RADIAN CORPORATION

HAZ 92

8501 Mo-Pac Blvd.
P.O. Box 201088
Austin, TX 78720-1088
(512)454-4797

RCN 269-069-02
28 February 1992

Dr. Bruce Swanton
New Mexico Environment Department
HRM Bureau
1190 St. Francis Drive
Santa Fe, New Mexico 87503

Dear Dr. Swanton:

We have enclosed a copy of the final *Chemical Data Acquisition Plan (CDAP)* for the sewage lagoon investigation activities to be conducted at Holloman AFB. This plan is being provided to you primarily to keep you informed of the progress made on this project. A copy was also provided to Mr. Jon Rinehart with the USEPA Region VI office.

Please contact me or Wally Hise if you have any questions regarding the document.

Sincerely,

Cris Hine

Cristian L. Hine
Project Director

cc: Mr. Ron Stirling/USACE
W Hise/Radian
Radian Project Team

Filed in Magazine shelf 3/4/92 bas

COPY Not Found

833d CSG/DEV
Holloman Air Force Base,
New Mexico

LIBRARY COPY

Chemical Data Acquisition Plan (CDAP)

Volume I
Sewage Lagoon Investigation

February 1992

Prepared Under Contract With:
US Army Corps of Engineers,
Omaha District

RADIAN CORPORATION

HAFB 03 ;

RADIAN
CORPORATION

DCN 92-269-069-02-03
RCN 269-069-02-02

(Mailing Address)
P.O. Box 201088
Austin, TX 78720-1088
(Shipping Address)
8501 North Mopac Blvd.
Austin, TX 78759
(512) 454-4797

CHEMICAL DATA ACQUISITION PLAN (CDAP)

SEWAGE LAGOON INVESTIGATION
HOLLOMAN AIR FORCE BASE, NM

Volume I

Prepared for:

49 SG/DEV
Holloman Air Force Base, NM

Prepared by:

Radian Corporation
8501 North MoPac Blvd.
P.O. Box 201088
Austin, Texas 78720-1088

Under Contract No. DACW45-91-D-0018 with:

U.S. Army Corps of Engineers
Omaha District
Omaha, Nebraska

February 1992

HOLLOMAN AIR FORCE BASE CHEMICAL
DATA ACQUISITION PLAN APPROVAL

This Chemical Data Acquisition Plan was developed for the sewage lagoon investigation to be conducted at Holloman Air Force Base, New Mexico. The signatures of key project personnel below indicate concurrence with the procedures specified in the plan and a commitment to communicate the plan and the philosophy of quality to all project personnel.

Wallace Hise, Program Manager

Signature Wallace Hise Date 27 Feb 92

Cristian L. Hine, Project Director

Signature Cristian L Hine Date 27 Feb 1992

Steve Gibson, Client Services Coordinator, Radian Analytical Services

Signature J. Steven Gibson Date 2/28/92

Jean M. Youngerman, Project QA Coordinator

Signature Jean M Youngerman Date 27 Feb 1992

This plan is approved for use in the Holloman AFB sewage lagoon investigation.

Ron Stirling, Project Manager, USACE

Signature _____ Date _____

Danielle Lakin, Project Chemist, USACE

Signature _____ Date _____

Chung-Rei Mao, Project QA Officer, MRD Laboratory

Signature _____ Date _____

CHEMICAL DATA ACQUISITION PLAN (CDAP)

		Page
1.0	TABLE OF CONTENTS	1-1
2.0	PROJECT DESCRIPTION	2-1
2.1	Background	2-1
2.2	Objectives	2-2
2.3	Environmental Setting	2-4
2.3.1	Meteorology	2-4
2.3.2	Physical Geography	2-6
2.3.3	Soils and Geology	2-8
2.3.4	Hydrology	2-9
3.0	CHEMICAL DATA QUALITY OBJECTIVES	3-1
3.1	Analytical Capability	3-2
3.2	Field Duplicate Samples	3-16
3.3	Definitions of Laboratory Quality Control Samples	3-17
4.0	PROJECT ORGANIZATION AND FUNCTIONAL AREA RESPONSIBILITIES	4-1
4.1	Roles and Responsibilities	4-1
4.2	Laboratory Qualifications	4-3
4.3	Subcontractor Qualifications	4-3
4.3.1	Drilling	4-3
4.3.2	Sludge Sampling	4-5
4.3.3	Survey Activities	4-5
5.0	FIELD ACTIVITIES	5-1
5.1	Sludge and Soil Samples	5-1
5.1.1	Sample Locations	5-1
5.1.2	Sampling Procedures	5-5
5.2	Soil Borings	5-8
5.2.1	Locations	5-8
5.2.2	Sampling Procedures	5-8
5.3	Analyses	5-10
5.3.1	Normal Samples	5-10

5.3.2 Quality Assurance/Quality Control Samples 5-10
5.4 Sample Containers, Preservation, and Holding Times 5-12
5.5 Monitor Well Installation Plan 5-15
5.5.1 Drilling Procedures 5-15
5.5.2 Monitor Well Installation 5-15
5.5.2.1 Monitor Well Screen and Casing 5-18
5.5.2.2 Sand Pack 5-18
5.5.2.3 Bentonite Seal 5-21
5.5.2.4 Grout Mixture 5-21
5.5.2.5 Surface Completions of Monitor Wells 5-21
5.5.3 Monitor Well Development 5-21
5.5.4 Surveying Requirements 5-22
5.5.5 Monitor Well Abandonment 5-24
5.6 General Information and Definitions 5-24
5.6.1 Laboratory Information 5-24
5.6.2 Decontamination Procedures for Sampling Equipment 5-26
5.6.3 Utility Clearance 5-26
5.6.4 Disposal of Drill Cuttings, Development Water and Purge Water 5-27
5.6.5 Site Restoration 5-27
5.6.6 Field Documentation 5-27
5.7 List of Equipment, Containers, and Supplies 5-28

6.0 SAMPLE CHAIN OF CUSTODY, PACKAGING, AND TRANSPORTATION 6-1

7.0 LABORATORY ANALYTICAL PROCEDURES 7-1

7.1 Metals by ICPES - EPA Method 6010 7-28
7.1.1 Soil Matrix 7-28
7.1.1.1 Sample Preparation 7-28
7.1.2 Sludge Matrix 7-28
7.1.2.1 Sample Preparation 7-28
7.1.3 Analytical Method 7-29
7.1.4 Method-Specific Data Quality Objectives 7-29
7.1.5 Preventive Maintenance 7-29
7.1.6 Instrument Calibration and Frequency 7-29
7.1.7 Internal Quality Control Checks 7-30
7.1.8 Corrective Action 7-30
7.1.9 Data Reduction, Validation, and Documentation 7-30
7.2 Arsenic by Furnace AA - SW 7060 7-30
7.2.1 Soil Matrix 7-30
7.2.1.1 Sample Preparation 7-31

7.2.2 Sludge Matrix 7-31
7.2.2.1 Sample Preparation 7-31
7.2.3 Analytical Method 7-31
7.2.4 Method-Specific Data Quality Objectives 7-31
7.2.5 Preventive Maintenance 7-32
7.2.6 Instrument Calibration and Frequency 7-32
7.2.7 Internal Quality Control Checks 7-32
7.2.8 Corrective Action 7-32
7.2.9 Data Reduction, Validation, and Documentation 7-32
7.3 Lead by Furnace AA - SW 7421 7-33
7.3.1 Soil Matrix 7-33
7.3.1.1 Sample Preparation 7-33
7.3.2 Sludge Matrix 7-33
7.3.2.1 Sample Preparation 7-33
7.3.3 Analytical Method 7-33
7.3.4 Method-Specific Data Quality Objectives 7-34
7.3.5 Preventive Maintenance 7-34
7.3.6 Instrument Calibration and Frequency 7-34
7.3.7 Internal Quality Control Checks 7-34
7.3.8 Corrective Action 7-34
7.3.9 Data Reduction, Validation, and Documentation 7-35
7.4 Mercury - SW 7471 (Cold-Vapor) 7-35
7.4.1 Soil Matrix 7-35
7.4.1.1 Sample Preparation 7-35
7.4.2 Sludge Matrix 7-35
7.4.2.1 Sample Preparation 7-35
7.4.3 Analytical Method 7-35
7.4.4 Method-Specific Data Quality Objectives 7-36
7.4.5 Preventive Maintenance 7-36
7.4.6 Instrument Calibration and Frequency 7-36
7.4.7 Internal Quality Control Checks 7-36
7.4.8 Corrective Action 7-36
7.4.9 Data Reduction, Validation, and Documentation 7-37
7.5 Selenium by Furnace AA - SW 7740 7-37
7.5.1 Soil Matrix 7-37
7.5.1.1 Sample Preparation 7-37
7.5.2 Sludge Matrix 7-37
7.5.2.1 Sample Preparation 7-37
7.5.3 Analytical Method 7-38
7.5.4 Method-Specific Data Quality Objectives 7-38
7.5.5 Preventive Maintenance 7-38
7.5.6 Instrument Calibration and Frequency 7-38
7.5.7 Internal Quality Control Checks 7-38

7.5.8 Corrective Action 7-39
7.5.9 Data Reduction, Validation, and Documentation 7-39
7.6 Thallium by Furnace AA - SW 7841 7-39
7.6.1 Soil Matrix 7-39
7.6.1.1 Sample Preparation 7-39
7.6.2 Sludge Matrix 7-39
7.6.2.1 Sample Preparation 7-40
7.6.3 Analytical Method 7-40
7.6.4 Method-Specific Data Quality Objectives 7-40
7.6.5 Preventive Maintenance 7-40
7.6.6 Instrument Calibration and Frequency 7-41
7.6.7 Internal Quality Control Checks 7-41
7.6.8 Corrective Action 7-41
7.6.9 Data Reduction, Validation, and Documentation 7-41
7.7 Organochlorine Pesticides and PCBs - SW 8080 7-41
7.7.1 Soil Matrix 7-41
7.7.1.1 Sample Preparation 7-41
7.7.2 Sludge Matrix 7-43
7.7.2.1 Sample Preparation 7-43
7.7.3 Analytical Method 7-44
7.7.4 Method-Specific Data Quality Objectives 7-44
7.7.5 Preventive Maintenance 7-45
7.7.6 Instrument Calibration and Frequency 7-45
7.7.7 Internal Quality Control Checks 7-45
7.7.8 Corrective Action 7-45
7.7.9 Data Reduction, Validation, and Documentation 7-45
7.8 Organophosphorus Pesticides - SW 8140 7-46
7.8.1 Soil Matrix 7-46
7.8.1.1 Sample Preparation 7-46
7.8.2 Sludge Matrix 7-47
7.8.2.1 Sample Preparation 7-47
7.8.3 Analytical Method 7-48
7.8.4 Method-Specific Data Quality Objectives 7-48
7.8.5 Preventive Maintenance 7-48
7.8.6 Instrument Calibration and Frequency 7-49
7.8.7 Internal Quality Control Checks 7-49
7.8.8 Corrective Action 7-49
7.8.9 Data Reduction, Validation, and Documentation 7-49
7.9 Chlorinated Herbicides - SW 8150 7-49
7.9.1 Soil Matrix 7-49
7.9.1.1 Sample Preparation 7-50
7.9.2 Sludge Matrix 7-50
7.9.2.1 Sample Preparation 7-50

7.9.3 Analytical Method 7-50
7.9.4 Method-Specific Data Quality Objectives 7-50
7.9.5 Preventive Maintenance 7-50
7.9.6 Instrument Calibration and Frequency 7-51
7.9.7 Internal Quality Control Checks 7-51
7.9.8 Corrective Action 7-51
7.9.9 Data Reduction, Validation, and Documentation 7-51
7.10 Volatile Organics - SW 8240 7-51
7.10.1 Soil Matrix 7-51
7.10.1.1 Sample Preparation 7-51
7.10.2 Sludge Matrix 7-52
7.10.2.1 Sample Preparation 7-52
7.10.3 Analytical Method 7-52
7.10.4 Method-Specific Data Quality Objectives 7-53
7.10.5 Preventive Maintenance 7-53
7.10.6 Instrument Calibration and Frequency 7-53
7.10.7 Internal Quality Control Checks 7-53
7.10.8 Corrective Action 7-53
7.10.9 Data Reduction, Validation, and Documentation 7-53
7.11 Semivolatile Organics - SW 8270 7-54
7.11.1 Soil Matrix 7-54
7.11.1.1 Sample Preparation 7-54
7.11.2 Sludge Matrix 7-55
7.11.2.1 Sample Preparation 7-55
7.11.3 Analytical Method 7-56
7.11.4 Method-Specific Data Quality Objectives 7-56
7.11.5 Preventive Maintenance 7-57
7.11.6 Instrument Calibration and Frequency 7-57
7.11.7 Internal Quality Control Checks 7-57
7.11.8 Corrective Action 7-57
7.11.9 Data Reduction, Validation, and Documentation 7-57
7.12 Polychlorinated Dioxins and Furans - SW 8280 7-58
7.12.1 Soil Matrix 7-58
7.12.1.1 Sample Preparation 7-58
7.12.2 Sludge Matrix 7-58
7.12.2.1 Sample Preparation 7-58
7.12.3 Analytical Method 7-58
7.12.4 Method-Specific Data Quality Objectives 7-59
7.12.5 Preventive Maintenance 7-59
7.12.6 Instrument Calibration and Frequency 7-59
7.12.7 Internal Quality Control Checks 7-60
7.12.8 Corrective Action 7-61
7.12.9 Data Reduction, Validation, and Documentation 7-61

7.13 Soil pH - SW 9045 7-61
7.13.1 Soil Matrix 7-61
7.13.1.1 Sample Preparation 7-62
7.13.2 Sludge Matrix 7-62
7.13.2.1 Sample Preparation 7-62
7.13.3 Analytical Method 7-62
7.13.4 Method-Specific Data Quality Objectives 7-62
7.13.5 Preventive Maintenance 7-63
7.13.6 Instrument Calibration and Frequency 7-63
7.13.7 Internal Quality Control Checks 7-63
7.13.8 Corrective Action 7-63
7.13.9 Data Reduction, Validation, and Documentation 7-63
7.14 Sulfide - SW 9030 7-64
7.14.1 Soil Matrix 7-64
7.14.1.1 Sample Preparation 7-64
7.14.2 Sludge Matrix 7-64
7.14.2.1 Sample Preparation 7-64
7.14.3 Analytical Method 7-64
7.14.4 Method-Specific Data Quality Objectives 7-65
7.14.5 Preventive Maintenance 7-65
7.14.6 Instrument Calibration and Frequency 7-65
7.14.7 Internal Quality Control Checks 7-65
7.14.8 Corrective Action 7-65
7.14.9 Data Reduction, Validation, and Documentation 7-66
7.15 Total Organic Carbon - SW 9060 7-66
7.15.1 Soil Matrix 7-66
7.15.1.1 Sample Preparation 7-66
7.15.2 Sludge Matrix 7-66
7.15.2.1 Sample Preparation 7-66
7.15.3 Analytical Method 7-67
7.15.4 Method-Specific Data Quality Objectives 7-67
7.15.5 Preventive Maintenance 7-67
7.15.6 Instrument Calibration and Frequency 7-67
7.15.7 Internal Quality Control Checks 7-67
7.15.8 Corrective Action 7-68
7.15.9 Data Reduction, Validation, and Documentation 7-68

8.0 CHEMICAL DATA QUALITY MANAGEMENT (CDQM) DELIVERABLES 8-1

9.0 REFERENCES 9-1

VOLUME II

APPENDIX A: RADIAN CORPORATION ANALYTICAL LABORATORY STANDARD OPERATING PROCEDURES

LIST OF FIGURES

		Page
2-1	Location Map of Holloman AFB	2-6
5-1	Sample Locations--Ponds C, D, E, and F	5-2
5-2	Sample Locations--Pond G	5-3
5-3	Sample Locations--Lakes Holloman Stinky	5-4
5-4	Locations of Proposed Borings, Proposed Upgradient Monitor Wells, and Monitor Well S2	5-9
5-5	USACE Boring Log	5-16
5-6	Typical Monitor Well Construction	5-19
5-7	Monitor Well Completion Form	5-20
5-8	Groundwater Development Record	5-23
5-9	A-E Quality Control Report	5-29
6-1	Example Sample Label and Custody Seal	6-2
6-2	Sample Chain-of-Custody Record	6-3

LIST OF TABLES

		Page
2-1	Summary of Preliminary Investigation Results	2-3
2-2	Meteorological Data for Holloman AFB	2-5
3-1	Estimated Precision and Accuracy Objectives for Soil and Sludge Samples	3-4
3-2	Analytical Method, Requested Detection Limits, and Maximum Contaminant Levels	3-6
4-1	Laboratory Certifications and Approvals Radian Corporation, Austin, Texas	4-4
5-1	Sample Intervals for Sludge and Soil Sample Locations	5-6
5-2	Number and Type of Analytical Sludge and Soil Samples	5-11
5-3	Summary of Sample Container, Preservation, and Holding Time	5-14
7-1	Analytical Methods	7-2
7-2	Summary of Internal Quality Control Procedures	7-15

2.0 PROJECT DESCRIPTION

Radian Corporation (Radian), under contract with the Omaha District U.S. Army Corps of Engineers (USACE), has prepared this Chemical Data Acquisition Plan (CDAP) for sampling sludge and soil from the sewage lagoons at Holloman Air Force Base (AFB), NM in support of the lagoon closure project.

2.1 Background

Holloman AFB submitted a Post-Closure Care Permit (PCCP) Application for the sewage lagoons in June 1991 to allow operation of the lagoons for wastewater treatment prior to final closure as hazardous waste management units. The application addresses Ponds A, B, C, D, E, F, and G, and includes a Delay-of-Closure Plan for these surface impoundments. As a condition for review of the PCCP application, the New Mexico Environment Department (NMED) is requiring a sampling and analysis program to be conducted in all impoundments downstream of Pond C, including Lakes Holloman and Stinky. The requirements are intended to demonstrate that hazardous constituents are not present in the sludge and underlying soil at levels that would adversely impact human health and the environment.

Additional requirements were imposed on Holloman AFB by EPA Region VI in a letter dated 20 June 1991 which requested that data be collected on the total organic carbon (TOC) content of soils from borings completed adjacent to the sewage lagoons. EPA intends to use these data for fate and transport modeling to determine permissible levels of contamination in the sewage lagoons during the delay-of-closure period.

In order to adequately address the NMED and EPA requirements and to prepare an approach that could be approved without significant modifications for unknown field conditions, a preliminary investigation was conducted by Radian in October 1991 to

determine the water depths and sludge thicknesses in the sewage lagoons. Results are summarized in Table 2-1. The work focused on Ponds C, D, E, F, and G, as well as Lakes Holloman and Stinky. At the time of the investigation, Lake Stinky was dry.

The following observations were made during the preliminary investigation:

- Sludge generally occurs in a layered fashion of brownish-red material (flocculent at the surface and more coarse with depth) grading to a soft black material high in organic matter. In all lagoons, the sludge is underlain by a grey clay (considered the natural bottom surface of the lagoons).

- There is no apparent mounding of sludge near the influent point to any lagoon, unlike the situation previously observed in Ponds A and B.

Based on the preliminary investigation, Radian prepared a strategy for investigation activities in the sewage lagoons. The approach to sludge and soil sampling was agreed upon after several conference calls involving personnel from Radian, USACE, Holloman AFB, NMED, EPA Region VI, and Headquarters Tactical Air Command (HQ TAC). The "Conceptual Plan for Sludge and Soil Sampling" (Radian, November 1991) summarizes the investigation approach. The NMED and EPA Region VI accepted and approved the Conceptual Plan in letters dated 18 November 1991 and 17 December 1991, respectively.

2.2 Objectives

The proposed sampling and analytical program will be structured to meet the requirements of the NMED and EPA, taking into consideration known field conditions at the present time. Sampling results will be used in part as a step toward final closure of the sewage lagoons. Specifically, the program is designed to meet the following objectives:

Table 2-1

Summary of Preliminary Investigation Results[a]

Pond	No. of Sample Locations	Water Depth (ft)			Sludge Thickness (in)		
		Minimum	Maximum	Average	Minimum	Maximum	Average
C	6	<2	7	4.5	Trace	10	6.5
D	8	4.5	6	5.5	0	1	Trace
E	9	4.5	6	5	4	13	10.25
F	4	5.5	5.5	5.5	6	10	7.5
G	12	1	4	3	3	8	5.5
Lake Holloman	11	1	8	5.5	4	20	6.25

[a]Field work conducted by Radian Corporation in October 1991.

- Generate data needed to support review of the PCCP application; and
- Generate data to characterize the lagoons and provide a preliminary estimate of the nature and extent of contamination, if any, and the resulting impact on final closure scenarios.

2.3 Environmental Setting

The following discussion of the meteorology, physical geography, soils, geology, and hydrology are from previous reports such as the Holloman AFB Records Search (CH2M Hill, August 1983) and the Holloman AFB RCRA Facility Assessment Report (A.T. Kearney, September 1988).

2.3.1 Meteorology

Holloman AFB is located in the Tularosa Basin with mountain ranges to the east and west. The climate is arid with low annual rainfall and low relative humidity. The mountain ranges have a dramatic influence on the local weather; they provide orographic lifting to produce summer thunderstorms and modify approaching weather systems. Holloman AFB receives most of its total annual rainfall from thunderstorm activity during the May through October period. The winter season is generally dry, characterized by clear skies and erratic snowfall from year to year. The period from March through May is characterized by a strong southerly wind flow and periods of blowing dust and sand. Meteorological data for Holloman AFB are presented in Table 2-2. Mean annual precipitation is 7.9 inches. The mean annual lake evaporation rate, commonly used to estimate the mean annual evapotranspiration rate, is an estimated 67 inches per year. Therefore, the annual net precipitation (mean annual precipitation minus mean annual evapotranspiration) for the Holloman AFB area is approximately minus 59 inches per year. As a result, site soils are generally dry.

Table 2-2

Meteorological Data for Holloman AFB[a]

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Annual Average or Extreme
Temperature (°F)													
Monthly mean	41	46	52	61	69	81	79	73	62	49	49	42	61
Mean daily high	54	60	66	76	84	93	91	86	76	63	63	55	75
Mean daily low	28	31	37	45	54	68	66	60	48	35	35	26	47
Record high	78	80	90	94	103	108	106	102	92	82	82	75	109
Record low	-11	0	9	23	26	52	54	38	26	3	3	2	-11
Precipitation (in)													
Monthly mean	0.5	0.4	0.3	0.2	0.4	0.7	1.2	1.3	1.2	0.9	0.3	0.5	7.9
Record maximum	1.9	1.4	3.0	0.8	2.9	3.6	3.7	4.4	3.9	4.2	2.5	2.4	4.4
Record minimum	0	T[b]	0	0	0	T	T	0.2	T	0	0	0	0
Relative humidity (%)													
4 a.m. mean	66	61	52	40	42	42	60	66	68	61	61	63	57
1 p.m. mean	42	35	27	19	20	19	31	35	38	34	34	37	31
Surface wind													
Mean velocity (Knots)	4	4	6	7	6	6	5	5	4	4	4	4	5
Prevailing direction	N	N	S	S	S	S	S	S	S	S	S	S	S

[a]Source: Holloman Air Force Base Installation Program Records Search; CH2M Hill; August 1983.
Period of record: September 1942 to December 1981.

[b]T = trace.

2.3.2 Physical Geography

Holloman AFB is located in the southern part of New Mexico in the Tularosa Basin, as shown in Figure 2-1. The basin is approximately 120 miles long and 35 miles wide, extending from the southern end of Chupadera Mesa almost to the Texas border. The Tularosa Basin is part of a structural basin which is more than 200 miles long and 24 to 60 miles wide, extending from southeastern Socorro County, New Mexico southward to Chiuahua, Mexico. In the vicinity of the Base, the Tularosa Basin is bounded 8 miles to the east by the Sacramento Mountains and 20 miles to the west by the San Andres Mountains.

Elevations within the Tularosa Basin range from 4,400 feet above mean sea level (ft-msl) at the northeast corner to 4,000 ft-msl in the southwest corner, sloping downward to the southwest. Elevations at the Base range from 4,100 to 4,028 ft-msl, excluding Tularosa Peak. Elevations in the Sacramento Mountains reach 12,000 ft-msl and range from 7,000 to 9,000 ft-msl within the San Andres Mountains.

The Tularosa Basin is a closed basin with regard to surface drainage. No surface water leaves the basin. Surface water is either lost to evaporation and infiltration or collects in the lowest point in the basin at or near Lake Lucero. This lake is located at the southwest edge of the gypsum dune field, known as White Sands National Monument, west of the Base. Surface water within the basin ultimately flows to Lake Lucero. Here, also a discharge point for groundwater, sulfate salts are concentrated by evaporation. The prevailing southwest winds then pick up and transport the salts, primarily gypsum, in a northeasterly direction to continue building the dune field of the White Sands National Monument.

The Base is crossed by several southwest trending "arroyos" or intermittent stream beds including Lost River (the largest), Dillard Draw, Malone Draw, and several smaller tributaries such as Red Arroyo and Arroyo Cavacita. Lost River is fed by

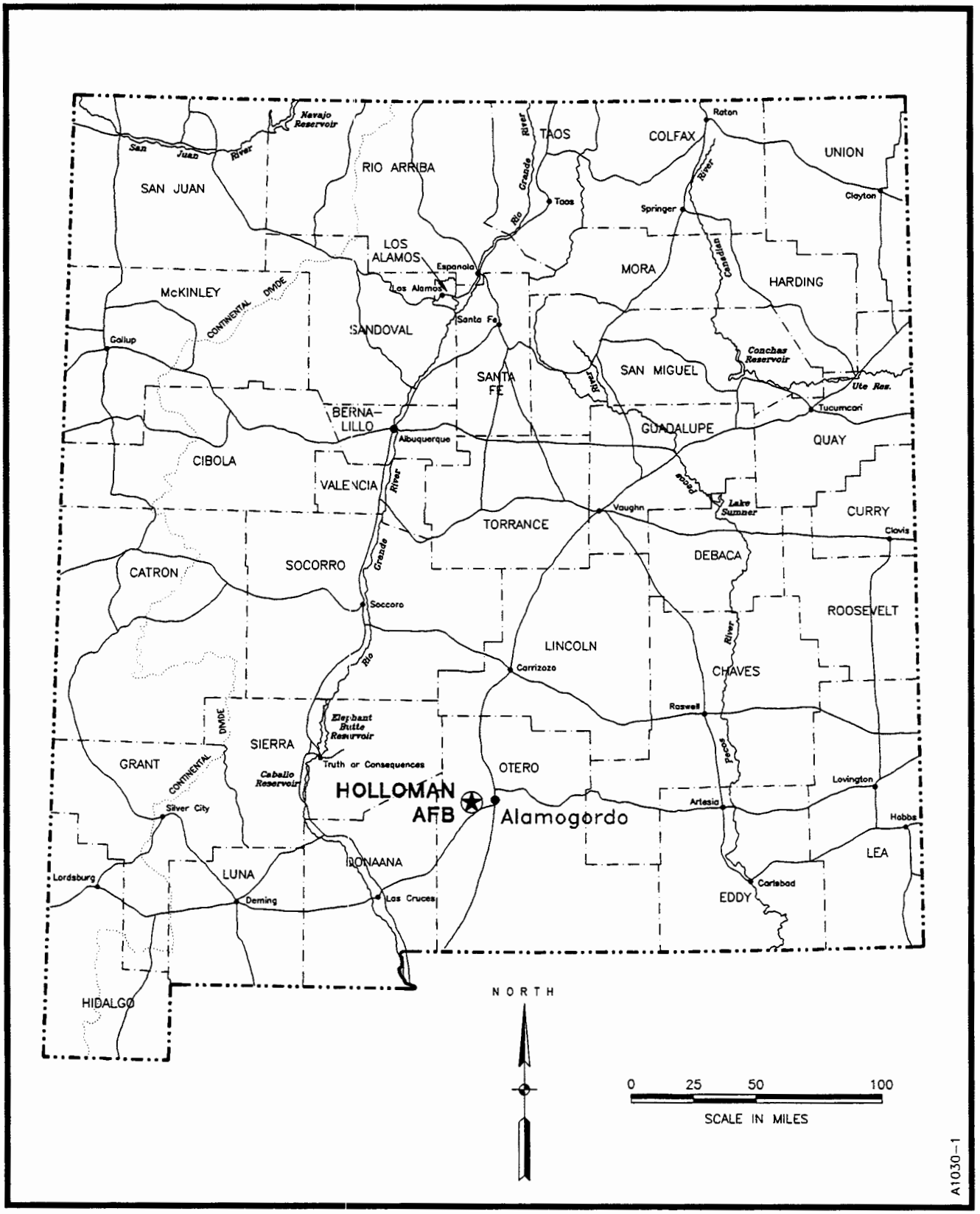


Figure 2-1. Location Map of Holloman AFB

groundwater seeps or springs. The river appears and disappears along its course as springs add water and evapotranspiration and infiltration recapture it.

2.3.3 Soils and Geology

Most of the Base is covered with well drained soils (fine sandy loam) formed in gypsiferous sediments of eolian (wind blown) or alluvial (stream deposition) origin. The soils are thin and overlie discontinuous beds of gypsum. The surface soils are nearly level with slopes ranging from 0 to 5 percent. Permeability of the soil horizons ranges from 4×10^{-4} to 1×10^{-3} cm/sec (moderately permeable).

Geologically, the Tularosa Basin is a graben structure, bounded on the east and west by mountains which are actually tilted fault blocks. The basin had its beginning over 270 million years ago when most of southern New Mexico was covered by a shallow sea. During the succeeding years, there were periods of inundation and each cycle left behind successive layers of sediments. Then, approximately 70 million years ago, a major mountain building episode occurred creating the Rocky Mountains. This upheaval caused the Tularosa area to be uplifted, forming a broad, gentle arch. As time passed, tectonic adjustments to the mountain building event took place and the top of this arch or dome collapsed (approximately 10 million years ago) along nearly vertical fault planes. The large area, which collapsed or settled, formed what is now the Tularosa Basin.

The fault planes have produced steep scarps clearly visible on the west side of the Sacramento mountains. The basin, itself, is underlain mostly by unconsolidated bolson deposits more than 4,000 feet thick in the vicinity of Holloman AFB. A bolson is a basin which has no surface drainage outlet. Bolson deposits refer to sediments carried by water into the closed basin or bolson. Only the uppermost bolson deposits are of significance to this investigation at this point in time.

2.3.4 Hydrology

Surface water resources within the Tularosa Basin are limited by the high evapotranspiration rate and low annual rainfall. Perennial streams occur in the mountainous regions surrounding the basin including Rio Tularosa, Rio Bonita, and Eagle Creek. Rio Bonita, located northeast of Tularosa and approximately 60 miles from Holloman AFB, discharges to Bonita Lake which in turn is tapped for water supply, some of which is transmitted by pipeline to the Base.

The intermittent streams and arroyos occurring within the basin are important drainage features only during the infrequent heavy rainfall, conveying surface water southwest to the basin's lowest elevation point (Lake Lucero).

Man-made and/or modified surface water features have some significance in an area otherwise devoid of lakes, rivers, and streams. The wastewater treatment system at Holloman AFB consists of six aeration/evaporation lagoons located in the southwest corner of the Base. Just southwest of these lagoons, a natural playa occurs, which receives discharge from the Base as well as seepage from the sewage lagoons. The inundated portion of the playa is referred to as Lake Holloman. Surface drainage within the undeveloped parts of the Base is controlled by the major arroyos, including Lost River and Dillard Draw and their tributaries. Surface flows are directed southwest toward the White Sands National Monument. Drainage within the developed portion of the Base flows by way of ditches and culverts to the southwest corner of the Base, in the vicinity of the wastewater treatment lagoons.

Groundwater occurs within the unconsolidated bolson fill at Holloman AFB. The Base obtains most of its water supply from wells installed in the fill. The Base well fields (Boles, Douglas, and San Andres) are located off-Base at the foot of the Sacramento

Mountains just south of Alamogordo. Groundwater beneath Holloman AFB is highly mineralized, containing dissolved solids in excess of 10,000 parts per million.

At the base of the Sacramento Mountains, the hydraulic gradient is quite steep but then flattens out quickly. In the vicinity of Holloman AFB, the ground surface slopes to the southwest gently but at a slightly higher rate than the water table. Depth to water table at the well fields near the mountains is 270 feet or more below land surface (bls), while at Holloman AFB the water table is 5 to 10 feet bls. Like surface drainage, groundwater flows predominately to the southwest, discharging by evapotranspiration. However, local groundwater flow direction appears to be influenced by the arroyos and draws. Potentiometric surface maps from the Holloman AFB Remedial Investigation (Walk, Haydel & Associates, Inc., 1989) indicate that groundwater flow is to the southeast at sites which are located northwest of Dillard Draw. The extent that the arroyos may effect groundwater flow throughout the Base is unknown.

The bolson fill is derived from limestone, dolomite and gypsum from the surrounding mountains. Fresh water recharges the bolson fill at the base of the mountains, which contains highly soluble materials such as gypsum. Groundwater quickly dissolves these formation minerals, and groundwater quality degrades with increased contact time. Therefore, groundwater under Holloman AFB is non-potable. The only potable groundwater in the vicinity is near the recharge area near the base of the mountains.

3.0 CHEMICAL DATA QUALITY OBJECTIVES

The overall objective of this work effort is to generate data to characterize the sewage lagoons and provide a preliminary estimate of the nature and extent of contamination, if any, and the resulting impact on final closure scenarios. The specific data quality objectives (DQOs) are to:

- Collect the samples specified in Section 5 to adequately determine the presence or absence of contamination in the sewage lagoons;
- Ensure data comparability through the use of standard methods and controlled systems to collect and analyze samples;
- Provide analytical results of known and acceptable precision and accuracy; and
- Gather data that could support an evaluation of the risks posed by the sewage lagoons to human health and the environment.

Measurement data representativeness is a function of a sampling strategy and will be achieved using the procedures discussed in Section 5, Field Activities. Potential for sample contamination will be minimized by the use of decontamination procedures specified in Section 5.6.2. Data comparability will be achieved using standard methods and standard units of measure as specified in the methods described in Section 7. Analytical imprecisional bias will be controlled through the use of a quality control (QC) program using prescribed QC samples and corrective actions specified in Section 7. Imprecision and bias in natural matrix samples will be estimated by standard QC methods such as matrix spikes, field duplicates, and trip blanks. Confirmation of chemical identity will be performed by gas chromatography (GC) analytical methods using second column confirmation procedures for samples with detected compounds or by mass spectroscopy.

A quality assurance/quality control (QA/QC) program will be used to ensure that the DQOs are met for the Holloman AFB project. QA/QC efforts are twofold. First, they provide the mechanism for ongoing control and evaluation of measurement data quality throughout the course of the project (i.e., system capability). Second, they specify quality control data to be used to define natural-matrix data quality for various measurement parameters, in terms of precision and accuracy. Control of measurement data quality (i.e., control of error sources that affect data quality) is possible for sample collection and analysis. However, matrix interference, or non-homogeneity, is not amenable to control and thus imprecision or bias due to these natural sources of error must be estimated from QC samples. For this project, sample collection error will be controlled through the use of standard sample collection methods and field logbooks. Sample analysis error will be controlled through the use of standard analytical methods, for which standard operating procedures (SOPs) are presented in Appendix A, performed on a capable analytical system, with quality control (QC) efforts as directed in published procedures. Natural matrix error will be estimated by standard QC methods such as matrix spikes, field duplicates, and trip blanks.

3.1 Analytical Capability

Efforts to control measurement error require that the analytical system be capable, in control, and appropriately sensitive for all analyses. System capability, in terms of accuracy and precision, may be documented by reporting system QC data (e.g., continuing calibration, quality control check samples (QCCS), and method spikes). System capability, in terms of sensitivity, may be documented through the use of maximum detection limits for system blanks (e.g., reagent, system and method blanks) and calibration standards. System control may be documented through the use of control charts or other statistical methods that indicate system performance over time.

Precision and accuracy objectives, in terms of maximum allowable imprecision and inaccuracy, for the various measurement parameters associated with site characterization efforts, are presented in Table 3-1. Data capture objectives for all constituents are 90 percent. Precision values presented in Table 3-1 represent a measure of variability for replicate measurements of the same parameter in clean-matrix, laboratory QC samples, expressed in terms of the coefficient of variation (CV, or relative standard deviation). CVs compared to precision objectives in Table 3-1 are calculated from data such as a series of continuing calibration results and QCCS results. Accuracy values for clean-matrix laboratory samples include components of both random error (i.e., variability due to imprecision) and systematic error (i.e., bias), and thus reflect the total analytical error for a given measurement, expressed as a percentage of the true value. The average relative percent difference between true and measured concentrations in continuing calibration and QCCS samples may be compared to accuracy objectives in Table 3-1. The basis for these estimates are, in most cases, described in the methods. The analytical laboratory will be able to document that the QA/QC procedure in each standard method, Chapter One and Method 8000 of SW846, 3rd edition, Method 1020 of Standard Methods for Examination of Water and Wastewater, 17th edition, or USACE Guidance Document ER 1110-1-263, was followed for all analytical work. Accuracy and precision estimates for samples in a natural matrix (which is much more difficult from an analytical standpoint) would not be expected to be within the objectives presented in Table 3-1.

Sample detection limits must normally be sensitive to concentrations at or below Resource Conservation and Recovery Act (RCRA) health limits which are presented in Table 3-2. It is important to note that for a number of compounds, the specified detection limit does not reach the RCRA limit for the methods included in this investigation. Natural sample detection limits will depend on dilution effects. In general, dilutions will be performed only as directed in each representative method. For target analytes on gas chromatography/mass spectrometry (GC/MS) and gas chromatography (GC) analyses, dilution will be performed if the target analyte concentrations exceed the

Table 3-1

Estimated Precision and Accuracy Objectives for Soil and Sludge Samples

Parameter	Method	Precision[a]	Accuracy[b]
Metals[c]	SW6010 ICPES	10%	±10%
Arsenic	SW7060 Graphite Furnace AA	15%	±15%
Lead	SW7421 Graphite Furnace AA	15%	±15%
Mercury	SW7471 Cold Vapor AA	15%	±15%
Selenium	SW7740 Graphite Furnace AA	15%	±15%
Thallium	SW7841	15%	±15%
Pesticides/PCBs	SW8080 GC/ECD	50%	See Method 8080, Table 3
Organophosphorus Pesticides	SW8140 GC/FPD	50%	See Method 8140, Table 3
Chlorinated Herbicides	SW8150 GC/ECD	50%	See Method 8150, Table 3
Volatile Organic Compounds	SW8240 GC/MS	50%	See Method 8240, Table 6
Semivolatile Organic Compounds	SW8270 GC/MS	50%	See Method 8270, Table 6
Dioxins and Furans	SW8280	50%	40-120%
Cyanide	SW9012	20%	85-115%
Sulfide	SW9030	20%	80-120%
Total Organic Carbon	SW9060	20%	80-120%

Table 3-1

(Continued)

[a] Coefficient of variation (CV or relative standard deviation) for replicate analytical determinations (exclusive of sampling variability). Average CV for a series of QCCS or continuing calibration samples will be compared to these objectives.

[b] Total error for a single measurement in a clean, laboratory-controlled matrix, including both systematic error (bias) and random error (variability due to imprecision), expressed as a percentage of the measured value. Average percent recovery for a series of QCCS or continuing calibration samples will be compared to these objectives.

[c] ICPES metals: antimony, barium, beryllium, cadmium, chromium, cobalt, copper, nickel, silver, tin, vanadium and zinc.

Table 3-2

Analytical Methods, Method Detection Limits, and Maximum Contaminant Levels

Parameter	Analysis		Reporting Limits[a]	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
METALS					
Antimony*	ICPES	SW-846:6010	10	32	d
Barium*	ICPES	SW-846:6010	1	4,000	d
Beryllium	ICPES	SW-846:6010	0.2	0.2	d
Cadmium*	ICPES	SW-846:6010	0.5	40	d
Chromium (total)*	ICPES	SW-846:6010	1	400 (Cr VI)	80,000[e] (Cr III)
Cobalt	ICPES	SW-846:6010	1	–	–
Copper*	ICPES	SW-846:6010	2	–	3200[e]
Nickel*	ICPES	SW-846:6010	2	2,000	d
Silver*	ICPES	SW-846:6010	1	200	400[f]
Tin	ICPES	SW-846:6010	60	–	48,000[e]
Vanadium*	ICPES	SW-846:6010	2	–	560[e]
Zinc*	ICPES	SW-846:6010	2	–	16,000[e]
Arsenic*	GFAA	SW-846:7060	0.4	80	24[f]
Lead*	GFAA	SW-846:7421	0.3	114	d
Mercury*	CVAA	SW-846:7471	0.02	20	24[e]
Selenium*	GFAA	SW-846:7740	0.5	–	400[e]
Thallium*	GFAA	SW-846:7841	0.5	–	6[e]
ORGANOCHLORINE PESTICIDES AND PCBs					
Aldrin	GC/ECD	SW-846:8080	0.001	0.04	d
alpha-BHC	GC/ECD	SW-846:8080	0.001	0.1	d
beta-BHC	GC/ECD	SW-846:8080	0.001	4	d
delta-BHC	GC/ECD	SW-846:8080	0.001	–	–
gamma-BHC (Lindane)	GC/ECD	SW-846:8080	0.001	0.5	d
Chlordane (technical)	GC/ECD	SW-846:8080	0.005	0.5	d
4,4'-DDD*	GC/ECD	SW-846:8080	0.001	3	d

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits[a]	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
4,4'-DDE*	GC/ECD	SW-846:8080	0.001	2	d
4,4'-DDT	GC/ECD	SW-846:8080	0.002	2	d
Dieldrin	GC/ECD	SW-846:8080	0.001	0.04	d
Endosulfan I*	GC/ECD	SW-846:8080	0.001	4	d
Endosulfan II	GC/ECD	SW-846:8080	0.003	–	4[e]
Endosulfan sulfate	GC/ECD	SW-846:8080	0.005	–	4[e]
Endrin	GC/ECD	SW-846:8080	0.001	20	24[f]
Endrin aldehyde	GC/ECD	SW-846:8080	0.002	–	–
Heptachlor	GC/ECD	SW-846:8080	0.001	0.2	d
Heptachlor epoxide	GC/ECD	SW-846:8080	0.001	0.08	d
Isodrin	GC/ECD	SW-846:8080	0.001	–	–
Kepone*	GC/ECD	SW-846:8080	0.001	–	–
Methoxychlor	GC/ECD	SW-846:8080	0.005	–	400[e]
Toxaphene	GC/ECD	SW-846:8080	0.050	0.6	d
PCB-1016	GC/ECD	SW-846:8080	0.010	0.09	d
PCB-1221	GC/ECD	SW-846:8080	0.020	0.09	d
PCB-1232	GC/ECD	SW-846:8080	0.020	0.09	d
PCB-1242	GC/ECD	SW-846:8080	0.010	0.09	d
PCB-1248	GC/ECD	SW-846:8080	0.010	0.09	d
PCB-1254*	GC/ECD	SW-846:8080	0.020	0.09	d
PCB-1260*	GC/ECD	SW-846:8080	0.020	0.09	d
ORGANOPHOSPHORUS PESTICIDES					
Dimethoate	GC/FPD	SW-846:8140	0.020	2,000	16[e]
Disulfoton	GC/FPD	SW-846:8140	0.020	3	d
Ethyl parathion	GC/FPD	SW-846:8140	0.015	500	d
Famphur	GC/FPD	SW-846:8140	0.050	–	–

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits*	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
Parathion methyl	GC/FPD	SW-846:8140	0.003	30	20[e]
Phorate	GC/FPD	SW-846:8140	0.015	–	–
Sulfotepp	GC/FPD	SW-846:8140	0.010	40	d
Thionazin	GC/FPD	SW-846:8140	0.100	–	–
o,o,o-Triethylphosphorthioate	GC/FPD	SW-846:8140	0.100	–	–
CHLORINATED HERBICIDES					
2,4-D	GC/ECD	SW-846:8150	0.120	800	d
2,4,5-T	GC/ECD	SW-846:8150	0.020	–	8,000[e]
2,4,5-TP (Silvex)	GC/ECD	SW-846:8150	0.017	–	640[e]
Dinoseb	GC/ECD	SW-846:8150	0.015	–	80[e]
VOLATILE ORGANICS					
Acetone*	GC/MS	SW-846:8240	10	8,000	d
Acetonitrile	GC/MS	SW-846:8240	10	500	d
Acrolein	GC/MS	SW-846:8240	7.5	–	–
Acrylonitrile	GC/MS	SW-846:8240	5	1	1.3[e]
Benzene	GC/MS	SW-846:8240	0.5	–	24[f]
Bromodichloromethane	GC/MS	SW-846:8240	0.5	0.5	5[e]
Bromomethane	GC/MS	SW-846:8240	1	100	112[e]
Carbon disulfide*	GC/MS	SW-846:8240	0.5	8,000	d
Carbon tetrachloride	GC/MS	SW-846:8240	0.5	5	d
2-Chloro-1,3-butadiene	GC/MS	SW-846:8240	2.5	–	1,600[e]
Chlorobenzene	GC/MS	SW-846:8240	0.5	2,000	1,600[e]
Chloroethane	GC/MS	SW-846:8240	1	–	–
Chloroform	GC/MS	SW-846:8240	0.5	100	115[e]
Chloromethane	GC/MS	SW-846:8240	1	–	–
3-Chloropropene	GC/MS	SW-846:8240	0.5	–	4,000[e]

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits*	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
Dibromochloromethane	GC/MS	SW-846:8240	0.5	–	1,600[e]
1,2-Dibromo-3-chloropropane	GC/MS	SW-846:8240	2	–	0.03[e]
1,2-Dibromoethane	GC/MS	SW-846:8240	0.5	–	0.008[e]
Dibromomethane	GC/MS	SW-846:8240	0.5	–	–
trans-1,4-Dichloro-2-butene	GC/MS	SW-846:8240	1	–	–
Dichlorodifluoromethane	GC/MS	SW-846:8240	2	20,000	16,000[e]
1,2-Dichloroethane	GC/MS	SW-846:8240	0.5	8	[d]
trans-1,2-Dichloroethene	GC/MS	SW-846:8240	0.5	–	1,600[e]
1,1-Dichloroethane	GC/MS	SW-846:8240	0.5	–	8,000[e]
1,1-Dichloroethene	GC/MS	SW-846:8240	0.5	10	1[e]
1,2-Dichloropropane	GC/MS	SW-846:8240	0.5	–	10[e]
cis-1,3-Dichloropropene	GC/MS	SW-846:8240	0.5	20	4[e]
trans-1,3-Dichloropropene	GC/MS	SW-846:8240	0.5	20	4[e]
Ethyl benzene	GC/MS	SW-846:8240	0.5	8,000	[d]
Ethyl methacrylate	GC/MS	SW-846:8240	0.5	–	7,200[e]
2-Hexanone	GC/MS	SW-846:8240	5	–	–
Iodomethane	GC/MS	SW-846:8240	0.5	–	–
Methylene chloride*	GC/MS	SW-846:8240	0.5	90	[d]
2-Butanone (MEK)	GC/MS	SW-846:8240	10	4,000	[d]
Methyl methacrylate	GC/MS	SW-846:8240	0.5	–	6,400[e]
4-Methyl-2-pentanone	GC/MS	SW-846:8240	5	4,000	[d]
Propanenitrile	GC/MS	SW-846:8240	10	–	–
Styrene	GC/MS	SW-846:8240	0.5	20,000	23[e]
1,1,1,2-Tetrachloroethane	GC/MS	SW-846:8240	0.5	300	269[e]
1,1,2,2-Tetrachloroethane	GC/MS	SW-846:8240	0.5	40	35[e]
Tetrachloroethene	GC/MS	SW-846:8240	0.5	10	14[f]

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits[a]	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
Toluene	GC/MS	SW-846:8240	0.5	20,000	16,000[f]
Tribromomethane	GC/MS	SW-846:8240	0.5	2,000	1,600[e]
1,1,1-Trichloroethane	GC/MS	SW-846:8240	0.5	7,000	7,200[e]
1,1,2-Trichloroethane	GC/MS	SW-846:8240	0.5	100	123[f]
Trichloroethene	GC/MS	SW-846:8240	0.5	60	64[e]
Trichlorofluoromethane	GC/MS	SW-846:8240	1	20,000	24,000[e]
1,2,3-Trichloropropane	GC/MS	SW-846:8240	0.5	500	400[e]
Vinyl Acetate	GC/MS	SW-846:8240	0.5	--	80,000[e]
Vinyl Chloride	GC/MS	SW-846:8240	1	--	0.4[e]
Xylenes (total)	GC/MS	SW-846:8240	0.5	200,000	160,000[e]
VOLATILE ORGANICS (Direct Injection)					
1,4-Dioxane	GC/MS	SW-846:8240	1	60	64[e]
Isobutanol	GC/MS	SW-846:8240	1	20,000	24,000[e]
Methacrylonitrile	GC/MS	SW-846:8240	1	8	[d]
SEMIVOLATILE ORGANICS					
Acenaphthene	GC/MS	SW-846:8270	1	--	4,800[e]
Acenaphthylene	GC/MS	SW-846:8270	1	--	--
Acetophenone	GC/MS	SW-846:8270	5	8,000	[d]
2-Acetylaminofluorene	GC/MS	SW-846:8270	1	--	--
4-Aminobiphenyl	GC/MS	SW-846:8270	1	--	--
Aniline	GC/MS	SW-846:8270	1	100	80[e]
Anthracene*	GC/MS	SW-846:8270	1	--	0.2[g]
Aramite	GC/MS	SW-846:8270	10	--	4,000[e]
Benzo(a)anthracene*	GC/MS	SW-846:8270	1	--	0.4[g]
Benzo(a)pyrene*	GC/MS	SW-846:8270	1	--	0.06[e]
Benzo(b)fluoranthene*	GC/MS	SW-846:8270	1	--	0.4[g]

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits*	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
Benzo(g,h,i)perylene	GC/MS	SW-846:8270	1	–	2.8[g]
Benzo(k)fluoranthene*	GC/MS	SW-846:8270	1	–	0.9[g]
Benzyl alcohol	GC/MS	SW-846:8270	1	–	240[e]
4-Bromophenyl phenyl ether	GC/MS	SW-846:8270	1	–	–
Butylbenzylphthalate*	GC/MS	SW-846:8270	1	20,000	16,000[f]
4-Chloro-3-methylphenol	GC/MS	SW-846:8270	1	–	–
4-Chloroaniline*	GC/MS	SW-846:8270	1	–	320[e]
Chlorobenzilate	GC/MS	SW-846:8270	1	–	1,600[e]
bis(2-Chloroethoxy)methane	GC/MS	SW-846:8270	1	–	–
bis(2-Chloroethyl)ether	GC/MS	SW-846:8270	1	0.6	[d]
bis(2-Chloroisopropyl)ether	GC/MS	SW-846:8270		–	–
2-Chloronaphthalene	GC/MS	SW-846:8270	1	–	–
2-Chlorophenol	GC/MS	SW-846:8270	1	400	[d]
4-Chlorophenyl phenyl ether	GC/MS	SW-846:8270	1	–	–
Chrysene*	GC/MS	SW-846:8270	1	–	14[g]
Diallate	GC/MS	SW-846:8270	1	–	11[e]
Dibenz(a,h)anthracene	GC/MS	SW-846:8270	1	–	0.05[e]
Dibenzofuran*	GC/MS	SW-846:8270	1	–	0.000005[e]
1,2-Dichlorobenzene	GC/MS	SW-846:8270	1	–	7,200[e]
1,3-Dichlorobenzene	GC/MS	SW-846:8270	1	–	–
1,4-Dichlorobenzene	GC/MS	SW-846:8270	1	–	290[e]
3,3'-Dichlorobenzidine	GC/MS	SW-846:8270	2	2	[d]
2,4-Dichlorophenol	GC/MS	SW-846:8270	1	200	240[e]
2,6-Dichlorophenol	GC/MS	SW-846:8270	1	–	–
Diethylphthalate	GC/MS	SW-846:8270	1	80,000	64,000[e]
p-Dimethylaminoazobenzene	GC/MS	SW-846:8270	1	–	–

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits*	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
7,12-Dimethylbenz(a)anthracene	GC/MS	SW-846:8270	5	–	–
3,3'-Dimethylbenzidine	GC/MS	SW-846:8270	2	–	0.08[e]
Dimethylphenethylamine	GC/MS	SW-846:8270	1	–	–
2,4-Dimethylphenol	GC/MS	SW-846:8270	1	–	1,600[e]
Dimethylpthalate	GC/MS	SW-846:8270	1	–	80,000[e]
4,6-Dinitro-2-methylphenol	GC/MS	SW-846:8270	5	–	–
Di-n-butylphthalate*	GC/MS	SW-846:8270	5	8,000	d
Di-n-octylphthalate*	GC/MS	SW-846:8270	1	–	1,600[e]
1,3-Dinitrobenzene	GC/MS	SW-846:8270	1	8	d
2,4-Dinitrophenol	GC/MS	SW-846:8270	5	200	160[e]
2,4-Dinitrotoluene	GC/MS	SW-846:8270	1	–	–
2,6-Dinitrotoluene	GC/MS	SW-846:8270	1	1	d
Diphenylamine	GC/MS	SW-846:8270	1	2,000	d
bis(2-Ethylhexyl)phthalate*	GC/MS	SW-846:8270	1	50	d
Ethylmethane sulfonate	GC/MS	SW-846:8270	1	–	–
Fluoranthene*	GC/MS	SW-846:8270	1	–	3,200[e]
Fluorene	GC/MS	SW-846:8270	1	–	3,200[e]
Hexachlorobenzene	GC/MS	SW-846:8270	1	–	0.4[e]
Hexachlorobutadiene	GC/MS	SW-846:8270	1	90	d
Hexachlorocyclopentadiene	GC/MS	SW-846:8270	1	600	560[e]
Hexachloroethane	GC/MS	SW-846:8270	1	80	d
Hexachlorophene	GC/MS	SW-846:8270	1.0	20	24[e]
Hexachloropropene	GC/MS	SW-846:8270	1	–	–
Indeno(1,2,3-c,d)pyrene	GC/MS	SW-846:8270	1	–	0.3[e]
Isophorone	GC/MS	SW-846:8270	1	2,000	1,700[e]
Isosafrole	GC/MS	SW-846:8270	1	–	–

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits[a]	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
Methapyrilene	GC/MS	SW-846:8270	1	–	–
3-Methylchloanthrene	GC/MS	SW-846:8270	1	–	–
Methyl methanesulfonate	GC/MS	SW-846:8270	1	–	–
2-Methyl naphthalene	GC/MS	SW-846:8270	1	–	–
2-Methylphenol	GC/MS	SW-846:8270	1	4,000	d
3-Methylphenol	GC/MS	SW-846:8270	1	4,000	d
4-Methylphenol	GC/MS	SW-846:8270	1	4,000	d
Naphthalene	GC/MS	SW-846:8270	1	–	320[e]
1,4-Naphthoquinone	GC/MS	SW-846:8270	1	–	–
1-Naphthylamine	GC/MS	SW-846:8270	1	–	–
2-Naphthylamine	GC/MS	SW-846:8270	1	–	–
2-Nitroaniline	GC/MS	SW-846:8270	5	–	–
3-Nitroaniline	GC/MS	SW-846:8270	5	–	–
4-Nitroaniline	GC/MS	SW-846:8270	5	–	–
Nitrobenzene	GC/MS	SW-846:8270	1	40	d
2-Nitrophenol	GC/MS	SW-846:8270	1	–	–
4-Nitrophenol	GC/MS	SW-846:8270	5	–	–
4-Nitroquinoline-N-oxide	GC/MS	SW-846:8270	10	–	–
N-Nitroso-di-n-butylamine	GC/MS	SW-846:8270	1	0.1	d
N-Nitrosodiethylamine	GC/MS	SW-846:8270	1	–	0.005[e]
N-Nitrosodiphenylamine	GC/MS	SW-846:8270	1	100	143[e]
N-Nitrosodipropylamine	GC/MS	SW-846:8270	1	0.1	d
N-Nitrosodimethylamine	GC/MS	SW-846:8270	1	–	–
N-Nitrosomethylethylamine	GC/MS	SW-846:8270	1	0.03	d
N-Nitrosomorpholine	GC/MS	SW-846:8270	1	–	–
N-Nitrosopiperidine	GC/MS	SW-846:8270	1	–	–

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits[a]	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
N-Nitrosopyrrolidine	GC/MS	SW-846:8270	1	0.3	[d]
5-Nitro-o-toluidine	GC/MS	SW-846:8270	1	–	–
Pentachlorobenzene	GC/MS	SW-846:8270	1	60	64[e]
Pentachloroethane	GC/MS	SW-846:8270	1	–	–
Pentachloronitrobenzene	GC/MS	SW-846:8270	1	200	30[e]
Pentachlorophenol	GC/MS	SW-846:8270	5	2,000	6[e]
Phenacetin	GC/MS	SW-846:8270	1	–	–
Phenanthrene*	GC/MS	SW-846:8270	1	–	5[h]
Phenol	GC/MS	SW-846:8270	1	50,000	48,000[e]
p-Phenylenediamine	GC/MS	SW-846:8270	5	–	480[e]
2-Picoline	GC/MS	SW-846:8270	1	–	–
Pronamide	GC/MS	SW-846:8270	1	6,000	6,400[e]
Pyrene*	GC/MS	SW-846:8270	1	–	2,400[f]
Pyridine	GC/MS	SW-846:8270	1	80	[d]
Safrole	GC/MS	SW-846:8270	1	–	–
1,2,4,5-Tetrachlorobenzene	GC/MS	SW-846:8270	1	20	24[e]
2,3,4,6-Tetrachlorophenol	GC/MS	SW-846:8270	2	2,000	2,400[e]
o-Toluidine	GC/MS	SW-846:8270	1	–	3[e]
1,2,4-Trichlorobenzene*	GC/MS	SW-846:8270	1	2,000	105[e]
2,4,5-Trichlorophenol	GC/MS	SW-846:8270	1	8,000	[d]
2,4,6-Trichlorophenol	GC/MS	SW-846:8270	1	40	63[e]
DIOXINS AND FURANS					
2,3,7,8-Tetrachlorodibenzo-p-dioxin	GC/MS	SW-846:8280	0.00008	–	0.000005[e]
Tetrachlorodibenzo-p-dioxins	GC/MS	SW-846:8280	0.00008	–	0.000005[e]
Tetrachlorodibenzo-p-furans	GC/MS	SW-846:8280	0.00006	–	0.000005[e]
Pentachlorodibenzo-p-dioxins	GC/MS	SW-846:8280	0.0002	–	0.000005[e]

Table 3-2

(Continued)

Parameter	Analysis		Reporting Limits[a]	Health-Based Levels (Soil)	
	Technique	Method (Soil)	Soil (mg/Kg)	RCRA[b] (mg/Kg)	Calculated[c] (mg/Kg)
Pentachlorodibenzo-p-furans	GC/MS	SW-846:8280	0.00008	–	0.000005[e]
Hexachlorodibenzo-p-dioxins	GC/MS	SW-846:8280	0.0002	0.0001	–
Hexachlorodibenzo-p-furans	GC/MS	SW-846:8280	0.0001	–	0.000005[e]
GENERAL					
Cyanide*	Colorimetric	SW-846:9012	1	2,000	1,600[e]
Sulfide*	Titrametric	SW-846:9030	50	–	–
Total Organic Carbon*	IR	SW-846:9060	2,000	–	–

[a] Method Detection Limit is the minimum concentration of a substance that can be measured and reported. Method Detection Limits are highly matrix dependent and may not always be achievable.

[b] Values taken from "Draft Preliminary Standards for RCRA Risk Assessment," Appendix 3, EPA Region VI, 20 February 1991; and 27 July 1990 Fed. Reg., "Corrective Action for SWMUs at Hazardous Waste Management Facilities; Proposed Rule," Appendix A.

[c] Values calculated using the reference dose (RfD) or slope factor (SF) with EPA's method for calculating action levels (Appendix 4 of "Draft Preliminary Standards for RCRA Risk Assessment," EPA Region VI, 20 February 1991; and 27 July 1990 Fed. Reg., "Corrective Action for SWMUs at Hazardous Waste Management Facilities," Appendix E. The source of the RfDs and SFs used in the calculation are designated by a footnote for each HBL value in this column.

[d] Values calculated using a RfD or SF are equivalent to the "RCRA" values.

[e] RfD or SF used in calculation of HBL from Health Effects Assessment Summary Tables, FY-1991 Annual, EPA, Washington D.C., January, 1991.

[f] RfD or SF used in calculation of HBL from Integrated Risk Information Service (IRIS), EPA, January, 1992.

[g] SF used in calculation of HBL calculated using method in Comparative Potency Approach for Estimating the Cancer RiskAssociated with Exposure to Mixtures of Polycyclic Aromatic Hydrocarbons, Interim Final, ICF-Clement Associates, Fairfax, Virginia, April 1, 1988.

[h] SF derived using methodology in "Docket Report on Health-Based Levels and Solubitities Used in the Evaluation of Delisting Petitions, Submitted Under 40 CFR Parts 260.20 and 260.22." Science Applications International Corporation, McLean, Virginia, November, 1989.

* Denotes chemicals previously detected at the Holloman AFB sewage lagoons.

IR = Infrared Spectrometry
ICPES = Inductively Coupled Plasma Emission Spectroscopy
GFAA = Graphite Furnace Atomic Absorption
CVAA = Cold Vapor Atomic Absorption
GC/MS = Gas Chromatography/Mass Spectrometry
SW-846 = Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, U.S. EPA, Office of Solid Waste and Emergency Response, November 1986, third edition.
EPA = Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020.
N/A = Not Applicable
IC = Ion Chromatography
GC/FPD = Gas Chromatography/Flame Photometric Detector
GC/ECD = Gas Chromatography/Electron Capture Detector
HML = California Department of Health Services; Hazardous Materials Laboratory

calibration range. For non-target analytes on GC/MS and GC analyses, dilutions will be performed when non-target analyte response interferes with target analyte response, and to achieve an internal standard response of approximately 20 percent of the maximum peak response. When samples are diluted after an initial undiluted analysis, data for target analytes with response within the calibration range for the undiluted analysis will be collected and reported with target analytes from diluted analyses, except in cases where method detection limits listed in the table exceed RCRA limits as previously discussed. For these compounds, high method detection limits will not result in unusable data. If natural sample detection limits exceed RCRA limits for any other compounds, the analytical laboratory must document what prompted the higher detection limits and the maximum concentrations that were allowable on the calibration curve. This level of effort is required on a sample-by-sample basis and may not be applied to batches of samples.

QC procedures used as an on-going control (i.e., feedback mechanism) for the analytical system are presented in Section 7, Table 7-2. For each method, control procedures, acceptance criteria and corrective actions are detailed. Data for each control procedure will be evaluated against these acceptance criteria to prove the analytical system was in control during sample analyses and thus, results are defensible. This table is a summary of information from SW-846 Chapter One and Method 8000 and individual methods. As such, it is intended to be used as a guide.

3.2 Field Duplicate Samples

Field duplicate samples will be analyzed for the purpose of assessing precision, including variability associated with both the laboratory analysis and the sample collection process. Duplicate samples will be collected at a minimum frequency of 5 percent of all field samples collected for both external quality assurance (QA) and internal quality control (QC) samples. The QA samples will be sent to the USACE Missouri River Division (MRD) laboratory for analysis. The QA field duplicates will be assigned the same sample

number as the initial sample so that results may be used as an independent assessment of combined sampling and analytical variability.

3.3 Definitions of Laboratory Quality Control Samples

The following quality control samples will be used to control and assess data quality:

- System blank - deionized water analyzed after calibration to assess system contamination.
- Reagent blank - reagent water taken through the digestion/extraction process as though it were an actual sample.
- Calibration check sample - a standard used to verify instrument calibration.
- QC check sample (QCCS) - known concentration of alternate-source reference materials spiked into an aliquot of deionized water. For dioxins and furans, the QCCS will be a second, independently prepared spike solution. This sample is taken through the digestion/extraction process as though it were an actual sample. The purpose of a QCCS analysis is to determine whether failure to meet QC acceptance criteria for a matrix spike is due to matrix interference in the sample, or to an out-of-control condition associated with the analytical system.
- Method spike - known concentration of standard materials (i.e., materials used for calibration purposes) spiked onto glass wool or for dioxins and furans, sodium sulfate (Na_2SO_4) (clean solid matrices). This sample is processed (i.e., extracted, digested) like all natural matrix samples. The purpose of a method spike, or blank spike, is to determine if the analytical system is in control, and capable, per method specifications.

- Matrix spike/matrix spike duplicates (MS/MSD) - splits from field samples spiked with known concentrations of reference materials and taken through the entire digestion/extraction process. The matrix spike allows the laboratory to assess the efficiency of extraction, accuracy of the analysis, and possible matrix effects. Analysis of a duplicate matrix spike, another aliquot of the sample spiked at the same concentration as the MS, allows the laboratory to assess precision at known concentrations.

- Surrogate spikes - For GC and GC/MS analyses, identifiable compounds not present in the sample matrix are added to every field sample.

- Duplicate analyses - samples split in the lab and treated as two independent samples. For Holloman AFB, approximately 5 percent of each sample batch will be analyzed in duplicate for sulfide and total organic carbon.

- ICPES interference check sample - an ICPES QC check sample which contains interferents and analyte concentrations at levels specified by EPA. Analyzed at the beginning and end of each sample analysis sequence, results are used to verify inter-element and background correction factors.

4.0 PROJECT ORGANIZATION AND FUNCTIONAL AREA RESPONSIBILITIES

Radian's project team for the Holloman AFB project will be composed of a Program Manager, a Project Director, and a Quality Assurance Coordinator. Roles and responsibilities of key personnel are discussed below.

4.1 Roles and Responsibilities

Mr. Wallace Hise will serve as the Program Manager for this project. In this role, Mr. Hise will have the overall responsibility, authority, and accountability for the project. He will function as the primary interface between the Corps of Engineers, Radian management, subcontractor management, and the project team. In executing these duties, he will:

- Have responsibility for meeting all contractual requirements for the task;
- Administer and supervise all contractual requirements for the task;
- Direct formulation of work plans in accordance with client directions;
- Have responsibility for assuring that required staffing levels and technical expertise are provided;
- Keep the USACE Project Manager informed on all aspects of the program including expenditures, progress, problems, and recommended solutions;
- Be available to the Radian Project Director for action on any problem requiring additional management or technical support;
- Keep Radian management informed on all matters relating to the program; and
- Review technical project outputs prior to issue.

Ms. Cris Hine will serve as the Project Director for this project. In this capacity, she will be responsible for organizing and directing the technical activities of the project and for reporting the results of these activities. She will have day-to-day interaction with the Technical Staff. In the execution of these duties, Ms. Hine will:

- Establish technical objectives and assist the Program Manager in the preparation and review of work plans;
- Be responsible for responding to work plan revisions;
- Advise the Program Manager of technical progress, expenditures, program needs, potential problems, and recommended solutions;
- Assure technical quality of reports, memoranda, and other communications through review of results;
- Maintain contact with the USACE Project Manager in areas that require decisions on technical matters; and,
- Confer with the Radian Program Manager in the selection of supporting technical staff and be responsible for reviewing their performance through the program.

Mrs. Jean Youngerman will serve as the Quality Assurance Coordinator (QAC). In this role, she will be responsible for development and execution of QA activities in all phases of the project, including test plan design, execution, data reduction, and reporting. Her responsibilities will include:

- Coordinating any external QA audit activities requested by the USACE;
- Serving as an in-house consultant to the Project Director and Task Leaders in defining data quality goals or requirements and in development of a project-specific, internal quality control system which is responsive to these goals;

- Coordinating preparation of the project quality assurance reports that document the project-specific policies, organization, objectives, functional activities, and specific QA and QC procedures and activities designed to achieve data quality goals or requirements;

- Providing independent review of the project approach, methods, and experimental design;

- Providing the mechanism whereby quality assurance problems may be brought to the immediate attention of the Project Director and Program Manager or, if warranted, may be brought directly to the attention of the Vice President of the technical staff through the Quality Assurance Director, for implementation of corrective action; and

- Documenting the results of all QA/QC activities in reports to Radian management and to clients.

Subcontractor staff managers assume ultimate responsibility for all operations in their subcontracts. Subcontractors and key personnel are discussed below.

4.2 Laboratory Qualifications

Radian laboratory qualifications are summarized in Table 4-1. All Holloman AFB samples will be analyzed by Radian Analytical Services. Radian's analytical laboratory client services representative will be Mr. Steve Gibson. Mr. Gibson will have ultimate responsibility for all analyses performed at Radian's laboratories.

4.3 Subcontractor Qualifications

4.3.1 Drilling

Radian has subcontracted Southwest Engineering, Inc. (SEI), Las Cruces, NM to provide all drilling services. SEI is a Small Business and a licensed New Mexico

Table 4-1

Laboratory Certifications and Approvals
Radian Corporation, Austin, Texas

Federal	
1.	U.S. EPA Regions IV, V, VI, IX for CLP Protocol; Full Inorganics
2.	U.S. EPA EMSL WS Drinking Water PE Participant
3.	U.S. EPA EMSL WP Waste Water
4.	U.S. EPA OSW PE Participant
5.	U.S. EPA Participant in the National Pesticide Survey
6.	U.S. Army Corps of Engineers; Validation
7.	U.S. Navy NEESA Approval
8.	U.S. Army; Martin Marietta for Hazwrap Programs
9.	U.S. Air Force; OEHL Audit and Approval
10.	U.S. Department of Agriculture; Import of Overseas Samples
State	
1.	New York DOH
2.	New Jersey DEP
3.	California DOHS
4.	Texas (TWC) Approval
5.	Oklahoma WRB
6.	South Carolina DOH/EC
7.	Kansas DHE
8.	Pennsylvania DER
9.	North Carolina DEH & NR
10.	Wisconsin DNR
Industrial Hygiene	
1.	AIHA Certification

water-well driller. Mr. Paul Pompeo will be assigned to this project. He is responsible to complete the work as stated in the USACE Scope of Services (SOS) and Radian's Statement of Work (SOW) for drilling services.

4.3.2 Sludge Sampling

The sludge and soil sampling at the ponds and lakes will be completed with the help of Quaternary Resource Investigations, Inc. (QRI), Baton Rouge, LA. QRI is a Small Business. Mr. Scott Elmer will be assigned to this project and will be responsible for following all sampling protocols outlined in the USACE SOS and Radian's SOW for sampling for this delivery order.

4.3.3 Survey Activities

The surveying of sludge and soil sampling locations, soil borings, and monitor wells will be completed by Moy Surveying, Las Cruces, NM. Moy Surveying is a Small Disadvantaged Business and is registered in the State of New Mexico. Mr. Jorge Moy will be asssigned to this project and will be responsible for following all survey protocols outlined in the USACE SOS and Radian's SOW for this delivery order.

5.0 FIELD ACTIVITIES

In order to achieve the objectives of this program, Radian will perform a series of field tasks at Holloman AFB. The activities were developed according to the USACE Scope of Services for Holloman AFB (23 December 1991) and are discussed in this section.

5.1 Sludge and Soil Samples

5.1.1 Sample Locations

The sample locations and intervals proposed in this CDAP are based on a preliminary survey of the sewage lagoons and lakes conducted by Radian in October 1991. The sample distribution within each lagoon was chosen such that a sample will be collected near each overflow to an adjacent lagoon, and the remaining samples will be distributed across the impoundment to provide the maximum information possible given 1) the limited number of samples to be collected, and 2) the relative size of the impoundments. Based on the preliminary survey, this approach is considered reasonable because no sludge mounds or "hot spots" are anticipated in the lagoons downstream of Ponds A and B.

Both sludge and underlying soil samples will be collected from Ponds C, E, F, G and Lake Holloman. In Pond D, Lake Stinky, and one Ditch and Overflow (DT-01) location only soil samples will be collected. In addition, soil samples will be collected from a former overflow from Pond D, and the ditch leading from the Pond G outfall to Lake Holloman. For each pond or lake, a sample location will be within 200 ft of the influent and effluent points. Figures 5-1, 5-2, and 5-3 illustrate the sample location and sample interval requirements for each core.

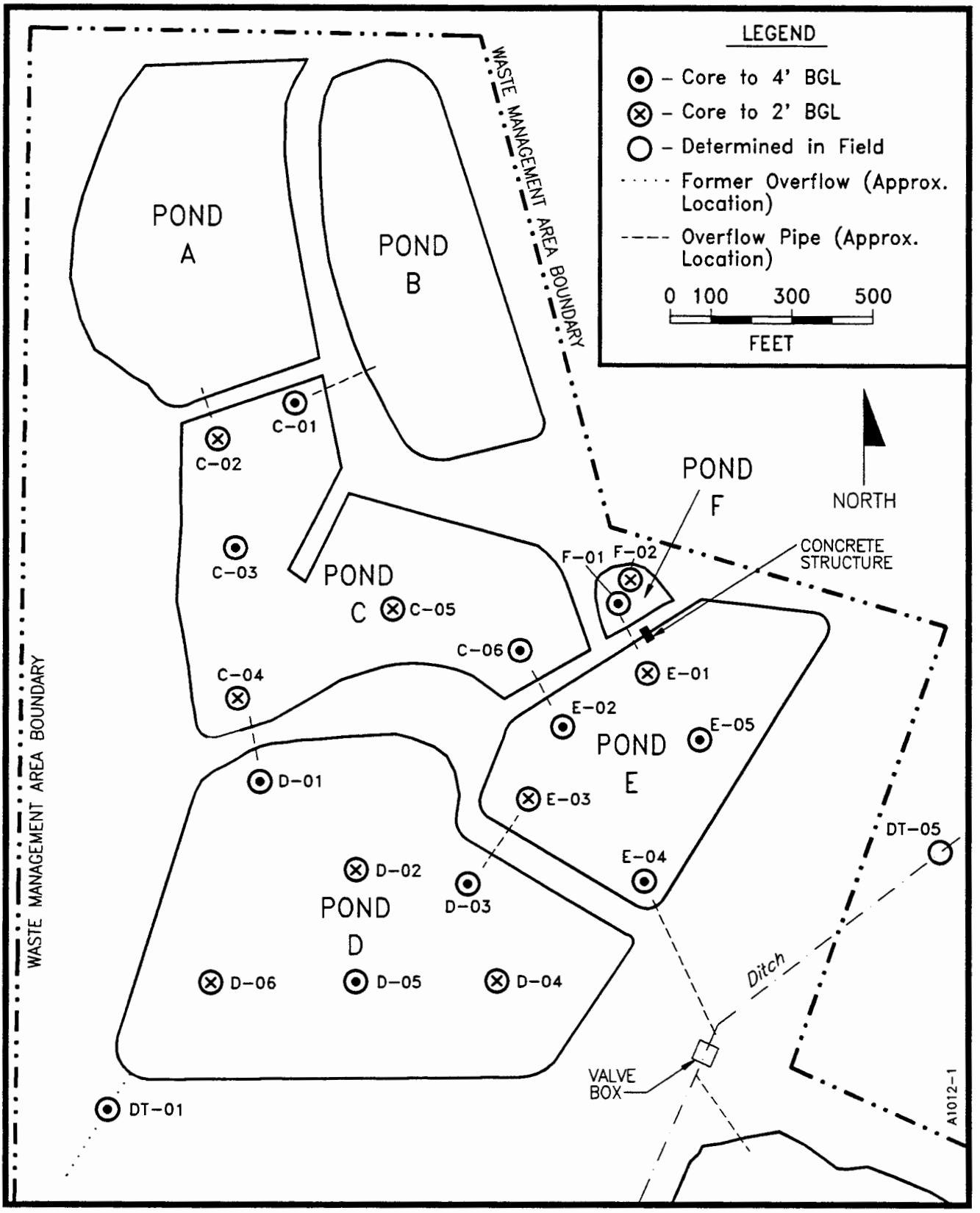


Figure 5-1. Sample Locations--Ponds C, D, E, and F

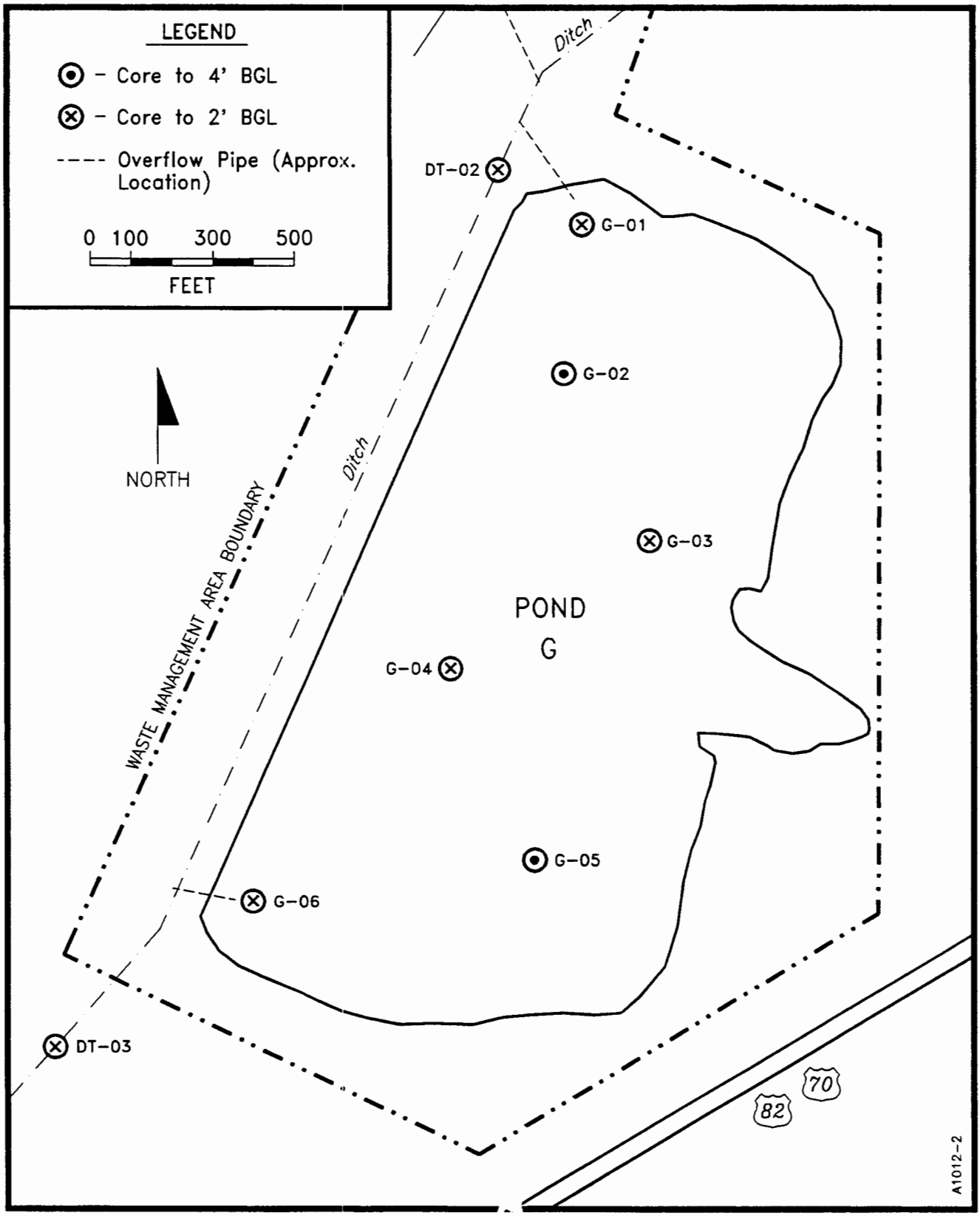


Figure 5-2. Sample Locations--Pond G

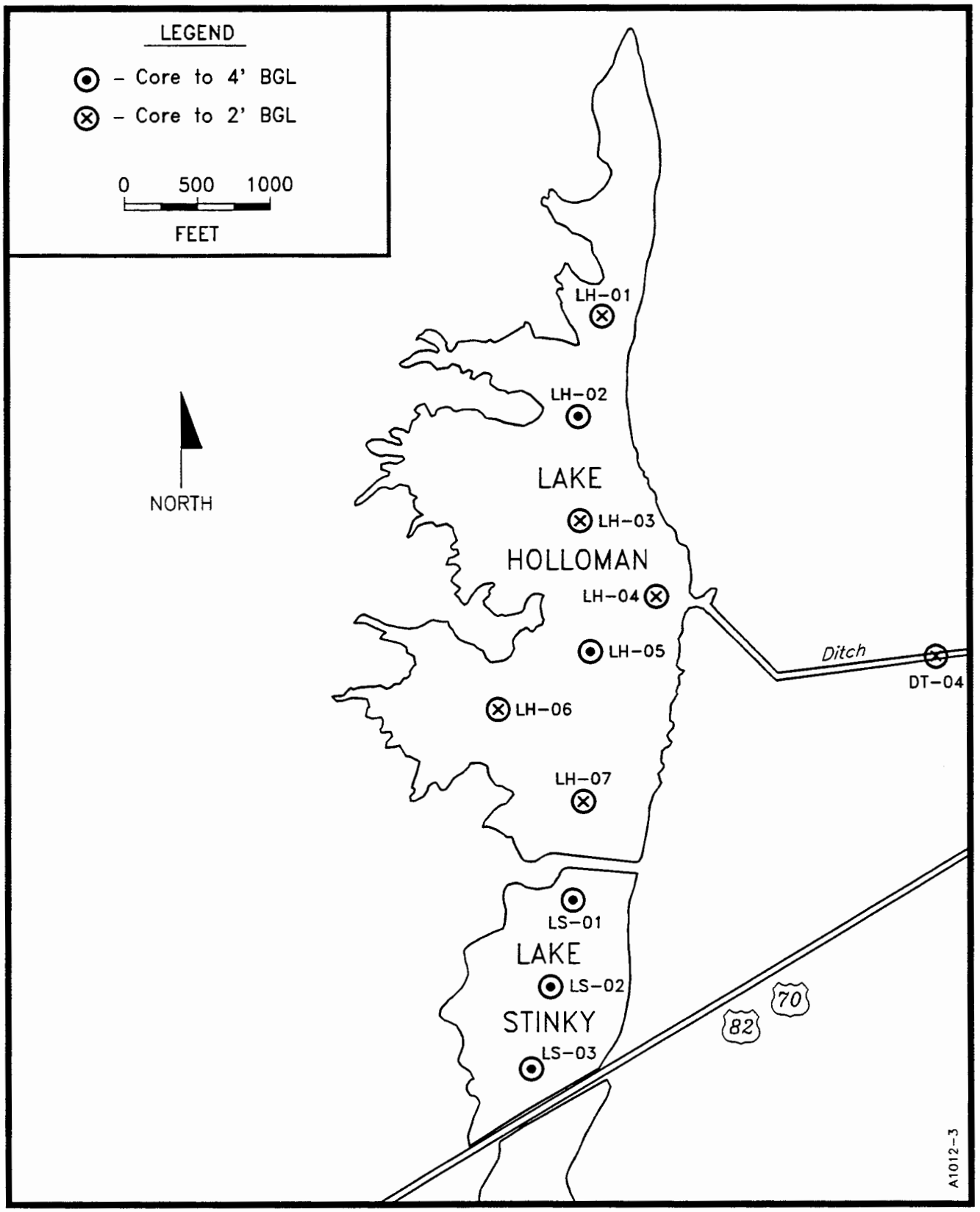


Figure 5-3. Sample Locations--Lakes Holloman and Stinky

5.1.2 Sampling Procedures

Sludge and underlying soil samples will be collected from a floating raft using either standard stainless steel split-spoons (ASTM Method D-1586), or a method known as "vibracoring". The Vibracore® technique obtains a continuous undisturbed core (consisting of sludge and underlying soil) to depths up to 20 ft below ground level (BGL). Either a thin-walled aluminum or lexan sampling tube will be used with the Vibracore® technique to collect the sample. Using either technique, the samples of the sludge and soil will be collected from the intervals specified in Table 5-1. Figures 5-1, 5-2 and 5-3 illustrate the sample location and interval requirements for each core.

After the samples are collected, they will be extracted from the core and handled with decontaminated stainless steel sampling equipment. Samples for volatile organics will be collected first (to minimize loss of volatile compounds) for each matrix, as appropriate, at the proposed sample intervals. After the volatile organic samples are collected, each sample interval will be placed in a separate decontaminated stainless steel sample bowl and homogenized prior to being containerized. These samples will be analyzed for the parameters outlined in Section 5.3. It is likely that some sample locations will require more than one sludge "core" to provide sufficient volume for all analyses. In addition to the parameters outlined in Section 5.3, two total organic carbon (TOC) soil samples will be collected from each pond. The samples will be collected from the 0 to 2 ft and 2 to 4 ft intervals (where 0 ft is the sludge/soil interface) from the same core. Visual, physical, and other characteristics of the soil cores will be recorded.

Each core will be backfilled with cement grout upon completion. The cement grout will consist of a mixture of one bag of Portland cement (ASTM C 150), 7 gallons of water and 3 to 5 lbs of bentonite powder.

Table 5-1

Sample Intervals for Sludge and Soil Sample Locations

		Intervals		
Site	Location	Sludge	0-2 ft	2-4 ft
Pond C	C-01	X	X	X
	C-02	X	X	
	C-03	X	X	X
	C-04	X	X	
	C-05	X	X	
	C-06	X	X	X
Pond D	D-01		X	X
	D-02		X	
	D-03		X	X
	D-04		X	
	D-05		X	X
	D-06		X	
Pond E	E-01	X	X	
	E-02	X	X	X
	E-03	X	X	
	E-04	X	X	X
	E-05	X	X	X
Pond F	F-01	X	X	X
	F-02	X	X	
Pond G	G-01	X	X	
	G-02	X	X	X
	G-03	X	X	

Table 5-1

(Continued)

		Intervals		
Site	Location	Sludge	0-2 ft	2-4 ft
	G-04	X	X	
	G-05	X	X	X
	G-06	X	X	
Lake Holloman	LH-01	X	X	
	LH-02	X	X	X
	LH-03	X	X	
	LH-04	X	X	
	LH-05	X	X	X
	LH-06	X	X	
	LH-07	X	X	
Lake Stinky	LS-01		X	X
	LS-02		X	X
	LS-03		X	X
Ditch and Overflow	DT-01*		X	X
	DT-02	X	X	
	DT-03	X	X	
	DT-04	X	X	
	DT-05	DIF	DIF	DIF
	Total Samples	30	40	18

*No sludge was encountered at the overflow location (DT-01); therefore, samples will be collected from the 0-2 and 2-4 ft intervals.

DIF = The two sample intervals will be determined in field.

5.2 Soil Borings

5.2.1 Locations

Soil samples will be collected from 2 borings located outside of the ponds, lakes, and ditches. As illustrated in Figure 5-4, one boring will be drilled in a hydrogeologically upgradient location near monitor well MW-1, and the second boring will be drilled in a hydrogeologically downgradient location near monitor well MW-3.

5.2.2 Sampling Procedures

In each of the 2 soil borings, samples will be collected at 5 ft intervals to 25 ft BGL. At each of the 5 intervals, a sample will be collected and analyzed in the laboratory for TOC. One of the 5 sample intervals will be analyzed for the additional parameters specified in Section 5.3. The sample analyzed for the additional parameters will be selected from the same vertical horizon (elevation) as the soil samples collected from the ponds.

Soil samples will be obtained using a stainless steel split-spoon sampler and handled using stainless steel sampling equipment. Samples for volatile organics will be collected first to minimize loss of volatile compounds. The samples for the other analyses will be collected from the selected interval, and homogenized prior to being containerized. After samples are collected, visual, physical, and other characteristics will be recorded on boring logs using the Unified Soil Classification System.

Each boring will be backfilled with cement grout upon completion. The cement grout will consist of a mixture of one bag of Portland cement (ASTM C 150), 7

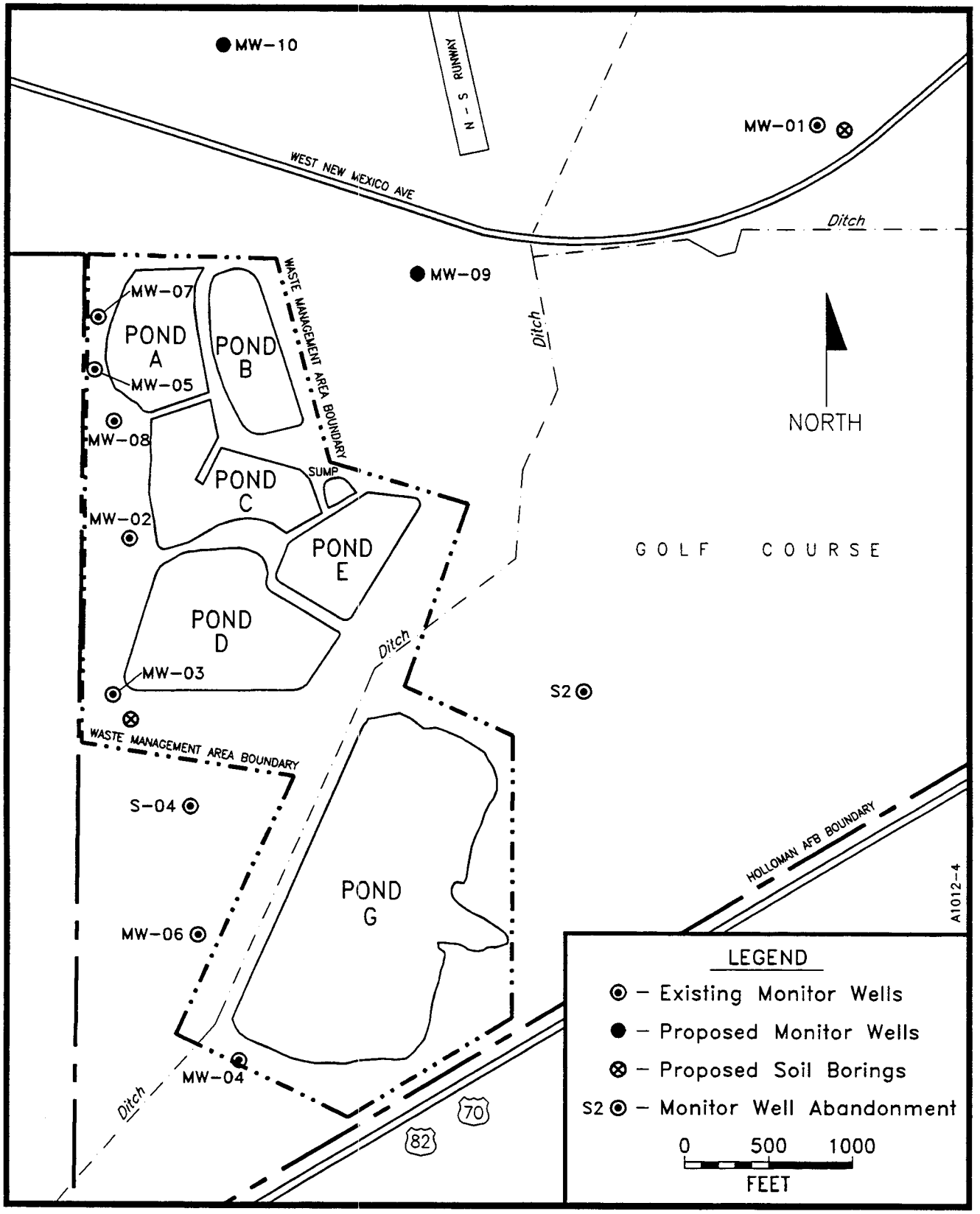


Figure 5-4. Locations of Proposed Borings, Proposed Upgradient Monitor Wells, and Monitor Well S2

gallons of water and 3 to 5 lbs of bentonite powder. Grout will be poured through the hollow-stem auger which will extend to at least 10 ft from the bottom of the boring. Grout will be poured until undiluted grout flows from the top of the boring, then the augers will be raised. This will continue until the augers are removed and the boring is filled with grout.

5.3 Analyses

5.3.1 Normal Samples

Table 5-2 presents a summary of the analyses to be conducted on sludge and soil samples. All samples will be analyzed for Appendix IX constituents (reference 40 CFR, Part 264). Selected soil samples will also be analyzed for TOC. Sample preparation and chemical analysis will be performed according to procedures published in Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846 (USEPA, 3rd edition, September 1986). All normal and QC samples will be analyzed by the Radian Analytical Services in Austin, Texas.

5.3.2 Quality Assurance/Quality Control Samples

A field QA/QC program will be used to ensure that data quality objectives are met. Sample collection error will be controlled through the use of standard sample collection methods and field logbooks. Natural matrix errors will be estimated by standard QA/QC methods such as matrix spikes, field duplicates, and trip blanks. The following paragraphs discuss the field QA/QC samples for analytical soil samples, and their collection frequency and procedures.

Table 5-2

Number and Type of Analytical Sludge and Soil Samples

Interval	Pond C	Pond D	Pond E	Pond F	Pond G	Lake Holloman	Lake Stinky	Pond G to LH Ditch	Pond D Overflow	Borings	Total Normal Samples
Sludge	6		5	2	6	7		4			30
0-2 ft	6	6	5	2	6	7	3	4	1		40
2-4 ft	3	3	3	1	2	2	3		1		18
Method	**Number of Analyses**										
SW-846:6010	15	9	13	5	14	16	6	8	2	2	90
SW-846:7060	15	9	13	5	14	16	6	8	2	2	90
SW-846:7421	15	9	13	5	14	16	6	8	2	2	90
SW-846:7471	15	9	13	5	14	16	6	8	2	2	90
SW-846:7740	15	9	13	5	14	16	6	8	2	2	90
SW-846:7841	15	9	13	5	14	16	6	8	2	2	90
SW-846:8080	15	9	13	5	14	16	6	8	2	2	90
SW-846:8140	15	9	13	5	14	16	6	8	2	2	90
SW-846:8150	15	9	13	5	14	16	6	8	2	2	90
SW-846:8240[1]	15	9	13	5	14	16	6	8	2	2	90
SW-846:8270	15	9	13	5	14	16	6	8	2	2	90
SW-846:8280[1]	15	9	13	5	14	16	6	8	2	2	90
SW-846:9012	15	9	13	5	14	16	6	8	2	2	90
SW-846:9030	15	9	13	5	14	16	6	8	2	2	90
SW-846:9060	2	2	2	2	2	2	2	0	0	10	24

Table 5-2

(Continued)

	QC Field Duplicate	QC Matrix Spike	QC Matrix Spike Duplicate	QA Field Duplicate	Total Analyses
Method	**Number of Analyses**				
SW-846:6010	5	5	5	5	110
SW-846:7060	5	5	5	5	110
SW-846:7421	5	5	5	5	110
SW-846:7471	5	5	5	5	110
SW-846:7740	5	5	5	5	110
SW-846:7841	5	5	5	5	110
SW-846:8080	5	5	5	5	110
SW-846:8140	5	5	5	5	110
SW-846:8150	5	5	5	5	110
SW-846:8240[1]	5	5	5	5	110
SW-846:8270	5	5	5	5	110
SW-846:8280[2]	5	0	0	5	110
SW-846:9012	5	5	5	5	110
SW-846:9030	5	5	5	5	110
SW-846:9060	1	1	1	1	28

[1]One trip blank will be sent with each ice chest containing volatile organic samples.
[2]Method SW-846:8280 does not include MS/MSD analyses. However, 5 percent (5 samples) will be analyzed in duplicate in the lab. Bottles need to be labeled appropriately as "duplicate sample".
QC are project specified and will be sent to Radian Analytical Services.
QA are USACE specified and will be sent to MRD Laboratory.

QA and QC Split Samples - QA and QC split samples (duplicates) will be collected for all analyses at a rate of 5 percent for each analyte. The soil will be homogenized and divided equally among all containers for both standard and duplicate samples.

Matrix Spike and Matrix Spike Duplicate (MS/MSD) - QC MS/MSD samples will be collected at a rate of 5 percent for each analysis. Additional volume may be necessary for sludge samples.

Trip Blanks - Trip blanks will consist of 40 mL VOA vials filled by the laboratory with Type I reagent grade water. Trip blanks will accompany all ice chests that contain volatile organic samples during both sampling activities and shipping procedures. No trip blanks will be sent with QA samples to the MRD laboratory.

5.4 Sample Containers, Preservation, and Holding Times

The sample containers, preservation measures, and holding times for the soil analyses to be conducted are summarized in Table 5-3. All containers used for chemical analyses will be pre-cleaned by the supplier, I-Chem or Eagle-Picher, in accordance with EPA protocol. The sample label will be affixed to the bottle, and labeled with the field sample number and the other required information in indelible ink (see Section 6.0). All soil and sludge samples collected for chemical analysis will be chilled to approximately 4°C with regular ice in a plastic bag during collection and shipment. The samples will be stored upright in a durable ice chest. Sufficient packing material (e.g., vermiculite) will be used to separate the bottles, filling any intervening voids.

Table 5-3

Summary of Sample Containers, Preservation, and Holding Times

Reference Method	Parameter	Container Type, No., and Volume[a]	Preservation and Storage Requirements	Maximum Holding Time (Preparation)	Maximum Holding Time (Analysis)
SW-846:6010	Ag, Ba, Be, Cd, Co, Cr, Cu, Ni, Sb, Sn, Va, Zn	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	6 months
SW-846:7060	As	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	6 months
SW-846:7421	Pb	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	6 months
SW-846:7471	Hg	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	28 days
SW-846:7740	Se	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	6 months
SW-846:7841	Tl	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	6 months
SW-846:8080	Organochlorine Pesticides/PCBs	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	14 days	40 days
SW-846:8140	Organophosphorus Pesticides	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	14 days	40 days
SW-846:8150	Chlorinated Herbicides	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	14 days	40 days
SW-846:8240	Volatile Organics	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/A	14 days
SW-846:8270	Semivolatile Organics Compounds	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	14 days	40 days
SW-846:8280	Dioxins and furans	(1) 250 mL glass, Teflon-lined cap	Refrigerated at 4°C	30 days	45 days
SW-846:9012	Cyanide	(1) 500 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	14 days
SW-846:9030	Sulfide	(1) 500 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/S	21 days
SW-846:9060	Total Organic Carbon	(1) 500 mL glass, Teflon-lined cap	Refrigerated at 4°C	N/A	28 days

[a]Samples may be combined in the specified container as follows:

8270/8080 in 500 mL glass.
8140/8150 in 500 mL glass.
Metals, cyanide, sulfide, TOC in 500 mL glass.
8280, (PCDDs and PCDFs) in 250 mL glass.
8240 in 250 mL glass.

5.5 Monitor Well Installation Plan

Two new upgradient monitor wells will be installed to provide additional background and hydrogeologic data. These monitor wells will be installed at the locations illustrated in Figure 5-4. Existing monitor well S-2, located east of the lagoons (Figure 5-4), will be abandoned during this investigation because it is not located upgradient of the lagoons and, therefore, will no longer be included in the RCRA monitoring network.

5.5.1 Drilling Procedures

All drilling will be accomplished using the hollow-stem auger method. This method performs well in unconsolidated sediments, allows the rig to operate without the use of drilling fluids, and permits easy collection of relatively undisturbed formation samples. For the depths and geology involved, this drilling method will provide fast and efficient performance. The hollow-stem auger rig will use 5-ft sections of at least 8-in. outer diameter and 3.75-in. inner diameter hollow-stem auger flight. The boring diameter will be such that there will be at least 2 inches of annular space between the formation exposed at the boring wall and the outside diameter of the centered well casing.

For the purpose of describing subsurface geology, soil samples will be collected continuously to the total depth drilled for each boring at a site. All lithological descriptions will be made by the geologist on site and recorded on the form shown in Figure 5-5. The samples will be visually classified according to the Unified Soil Classification System, and the completed boring logs will be included in the final report.

5.5.2 Monitor Well Installation and Construction

Each monitor well will be installed to provide representative water samples from the uppermost water bearing zone. The exact depths of the wells and the screened

DRILLING LOG

HOLE NO.

G1773

1. COMPANY NAME RADIAN CORPORATION	2. DRILLING SUBCONTRACTOR SOUTHWEST ENG INC
SHEET 1 OF SHEETS	
3. PROJECT HOLLOMAN AFB	4. LOCATION
5. NAME OF DRILLER	6. MANUFACTURER'S DESIGNATION OF DRILL
7. SIZES AND TYPES OF DRILLING AND SAMPLING EQUIPMENT	8. HOLE LOCATION
	9. SURFACE ELEVATION
	10. DATE STARTED / 11. DATE COMPLETED
12. OVERBURDEN THICKNESS	15. DEPTH GROUNDWATER ENCOUNTERED
13. DEPTH DRILLED INTO ROCK	16. DEPTH TO WATER AND ELAPSED TIME AFTER DRILLING COMPLETED
14. TOTAL DEPTH OF HOLE	17. OTHER WATER LEVEL MEASUREMENTS (SPECIFY)

18. GEOTECHNICAL SAMPLES	DISTURBED	UNDISTURBED	19. TOTAL NUMBER OF CORE BOXES

20. SAMPLES FOR CHEMICAL ANALYSIS	VOC	METALS	OTHER (SPECIFY)	OTHER (SPECIFY)	OTHER (SPECIFY)	21. TOTAL CORE RECOVERY %

22. DEPOSITION OF HOLE	BACKFILLED	MONITORING WELL	OTHER (SPECIFY)	23. SIGNATURE OF INSPECTOR

ELEV. a	DEPTH b	DESCRIPTION OF MATERIALS c	FIELD SCREENING RESULTS d	GEOTECH SAMPLE OR CORE BOX NO. e	ANALYTICAL SAMPLE NO. f	BLOW COUNTS g	REMARKS h

PROJECT

HOLE NO.

Figure 5-5. USACE Boring Log

DRILLING LOG

HOLE NO.

61774

PROJECT HOLLOMAN AFB RI/FS

INSPECTOR

SHEET OF SHEETS

ELEV. a	DEPTH b	DESCRIPTION OF MATERIALS c	FIELD SCREENING RESULTS d	GEOTECH SAMPLE OR CORE BOX NO. e	ANALYTICAL SAMPLE NO. f	BLOW COUNTS g	REMARKS h

PROJECT

HOLE NO.

Figure 5-5. (Continued)

intervals will be decided by the on-site geologist. The depths and construction will depend on the geology and groundwater conditions encountered during drilling.

5.5.2.1 Well Screen and Casing

The screen construction will be 2-in. diameter, 0.010-in. slotted, Schedule 40 PVC continuous wrap design which meets ASTM F 480-81. The material lengths selected will be based on site-specific groundwater and geologic conditions encountered (a 10-ft screen is anticipated). The screen will be joined to a 2-in. diameter, Schedule 40 PVC (which also meets ASTM F 480-81), flush threaded casing. The casing will extend from the top of the screen to at least 2 ft above ground surface. Since all well screen and casing materials will be centered in the borehole through the use of the hollow-stem auger drilling method, centralizers will not be necessary for the alignment of the well. Prior to installation, the casing and screen sections will be thoroughly washed with potable water using a high-temperature, high-pressure sprayer. No solvent PVC or other glue will be used in the construction of the wells. A typical monitor well construction schematic is shown in Figure 5-6. A sample form for recording well completion data in the field is shown in Figure 5-7. Monitor well completion diagrams will be submitted in the final report.

5.5.2.2 Sand Pack

After the casing and screen have been installed for each well, a sand pack will be emplaced in the annular space around the well. The sand pack will consist of washed and bagged rounded sand with a 16-40 gradation. The pack will be poured between the well casing and inside wall of the hollow-stem auger. The augers will be retracted slowly while the sand is being added. Frequent measurements of the sand pack will be made with a weighted tape to ensure that bridging has not occurred and to determine the depth of the sand pack in relation to the screened interval. The sand pack will extend to approximately 2 ft above the well screen.

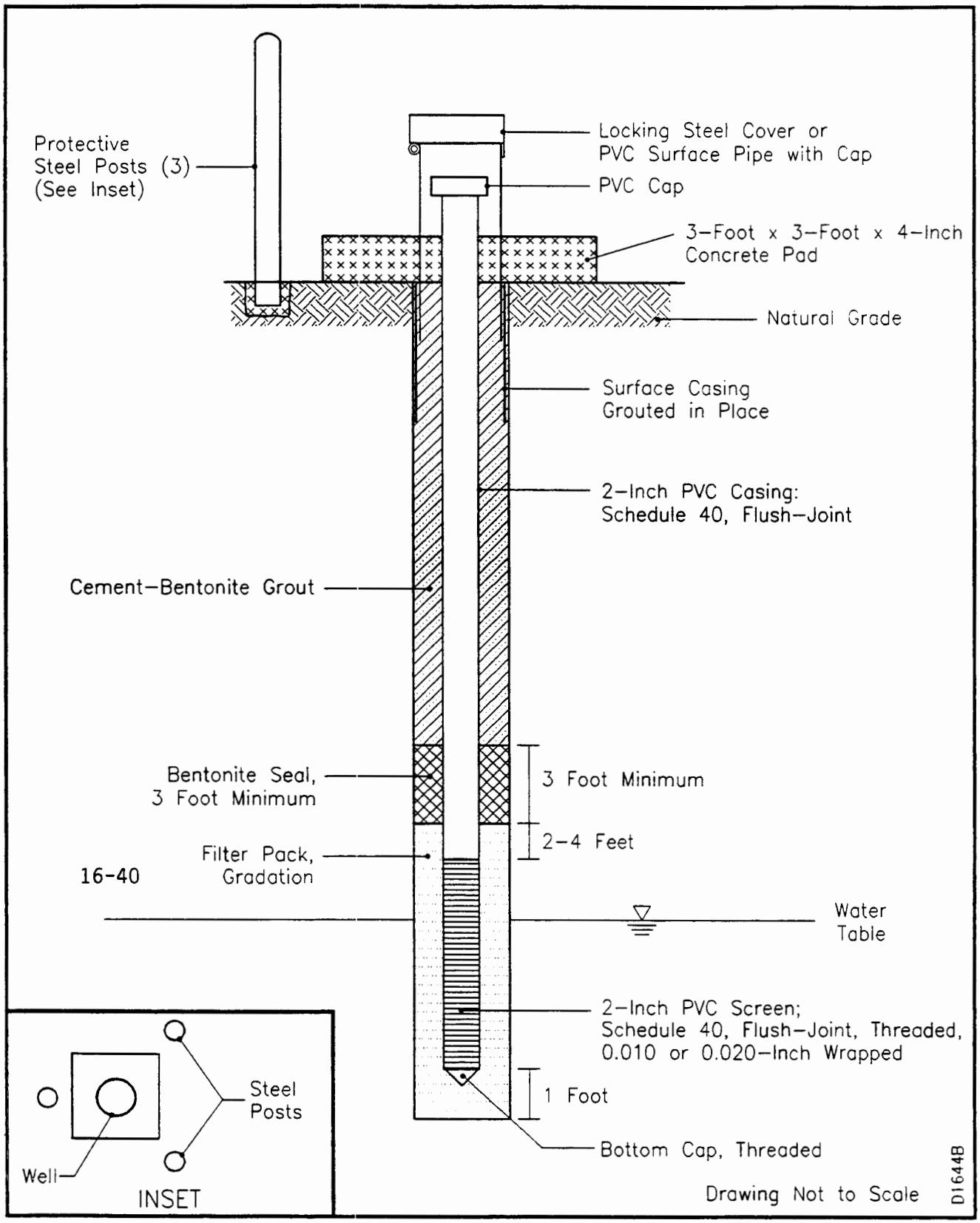
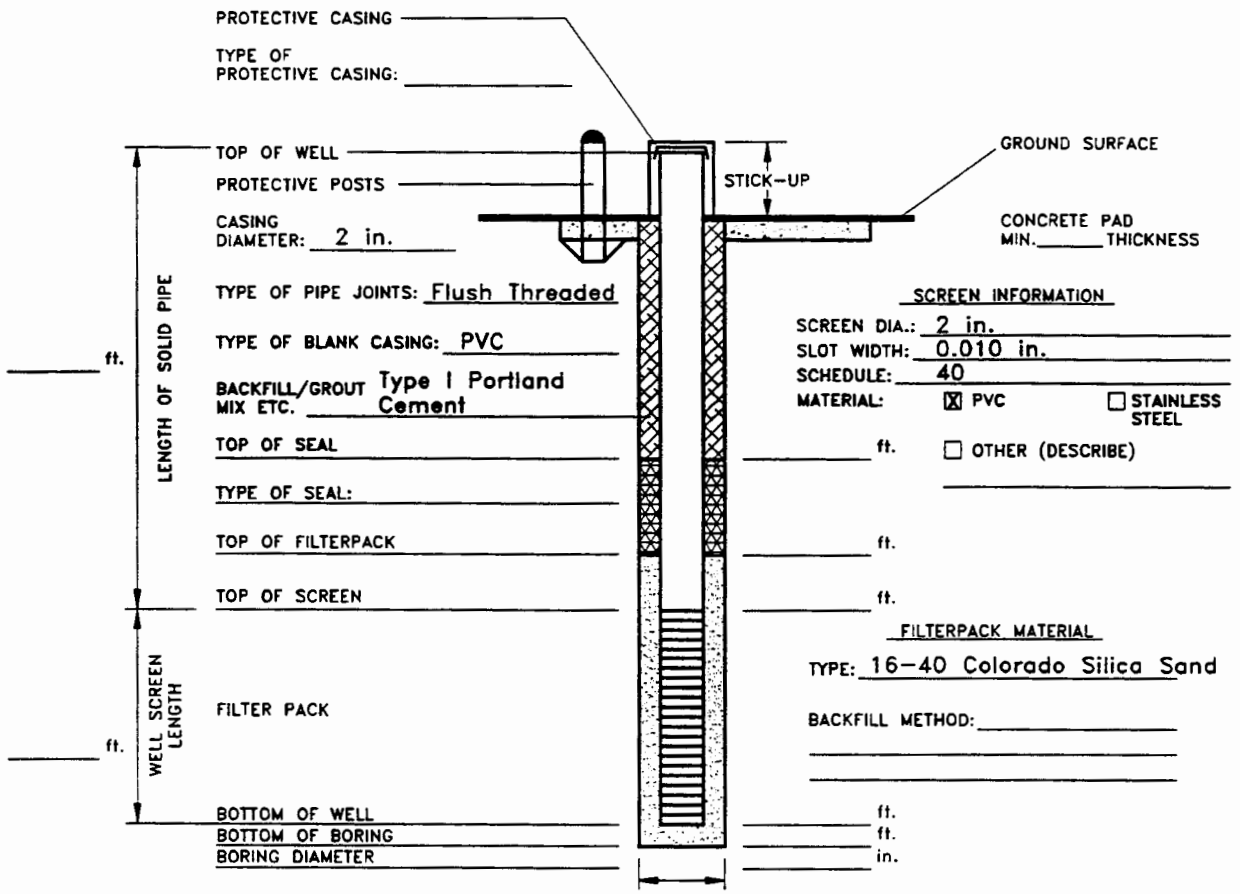


Figure 5-6. Typical Monitor Well Construction

ELEVATION GROUND WATER			PROJECT HOLLOMAN AFB
DATE INSTALLED	STARTED	COMPLETED	LOCATION (Coordinates or Station)
ELEVATION TOP OF HOLE			SIGNATURE OF INSPECTOR/INSTALLER
DRILLING METHOD			WELL NO. (as shown on drawing: title and file number)

MONITORING WELL CONSTRUCTION DIAGRAM

(ALL MEASUREMENTS FROM GROUND SURFACE)



WELL DEVELOPMENT

METHOD:

TIME SPENT DEVELOPING:

VOLUME OF WATER REMOVED:

VOLUME OF WATER ADDED:

DESCRIPTION OF PREDEVELOPMENT WATER:

DESCRIPTION OF POST DEVELOPMENT WATER:

WATER LEVEL SUMMARY

WATER LEVEL MEASUREMENTS

DATE/TIME/LEVEL

DEPTH FROM TOP CASING

AFTER DEVELOPMENT:

G1775

Figure 5-7. Monitor Well Completion Form

5.5.2.3 Bentonite Seal

To provide an adequate seal, at least 3 ft of bentonite pellets will be placed above the sand pack. As with the sand pack, the bentonite will be tremied through the augers.

5.5.2.4 Grout Mixture

Neat cement grout will be emplaced from above the top of the bentonite seal to land surface. Cement grout shall consist of a mixture of not more than 7 gallons of water and 3 pounds of powdered bentonite to each 94-pound sack of Portland Cement (ASTM C 150).

5.5.2.5 Surface Completions of Monitor Wells

Above-ground surface completion will be used for all monitor wells. The PVC well casing will be extended approximately 2 ft above land surface and a suitable vented cap or other casing cap will be provided for each well. The extended PVC casing will be shielded with at least a 4 in. diameter steel protective casing. The protective steel casing will be placed over the PVC well casing and cap and will be seated in a 3-ft by 3-ft by 4-in. thick concrete surface pad. All protective casings will have keyed-alike locks and caps. Three 2-in. diameter steel guard posts, 5 ft in total length, will be installed and cemented in separate post holes outside the concrete pad. The guard posts will be placed approximately 2 ft below and 3 ft above the pad surface.

5.5.3 Monitor Well Development

Each new monitor well will be developed as soon as is practical after completion, but not earlier than 48 hours after grouting is completed in order to allow the

cement grout to set up. The monitor wells will be developed by pumping, surging, and/or bailing without the use of any additives. Temperature, pH, and specific conductivity will be measured during development activities and recorded on the Well Development Record shown in Figure 5-8. Development will continue until these parameters have stabilized (less than 10 percent change between four consecutive readings) and the water is clear and free of sediment to the fullest extent possible. If the parameters have not stabilized after 4 hours of continuous development activities, the USACE-PM will be contacted for further direction.

A water sample will be collected in a clear glass container both before and after well development and then photographed side by side. The photograph will be taken against a white background and a 35-mm slide will be submitted as a part of the well log. Fines remaining in the water will not be allowed to settle out prior to taking the photograph. The depth of any sediment which collects in the bottom of the jar after the sample is allowed to settle will be noted on the record of well development. The nephelometric turbidity of the water will be determined in accordance with ASTM D-1889 and the results will be shown on the final well completion form.

5.5.4 Surveying Requirements

A registered professional land surveyor will be retained to survey the vertical elevations and coordinates of the wells and the tops of the boreholes. The following are the survey requirements for the well and boreholes:

- Determine ground elevations of borings and monitor wells to the closest 0.1 foot;
- Determine elevation of the mark point notch in the top of the PVC well to the closest 0.01 foot; and
- Determine coordinates of the well to the nearest 1.0 foot.

GROUND WATER DEVELOPMENT RECORD

Well ID _____
Time/Date Start Development _____
Installation ID _____
Project _____
Initial/Final Groundwater Depth _____/_____ (FT) Below Measuring Point
Initial/Final Depth to Bottom of Well _____/_____(FT) Below Measuring Point
Time/Date Finish Development _____
Logger Code _____
Type, Size/Capacitiy of Pump or Bailer _____
Total Volume to Purge for 3/5 (circle one) Well Volumes _____ Gallons
Actual Purged Volume _____ Gallons

Time	Cumulative Volume (gallons)	Clarity/Color	pH	Specific Conductivity (µmhos)	Temp °C	Comments

Figure 5-8. Groundwater Development Record

Elevations will be referenced to the National Geodetic Vertical Datum of 1929, if easily accessible, or to an existing local vertical datum. Coordinates will be referenced to the State Plane Coordinate System, if easily accessible, or to an existing local grid system. Flags or buoys will mark the sampling locations within the lakes and ponds. These markers will be used to survey the sampling locations within a one-foot degree of accuracy.

Two permanent control monuments with brass, bronze, or aluminum alloy caps will be set in accessible locations within the limits of the work at each site. These monuments will be set no closer than 500 feet to each other. Coordinates and elevations will be established to the closest 0.01 foot for each monument.

Each well will be labelled with a permanent corrosion-resistant tag on the outer steel protective casing. The tag will identify the well number, depth, date of installation, the U.S. Army Corps of Engineers, Omaha District, and the adjusted top of casing elevation. The well will also be clearly identified as a groundwater monitoring well.

5.5.5 Monitor Well Abandonment

Abandonment of monitor well S-2 will be accomplished by filling the well casing with grout using a tremie pipe, and removing above-ground completion features.

5.6 General Information and Definitions

5.6.1 Laboratory Information

All normal and QC sample analyses, except for dioxins and furans, will be conducted by Radian Analytical Services at the following address:

Sample Control
Radian Corporation - Summit Park
14046 Summit Dr. Suite 101
Austin, Texas 78728
(512) 244-0855

If Saturday delivery is required, contact Mr. Steve Gibson and ship the samples Federal Express, Deliver Saturday (**DO NOT CHECK HOLD FOR PICK-UP**) to the following address:

Sample Control
Radian Corporation
2106 Denton Dr.
Austin, Tx 78759
(512) 454-4797

All normal and QC sample analyses for dioxins and furans, SW-846 Method 8280, will be sent to the following address:

Enseco-California Analytical Laboratories
2544 Industrial Blvd.
West Sacramento, CA 95691
(916) 372-1393

External QA Samples required by the USACE Missouri River Division Laboratory will be shipped to the following address:

U.S. Army Engineer Division, Missouri River
Attn: CEMRD-ED-LC (Dick Kissinger)
420 South 18th Street
Omaha, NE 68102
(402) 444-4314

5.6.2 Decontamination Procedures for Sampling Equipment

To ensure that sludge and soil sampling equipment are not contaminated or cross-contaminated by materials and equipment used in the course of the investigation, the following procedures will be used to decontaminate all sampling equipment between and before usage:

- Wash with ALCONOX® detergent;
- Rinse with potable water;
- Rinse with reagent grade hexane;
- Rinse with reagent grade water; and
- Allow to air dry.

The drilling augers and rods will be decontaminated with a high pressure, high temperature steam cleaner between each boring and monitor well.

5.6.3 Utility Clearance

Utility clearance support will be provided by Holloman AFB personnel. A digging permit is required before activities begin. Permits are granted by providing plans for boring and well locations to the appropriate personnel (i.e., plumbing, electric, and sewer) for review. Based on the review of the plans, the Base may or may not visit each site. For the sites that require a visit, the necessary individuals will go to the site , inspect the staked drilling locations, and determine if activities can commence. After the site has been cleared, the digging permit will be signed by the required Base personnel.

5.6.4 Disposal of Drill Cuttings, Development Water and Purge Water

All drill cuttings (except cuttings from the upgradient monitor well boring) and sample waste will be considered potentially contaminated. Cuttings, used sampling equipment, and protective clothing will be drummed, placed on pallets, and labelled. At the completion of all drilling activities, the pallets will be collected and transported to a location on Base specified by the BEC.

All drums will be adequately labeled prior to being moved to the staging area. Drums will not be labeled using a "Magic Marker" or equivalent felt-tip marker, or be labeled on the top. At a minimum, drums will be labeled as to the type of material contained, site number and location, boring numbers, and the telephone number of the BEC. The eventual disposal of the contents of these drums will be determined by the analytical results which will be provided by Radian in sufficient detail to enable the BEC to properly prepare a manifest for ultimate shipment of the drums to a disposal facility. Radian will not be responsible for off-Base disposal of any drums that contain contaminated material.

5.6.5 Site Restoration

The site will be restored to its original state within 10 working days of completion of the field investigation. The restoration efforts will meet the approval of the BEC. Appropriate photographs will be taken both before and after field work activities to document this restoration.

5.6.6 Field Documentation

A Field Log Book will be kept by the Radian Supervising Geologist. The field log book will serve primarily as a daily log of activities carried out during the investigation.

Any observations during drilling activities not included in the drilling log will be recorded in this book. Other observations may be included as the situation dictates for a thorough record to reconstruct the events concerning all field activities. The field log book is a bound book with sequentially numbered pages and with a unique document control number.

The Supervising Geologist will also complete A-E Daily Quality Control Reports (A-E DQCR), shown in Figure 5-9, at the end of each day. These reports will be sent to the USACE-PM and the BEC.

5.7 List of Equipment, Containers, and Supplies

The implementation of the field activities will require specific equipment, containers, and supplies for the collection of field samples as summarized below.

Sampling Equipment

- Vibracore® sampling equipment and thin-walled aluminum tubes;
- Hollow-stem auger drill rigs;
- Stainless steel split-spoon samplers;
- Stainless steel compositing bowls and sampling equipment;
- DOT - approved drums for soil collection;
- Pumps; and
- Surge blocks.

Sampling Bottles and Shipping Materials

- 250 ml wide-mouth glass with Teflon cap;
- 500 ml wide-mouth glass with Teflon cap;

A-E DAILY QUALITY CONTROL REPORT

Date_____

Day	S	M	T	W	TH	F	S

COE Project Manager_____
Project_____
Job No._____
Contract No._____

SUB-CONTRACTORS ON SITE:
EQUIPMENT ON SITE:
WORK PERFORMED (INCLUDING SAMPLING):

Figure 5-9. A-E Daily Quality Control Report

Project_____ Report No._____

Job No._____ Date_____

QUALITY CONTROL ACTIVITIES (INCLUDING FIELD CALIBRATIONS):
HEALTH AND SAFETY LEVELS AND ACTIVITIES:
PROBLEMS ENCOUNTERED/CORRECTIVE ACTION TAKEN:
SPECIAL NOTES:
TOMORROW'S EXPECTATIONS:

BY_____ TITLE_____

Figure 5-9. (Continued)

- Bottle mesh;
- Plastic freezer bags;
- Ice chests; and
- Packaging and shipping materials.

Decontamination Equipment

- ALCONOX® soap;
- Hexane (Pesticide Grade);
- Reagent grade water;
- Squirt bottles;
- Plastic sheeting;
- Distilled water; and
- General decontamination equipment.

Miscellaneous Field Gear and Instrumentation

- Protective gloves;
- Saranex-coated tyvek coveralls;
- Full-face air purifying respirators and cartridges;
- First aid kit;
- Eye wash;
- pH and conductivity meters;
- pH buffers and conductivity standards;
- Water-level probe;
- Tape measure; and
- Turbidity meter.

6.0 SAMPLE CHAIN OF CUSTODY, PACKING, AND TRANSPORTATION

A sample label, shown in Figure 6-1, will be affixed to all sampling containers submitted for laboratory analysis. Sample labels identify the sample by documenting the sample type, sampler(s) initials, sampling locations, depth, time, and date. The unique number assigned to each sample is also noted on the sample label. Indelible ink will be used to complete all sample labels.

A chain-of-custody form, shown in Figure 6-2, will be used to record the number of samples collected and the corresponding laboratory analyses; indelible ink will be used. Information on this form includes time and date of sampling, sample number, type of sample, sampler's name, preservatives used, and any special instructions. Samples collected for matrix spike/matrix spike duplicate analysis will be identified on the chain-of-custody form. A copy of the chain-of-custody form will be retained by the sampler, and will be maintained in a file of field documentation.

All samples will be kept cool with regular ice in a plastic bag during collection and shipment. The samples will be stored upright in a durable ice chest. Sufficient packing material (i.e., vermiculite) will be used to separate the bottles, filling any intervening voids. Fresh ice will be placed in the cooler prior to shipment.

The ice will be placed above and around the top of the sample containers. The remaining space will be filled with additional packing material. The chain-of-custody form will be sealed in a plastic Zip-loc® bag and affixed to the top lid of the cooler. The cooler will be secured by completely wrapping it with strapping tape around both ends. If there is a drain on the cooler, it will be taped shut. The cooler will be labeled with "This Side Up" arrows on two opposing sides. Custody seals will also be affixed to coolers to indicate tampering.

ATTENTION:
BEFORE OPENING
NOTE IF CONTAINER WAS
TAMPERED WITH.

CUSTODY # _____

ATTENTION:
BEFORE OPENING
NOTE IF CONTAINER WAS
TAMPERED WITH.

8-90-12896

Field Number _____
Sample Type: _____
Client: _____
Location: _____
Preservative: _____
Sampler: _____
Date: _____
Comment: _____

6-89-31426

Figure 6-1. Example Sample Label and Custody Seal

RADIAN CORPORATION

Chain of Custody Record

Page _____ of _____

PROJECT

SITE

COLLECTED BY *(Signature)*

FIELD SAMPLE I.D.	SAMPLE MATRIX	DATE/TIME	NO. OF CONTAINERS	ANALYSES								REMARKS	SAM ID NO. *(for lab use only)*

REMARKS	RELINQUISHED BY:	DATE	TIME

RECEIVED BY:	DATE	TIME	RELINQUISHED BY:	DATE	TIME	RECEIVED BY:	DATE	TIME	RELINQUISHED BY:	DATE	TIME

LAB USE ONLY

RECEIVED FOR LABORATORY BY:	DATE	TIME	AIRBILL NO.	OPENED BY:	DATE	TIME	TEMP°C	SEAL #	CONDITION

REMARKS:

Figure 6-2. Sample Chain-of-Custody Record

Sludge and soil samples will be shipped to the laboratory by overnight courier on a daily basis.

7.0 LABORATORY ANALYTICAL PROCEDURES

The methods and procedures that will be used to prepare and analyze samples are discussed in this section. Most chemical analyses will be performed according to the following publications:

- SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, U.S. EPA, Office of Solid Waste and Emergency Response, November 1986, third edition;
- EPA, Methods for Chemical Analysis of Water and Wastes, EPA Publication No. 600/4-79-020, March 1983; and
- ASTM, 1990 Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA, 1990.

Laboratory-specific Standard Operating Procedures (SOPs) for most methods are provided in Appendix A. The dioxin and furan SOP from Enseco-Cal Labs will be delivered under separate cover. Individual parameters and analytical methods to be used are listed in Table 7-1.

Most analytical methods to be used in this project require the measurement system to initially satisfy specific criteria for calibration linearity, reference material recovery, and freedom from contamination. Results of control samples, which are analyzed at a 5 percent frequency to monitor any changes in the quality of data being produced, indicate which corrective actions are necessary to correct an out-of-control condition. An out-of-control condition is defined as:

- Detection of any compounds of interest in a reagent blank at ≥ 5 times the limit of detection.

Table 7-1

Analytical Methods

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
METALS					
Antimony	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	10
Barium	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	1
Beryllium	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	0.2
Cadmium	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	0.5
Chromium	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	1
Cobalt	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	1
Copper	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	2
Nickel	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	2
Silver	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	1
Tin	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	60
Vanadium	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	2
Zinc	Acid Digestion	SW-846:3050	ICPES	SW-846:6010	2
Arsenic	Acid Digestion	SW-846:3050	GFAA	SW-846:7060	0.4
Lead	Acid Digestion	SW-846:3050	GFAA	SW-846:7421	0.3
Mercury	Acid Digestion	SW-846:7471	CVAA	SW-846:7471	0.02
Selenium	Acid Digestion	SW-846:3050	GFAA	SW-846:7740	0.5
Thallium	Acid Digestion	SW-846:3050	GFAA	SW-846:7841	0.5
ORGANOCHLORINE PESTICIDES AND PCBs					
Aldrin	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
alpha-BHC	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
beta-BHC	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
delta-BHC	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
gamma-BHC (Lindane)	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Chlordane (technical)	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.005
4,4'-DDD	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
4,4'-DDE	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
4,4'-DDT	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.002
Dieldrin	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Endosulfan I	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Endosulfan II	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.003
Endosulfan sulfate	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.005
Endrin	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Endrin aldehyde	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.002
Heptachlor	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Heptachlor epoxide	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Isodrin	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Kepone	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.001
Methoxychlor	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.005
Toxaphene	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.050
PCB-1016	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.010
PCB-1221	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.020
PCB-1232	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.020
PCB-1242	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.010
PCB-1248	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.010

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
PCB-1254	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.020
PCB-1260	Extraction	SW-846:3540/3550	GC/ECD	SW-846:8080	0.020
ORGANOPHOSPHORUS PESTICIDES					
Dimethoate	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.020
Disulfoton	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.020
Ethyl parathion	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.015
Famphur	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.050
Parathion methyl	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.003
Phorate	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.015
Sulfotepp	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.010
Thionazin	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.100
o,o,o-Triethylphosphorthioate	Extraction	SW-846:3540/3550	GC/FPD	SW-846:8140	0.100
CHLORINATED HERBICIDES					
2,4-D	Extraction/Esterification	SW-846:8150	GC/ECD	SW-846:8150	0.120
2,4,5-T	Extraction/Esterification	SW-846:8150	GC/ECD	SW-846:8150	0.020
2,4,5-TP (Silvex)	Extraction/Esterification	SW-846:8150	GC/ECD	SW-846:8150	0.017
Dinoseb	Extraction/Esterification	SW-846:8150	GC/ECD	SW-846:8150	0.015
VOLATILE ORGANICS					
Acetone	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	10
Acetonitrile	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	10
Acrolein	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	7.5
Acrylonitrile	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	5

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
Benzene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Bromodichloromethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Bromomethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	1
Carbon disulfide	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Carbon tetrachloride	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
2-Chloro-1,3-butadiene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	2.5
Chlorobenzene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Chloroethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	1
Chloroform	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Chloromethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	1
3-Chloropropene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Dibromochloromethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,2-Dibromo-3-chloropropane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	2
1,2-Dibromoethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Dibromomethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
trans-1,4-Dichloro-2-butene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	1
Dichlorodifluoromethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	2
1,2-Dichloroethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
trans-1,2-Dichloroethene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,1-Dichloroethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,1-Dichloroethene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,2-Dichloropropane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
cis-1,3-Dichloropropene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
trans-1,3-Dichloropropene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Ethyl benzene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Ethyl methacrylate	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
2-Hexanone	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	5
Iodomethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Methylene chloride	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
2-Butanone (MEK)	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	10
Methyl methacrylate	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
4-Methyl-2-pentanone	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	5
Propanenitrile	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	10
Styrene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,1,1,2-Tetrachloroethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,1,2,2-Tetrachloroethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Tetrachloroethene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Toluene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Tribromomethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,1,1-Trichloroethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
1,1,2-Trichloroethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Trichloroethene	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Trichlorofluoromethane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	1
1,2,3-Trichloropropane	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
Vinyl Acetate	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Vinyl Chloride	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	1
Xylenes (total)	Purge and Trap	SW-846:5030	GC/MS	SW-846:8240	0.5
Volatile Organics (Direct Injection)					
1,4-Dioxane	Direct Injection	SW-846:8240	GC/MS	SW-846:8240	20
Isobutanol	Direct Injection	SW-846:8240	GC/MS	SW-846:8240	20
Methacrylonitrile	Direct Injection	SW-846:8240	GC/MS	SW-846:8240	20
SEMIVOLATILE ORGANICS					
Acenaphthene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Acenaphthylene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Acetophenone	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
2-Acetylaminofluorene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
4-Aminobiphenyl	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Aniline	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Anthracene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Aramite	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	10
Benzo(a)anthracene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Benzo(a)pyrene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Benzo(b)fluoranthene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Benzo(g,h,i)perylene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Benzo(k)fluoranthene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Benzyl alcohol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
4-Bromophenyl phenyl ether	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Butylbenzylphthalate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
4-Chloro-3-methylphenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
4-Chloroaniline	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Chlorobenzilate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
bis(2-Chloroethoxy)methane	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
bis(2-Chloroethyl)ether	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
bis(2-Chloroisopropyl)ether	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1.0
2-Chloronaphthalene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2-Chlorophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
4-Chlorophenyl phenyl ether	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Chrysene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Diallate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Dibenz(a,h)anthracene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Dibenzofuran	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1,2-Dichlorobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1,3-Dichlorobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1,4-Dichlorobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
3,3'-Dichlorobenzidine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	2
2,4-Dichlorophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2,6-Dichlorophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Diethylphthalate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
p-Dimethylaminoazobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
7,12-Dimethylbenz(a)anthracene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
3,3'-Dimethylbenzidine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	2
Dimethylphenethylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2,4-Dimethylphenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Dimethylpthalate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
4,6-Dinitro-2-methylphenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
Di-n-butylphthalate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1.0
Di-n-octylphthalate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1,3-Dinitrobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2,4-Dinitrophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
2,4-Dinitrotoluene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2,6-Dinitrotoluene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Diphenylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
bis(2-Ethylhexyl)phthalate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Ethylmethane sulfonate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Fluoranthene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Fluorene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Hexachlorobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Hexachlorobutadiene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Hexachlorocyclopentadiene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Hexachloroethane	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
Hexachlorophene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1.0
Hexachloropropene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Indeno(1,2,3-c,d)pyrene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Isophorone	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Isosafrole	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Methapyrilene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
3-Methylchloanthrene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Methyl methanesulfonate	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2-Methyl naphthalene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2-Methylphenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
3-Methylphenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
4-Methylphenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Naphthalene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1,4-Naphthoquinone	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1-Naphthylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2-Naphthylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2-Nitroaniline	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
3-Nitroaniline	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
4-Nitroaniline	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
Nitrobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2-Nitrophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
4-Nitrophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
4-Nitroquinoline-N-oxide	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	10
N-Nitroso-di-n-butylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosodiethylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosodiphenylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosodipropylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosodimethylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosomethylethylamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosomorpholine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosopiperidine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
N-Nitrosopyrrolidine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
5-Nitro-o-toluidine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Pentachlorobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Pentachloroethane	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Pentachloronitrobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Pentachlorophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
Phenacetin	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Phenanthrene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Phenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
p-Phenylenediamine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	5
2-Picoline	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Pronamide	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Pyrene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1

Table 7-1

(Continued)

Parameter	Preparation		Analysis		Reporting Limit[a]
	Technique	Method	Technique	Method (Soil)	Soil (mg/kg)
Pyridine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
Safrole	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1,2,4,5-Tetrachlorobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2,3,4,6-Tetrachlorophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	2
o-Toluidine	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
1,2,4-Trichlorobenzene	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2,4,5-Trichlorophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
2,4,6-Trichlorophenol	Extraction	SW-846:3540/3550	GC/MS	SW-846:8270	1
DIOXINS AND FURANS					
2,3,7,8-Tetrachlorodibenzo-p-dioxin	Extraction	SW-846:8280	GC/MS	SW-846:8280	0.00008
Tetrachlorodibenzo-p-dioxins	Extraction	SW-846:8280	GC/MS	SW-846:8280	0.00008
Tetrachlorodibenzo-p-furans	Extraction	SW-846:8280	GC/MS	SW-846:8280	0.00006
Pentachlorodibenzo-p-dioxins	Extraction	SW-846:8280	GC/MS	SW-846:8280	0.0002
Pentachlorodibenzo-p-furans	Extraction	SW-846:8280	GC/MS	SW-846:8280	0.00008
Hexachlorodibenzo-p-dioxins	Extraction	SW-846:8280	GC/MS	SW-846:8280	0.0002
Hexachlorodibenzo-p-furans	Extraction	SW-846:8280	GC/MS	SW-846:8280	0.0001
GENERAL					
Cyanide	Distillation	SW-846:9012	Colorimetric	SW-846:9012	1
Sulfide	Distillation	SW-846:9030	Titrametric	SW-846:9030	50
Total Organic Carbon	Acid Treatment	SW-846:9060	IR	SW-846:9060	2,000

Table 7-1

(Continued)

[a] Reporting Limit is the minimum concentration of a substance that can be measured and reported. Reporting Limits are highly matrix dependent and may not always be achievable. Detection limits for sludge samples are often higher due to water content.

IR	=	Infrared Spectrometry
ICPES	=	Inductively Coupled Plasma Emission Spectroscopy
GFAA	=	Graphite Furnace Atomic Absorption
CVAA	=	Cold Vapor Atomic Absorption
GC/MS	=	Gas Chromatography/Mass Spectrometry
SW-846	=	Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, U.S. EPA, Office of Solid Waste and Emergency Response, November 1986, third edition.
EPA	=	Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020.
N/A	=	Not Applicable
IC	=	Ion Chromatography
GC/FPD	=	Gas Chromatography/Flame Photometric Detector
GC/ECD	=	Gas Chromatography/Electron Capture Detector

- Failure to meet the acceptance criteria for recovery of any compound of interest in a QC sample.

- Exceeding the action limit for matrix spike recovery and subsequent failure to meet the acceptance criteria for a QC check sample for the same parameter(s). Any parameter which fails the matrix spike test but passes the QC check sample test will be flagged as suspect for the parameter due to matrix effects.

When an out-of-control situation is detected, efforts are undertaken to determine the cause. Corrective actions for routine QC checks are outlined in Table 7-2. Procedures related to corrective actions are described below.

During the course of the Holloman AFB Investigation, it will be the responsibility of the laboratory QC officers, Project Director, Task Leaders, and other project team members to see that all measurement procedures are followed as specified and that measurement data meet the prescribed acceptance criteria. In the event a problem arises, it is imperative that prompt action be taken to correct the problem(s). Laboratory supervisors will initiate corrective action in the event of QC results which exceed acceptability limits. Corrective action may also be initiated upon identification of some other problems or potential problems. Corrective action may also be initiated by the Laboratory QC officer based upon QC data or other anomalies noted during data review.

For this project, the following corrective actions will be implemented when surrogate spike compounds are recovered outside the method criteria:

- Check to be sure there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.

- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Analyze an extracted quality control check sample (QCCS).

Table 7-2

Summary of Internal Quality Control Procedures

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:6010	Metals (ICPES)	Laboratory Mixed standard calibration	Daily	r≥0.995	Repeat calibration
		QC check sample analysis (second source QC check sample)	10%, minimum of 1 per batch	Measured value within ±10% of true value for element of interest	Repeat calibration
		Preparation blank	1 per digestion batch ≤20 samples	≤5 x Method detection limit	1) Reanalyze 2) Clean system 3) Reanalyze 4) Redigest samples if reanalysis fails
		Calibration blank	10%	≤5 x Method detection limit	1) Rerun 2) Clean system 3) Reanalyze sample 4) Redigest samples if reanalysis fails
		Matrix spike analysis	5%	75-125% of true value	1) Analyze method spike (or QCCS) 2) If method spike is ok; flag data 3) If method spike not ok; see lab supervisor and reanalyze samples
		Matrix spike duplicate	5%	Relative percent difference ≤20% and 75-125% of true value	1) Analyze method spike (or QCCS) 2) If method spike is ok; flag data 3) If method spike not ok; see lab supervisor and reanalyze samples
		ICP interference check	Run at beginning and end of daily run	80-120% of true value for EPA check sample elements	1) See lab manager 2) Repeat calibration
		ICP linear range check	Quarterly	Measured value within ±15% of expected value	Tests upper limit of ICP linear range
		Instrument detection limit	Quarterly	≤ current LOD	Used to verify current IDL

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:6010 (Continued)	Metals (ICPES) (Continued)	Field Duplicate field sample	5%, minimum one per program	None	Determine sampling/analytical variability
SW-846:7060 SW-846:7421 SW-846:7471 SW-846:7740 SW-846:7841	Metals (AA) Arsenic Lead Mercury Selenium Thallium	Laboratory Multipoint calibration	Daily, prior to analyses	r≥0.995	1) Repeat test 2) Take corrective action 3) Repeat calibration and test
		QC check sample	10%, or minimum of one per batch	Measured value within ±15% of expected value (±20% for Mercury)	Repeat calibration
		Calibration blank	10%, or minimum of one per batch	≤5 x MDL	1) Clean system 2) Reanalyze
		Preparation blank	10%, or minimum of one per batch	≤5 x MDL (≤10 x MDL for Mercury)	1) Reanalyze 2) Clean system 3) Redigest and reanalyze
		Matrix spike	5%, or minimum of 1 per batch	75-125% Recovery	1) Run check sample (QCCS) 2) Correct problem 3) If QCCS fails, reanalyze samples 4) If not, flag data
		Matrix Spike Duplicate	5%, or minimum of 1 per batch	Within 20% RPD and 75-125% Recovery	1) Run check sample (QCCS) 2) Correct problem 3) If QCCS fails, reanalyze samples 4) If not, flag data
		LOD check	Quarterly	≤current LOD	Used to verify current LOD
		Field Duplicate sample	5%, 1 per 20 samples	None	Determine sampling/analytical variability
SW-846:8080	Organochlorine Pesticides and PCBs	Laboratory Multipoint calibration (minimum of 5 points)	Initially, as required	RSD ≤20% or r≥0.995	Repeat calibration
		Single point calibration	Daily prior to sample analyses	RPD ≤15%	Repeat 5-point calibration

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:8080 (Continued)	Organochlorine Pesticides and PCBs (Continued)	DDT and endrin degradation check sample	Daily prior to analyses	Degradation ≤20% (see method)	1) Follow maintenance in Method 8000, see Section 7.7 2) Recalibrate
		Surrogate spikes	Every sample	Based on CLP method	1) Evaluate system 2) Recalculate data and/or reanalyze extract 3) Flag data
		Extraction blank	5%	≤ MDL	1) Clean system 2) Reanalyze 3) Flag data
		Method blank	Daily	≤MDL	1) Clean system 2) Reanalyze
		QC check sample (QCCS)	5%	Laboratory derived	1) Evaluate system 2) Repeat test for criteria that failed
		Matrix spike	5%	CLP limits	1) Analyze QCCS 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples
		Matrix spike duplicate	5%	RPD <50% and recovery within method specified limits (Table 3)	1) Analyze QCCS 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples
		Field Duplicate field samples	5%; minimum one per program	None	Will be used to determine sampling/analytical variability

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:8140	Organophosphorus Pesticides	Laboratory Multipoint calibration (minimum 5 points)	Initially and as required by daily check	RPD ≤20% or r>0.995	Repeat calibration
		Calibration check sample	Daily prior to sample analyses	RPD ≤15%	Repeat 5-point calibration
		QC check sample	5%	Laboratory derived	1) Evaluate system 2) Repeat test for criteria that failed
		Surrogate spikes	Every sample	Laboratory derived	1) Evaluate system 2) Recalculate data and/or reanalyze extract 3) Analyze QCCS, if QCCS fails, reextract and reanalyze sample 4) Flag data and report analysis and reanalysis results
		System blank	Daily	≤ MDL	1) Clean system 2) Reanalyze
		Extraction blank	5%	≤MDL	1) Clean system 2) Reanalyze 3) Flag data
		Matrix spike	5%	Laboratory derived	1) Analyze QCCS 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples
		Matrix spike duplicate	5%	RPD <50% and recovery within method specified limits	1) Analyze QCCS 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:8140 (Continued)	Organophosphorus Pesticides (Continued)	Field Duplicate field samples	5%; minimum one per program	None	Will be used to determine sampling/analytical variability
SW-846:8150	Herbicides	Laboratory Multipoint calibration (minimum of 5 points)	Initially, and as required by daily check	RSD ≤20% for RFs	Repeat calibration
		Single point calibration	Daily, prior to sample analyses	RPD≤15%	Repeat multipoint calibration
		Surrogate spikes	Every sample	Laboratory derived	1) Evaluate system 2) Recalculate data and/or reanalyze extract 3) Flag data
		Quality control check sample (QCCS)	5%	Laboratory derived	1) Recalibrate 2) Reanalyze affected samples
		System blank	Daily	≤MDL	1) Clean system 2) Reanalyze
		Method blank	5%	<MDL	1) Clean system 2) Reanalyze 3) Flag data
		Matrix spike	5%	Laboratory derived	1) Analyze QCCS 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples
		Matrix spike duplicate	5%	RPD ≤50% and recovery within method specified limits	1) Analyze QCCS 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples
SW-846:8150 (Continued)	Herbicides (Continued)	Field Duplicate field samples	5% minimum one per program	None	Will be used to determine sampling and analytical variability

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:8240	Volatile Organic Compounds	Laboratory Check of mass spectral ion intensities using BFB	Daily prior to sample analysis, or every 12 hours	Refer to method (Table 3)	1) Retune instrument 2) Repeat BFB analysis
		5-point calibration at 10-200 ppb range	Initial calibration; and as required	RF variability for specific compounds <30% RSD	Repeat calibration
		System performance check compounds	Every 12 hours	RF ≤0.300 (0.250 for bromoform)	1) Evaluate system 2) Repeat calibration
		Calibration check compounds	Every 12 hours	RSD <25%	1) Evaluate system 2) Repeat test 3) Recalibrate
		Surrogate spikes	Every sample	Laboratory derived	1) Evaluate system 2) Recalculate data and/or reanalyze extract 3) Flag data
		Internal standards	Every sample	Refer to method	1) Inspect mass spectrometer 2) Correct problem 3) Repeat calibration 4) Reanalyze samples
		Method Blank	Daily prior to analyses	<DL except for common laboratory contaminants which may be 5 x DL	1) Run solvent blank 2) Reanalyze blank and samples
		Quality Control Check Sample	5%	Refer to method	1) Evaluate system 2) Repeat test for criteria that failed

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:8240 (Continued)	Volatile Organic Compounds (Continued)	Matrix spike	5%	Refer to method (Table 6)	1) Run check samples (QCCS) 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples
		Matrix spike duplicate	5%	≤50% RPD and recovery within limits of method (Table 6)	1) Run check sample (QCCS) 2) Correct problem 3) If QCCS is ok; flag data 4) If QCCS is not ok; reanalyze samples
		Field Duplicate field samples	5%	None	Used to determine sampling/analytical variability
		Trip blank	5%; or one per sampling event	None	Will be used to determine sources of contamination
SW-846:8270	Semivolatile Organic Compounds	Laboratory Check of mass spectral ion intensities using DFTPP	Daily prior to sample analysis or every 12 hours	Refer to method	Retune instrument Repeat DFTPP analysis
		5-point calibration at 10-200 ppb range	Initial calibration	RF variability for specific compounds <30% RSD	Repeat calibration
		System performance check compounds	Every 12 hours	Minimum average response factor of 0.050	1) Evaluate system 2) Repeat calibration
		Calibration check compounds (CCC)	Every 12 hours	Single-point RF for each CCC within 30% of average multi-point RF	1) Evaluate system 2) Take corrective action 3) Repeat test 4) See lab manager
		Surrogate spikes	Every sample	Based on method (Table 8)	1) Evaluate system 2) Recalculate data and/or reanalyze extract 3) Flag data

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:8270 (Continued)	Semivolatile Organic Compounds (Continued)	Internal standards	Every sample	Refer to method	1) Inspect mass spectrometer 2) Correct problems and repeat calibration 3) Reanalyze samples
		Extraction blank	5% or daily	<DL except for common laboratory contaminants which may be 5 x DL	1) Run solvent blank 2) Evaluate system
		Matrix spike	5%	Refer to method (Table 6)	1) Run check sample (QCCS) 2) Correct problem 3) If QCCS fails, reanalyze samples 4) Flag data
		Matrix spike duplicate	5%	≤50% RPD and recovery within limits of method (Table 6)	1) Run check samples (QCCS) 2) Correct problem 3) If QCCS fails, reanalyze samples 4) Flag data
		Field Duplicate field sample	5%	None	Will be used to determine sampling/analytical variability
SW-846:8280	Dioxins and Furans	Laboratory Initial calibration Multipoint, 5 levels in triplicate	Yearly, with fresh standards	Relative standard deviation ≤15%	1) Repeat initial calibration 2) Evaluate system 3) Repeat calibration
		Single-point check	Daily	Agreement within 30% of value predicted from multipoint calibration curve	1) Repeat single point check 2) Repeat multipoint
		TCDD chromatography check	Daily	25% valley between 1,2,3,4-TCDD and 2,3,7,8-TCDD	Replace column

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:8280 (Continued)	Dioxins and Furans (Continued)	PCDD/PCDF retention time window check	Daily, unless retention times of internal standards vary >0.2 minutes	Less than ±0.2 minutes variation on internal standards	Rerun retention time standard, adjust SIM windows
		Sensitivity check	Daily	>150,000 area counts from 322 ion from 1 μl of 1.0 ppm C_{13}-2,3,7,8-TCDD	1) Evaluate instrument 2) Take corrective action
		Method blank	5%	≤MDL	Used to assess contamination
		Duplicate analyses	5%	Not specified	Obtain third value
		Surrogate spike	Every sample	Method specified limits of 40-120%	Flag data
		Lab Check Standard (LCS)	5%	40 - 120% Recovery	1) Evaluate system 2) Recalculate data 3) Reanalyze standard 4) Correct problem 5) Reanalyze affected samples
		Field Duplicate samples	5%	None	Used to assess sampling/analytical variability

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:9012	Cyanide	Laboratory Calibration curve	Daily, prior to sample analyses	r≥0.995	Repeat calibration
		QC Check standard	10%	±15% error	1) Reanalyze 2) Repeat calibration 3) Reanalyze affected samples
		Reagent blank	1 per batch ≤20 samples	<0.01 μg/L	1) Clean instrument/equipment 2) Rerun test
		Duplicate analysis	5%	RPD ≤20%	Obtain third value
		Matrix spike	5%, or minimum of 1 per batch	75 - 125%	1) Check calculations 2) Analyze QCCS 3) If QCCS ok; flag data 4) If QCCS not ok; reanalyze samples
		Matrix spike duplicate	5%, or minimum of 1 per batch	RPD ≤20% and recovery within 75 - 125%	1) Check calculations 2) Analyze QCCS 3) If QCCS ok; flag data 4) If QCCS not ok; reanalyze samples
		Field Duplicate sample	5%	None	Used to assess sampling/analytical variability
SW-846:9030	Sulfide	Laboratory Standardize Iodine solution	Daily	RPD ≤5% for duplicates	Repeat standardization
		Standardize titrant	Daily	RPD ≤5% for duplicates	Repeat standardization
		Matrix spike	10%	75-125% Recovery	1) Check calculations 2) Reanalyze 3) Flag data

Table 7-2

(Continued)

Analytical Method	Parameter	Quality Control Check	Frequency[a]	Acceptance Criteria	Corrective Action
SW-846:9030 (Continued)	Sulfide (Continued)	Matrix spike duplicate	10%	RPD ≤20% and 80 - 120% Recovery	1) Check calculations 2) Reanalyze 3) Flag data
		Blank	One per batch ≤20 samples	≤MDL	1) Reanalyze blank 2) Reanalyze samples
		Duplicate analyses	10%	RPD ≤15%	1) Obtain third value
		Field Duplicate sample	5%	None	Used to assess sampling/analytical variability
SW-846:9060	Total Organic Carbon (TOC)	Laboratory Calibration	Daily, prior to sample analyses	N/A	N/A
		QC check standard	10% or minimum of 1 per batch	±20% error	Repeat calibration
		Duplicate analysis	10%	RPD <20%	1) Obtain 3rd value 2) Flag data
		Field Duplicate samples	5%	None	Used to assess sampling/analytical variability

[a] Frequencies for duplicate samples and field blanks are computed based on the total number of samples taken for and the number of analyses specified in the SOW.

QCCS = Quality Control Check Samples
MDL = Method Detection Limit
N/A = Not Applicable
RF = Response Factor
DL = Detection Limit
RPD = Relative Percent Difference

- If the QCCS compounds are recovered within criteria, flag data as matrix effect.
- If the QCCS compounds are recovered outside criteria, reextract and reanalyze the sample, report both sets of results.

A brief description of the analysis and the corrective action taken will be included in the laboratory report. These corrective actions are summarized in Table 7-2.

To meet the State of New Mexico's requirement for a calibration check near the PQL, Radian proposes to analyze a second-source calibration standard for each method. This check standard will be a representative subset of the analytes to be determined.

For this project, all samples will be reported on a dry-weight basis. The dry-weight calculation will be based on a moisture analysis.

The data analysis required to calculate sample concentrations will proceed according to procedures outlined in the analytical methods identified in Table 7-2. Data reduction involves taking instrument responses or other raw data and calculating concentrations for each target analyte. Data validation involves examining the systems producing the data to be sure they are operating properly and quality objectives have been met. Data will be reviewed and validated by the laboratory QC officer. Data will be validated for conformance with method specifications including:

- Calibration;
- Duplicate analysis;
- Blank analysis;
- Spike analysis;
- Sample data calculations; and
- Quality control sample frequency.

The quality control activities implemented in this project will provide a basis for assessing the accuracy and precision of all data. If the recoveries for the dioxin/furan spikes are below the control limits presented in Table 7-2, and the signal-to-noise ratio of the compound of interest is >10:1, then the data will be deemed acceptable and reported. Frequencies and acceptance criteria for these tests are presented in Table 7-2. Calculations are presented below.

Accuracy

For this project, accuracy of the measurement data will be assessed and controlled by continuing calibration check samples (CCCS), quality control check samples (QCCS), and method spikes (blank spikes). These results will be used to control accuracy within acceptable limits by requiring that they meet specific criteria. As CCCS, QCCS, and method spike samples are analyzed, recoveries will be calculated and compared to pre-established acceptance limits. Recovery is calculated as the measured value divided by the actual value times 100. Overall inaccuracy will be calculated as the average of (100 - %recovery). This inaccuracy estimate includes systematic bias and random bias and will be compared to Table 3-1 to determine data acceptability.

Precision

For this project, precision will be assessed and controlled through the use of sequential CCCS, QCCS, and duplicate analyses. The coefficient of variation (CV) will be used to estimate precision for sequential CCCS and QCCS and is calculated by:

$$CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

The relative percent difference (RPD) will be used to estimate precision for analytical duplicates and is calculated by:

$$RPD = \frac{X_1 - X_2}{(X_1 + X_2)/2} \times 100$$

The standard analytical methods and procedures that will be used for soil and sludge samples are briefly discussed in the following subsections.

7.1 Metals by ICPES - EPA Method 6010

7.1.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of antimony, barium, beryllium, cadmium, chromium, cobalt, copper, nickel, silver, tin, vanadium, and zinc at the Holloman AFB sewage lagoons listed in 5-1.

7.1.1.1 Sample Preparation

Soil samples will be prepared according to EPA Method 3050. The laboratory-specific SOP is presented in Appendix A.

7.1.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of antimony, barium, beryllium, cadmium, chromium, cobalt, copper, nickel, silver, tin, vanadium, and zinc at the Holloman AFB sewage lagoons listed in Table 5-1.

7.1.2.1 Sample Preparation

Sludge samples will be prepared according to EPA Method 3050. The laboratory-specific SOP is presented in Appendix A.

7.1.3 Analytical Method

Metals (antimony, barium, beryllium, cadmium, chromium, cobalt, copper, nickel, silver, tin, vanadium, and zinc) will be determined by EPA Method 6010 which allows the simultaneous, or sequential, measurement of elements using Inductively Coupled Plasma Emission Spectroscopy (ICPES). This method measures the element emitted light by optical spectrometry. Samples are nebulized, and the resulting aerosol is transported to the plasma torch. Element specific atomic-line emission spectra are produced which are dispersed by a grating spectrometer and monitored for intensity by photomultiplier tubes.

7.1.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.1.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.1.6 Instrument Calibration and Frequency

Detailed calibration procedures for ICPES systems are described in SW-846, 3rd ed. A response factor (RF) is calculated daily for each metal based on three exposures of a calibration standard and calibration blank. The RF is calculated and stored in the ICPES computer.

7.1.7 Internal Quality Control Checks

Following calibration, a mid-level calibration check sample is analyzed. Calibration is verified by analyzing a QC check standard (prepared independently of calibration standards) every 10 samples. Additional internal quality control checks are presented in Table 7-2.

7.1.8 Corrective Action

Following calibration, a mid-level calibration check sample is analyzed; agreement between the measured value and the expected value must be within 5 percent for analyses to proceed. Calibration is verified by analyzing a QC check standard (prepared independently of calibration standards) every 10 samples; agreement within ± 15 percent of the expected value is required for all metals analyzed by ICPES. A summary of corrective action procedures is presented in Table 7-2.

7.1.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.2 Arsenic by Furnace AA - SW 7060

7.2.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of arsenic at the Holloman AFB sewage lagoons listed in Table 5-1.

7.2.1.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion Procedure of Sludges - Method 3050 Digestions."

7.2.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of arsenic at the Holloman AFB sewage lagoons listed in Table 5-1.

7.2.2.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion of Sludges - Method 3050 Digestions."

7.2.3 Analytical Method

Following the laboratory SOP, a sample aliquot will be placed in a graphite tube in the furnace, evaporated, charred, and atomized. Radiation from a given excited element is passed through the vapor containing ground-state atoms of arsenic. The intensity of the radiation decreases in proportion to the amount of ground-state atoms present. A monochromator isolates the characteristic radiation from the hollow cathode tube or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

7.2.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.2.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.2.6 Instrument Calibration and Frequency

A multi-point calibration curve with a correlation coefficient of greater than 0.995 must be generated daily, prior to analyses.

7.2.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.2.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.2.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.3 Lead by Furnace AA - SW 7421

7.3.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of lead at the Holloman AFB sewage lagoons listed in Table 5-1.

7.3.1.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion Procedure of Sludges - Method 3050 Digestions."

7.3.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of lead at the Holloman AFB sewage lagoons listed in Table 5-1.

7.3.2.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion Procedure of Sludges - Method 3050 Digestions."

7.3.3 Analytical Method

Following the laboratory SOP, a sample aliquot will be placed in a graphite tube in the furnace, evaporated, charred, and atomized. Radiation from a given excited element is passed through the vapor containing ground-state atoms of lead. The intensity of the radiation decreases in proportion to the amount of ground-state atoms present. A

monochromator isolates the characteristic radiation from the hollow cathode tube or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

7.3.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.3.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.3.6 Instrument Calibration and Frequency

A multi-point calibration curve with a correlation coefficient of greater than 0.995 must be generated daily, prior to analyses.

7.3.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.3.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.3.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.4 Mercury - SW 7471 (Cold-Vapor)

7.4.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of mercury at the Holloman AFB sewage lagoons listed in Table 5-1.

7.4.1.1 Sample Preparation

Soil samples will be prepared as directed in Method 7471.

7.4.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of mercury at the Holloman AFB sewage lagoons listed in Table 5-1.

7.4.2.1 Sample Preparation

Sludge samples will be prepared as directed in Method 7471.

7.4.3 Analytical Method

Following EPA Method 7471, mercury in the sample is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes

through a cell positioned in the light path of an atomic absorption spectrometer where absorbance due to mercury is measured.

7.4.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.4.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.4.6 Instrument Calibration and Frequency

A multi-point calibration curve with a correlation coefficient of greater than 0.995 must be generated daily, prior to analyses.

7.4.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.4.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.4.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.5 Selenium by Furnace AA - SW 7740

7.5.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of selenium at the Holloman AFB sewage lagoons listed in Table 5-1.

7.5.1.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion Procedure For Sludge - Method 3050 Digestions."

7.5.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of selenium at the Holloman AFB sewage lagoons listed in Table 5-1.

7.5.2.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion Procedure For Sludge - Method 3050 Digestions."

7.5.3 Analytical Method

Following EPA Method 7740 and the laboratory SOP, a sample aliquot will be placed in a graphite tube in the furnace, evaporated, charred, and atomized. Radiation from a given excited element is passed through the vapor containing ground-state atoms of selenium. The intensity of the radiation decreases in proportion to the amount of ground-state atoms present. A monochromator isolates the characteristic radiation from the hollow cathode tube or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

7.5.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.5.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.5.6 Instrument Calibration and Frequency

A multi-point calibration curve with a correlation coefficient of greater than 0.995 must be generated daily, prior to analyses.

7.5.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.5.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.5.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.6 Thallium by Furnace AA - SW 7841

7.6.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of thallium at the Holloman AFB sewage lagoons listed in Table 5-1.

7.6.1.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion Procedure For Sludges - Method 3050 Digestions."

7.6.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of thallium at the Holloman AFB sewage lagoons listed in Table 5-1.

7.6.2.1 Sample Preparation

Samples will be prepared following EPA Method 3050 and the laboratory-specific SOP provided in Appendix A, "Acid Digestion Procedure For Sludges - Method 3050 Digestions."

7.6.3 Analytical Method

Following the laboratory SOP, a sample aliquot will be placed in a graphite tube in the furnace, evaporated, charred, and atomized. Radiation from a given excited element is passed through the vapor containing ground-state atoms of thallium. The intensity of the radiation decreases in proportion to the amount of ground-state atoms present. A monochromator isolates the characteristic radiation from the hollow cathode tube or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

7.6.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.6.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.6.6 Instrument Calibration and Frequency

A multi-point calibration curve with a correlation coefficient of greater than 0.995 must be generated daily, prior to analyses.

7.6.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.6.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.6.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.7 Organochlorine Pesticides and PCBs - SW 8080

7.7.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of organochlorine pesticides and PCBs at the Holloman AFB sewage lagoons listed in Table 5-1.

7.7.1.1 Sample Preparation

Prior to analysis, samples will be prepared using either Method 3540 or Method 3550. Method 3540 and Method 3440 are procedures for extracting nonvolatile and

semivolatile organic compounds from soils and sludges. Both processes ensure intimate contact of the sample matrix with the extraction solvent.

Using Method 3540, the solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and as necessary, exchanged into hexane.

Using Method 3550, the sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The solvent is then extracted using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

Method 3620 may be used to cleanup the extracts. Florisil is a magnesium silicate with acidic properties. The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with hexane. The eluate is analyzed.

Method 3640, gel permeation chromatography (GPC), is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules that may be used to cleanup the extracts. The packing gel is porous and is characterized by the range or uniformity of that pore size. The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent the product is then concentrated.

Method 3660 will be used to cleanup the extract for analysis for PCBs. Sulfur is encountered in many sediment samples. Method 3660 is used after Method 3620 is employed. The solubility of sulfur in various solvents is very similar to the organochlorine pesticides; therefore, the sulfur interference follows along with the pesticides through the

normal extraction and cleanup techniques. To eliminate this interference, the sample is mixed with mercury and the extract is removed from the sulfur cleanup reagent.

7.7.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of organochlorine pesticides and PCBs at the Holloman AFB sewage lagoons listed in Table 5-1.

7.7.2.1 Sample Preparation

Prior to analysis, samples will be prepared using either Method 3540 or Method 3550. Method 3540 and Method 3440 are procedures for extracting nonvolatile and semivolatile organic compounds from soils and sludges. Both processes ensure intimate contact of the sample matrix with the extraction solvent.

Using Method 3540, the solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and as necessary, exchanged into hexane.

Using Method 3550, the sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The solvent is then extracted using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

Method 3620 may be used to cleanup the extracts. Florisil is a magnesium silicate with acidic properties. The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with hexane. The eluate is analyzed.

Method 3640, gel permeation chromatography (GPC), is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules that may be used to cleanup the extracts. The packing gel is porous and is characterized by the range or uniformity of that pore size. The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent the product is then concentrated.

Method 3660 will be used to cleanup the extract for analysis for PCBs. Sulfur is encountered in many sediment samples. Method 3660 is used after Method 3620 is employed. The solubility of sulfur in various solvents is very similar to the organochlorine pesticides; therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. To eliminate this interference, the sample is mixed with mercury and the extract is removed from the sulfur cleanup reagent.

7.7.3 Analytical Method

Method 8080 is a gas chromatographic method using electron capture detection or halide-specific detection. This method is used to determine the concentration of certain organochlorine pesticides and polychlorinated biphenyls with second column confirmation. Operating parameters and interferences are described in Method 8080 and the laboratory-specific SOP in Appendix A.

7.7.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.7.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.7.6 Instrument Calibration and Frequency

Calibration will be performed as directed in the method and described in Table 7-2.

7.7.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.7.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.7.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.8 Organophosphorus Pesticides - SW 8140

7.8.1 Soil Matrix

Soil samples will be analyzed by Method 8140 to determine the natural concentrations of organophosphorus pesticides at the Holloman AFB sewage lagoons listed in Table 5-1.

7.8.1.1 Sample Preparation

Prior to analysis, samples will be prepared using either Method 3540 or Method 3550. Method 3540 and Method 3440 are procedures for extracting nonvolatile and semivolatile organic compounds from soils and sludges. Both processes ensure intimate contact of the sample matrix with the extraction solvent.

Using Method 3540, the solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and as necessary, exchanged into hexane.

Using Method 3550, the sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The solvent is then extracted using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

Method 3620 may be used to cleanup the extracts. Florisil is a magnesium silicate with acidic properties. The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with hexane. The eluate is analyzed.

Method 3640, gel permeation chromatography (GPC), is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules that may be used to cleanup the extracts. The packing gel is porous and is characterized by the range or uniformity of that pore size. The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent the product is then concentrated.

7.8.2 Sludge Matrix

Sludge samples will be analyzed by Method 8140 to determine the natural concentrations of organophosphorus pesticides at the Holloman AFB sewage lagoons listed in Table 5-1.

7.8.2.1 Sample Preparation

Prior to analysis, samples will be prepared using either Method 3540 or Method 3550. Method 3540 and Method 3440 are procedures for extracting nonvolatile and semivolatile organic compounds from soils and sludges. Both processes ensure intimate contact of the sample matrix with the extraction solvent.

Using Method 3540, the solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and as necessary, exchanged into hexane.

Using Method 3550, the sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The solvent is then extracted using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

Method 3620 may be used to cleanup the extracts. Florisil is a magnesium silicate with acidic properties. The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with hexane. The eluate is analyzed.

Method 3640, gel permeation chromatography (GPC), is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules that may be used to cleanup the extracts. The packing gel is porous and is characterized by the range or uniformity of that pore size. The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent the product is then concentrated.

7.8.3 Analytical Method

Method 8140 is a gas chromatographic method using flame photometric detection or thermionic detection. This method is used to determine the concentration of certain organophosphorus pesticides. Second column confirmation analyses will be performed for all target analytes detected. Operating parameters and interferences are described in Method 8140 and the laboratory-specific SOP in Appendix A.

7.8.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.8.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and

available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.8.6 Instrument Calibration and Frequency

Calibration will be performed as directed in the method and as summarized in Table 7-2.

7.8.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.8.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.8.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.9 Chlorinated Herbicides - SW 8150

7.9.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of chlorinated herbicides at the Holloman AFB sewage lagoons listed in Table 5-1.

7.9.1.1 Sample Preparation

Soil samples will be prepared as directed in Method 8150.

7.9.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of chlorinated herbicides at the Holloman AFB sewage lagoons listed in Table 5-1.

7.9.2.1 Sample Preparation

Sludge samples will be prepared as directed in Method 8150.

7.9.3 Analytical Method

Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Second column confirmation analyses will be performed for all target analytes detected. A description of the method will be found in Method 8150, or the laboratory SOP provided in Appendix A.

7.9.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.9.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.9.6 Instrument Calibration and Frequency

Five-point calibration curves are prepared daily. QCCS samples are analyzed to verify calibration at a frequency of 5 percent of samples analyzed.

7.9.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.9.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.9.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.10 Volatile Organics - SW 8240

7.10.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of volatile organics at the Holloman AFB sewage lagoons listed in Table 5-1.

7.10.1.1 Sample Preparation

Sample preparation for analysis of soil samples by Method 8240 will follow Method 5030, purge and trap. The procedure for low-level concentrations will be followed when possible given the samples at hand. The laboratory-specific SOP is provided in

Appendix A. Prior to determination of the three compounds, 1,4-dioxane, isobutanol, and methacrylonitrile, these compounds will be extracted from soils with water. The resulting aqueous extract will then be analyzed by direct injection.

7.10.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of volatile organics at the Holloman AFB sewage lagoons listed in Table 5-1.

7.10.2.1 Sample Preparation

Sample preparation for analysis of sludge samples by Method 8240 will follow Method 5030, purge and trap. The procedure for mid-level concentrations will be followed. The laboratory-specific SOP is provided in Appendix A. Prior to determination of the three compounds, 1,4-dioxane, isobutanol, and methacrylonitrile, these compounds will be extracted from sludge samples with water. The resulting aqueous extract will then be analyzed by direct injection.

7.10.3 Analytical Method

The presence and concentration of purgeable halocarbon and organic compounds (volatile organics) in soil and sludge samples will be determined by EPA Method 8240 with a capillary column. The laboratory-specific SOP is provided in Appendix A. This method uses a purge and trap gas chromatographic/mass spectrometer (GC/MS) technique. An inert gas is bubbled through water to transfer the purgeable organic compounds from the liquid to the vapor phase. The vapor is then swept through a sorbent trap where the purgeables are trapped. The trap is backflushed and heated to desorb the purgeable organics onto a gas chromatographic capillary column where they are separated and then detected with a mass spectrometer. The analysis will include a 10 peak library search for tenatively identified compounds (TICs).

7.10.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.10.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.10.6 Instrument Calibration and Frequency

Calibrations will be performed daily using a five point calibration curve and checked every 12 hours with a continuing calibration check sample.

7.10.7 Internal Quality Control Checks

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.10.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.10.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.11 Semivolatile Organics - SW 8270

7.11.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of semivolatile organics at the Holloman AFB sewage lagoons listed in Table 5-1.

7.11.1.1 Sample Preparation

Soil samples will be prepared using either Method 3540, soxhlet extraction, or Method 3550, sonication. Laboratory SOPs are provided in Appendix A. Method 3540 and Method 3440 are procedures for extracting nonvolatile and semivolatile organic compounds from soils and sludges. Both processes ensure intimate contact of the sample matrix with the extraction solvent.

Using Method 3540, the solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and as necessary, exchanged into hexane.

Using Method 3550, the sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The solvent is then extracted using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

Method 3640, gel permeation chromatography (GPC), is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules that may be used to cleanup the extracts. The packing gel is porous and is characterized by the range or uniformity of that pore size. The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period.

The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent the product is then concentrated.

Method 3650, acid-base partition cleanup, may be used. The solvent extract is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and then ready for analysis for the acid analytes.

7.11.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of semivolatile organics at the Holloman AFB sewage lagoons listed in Table 5-1.

7.11.2.1 Sample Preparation

Sludge samples will be prepared using either Method 3540, soxhlet extraction, or Method 3550, sonication. Laboratory SOPs are provided in Appendix A. Method 3540 and Method 3440 are procedures for extracting nonvolatile and semivolatile organic compounds from soils and sludges. Both processes ensure intimate contact of the sample matrix with the extraction solvent.

Using Method 3540, the solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and as necessary, exchanged into hexane.

Using Method 3550, the sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The solvent is then extracted using sonication. The extract is

separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

Method 3640, gel permeation chromatography (GPC), is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules that may be used to cleanup the extracts. The packing gel is porous and is characterized by the range or uniformity of that pore size. The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent the product is then concentrated.

Method 3650, acid-base partition cleanup, may be used. The solvent extract is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and then ready for analysis for the acid analytes.

7.11.3 Analytical Method

Method 8270 is a capillary column GC/MS technique used for determining acidic, basic, and neutral organic compounds that are soluble in methylene chloride; methylene chloride extraction is the basis of Methods 3540 and 3550. Operating parameters and interferences are described in Methods 8270, 3540, and 3550 and in the laboratory-specific SOP presented in Appendix A. The analysis will include a 20 peak library search for tenatively identified compounds (TICs), which will include symtrinitrobenzene.

7.11.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.11.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.11.6 Instrument Calibration and Frequency

Calibrations will be performed daily using a five point calibration curve and checked every 12 hours with a continuing calibration check sample.

7.11.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.11.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.11.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.12 Polychlorinated Dioxins and Furans - SW 8280

7.12.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentrations of dioxins and furans at the Holloman AFB sewage lagoons listed in Table 5-1.

7.12.1.1 Sample Preparation

Soil samples will be prepared and cleaned up as necessary according to Method 8280.

7.12.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentrations of polychlorinated dioxins and furans at the Holloman AFB sewage lagoons listed in Table 5-1.

7.12.2.1 Sample Preparation

Sludge samples will be prepared and cleaned up, as necessary, according to Method 8280.

7.12.3 Analytical Method

Method 8280 is used to determine polychlorinated dioxins and furans (PCDD/PCDF). Retention time windows are determined for each isomer group. This is accomplished by injection of a PCDD/PCDF retention time standard which contains the first and last eluter from each isomer group. The isomer group retention time analysis is performed once at the beginning of each project and again if retention times shift more than

0.2 minutes. Adequate sensitivity is also verified from the retention time standard which contains $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 1.0 μg/mL.

7.12.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.12.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request.

7.12.6 Instrument Calibration and Frequency

Response factors for each PCDD/PCDF isomer class are determined from an initial five point calibration at 0.2, 0.5, 1.0, 2.0, and 5.0 μg/mL concentrations. This five-point calibration is performed in triplicate and the average response factors are calculated. The response factors determined for each isomer class must not have a percent RSD greater than 15 percent. Radian uses a calibration standard containing the following analytes:

- 2,3,7,8-TCDF,
- 1,2,3,7,8-PeCDF,
- 2,3,4,7,8-PeCDF,
- 1,2,3,4,7,8-HxCDF,
- 1,2,3,6,7,8-HxCDF,
- 2,3,4,6,7,8-HxCDF,
- 1,2,3,7,8,9-HxCDF,
- 1,2,3,4,6,7,8-HpCDF,
- 1,2,3,4,7,8,9-HpCDF,

- OCDF,
- 2,3,7,8-TCDD,
- 1,2,3,7,8-PeCDD,
- 1,2,3,4,7,8-HxCDD,
- 1,2,3,6,7,8-HxCDD,
- 1,2,3,7,8,9-HxCDD,
- 1,2,3,4,6,7,8-HpCDD, and
- OCDD.

Where more than one isomer per isomer group is present, the average response factor is used.

For quantitation, the following mixture of internal standards is contained in the calibration standard solutions. This mixture is also added to each sample before extraction:

- $^{13}C_{12}$-2,3,7,8-TCDD,
- $^{13}C_{12}$-2,3,7,8-TCDF,
- $^{13}C_{12}$-1,2,3,7,8-PeCDD,
- $^{13}C_{12}$-1,2,3,6,7,8-HxCDD,
- $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD, and
- $^{13}C_{12}$-OCDD.

Each isomer class is quantitated using a C-13 or C_{13} internal standard from that class.

7.12.7 Internal Quality Control Checks

A TCDD chromatographic test mixture is analyzed daily to verify that there is at least 25 percent valley resolution between 2,3,7,8-TCDD and 1,2,3,4-TCDD.

The 1.0 μg/mL PCDD/PCDF standard is analyzed at the beginning of each working day to verify that the response factors obtained for that day agree to within ± 30 percent of those obtained from the initial five-point calibration in triplicate. Also, isotope ratio for each PCDD/PCDF isomer class are verified to be within ± 15 percent of their theoretical values.

For PCDD/PCDF analyses, the mixture of internal standards also serves as the surrogate spikes. Surrogate recoveries are determined relative to $^{13}C_{12}$-1,2,3,4-TCDD, which is added to each extract prior to analysis. Surrogate response factors are determined from analysis of a $^{13}C_{12}$-TCDD spiked aliquot of the internal standard/surrogate solution. The acceptance criteria are 40 - 120 percent recovery of each PCDD/PCDF spike compound. The spike concentration is 25 ng of $^{13}C_{12}$-1,2,3,4-TCDD.

Additional daily QC checks are summarized in Table 7-2.

7.12.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.12.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.13 Cyanide - SW 9012

7.13.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentration of cyanide at the Holloman AFB sewage lagoons listed in Table 5-1.

7.13.1.1 Sample Preparation

Cyanide in soil samples will be released by refluxing the samples with strong acid and distillation of hydrocyanic acid into an alkaline scrubbing solution. This scrubbing solution is subsequently analyzed for cyanide.

7.13.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentration of cyanide at the Holloman AFB sewage lagoons listed in Table 5-1.

7.13.2.1 Sample Preparation

Cyanide in sludge samples will be released by refluxing the samples with strong acid and distillation of hydrocyanic acid into an alkaline scrubbing solution. This scrubbing solution is subsequently analyzed for cyanide.

7.13.3 Analytical Method

Method 9012 is used to determine the concentration of inorganic cyanide in an aqueous waste or leachate. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry.

7.13.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.13.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.13.6 Instrument Calibration and Frequency

A daily calibration curve is prepared using a blank and a minimum of five standards, with a correlation coefficient greater than 0.995. A high and a low standard are distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. The distilled standards must agree within ±15 percent of the undistilled standards.

7.13.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.13.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.13.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.14 Sulfide - SW 9030

7.14.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentration of sulfide at the Holloman AFB sewage lagoons listed in Table 5-1.

7.14.1.1 Sample Preparation

Sulfide in soil samples will be released by refluxing with strong acid and distillation of the resulting hydrogen sulfide into a scrubbing solution containing zinc acetate. The zinc sulfide which forms is separated and the sulfide content determined.

7.14.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentration of sulfide at the Holloman AFB sewage lagoons listed in Table 5-1.

7.14.2.1 Sample Preparation

Sulfide in sludge samples will be released by refluxing with strong acid and distillation of the resulting hydrogen sulfide into a scrubbing solution containing zinc acetate. The zinc sulfide which forms is separated and the sulfide content determined.

7.14.3 Analytical Method

Method 9030 is used to determine the concentration of total sulfides in zinc sulfide precipitate. Excess iodine is added to a sample which has been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic

conditions. The excess iodine is back-titrated with sodium thiosulfate or phenylarsine oxide.

7.14.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.14.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.14.6 Instrument Calibration and Frequency

The thiosulfate solution is standardized daily against primary standard potassium dichromate. The iodine solution is standardized daily against the standardized thiosulfate solution. The iodine solution is considered acceptable if the RPD is less than 5 percent.

7.14.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.14.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.14.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

7.15 Total Organic Carbon - SW 9060

7.15.1 Soil Matrix

Soil samples will be analyzed to determine the natural concentration of total organic carbon at the Holloman AFB sewage lagoons listed in Table 5-1.

7.15.1.1 Sample Preparation

Soil samples will be air dried and ground to pass through a 100 mesh sieve. An aliquot of the sized sample will be taken and treated with hydrochloric acid to remove inorganic carbon. The treated solid will be dried at 105°C, dried, and weighed.

7.15.2 Sludge Matrix

Sludge samples will be analyzed to determine the natural concentration of total organic carbon at the Holloman AFB sewage lagoons listed in Table 5-1.

7.15.2.1 Sample Preparation

Sludge samples will be air dried and ground to pass through a 100 mesh sieve. An aliquot of the sized sample will be taken and treated with hydrochloric acid to remove inorganic carbon. The treated solid will be dried at 105°C, dried, and weighed.

7.15.3 Analytical Method

Total organic carbon is measured using a carbonaceous analyzer by quantitatively converting the organic carbon in a sample to carbon dioxide which is measured by differential thermol conductivity using sequential removal of water and carbon dioxide.

7.15.4 Method-Specific Data Quality Objectives

Method-specific DQOs are presented in Table 7-2 as "Acceptance Criteria."

7.15.5 Preventive Maintenance

A preventive maintenance program will be followed to ensure the availability and accuracy of instruments. Records of repairs and adjustments will be maintained and available for inspection, upon request. Laboratory SOPs of instrument maintenance procedures are presented in Appendix A.

7.15.6 Instrument Calibration and Frequency

The instrument used to determine organic carbon is calibrated daily prior to use. QCCS samples are analyzed to verify calibration at a frequency of 10 percent of samples analyzed; recovery must be within 20 percent of the expected value.

7.15.7 Internal Quality Control Checks

Internal QC checks are presented in Table 7-2.

7.15.8 Corrective Action

Corrective actions are presented in Table 7-2.

7.15.9 Data Reduction, Validation, and Documentation

Data will be reduced, validated, and reported according to laboratory Standard Operating Procedures (SOPs).

8.0 CHEMICAL DATA QUALITY MANAGEMENT (CDQM) DELIVERABLES

The following CDQM deliverables will be prepared for this project:

- Chemical Data Acquisition Plan (this document);
- Site Safety and Health Plan;
- A-E Daily Quality Control Reports;
- A-E Sampling and Quality Control Summary Report; and
- Site Decision Report.

9.0 REFERENCES

1. CH2M Hill, 1983: Installation Restoration Program Records Search for Holloman Air Force Base, New Mexico, Gainesville, FL.

2. A.T. Kearney, Inc., 1990: RCRA Facility Assessment Preliminary Review/Visual Site Inspection Report, Redwood City, CA.

3. Walk, Haydel & Associates, 1989: Installation Restoration Program Remedial Investigation Report for Holloman Air Force Base, New Mexico, New Orleans, LA.

4. EPA, SW-846, 1989: "Test Methods for Evaluating Solid Waste - Physical/Chemical Method." Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C., SW-846, fourth edition, revised 1989.

5. Kim, Yongmoo, 1991: "Draft Preliminary Standards for RCRA Risk Assessment," EPA Region 6, Dallas, Texas. February 20, 1991.

833d CSG/DEV
Holloman Air Force Base,
New Mexico

LIBRARY COPY

Chemical Data Acquisition Plan (CDAP)

Volume II - Appendices
Sewage Lagoon Investigation

February 1992

Prepared Under Contract With:
US Army Corps of Engineers,
Omaha District

RADIAN
CORPORATION

RADIAN
CORPORATION

DCN 92-269-069-02-03
RCN 269-069-02-02

8501 Mo-Pac Blvd.
P.O. Box 201088
Austin, TX 78720-1088
(512)454-4797

CHEMICAL DATA ACQUISITION PLAN (CDAP)

SEWAGE LAGOON INVESTIGATION
HOLLOMAN AIR FORCE BASE, NM

Volume II

Prepared for:

49 SG/DEV
Holloman Air Force Base, NM

Prepared by:

Radian Corporation
8501 North MoPac Blvd.
P.O. Box 201088
Austin, Texas 78720-1088

Under Contract No. DACW45-91-D-0018 with:

U.S. Army Corps of Engineers
Omaha District
Omaha, Nebraska

February 1992

APPENDIX A

RADIAN CORPORATION ANALYTICAL LABORATORY STANDARD OPERATING PROCEDURES

CROSS-REFERENCE TABLE OF SOPS

Method or Procedure No.	Reference:	Title of SOP
325-AD-001		General Training
320-CH-019		Analysis of Chlorinated Herbicides by EPA method SW-846-8150 (3rd Ed.)
321-CH-011		Analysis of Appendix IX Organophosphorus Pesticides by EPA Method SW-846-8140 (3rd Ed.)
320-DG-003		Acid Digestion of Sludges - Method 3050-Digestions
321-CH-008		Analysis of Appendix IX Organochlorine Pesticides and PCBs by EPA Method SW-846-8080 (3rd Ed.)
321-MS-009		Analysis of Purgeable Volatile Appendix VIII Compounds Using USEPA SW-846 Method 8240
321-SP-008		Operation of the Ultratip Probe Sonication System
321-SP-020		Sonication Extraction by EPA Method SW-846-3550
325-AA-003	EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 270.2	Analysis of Selenium by Graphite Furnace
325-IN-001		Equipment Maintenance
321-SP-024		Special Procedure When Preparing Samples for GC/ECD Analysis
325-AA-004	EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 239.2	Analysis of Lead by Graphite Furnace
321-MS-010		Analysis of Appendix IX Semivolatile Compounds by EPA Method SW-846-8270
320-MT-001	EPA 200.7 SW846 3rd Method 6010	Inductance Coupled Plasma Emission Spectroscopy
325-IN-001		Equipment Maintenance
325-GC-005	EPA Method 8000, SW846, 3rd Ed.	Documentation and Data Review
338		Determination of Organic Lead Compounds by Flame Atomic Absorption Spectrometry
321-SP-013		Soxhlet Extraction by EPA Method SW-846-3540, 3rd Ed.
321-SP-026		Method 8280 for Analysis of Dioxins and Furans
325-SP-018		Sample Preparation for Chlorinated Herbicides in Sludge or Solid Matrices
325-SP-039		Sulfur Cleanup by SW-846, Method 3660
325-SP-014		Alumina Column Cleanup - Method SW-846-3611, 3rd Ed.
325-SP-011		Acid-Base Cleanup Extraction - EPA Method SW-846-3650, 3rd Ed.
325-SP-034		Silica Gel Cleanup for Analysis of PNA's
325-SP-038		Florisil Column Cleanup
321-MS-011	SW-846 3rd Ed., Method 8280	GC/MS PCDD/PCDF Analysis
325-AA-005	EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 279.2	Analysis of Thallium by Graphite Furnace
325-AA-001	EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 206.2	Analysis of Arsenic by Graphite Furnace

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY:	PROCEDURE NO: 325-AD-001	PAGE: 1 of 22
TITLE: General Training	REVISION NO: Original	EFFECTIVE DATE: 8/2/88
	SUPERSEDES: N/A	

REFERENCES: 320-AD-001

SATELLITE FILES: All

REASON FOR REVISION: Original

1.0 INTRODUCTION

This Standard Operating Procedure addresses training within the Analytical Chemistry Department of Radian Corporation. To simplify the process of training, we hire capable people with some preliminary education and training. However, any laboratory staff member must be taught the important aspects of a new task and the techniques needed to obtain results which conform to the Radian Quality Specifications (form attached). Standard Operating Procedures for specific laboratory procedures are essential in the performance of analytical work which will meet these Quality Specifications. The combination of the use of the correct Standard Operating Procedures and documented training in the Analytical Chemistry Department ensure that all staff analysts will deliver quality analytical work.

2.0 PURPOSE

The purpose of this Standard Operating Procedure is to orient employees in specific aspects of training. In addition, this Standard Operating Procedure defines the selection and documentation procedures for training, and the use of Standard Operating Procedures, the Detailed Project Work Plan form and the Corrective Action Report form. Special requirements for Safety and Quality Assurance/Quality Control are also defined.

WRITER: NAME/DATE:		
ACTIVITY MGR: NAME/DATE	NAME/DATE	NAME /DATE
R A Magee 7/7/88	Jean Zeller 7/26/88	8/2/88

7-87-27815

is obtained from the Document Control Officer, make the revisions and route the revised Standard Operating Procedure for review and signatures.

3.6 New Standard Operating Procedures should be written as needed, reviewed, and routed for signatures. See SOP 320-AD-001 for SOP procedures.

3.7 The "Corrective Action Report" (CAR) form (attached) is for communication and documentation on situations requiring action. The form allows documentation of the situation and subsequent action. The originator fills out Part 1 and distributes the copies. The reply/resolution is completed by the Technical Director.

4.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/AC)

4.1 Each laboratory has a Standard Operating Procedure for QA/QC criteria and procedures. The QA/QC results are used to evaluate how the process went, usually by tests of precision and accuracy.

4.2 Goals for precision and accuracy are often set based on previous experience of the laboratory, the EPA CLP experience, or the Quality Assurance Project Plan for the program. The supporting the QA/QC data and documentation ensure that the analytical data are of known quality.

4.3 Control charts are used to monitor instrument and/or method performance. If the value plotted (usually response), fails to meet the QC requirements, corrective action is required before proceeding with analyses. Indicate actions or changes on the chart and/or in a notebook. The existence of a control chart provides documentation that the instrument operated correctly on the day a given measurement was made and/or that documented problems were addressed.

ATTACHMENTS

1. Radian Quality Specification
2. Standard Operating Procedure Training Form
3. Analytical Method System Training Form
4. Detailed Project Work Plan Form
5. Corrective Action Report Form

PREFACE

A "Radian Quality Project" is defined as one which conforms to the specifications set forth in this document. The document was developed by a representative group of senior operations, technical, and G&A staff members. Initially, the group was asked if a quality specification for a generic Radian project could be written. About half the group felt it was possible; the other half was not optimistic. After its development, however, the group was unanimously supportive and enthusiastic about the specification.

Ten quality specifications are included: two procedural specs, seven project specs, and one developmental spec. Each specification can be met only if each subspecification accompanying it is met. Guidelines are not mandatory, but experience has shown that following the guidelines facilitates meeting spec.

A "Radian Quality Project" meets all ten specifications. It can legitimately be argued that a project of satisfactory quality could be achieved without meeting all of the specs, particularly the procedural and developmental ones. The group believes adherence to these specs increases the probability of a successful project so greatly, however, that they merit inclusion as hard specs.

The project team, subject to supervisory review, determines whether a completed project meets spec. The specification is, of course, reviewed regularly by project team members during the execution of the project to insure that it is being met. At project conclusion, prior to wrap-up, the Program Manager (PM) and Project Director (PD) jointly mark the reporting blocks in this spec. The project team then reviews their assessment during the wrap-up meeting and any differences are discussed and reconciled. If it is ultimately determined that all reporting blocks can be marked "yes," the project meets spec. The completed Quality Specification/Report is then routed to the PD's Division Manager for inclusion in the Division Manager's Notebook. Copies should be sent to the PM's Section Manager and to the Division Managers of other project participants. Audits of completed Quality Specification/Reports will be conducted by Division Managers and Operations Staff Section Managers.

The spec calls for peer review of the project at several points during its execution. The peer reviewer(s) should be a technically qualified staff member not working on the project. The reviewer(s) should be selected prior to project kickoff and his/her review time budgeted into the project. Any questions concerning the review process should be addressed by the PD's Division Manager.

At first glance it may look as if adherence to this specification will increase the cost of the project. The specification development group is convinced, however, that careful adherence to the spec will, on the average, reduce project execution costs. The spec is also designed so that it may be applied effectively and efficiently to projects ranging from the very small to the very large. Finally, quality control reporting has been made very simple so that it requires very little time.

Quality work is absolutely essential to Radian's continuing success. In order to maintain our reputation and assure our future growth and profitability, we must consistently produce high quality products. This will occur if every Radian PM, PD, and Task Leader (TL) uses the spec as it was intended, i.e., as a guide in planning, controlling, and wrapping up projects.

HOW TO USE THIS QUALITY SPECIFICATION

This spec will be applied to all projects, large and small. (The Project Instructions for a very small project, of course, may be contained on a single page.) The spec may be met by following the steps listed below.

1. The PM and PD commit to meeting the spec before the project is bid.
2. The PM and PD carefully read the spec prior to proposal preparation.
3. The PM and PD bid the project in such a manner that the spec can be met.
4. The PM and PD execute the Proposal Checklist Report in Attachment D to the spec at the time the proposal is prepared.
5. The PM and PD reread the spec prior to project initiation.
6. The PM and PD develop Project Instructions which will produce a project which meets the spec.
7. The PM and PD execute the Project Kickoff Report in Attachment D.
8. At major milestones (designated in the Project Instructions), the PM and PD review project progress against the quality spec and take any corrective measures necessary to ensure that the spec is being met.
9. At conclusion of the project, the Project Quality Specification/Report is filled out, reviewed, and distributed in accordance with the instructions contained in the Preface above. The project is judged to have met the quality specification if all specifications and all subspecifications accompanying them are met.

B. PROJECT SPECIFICATIONS

	YES	NO
1. Were the project objectives met?	☐	☐
a. Were the objectives clearly stated and documented in the Project Instructions at the onset of the project?	☐	☐
b. Did peer and client review of the objectives at the onset of the project find that the objectives addressed the client's needs in solving his/her problems?	☐	☐
c. If changes were made in the project objectives during the execution of the project, were those changes documented in writing and did both Radian and the client agree to such changes at that time?	☐	☐
d. Did peer and client review find that the product met the objectives?	☐	☐
e. Were all contract deliverables (interim and final) provided?	☐	☐

	YES	NO
2. Was the work technically sound?	☐	☐
a. Was a detailed work plan developed and was peer review positive after incorporation of reviewer comments?	☐	☐
b. Was the need for a specific, written Quality Assurance Project Plan (QAPP) evaluated by the PM/PD and, if required, was the resulting QAPP approved by the QA Officer/Designee?	☐	☐
c. Were appropriate technical milestones provided in the Project Instructions?	☐	☐
d. Was proper peer review conducted and appropriate corrective action taken at each milestone?	☐	☐
e. Did peer review find that all appropriate data and associated data quality measures were developed and addressed in the findings?	☐	☐
f. Did peer review find that conclusions were complete and supported by the findings?	☐	☐
g. Was the QAPP, if required, correctly and completely implemented?	☐	☐
h. Was final peer review positive?	☐	☐

	YES	NO
3. Was the client pleased with the work?	☐	☐
a. Did the client say he/she was pleased with the work when asked?	☐	☐
b. Did the client say he/she was pleased with the report when asked?	☐	☐
c. Was the client pleased with our responsiveness, adherence to schedule, and the timeliness of our services?	☐	☐
d. Did the work put us in a favorable position to obtain follow-on?	☐	☐
e. If the client commented to others about the program, were the comments positive?	☐	☐
f. If applicable, were award fee results high?	☐	☐

	YES	NO
4. Was the work conducted in a professionally safe manner?	☐	☐
a. If the project involved field operations, was a safety plan prepared and approved? If field operations were not involved, did the PM/PD evaluate the need for a project-specific safety plan prior to the initiation of work?	☐	☐
b. If a project-specific safety plan was required for an activity, was peer review positive after incorporation of reviewer comments?	☐	☐
c. Were all Radian team members properly trained in the procedures outlined in the *Radian Health and Safety Manual* and in project-specific safety procedures (including client-dictated practices) prior to the initiation of work?	☐	☐
d. Did all Radian personnel comply with applicable safety procedures during performance of the work?	☐	☐
e. Were all affected Radian personnel satisfied with the level of safety procedures used on the project or, if not, were the safety procedures used found to be adequate after a review by senior technical staff management?	☐	☐

ATTACHMENTS TO PROJECT QUALITY SPECIFICATION/REPORT

ATTACHMENT A
PROJECT INSTRUCTIONS OUTLINE

A set of Project Instructions must be issued by the PM/PD team before execution begins on any Radian project. The Project Instructions should contain at least the information described below. Any additional sections may be included at the discretion of the PM/PD team. A copy of sections 1 and 2 will be forwarded to the Marketing Support Office (Room 4-233, Austin).

1.0 IDENTIFYING DATA–Radian project number, project title, client, client's contract number, contract type, effective date, and duration.

2.0 PROJECT SUMMARY–A brief (half-page) description of the work to be performed.

3.0 SCOPE–The scope of work in task statement form.

4.0 PERSONNEL–All personnel who will be involved with the project, both technical and contractual, for both the sponsor and Radian. Peer reviewers and their responsibilities.

5.0 PROJECT ORGANIZATION–The project organization formed by Radian to execute the project. The project organization chart. The Radian secretary in charge of the project.

6.0 BUDGETS–Budgetary responsibilities of each individual in the project organization. Labor, materials, and supplies budgets. Time-phased labor expenditures for each team member.

7.0 SCHEDULE–The project schedule. The individual responsible for each milestone.

8.0 CONFIDENTIALITY–All confidentiality considerations clearly defined.

9.0 SAFETY–All safety considerations clearly defined.

10.0 REPORTS–All required reports listed, any special formats cited, and the specific individual responsible for editing, approving, and getting each report out on time designated.

11.0 CORRESPONDENCE–Distribution instructions and mailing addresses for each type of correspondence going both to the client and to Radian.

12.0 PROJECT FILE–The location of the master project file, any pertinent format data, and the individual responsible for maintaining the file.

13.0 DETAILED WORK PLAN–The technical plan prepared by PM, PD and TLs. This must describe the technical aspects of implementing the work in adequate detail to allow the peer reviewers to fully critique the planned approach, methods, and experimental designs including the Quality Assurance Project Plan (QAPP). This objective may be achieved by a single document or a combination of individual test plans, safety plans, QAPPs, oral presentations or other project planning materials.

14.0 SUBCONTRACTOR MANAGEMENT–Project Instructions for any subcontractors/consultants/external laboratories.

ATTACHMENT B
REPORT PRESENTATION GUIDELINES

1. Did the report properly and fairly document the project, its findings, conclusions, and recommendations?
2. Did the report receive a thorough technical review?
3. Did the report comply with the Radian (or a client-specified) format as outlined in the *Radian Style and Format Guide: THE WRITE STUFF*?
4. Was the report well written, i.e., clear, concise, well organized, and internally consistent in presentation?
5. Did the report receive a thorough editorial review?
6. Were all typos and grammatical errors identified and corrected?
7. Was one typeface used throughout the report?
8. Were appropriate credits and/or references given throughout the report?
9. Were all abbreviations and/or acronyms defined in the report?
10. Did all draft reports possess a final report quality when presented to the client?

Distribution:
PM Section Mgr _____
PD Div Mgr _____
PD Group Ldr _____
PD Dept. Hd _____

ATTACHMENT D
PROPOSAL CHECKLIST/PROJECT KICKOFF REPORT

PROPOSAL CHECKLIST REPORT

Radian Proposal No. ____ ____ ____ ____ Radian Project No. ____ ____ ____

Proposal/Project Title _____

Bid Price _____

Budget Review Checklist

1. What is our best estimate of the cost to do this job? Has this estimate included contingencies?
2. Did we bid this price?
3. If no, and we bid lower, why and what funds will make up the difference?
4. If legitimate technical problems require more funds than allocated to the job, how will we secure additional funds or reduce the project scope?
5. At what point will the client be made aware of this contingency plan?
6. How will agreement on budget modifications resulting from changes in scope be reached?
7. Have any additional capital assets required to execute this project been approved and budgeted?
8. Do the PM and PD understand that if costs to execute this project exceed allocated funds and if the contingency plan (or an alternate contingency plan) does not provide additional funding or scope reduction to bring project within budget, then the project is overrun and does not meet the project specification?

PM _____ (Date) PD _____ (Date)

PROJECT KICKOFF REPORT

Radian Project No./Title _____

Budget _____ Start Date _____ Completion Date _____

PM _____ PD _____

Peer Reviewers _____

Project Secretary _____

Provide answer and date for each:

1. Project Instructions Prepared? _____ Peer Review Positive? _____
   Copies of Sections 1.0 and 2.0 sent to Marketing Support Office? _____
2. Quality Assurance Plan Needed? _____ Prepared? _____
   Peer Review Positive? _____
3. Safety Plan Needed? _____ Prepared? _____
   Peer Review Positive? _____
4. Masterfile Input Forms Submitted? _____
   Invoicing Instructions Submitted? _____
5. Budget Review Checklist Reviewed? _____
   Budget Commitment (see Item 8 above):

PM _____ (Date) PD _____ (Date)

Peer Reviewers _____ (Date) _____ (Date)

10/83/14698

RADIAN CORPORATION

RECORD OF ANALYTICAL METHOD/SYSTEM TRAINING FOR _____ AREA

Name: _____ Analytical Method/System: _____

Pertinent Documentation (Radian Standard Operating Procedures, Published Methods): _____

_____

Equipment or Instrument Involved: _____

_____

_____

Details of Training: (If not pertinent indicate with NA)

	INITIALS Analyst	Trainer	Date
A. Studied pertinent documents.	_____	_____	_____
B. Performed task with trainer.	_____	_____	_____
C. Performed task or method independently with review by trainer (using check sample if appropriate, attach results)	_____	_____	_____
D. Performed basic maintenance with trainer.	_____	_____	_____
E. Performed basic maintenance independently with review by trainer.	_____	_____	_____

Lab Manager Training Record Review (initials, date):

_____ _____ _____ _____

_____ _____ _____ _____

QC Requirements (minimum listed, check for minimum - charge for more):

System Blanks(10%)_____ Reagent Blanks(10%)_____ Recovery Check(10%)_____

Duplicate Analyses(10%)_____ Linearity Check(4pts)_____ LLD_____ LLQ_____

Matrix Spike(5%)_____ Internal Standard(s):_____

Surrogate(s):_____ Other:_____

Safety Precautions:

Routine:_____

Other:_____

Potential Problems:_____

Budget (people, hours, ODCs & charge numbers):_____

Prepared by:_____

Approval: PD or TL_____ Date_____

Part II Reply / Resolution (Furnished by Technical Director)

Proposed by: Date: CAR #:

Description: Scheduled Implementation:

Part III Implemented Correction Action (by:)

Description: Date Implemented:

Part IV Follow-Up Required: Yes ☐ No ☐ (by:)

Verified by: Date: Comments:

Information Copies, Distributed by Technical Director:

Corrective Action Report (CAR)

Part I Initial Information (Furnished by Originator)

Originator:

Urgency Level:

Requires resolution for immediate job ☐

Date:

Requires resolution for future jobs ☐

To Lab Manager Responsible for Action: _____

Present Situation Requiring Action:

Site / Lab: Type: QC Limit ☐ Documentation ☐ System ☐ Other ☐

Date / Time Identified:

Description of Situation: (attach supporting data if available)

Recommended Corrective Action or Improvement:

Description: Implemented by:

Department Head Copy (Pink)

CONFIDENTIAL

RADIAN

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Gas Chromatography	PROCEDURE NO: 320-CH-019	PAGE: 1 of 48
TITLE: ANALYSIS OF CHLORINATED HERBICIDES BY EPA METHOD SW-846-8150 (3rd Ed.)	REVISION NO: 1	EFFECTIVE DATE: 5/3/90
	SUPERSEDES: 321-CH-009	

REFERENCES: 321-SP-001, 321-SP-004, 321-SP-018, 321-SP-019, 321-CH-001, 321-CH-003, 321-CH-004

SATELLITE FILES: 1-169

REASON FOR REVISION: Updated SOP

1.0 PURPOSE

1.1 To provide a procedural guide for the application of EPA SW-846-8150 (see Appendix I) to the analysis of chlorinated herbicides in hazardous wastes.

1.2 To describe modifications to Method 8150 necessary to optimize performance for the analytical instrumentation in the Radian Analytical Chemistry Laboratories.

2.0 SCOPE AND APPLICABILITY

2.1 Chlorinated herbicides may be analyzed in water, soil, or sludge matrices with analytical sensitivity in the low ppb range. Appendix II of this SOP provides a table of target species and method detection limits (MDL).

3.0 METHOD SUMMARY

3.1 SW-846-8150 describes gas chromatographic conditions and calibration criteria for the analysis of various chlorinated herbicides. The sample is extracted as described in SOP 321-SP-019. After the methylene chloride extraction, the extract is esterified with diazomethane. An aliquot is injected into the gas chromatograph equipped with an electron capture detector.

4.0 INTERFERENCES

4.1 Matrix interferences can be caused by the co-extraction of contaminants originating either in the sample or in the extraction process itself. Reagent water method blanks should be run to insure that glassware and reagents used in sample processing are interference-free. The nature and extent of interferences co-extracted from the samples will vary considerably from source to source. Organic acid, especially chlorinated acids, and phenols may cause interference with the determination.

WRITER/NAME/DATE: Clifford Mayer 12/13/89	Gary Nelson 5/3/90	
ACTIVITY MGR: NAME/DATE Marilyn Melton 12/20/89	NAME/DATE Fred Shore 2/5/90	NAME /DATE Paul H Wale 4/3/90

7-87-27815

5.4.2 Stock Preparation

Compound	Original Conc. ug/mL	Volume Spike (uL) in 1 mL MeOH	Final Conc.*
2,4-D	5000	200	1000 ug/mL
Silvex	5000	200	1000 ug/mL
2,4,5-T (Silvex)	5000	200	1000 ug/mL
Dinoseb	5000	200	1000 ug/mL
Dicamba	5000	200	1000 ug/mL
2,4-DB	5000	200	1000 ug/mL
Dalapon	5000	200	1000 ug/mL
Dichloroprop	5000	200	1000 ug/mL
MCPP	Neat	200 mg/10 mL	20,000 ug/mL
MCPA	Neat	200 mg/10 mL	20,000 ug/mL

5.4.3 Working Standard Preparation

Use stock solution (1000 ug/mL) concentration for Standard # 1 and #2; dilute stock solution (1000 ug/mL) 1/10 = 100 ug/mL for Standard #3, 4, and 5:

	#1	#2	#3	#4	#5
Dilution of compounds 1-8 (Resulting Conc.)	1.0	0.5	0.25	0.10	0.05 ug/mL
uL of Stock Solution Der. in 10 mL	10 uL	5 uL	25 uL*	10 uL*	5 uL*

*Dilute 1/10 = 100 ng/uL for Standard # 3, 4, and 5

	#1	#2	#3	#4	#5
Dilution of compounds 9-10 (Resulting Conc.)	200	160	80	40	20 ug/mL
uL of Stock Sol. (20,000 ug/mL) Der. in 10 mL	100 uL	80 uL	40 uL	20 uL	10 uL

5.4.4 Quality Control Check Standard Preparation

Prepare standard from EPA QC standard or standard from second source using a concentration high enough so only a few uL can be used to get desired concentration in 10 mL. If the solvent is not MeOH or hexane, evaporate to dryness before methylating. (Desired concentration is 250 pg/uL for all but MCPP and MCPA, which should be approximately 80,000 pg/uL or 80 ug/mL.)

Alternate temperature programs may be used if all analytes can be separated and quantitated.

7.3.3 Instrument Parameters C

Column: 6' x 2mm, 1.5% OV-1 + 1.5 OV-225 on Gas Chrom-Q
Inlet Temperature: 220°C
Detector Temperature: 320°C
Carrier Gas: 5% methane/95% argon @ 30 mL/min
Makeup Gas: none
Oven Temperature: Initial — 50°C for 1 minute
Ramp 1 -- 10°C/minute to 185°C
hold @ 185°C for 5 min
Ramp 2 -- 20°C/minute to 200°C
Injection Volume: 2 uL

7.3.4 Instrument Parameters D

Column: DB-5, 30m x 0.53 mm (J & W Scientific)
Inlet Temperature: 210°
Detector Temperature: 300
Carrier Gas: Helium @ 15mL/min
Makeup Gas: 5% methane/95% argon @ 15mL/min.
Oven Temperature: 180° Isothermal
Injection Volume: 2 mL

7.3.4 Instrument Parameters E

Column: DB-608, 30m X 0.53mm (J&W Scientific)
Inlet Temperature: 210°C
Detector Temperature: 300°C
Carrier Gas: Helium @ 15mL/minute
Makeup Gas: 5% methane/95% Argon @ 15mL/minute
Oven Temperature: 180°C Isothermal
Injection volume: 2mL

8.4 Concentration Factor

MDLs quoted on SAM® are for a water matrix and assume a 1L sample size taken to a 10 mL final volume. A concentration factor (CF) needs to be calculated for entry into SAM so that the MDLs will be adjusted for sample sizes other than 1L, dilution in the lab, and dilution effects due to sample cleanup techniques, and matrix, if different from water.

$$\text{CF Water} = \left[\frac{\text{Ideal Volume One (L)}}{\text{Actual Volume (L)}}\right] [\text{DF}]$$

$$\text{CF Soil} = \left[\frac{\text{Ideal Weight One (kg)}}{\text{Dry Weight (kg)}}\right] [\text{DF}]$$

8.5 Dilution Factor

The dilution factor (DF) takes into account the analytical lab dilution, extraction dilution, and sample cleanup dilution.

DF = [GC dilution] [Extraction dilution] [Cleanup dilution]

8.6 Example Calculations for CF and DF

8.6.1 Case 1: Water sample. Sample prep extracts an aqueous sample of 900 mL. The extract is evaporated to dryness. Then extract is redissolved in hexane, methylated, and brought to a final volume of 10 mL. It requires a 1/10 dilution for GC analysis:

$$\text{DF} = [10] \left[\frac{10\ \text{mL}}{10\ \text{mL}}\right] = 10$$

$$\text{CF} = \left[\frac{1\text{L}}{0.90}\right] [10] = 11$$

If the method quoted MDL for silvex is 0.15 ug/L, the actual DL for this sample would be 1.6 ug/L.

8.6.2 Case 2: Soil Sample. Sample prep extracts 1 gm of soil with a moisture content of 10%. The extract is evaporated to dryness. Then extract is redissolved in hexane, methylated, and brought to a final volume of 10 mL. GC analysis requires a 1/20 dilution:

$$\text{DF} = [20] \left[\frac{10\ \text{mL}}{10\ \text{mL}}\right] = 20$$

$$\text{CF} = \left[\frac{1\text{L}}{(0.001\text{kg})(.90)}\right] [20] = 22{,}222$$

If the method quoted MDL for silvex is 0.15 ug/L, the actual DL would be 3300 ug/kg.

calibration standards (preferably 100 pg/uL). If the response for any analyte varies from the original response by more than ±15%, this may indicate that the calibration sample has changed or that maintenance of tha analytical equipment is required. A freshly prepared calibration sample should be analyzed. If the sample fails the calibration criteria, then the following items should be done:

1. Replace septum every 75 injections or sooner.
2. Clean or replace the inlet splitter.
3. Clean or remove the front portion of the column.
4. Check the autosampler for carryover or non-reproducibility.
5. Bake-out the column and detectors.
6. Solvent rinse the capillary column.
7. Clean or replace the ECD.

If the problem involves poor peak resolution, peak tailing, non-symmetrical peaks, and none of the above maintenance items solves the problem, then change the column. The useful lifetime of the column depends on factors such as, number of samples analyzed, purity of carrier gas, contamination level of samples and frequency of routine maintenance. Every time a column is replaced a 72-hour retention time study is performed (see Section 9.4) and a new five-point calibration curve must be run.

9.3 Analytical Sequence

The following is a typical work day sequence of standards and samples after the five-point calibration has been achieved:

1. System blank (solvent only)
2. Calibration check
3. Reagent blank
4. 10 samples
5. Sample duplicate
6. Calibration check
7. Repeat 4 through 6

9.4 Retention Time Windows

9.4.1 72-Hour Retention Time Study

Each column used for Method 8150 must undergo a 72-hour retention time study with the results archived in the lab for the lifetime of the column. Details for performing the study appear in SW-846 Method 8000 Section 7.5. Retention time windows which exceed 1.5% for capillary columns indicate a problem. Corrective action should be taken which may include:

result for the unspiked sample may not be reported for regulatory compliance purposes.

9.8 Method Blanks and System Blanks

9.8.1 A method blank is performed with each extraction batch and is carried through the entire sequence. An out-of-control blank is defined as one which contains target analytes at or above the method MDL or non-target analytes at a level that would require further dilution (i.e., effective elevation in sample MDLs) to bring the analysis on scale. The out-of-control blank is documented via the Radian Malfunction Form or Corrective Action Report shown in Appendix VII. The results for the samples should be reported without performing any means of background subtraction. Presence of the target analyte in a blank is documented with a B flag in the results field and should be documented in the comments section of SAM.

9.8.2 System blanks are internal lab discretionary checks and are not reported routinely on SAM.

10.0 DOCUMENTATION

10.1 Labeling of Chromatograms

In order to provide analytical traceability, chromatograms should be labeled with the following items of information. Labs equipped with data systems can program the information into the report header. Laboratories with integrators will need to manually label each chromatogram. In this case, predesigned stamps have proven useful.

SAM Number
Standard ID#
Instrument Number
Analysis Date
Analysis Time
Unique File Number (Run Number)
Analyst Initials
Dilution Used
Injection Volume

10.2 Notebook Documentation

10.2.1 All manual sample calculations should be documented in a Radian bound notebook. Pages should be numbered sequentially and contain the following information:

SAM Number and Fraction Number
Unique File Number
Standard Number - if any
Analysis Date and Time (if not incorporated in the unique file number)
Instrument Number (if not incorporated in the unique file number)

11.2 Only positively confirmed results above the MDL are routinely reported in the Radian Analytical Labs. The C (confirmed) flag will appear in the SAM field to document the confirmation status of the result when second column confirmation was required by the client. In those cases where a confirmation was not performed at the client or project request, the V (second column not requested) flag should appear in the result field. Results which underwent a second column analysis but were not confirmed can be reported on a project requested basis. The X (false positive) flag is used in these cases.

11.3 Confirmed results below the MDL can be reported on a project requested basis. In these cases, the result is flagged with an E (estimated) flag on SAM to indicate the non-quantitative nature of below MDL reporting.

Unconfirmed results below the MDL should not be reported.

Appendices

Appendix I.	EPA Method SW-846-8150 (See following 20 pages)
Appendix II.	Method 8150 MDLs
Appendix III.	Site-Specific Instrumentation Information for Radian Labs
Appendix IV.	Relative Elution Orders for Each Set of Instrument Parameters
Appendix V.	Summary of Method 8150 Quality Control
Appendix VI.	Example of QC Control Chart for Surrogate Recovery
Appendix VII.	Radian Malfunction Form and Corrective Action Report
Appendix VIII.	Appendix B to Part 136, 49 Federal Register 43430, Oct. 26, 1984
Appendix IX.	Derivitization Procedure (Austin)

METHOD 8150

CHLORINATED HERBICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.3 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.4 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 4-mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.1.2 Column 2: 1.8-m x 4-mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.1.3 Column 3: 1.98-m x 2-mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopack C or equivalent.

4.1.2 **Detector:** Electron capture (ECD).

4.2 Erlenmeyer flasks: 250- and 500-mL Pyrex, with 24/40 ground-glass joint.

4.3 Beaker: 500-mL.

4.4 Diazomethane generator: Refer to Section 7.3 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 **Diazald kit:** recommended for the generation of diazomethane using the procedure given in Section 7.3.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150-mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Section 7.3.3.

4.5 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw cap.

4.6 Separatory funnel: 2-L, 125-mL, and 60-mL.

4.7 Drying column: 400-mm x 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.8.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.8.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.11 Microsyringe: 10-uL.

4.12 Wrist shaker: Burrell Model 75 or equivalent.

4.13 Glass wool: Pyrex, acid washed.

4.14 Balance: Analytical, capable of accurately weighting to the nearest 0.0001 g.

4.15 Syringe: 5-mL.

4.16 Glass rod.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commerically prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.10.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

5.11 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.12 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.12.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.11.

5.12.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with diethyl ether.

5.12.3 Analyze each calibration standard according to Section 7.0.

5.13 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

7.1.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125-mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.3 **Solvent cleanup:**

7.1.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.1.3.2 Combine ether extracts in a 125-mL Erlenmeyer flask containing 1.0 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

7.1.3.3 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.1.3.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the

7.2.3 **Solvent cleanup:**

7.2.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into a 250-mL Erlenmeyer flask, and pour the organic layer into a 125-mL Erlenmeyer flask containing about 0.5 g of acidified sodium sulfate. Repeat the extraction twice more with 10-mL aliquots of diethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.2.3.2 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.3 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.2.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.2.3.5 Determine the original sample volume by refilling the sample bottle to the mark with water and transferring to a 1-liter graduated cylinder. Record the sample volume to the nearest 5 mL.

Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 min or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 min of total esterification.

7.3.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 min.

7.3.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.4 Gas chromatography conditions (Recommended):

7.4.1 **Column 1a:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.2 **Column 1b:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 140°C for 6 min and then programmed at 10°C/min to 200°C and held.

7.4.3 **Column 2:** Set 5% methane/95% argon carrier gas at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.4 **Column 3:** Set nitrogen (ultra-high purity) carrier gas at 25-mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 10°C/min to 150°C and held.

7.5 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.5.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.5.2 The following gas chromatographic columns are recommended for the compounds indicated:

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

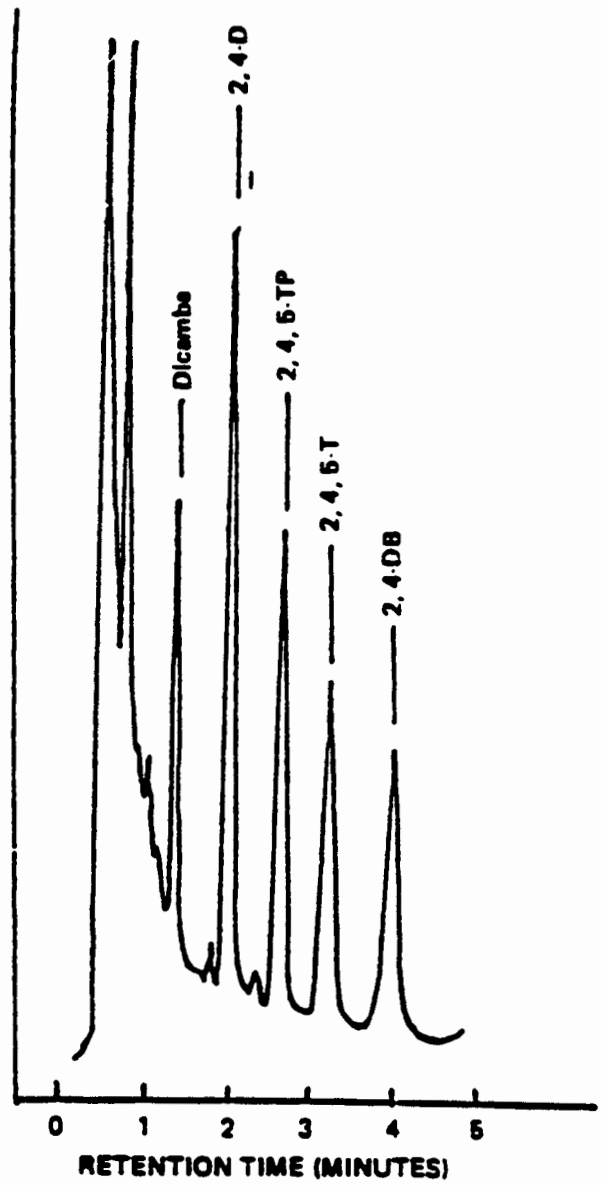


Figure 2. Gas chomatogram of chlorinated herbicides.

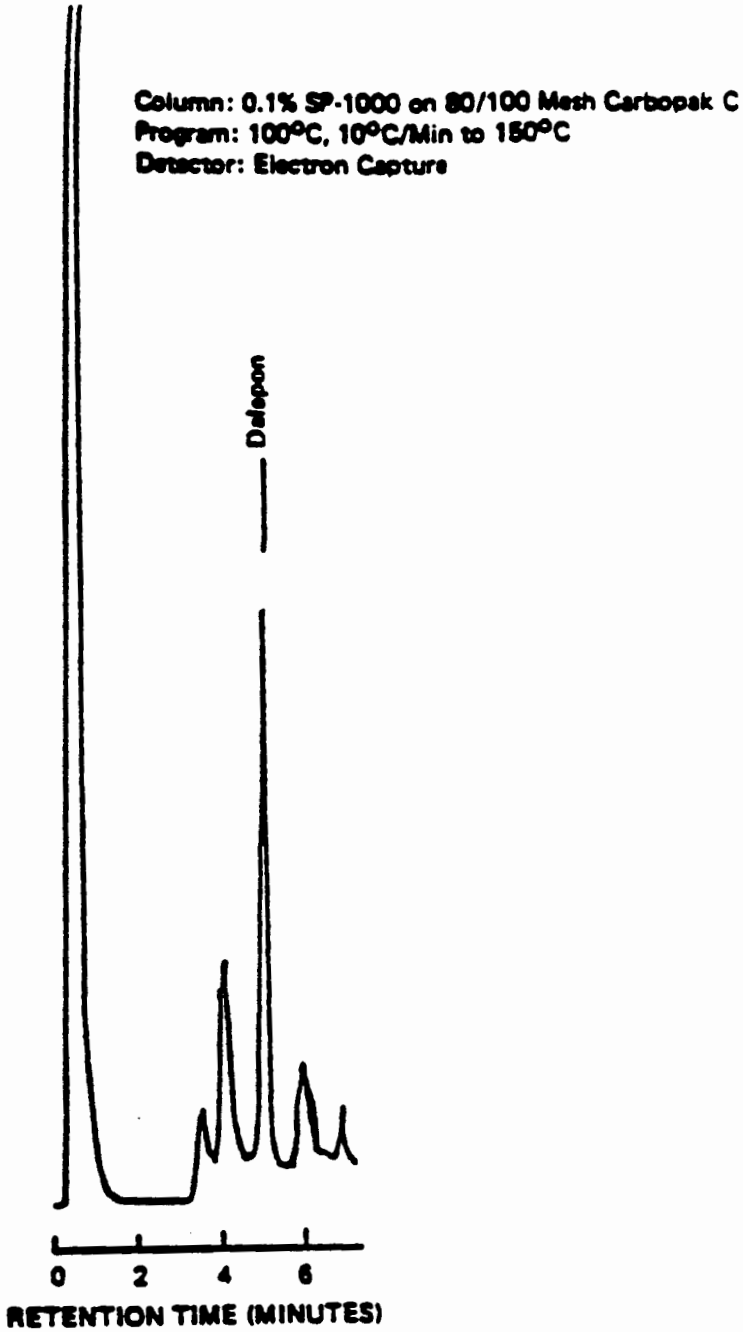


Figure 4. Gas chromatogram of dalapon, column 3.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using reagent water and effluents from publicly owned treatment works (POTW), the average recoveries presented in Table 3 were obtained. The standard deviations of the percent recoveries of these measurements are also included in Table 3.

10.0 REFERENCES

1. U.S. EPA, National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio, 1971.

2. Goerlitz, D.G., and W.L. Lamar, "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography," U.S. Geol. Survey Water Supply Paper, 1817-C, 1967.

3. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. U.S. EPA, "Extraction and Cleanup Procedure for the Determination of Phenoxy Acid Herbicides in Sediment," EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi, 1972.

5. "Pesticide Methods Evaluation," Letter Report #33 for EPA Contract No. 68-03-2697. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

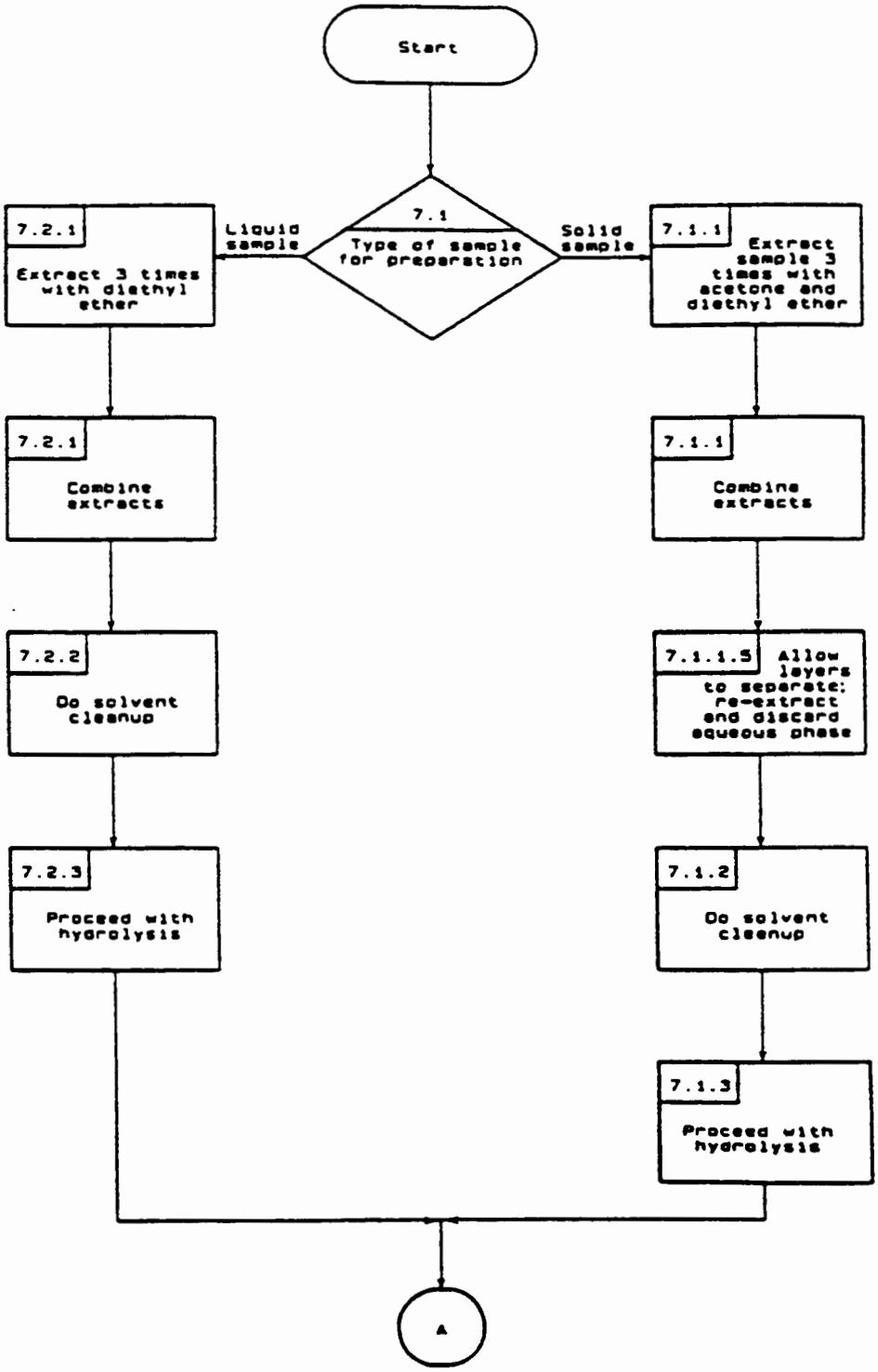
6. McNair, H.M. and E.J. Bonelli, "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1969.

7. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995, 1975.

8. Glaser, J.A. et.al., "Trace Analysis for Wastewaters," Environmental Science & Technology, 15, 1426, 1981.

9. U.S. EPA, "Method 615. The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, June 1982.

METHOD 8150
CHLORINATED HERBICIDES



Revision 0
Date September 1986

APPENDIX II. Detection Limits for Chlorinated Herbicides EPA Method 8150

Compound	Method Detection Limit* (ug/L)
2,4-D	1.2
2,4,5-TP (Silvex)	0.17
2,4,5-T	0.20
Dinoseb	0.15
Dicamba	0.27
2,4-DB	0.91
Dalapon	5.8
MCPP	192
MCPA	249
Dichloroprop	0.65

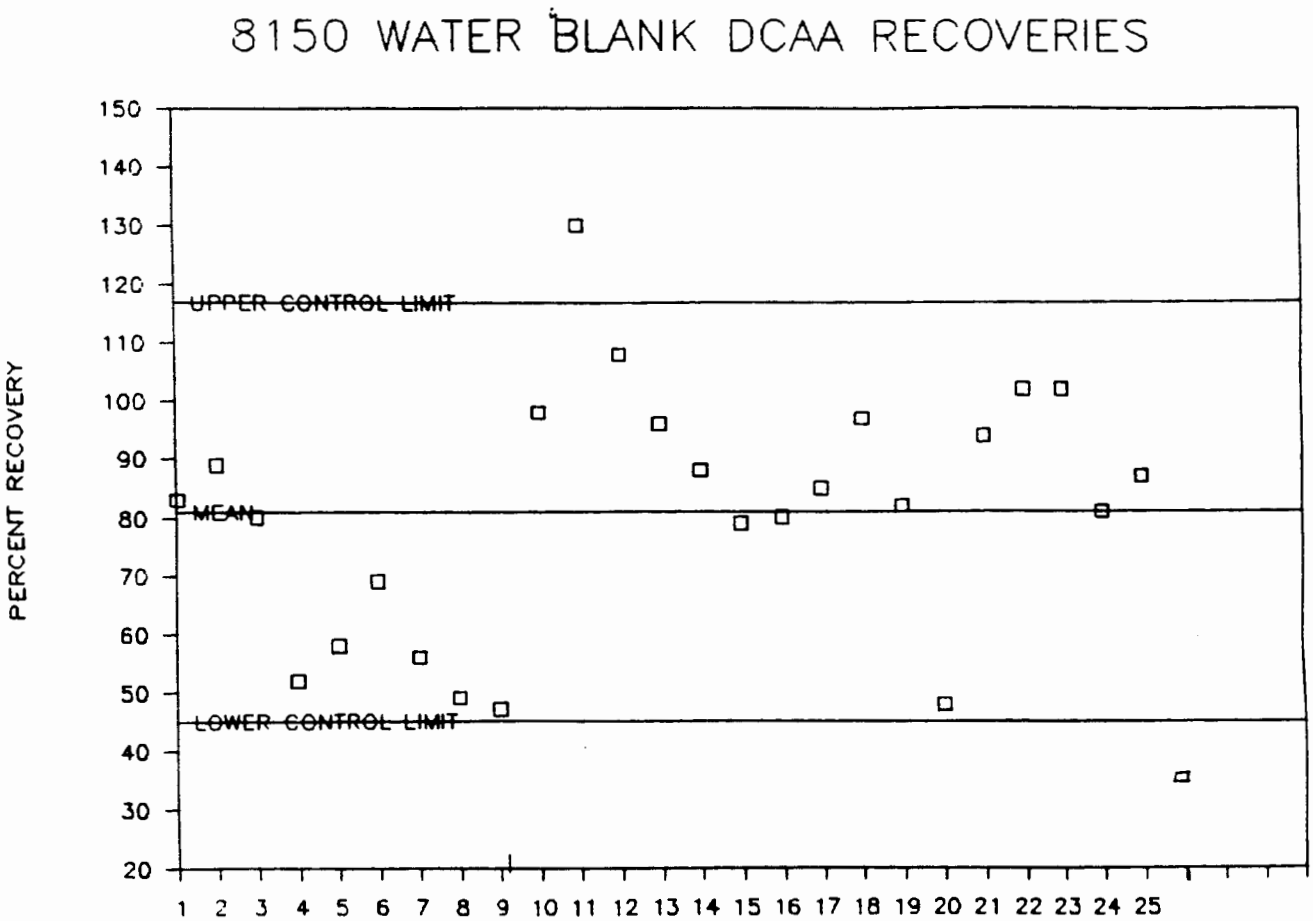
For soils MDL, multiply stated MDL x 100 (assuming 10 gm ext) = ug/kg
* From SW-846-8150 (3rd Ed.) except for Dinoseb, which is higher.

APPENDIX IV. Elution Order of Chlorinated Herbicides

Compound	Retention Time (minutes) Instrument Parameters A	Instrument Parameters B	Instrument Parameters C	Instrument Parameters D	Instrument Parameters E
DCAA	8.3	10.1	13.6	4.2	3.4
2,4-D	10.9	13.8	15.8	6.3	5.8
2,4,5-TP (Silvex)	13.5	15.8	16.5	9.6	7.7
2,4,5-T	14.1	17.4	17.5	10.6	9.7
Dinoseb	15.6	17.7	19.2	13.6	10.3
Dicamba			13.9		
2,4-DB			18.2		
Dalapon			3.26		
MCPP			* 14.1		
MCPA			* 14.7		
Dichloroprop			15.0		

* = Coelute

APPENDIX VI. Example of QC Control Chart for Surrogate Recovery



APPENDIX VII. Radian Malfunction Form and Corrective Action Report

RADIAN CORPORATION

MALFUNCTION REPORT

Malfunction Report Number _____

Malfunction Type _____
1 - QC Limits Exceeded
2 - Documentation
3 - Other (explain)

Urgency Level _____
1 - Requires immediate attention
2 - Should be addressed within 7 days
3 - Requires written explanation within 14 days

Laboratory: _____ Reported to: _____

Location: _____ Position: _____

Contract: _____

Date/Time of Malfunction: _____ Date Reported: _____

Malfunction Reported by: _____

Matrix: ☐ Solid ☐ Water ☐ Air ☐ Other _____

Description of Problem: _____

Action: _____

Date/Time Resolved: _____ By Whom: _____

(Upon completion, send copies to distribution listed and return original to person who reported the malfunction.)

Distribution: _____ _____ _____ _____ _____ _____

White - Original Yellow - Laboratory Supervisor's Copy Pink - Originator's Copy

7-87-27815

APPENDIX VII. (Continued)

Part II Reply / Resolution (Furnished by Technical Director)

Proposed by: Date: CAR #:

Description: Scheduled Implementation:

Part III Implemented Correction Action (by:)

Description: Date Implemented:

Part IV Follow-Up Required: Yes ☐ No ☐ (by:)

Verified by: Date: Comments:

Information Copies, Distributed by Technical Director:

APPENDIX VIII. (Continued)

MDL = 2.681 (S_{blank})

where 2.681 is equal to $t_{12, .99}$

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	10	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
∞	∞	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.5.3)

3.10 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.12 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 7.5.1)

3.14 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1.)

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [illegible] for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from

CONFIDENTIAL

RADIAN CORPORATION RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Gas & Liquid Chromatography Lab	PROCEDURE NO: 321-CH-011	PAGE: 1 of 6
TITLE: ANALYSIS OF APPENDIX IX ORGANOPHOSPHORUS PESTICIDES BY EPA METHOD SW-846 - 8140 (Third Ed.)	REVISION NO: 1	EFFECTIVE DATE: 27 June 1987
	SUPERCEDES: 19 June 1986	

REFERENCES: 321-SP-001, -004, -012; 321-CH-001, -003, -004

SATELLITE FILES: 1-177, 1-167

REASON FOR REVISION: Updated Procedure

1.0 PURPOSE

1.1 To provide a procedural guide for the application of EPA SW-846 Method 8140 (see Appendix A) to the analysis of Appendix IX Organophosphorus Pesticides in hazardous wastes.

1.2 To describe modifications to Method 8140 to optimize performance for the analytical instrumentation in this laboratory.

2.0 PROCEDURE

2.1 Extraction Procedure

Water samples are extracted at a neutral pH with methylene chloride as a solvent using a continuous liquid-liquid extractor. See SOP 321-SP-012. A one liter sample is required for the detection limits listed in Table 2.

2.2 Gas Chromatographic Procedure

The gas chromatographic analyses are carried out using a packed column with a flame photometric detector in the phosphorus-specific mode. The GC conditions are as follows:

Instrument: Tracor 570 with FPD detector (phosphorus mode)
GC Column: 6' x 2 mm ID glass column packed with 5% OV-210 on Supelcoport.

Instrument Parameters:

Oven Temperature: Initial = 160°C for 5 minutes
Ramp @ 10°C per minute
Final = 240°C for 17 minutes

WRITER: NAME/DATE		
6-9-87		6/27/87
ACTIVITY MGR: NAME/DATE	NAME/DATE	NAME/DATE
6-16-87	6/17/87	6-18-87

maintained daily plotting the detector response of a selected organophosphorus pesticide at the 2 ng/uL level. Lines are drawn parallel to the time axis at the mean value and at plus and minus 2 and 3 standard deviations. The line at 2 standard deviations is the warning limit and the line at 3 standard deviations is the control limit.

TABLE 2. DETECTION LIMITS AND PERCENT RECOVERY DATA FOR APPENDIX IX ORGANOPHOSPHORUS PESTICIDES BY EPA METHOD 8140

Compound	Instrument Detection Limit (ng) (total ng)	Method Detection Limit (ug/L)	Mean Percent Extraction Recovery	Spike Level ug/L
Sulfotepp	0.02	0.10	57	5.4
Phorate	0.02	0.10	65	5.4
Disulfoton	0.04	0.20	53	5.2
Methyl Parathion	0.04	0.20	75	5.2
Ethyl Parathion	0.03	0.15	76	5.5
Famphor	0.10	0.50	66	5.0

11/83/14698

METHOD 8140

ORGANOPHOSPHORUS PESTICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8140 is a gas chromatographic (GC) method used to determine the concentration of various organosphosphorus pesticides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8140 is used to analyze unfamiliar samples, compound identifications should be supported by at least two additional qualitative techniques if mass spectroscopy is not employed. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

2.0 SUMMARY OF METHOD

2.1 Method 8140 provides gas chromatographic conditions for the detection of ppb levels of organophosphorus pesticides. Prior to analysis, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph, and compounds in the GC effluent are detected with a flame photometric or thermionic detector.

2.2 If interferences are encountered in the analysis, Method 8140 may also be performed on extracts that have undergone cleanup using Method 3620 and/or Method 3660.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 The use of Florisil cleanup materials (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85% and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorous pesticides as a function of Florisil fractions. Use of phosphorus- or halogen-specific detectors, however, often obviates the necessity for cleanup for relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is no less than 85%.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.4.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.4.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

4.9 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1a:** Set helium carrier gas flow at 30 mL/min flow rate. Column temperature is set at 150°C for 1 min and then programmed at 25°C/min to 220°C and held.

7.2.2 **Column 1b:** Set nitrogen carrier gas flow at 30 mL/min flow rate. Column temperature is set at 170°C for 2 min and then programmed at 20°C/min to 220°C and held.

7.2.3 **Column 2:** Set helium carrier gas at 25 mL/min flow rate. Column temperature is set at 170°C for 7 min and then programmed at 10°C/min to 250°C and held.

7.2.4 **Column 3:** Set nitrogen carrier gas at 30 mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 25°C/min to 200°C and held.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

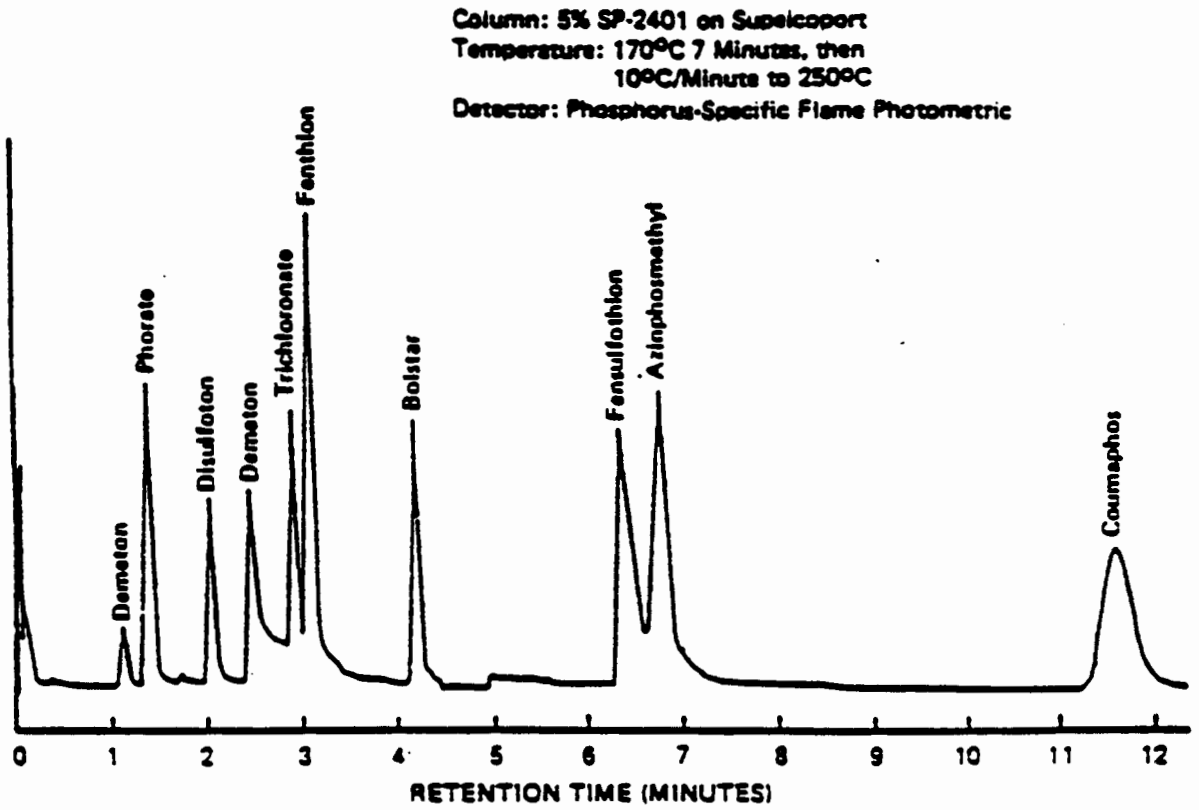


Figure 1. Gas chromatogram of organophosphorus pesticides (Example 1).

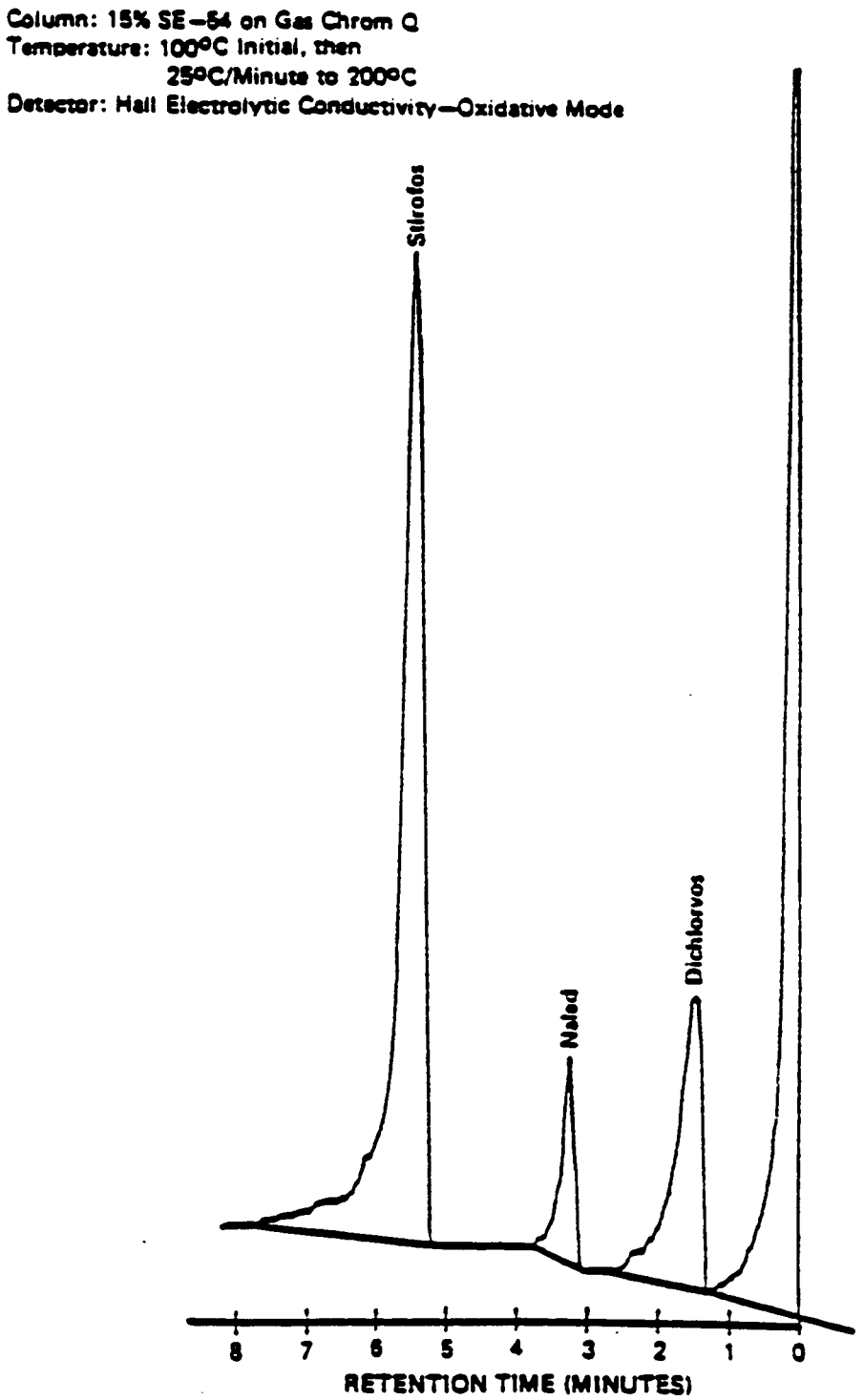


Figure 3. Gas chromatogram of organophosphorus pesticides (Example 3).

8.2.1 Select a representative spike concentration for each analyte to be measured. The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation:

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The GC/MS operating conditions and procedures for analysis are those specified in Method 8270.

8.4.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns and additional cleanup.

9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision studies have been conducted using spiked wastewater samples. The results of these studies are presented in Table 3.

TABLE 3. SINGLE-OPERATOR ACCURACY AND PRECISION[a]

Parameter	Average recovery (%)	Standard deviation (%)	Spike range (ug/L)	Number of analyses
Azinphos methyl	72.7	18.8	21-250	17
Bolstar	64.6	6.3	4.9-46	17
Chlorpyrifos	98.3	5.5	1.0-50.5	18
Coumaphos	109.0	12.7	25-225	17
Demeton	67.4	10.5	11.9-314	17
Diazinon	67.0	6.0	5.6	7
Dichlorvos	72.1	7.7	15.6-517	16
Disulfoton	81.9	9.0	5.2-92	17
Ethoprop	100.5	4.1	1.0-51.5	18
Fensulfothion	94.1	17.1	23.9-110	17
Fenthion	68.7	19.9	5.3-64	17
Merphos	120.7	7.9	1.0-50	18
Mevinphos	56.5	7.8	15.5-520	16
Naled	78.0	8.1	25.8-294	16
Parathion methyl	96.0	5.3	0.5-500	21
Phorate	62.7	8.9	4.9-47	17
Ronnel	99.2	5.6	1.0-50	18
Stirophos	66.1	5.9	30.3-505	16
Tokuthion	64.6	6.8	5.3-64	17
Trichloronate	105.0	18.6	20	3

[a]Information taken from Reference 4.

CONFIDENTIAL

RADIAN CORPORATION **RESEARCH & ENGINEERING**

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Chemistry Department	PROCEDURE NO: 320-DG-003	PAGE: 1 of 4
TITLE: Acid Digestion of Sludges - Method 3050 Digestions	REVISION NO: 0	EFFECTIVE DATE: 1/90
	SUPERCEDES: N/A	

REFERENCES
N/A

SATELLITE FILES:
Inorganics

REASON FOR REVISION:
Original -- Commonality

1.0 PURPOSE

1.1 Method 3050 is an acid digestion procedure used to prepare sludge and soil or similar samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3050 may be analyzed by ICP for all the listed metals, or FLAA or GFAA as indicated below:

FLAA		GFAA
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Arsenic	Nickel	Cadmium
Barium	Potassium	Chromium
Beryllium	Selenium	Cobalt
Calcium	Sodium	Iron
Cadmium	Silver	Molybdenum
Chromium	Tin	Selenium
Cobalt	Thallium	Thallium
Copper	Vanadium	Vanadium
Iron	Zinc	
Lead		

1.2 Method 3050 may also be applicable to the analysis of other metals in sludge-type samples. However, prior to using this method for metals, it must be evaluated using the specific metal and matrix.

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide.

WRITER NAME/DATE		
Lisa D Lopez 12/21/89		
ACTIVITY MGR. NAME/DATE	NAME/DATE	NAME/DATE
Dan Wagner 12/21/89	David H. Dale 2/1/90	Fred L Shore 2/7/90

6.2 Heat the sample to 95°C and reflux for 10 to 15 minutes. Do not boil the sample. Allow the sample to cool and add 5 mL of concentrated nitric acid. Cover and reflux for approximately 30 minutes. Repeat this last step to ensure complete oxidation.

6.3 Evaporate the solution to a volume of 15 to 20 mL and cool. Add 3 mL of Type II water and 2 mL of 30% hydrogen peroxide. Cover the sample and heat slowly until the effervescence subsides. Cool.

6.4 Add additional 30% hydrogen peroxide in 1 mL aliquots with warming until the effervescence is minimal or the general sample appearance is unchanged.

6.4.1 If the sample is being prepared for ICAP analysis or flame AAS analysis of the metals listed in Section 1.1 or the ICAP analysis of As and/or Se then add 5 mL of concentrated HCl and 10 mL of water to the sample. Cover the beaker and reflux for an additional 15 minutes. Cool.

NOTE: The HCl may be omitted if the lab supervisor approves and the client is notified. The addition of the HCl may lead to reduced silver recoveries.

6.4.2 If the sample is being prepared for the graphite furnace analysis of any of the metals listed in Section 1.1, reduce the volume to 15 to 20 mL. Cool.

6.5 Filter or centrifuge the sample to remove any remaining particulate. Bring to a final volume of 100 mL with water in a volumetric flask.

7.0 SAFETY

7.1 Follow normal laboratory safety procedures as outlined in the Radian Corporation Health and Safety Manual and the site specific laboratory safety SOP.

8.0 QUALITY CONTROL

8.1 Prepare at least one reagent blank with each batch of samples to determine if contamination is occurring. A minimum of one blank should be run for every 20 samples.

CONFIDENTIAL

RADIAN CORPORATION RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Gas & Liquid Chromatography Lab	PROCEDURE NO: 321-CH-008	PAGE: 1 of 10
TITLE: ANALYSIS OF APPENDIX IX ORGANOCHLORINE PESTICIDES & PCBs BY EPA METHOD SW-846-8080 (Third Edition)	REVISION NO: 1	EFFECTIVE DATE: 27 June 1987
	SUPERCEDES: 19 June 1986	

REFERENCES: 321-SP-001, -004, -012, -013, -020; 321-CH-001, -004

SATELLITE FILES: 1-169, 1-177

REASON FOR REVISION: Updated Procedure

1.0 PURPOSE

1.1 To provide a procedural guide for the application of EPA Method SW-846-8080 (see Appendix A) to the analysis of Appendix IX organochlorine pesticides and PCBs in hazardous wastes.

1.2 To describe the modifications to Method 8080 which are necessary to facilitate performance of the analyses.

2.0 PROCEDURE

The chlorinated pesticides described in the scope and application section (1.0) of Method 8080 are analyzed by a modified procedure described below.

2.1 Modification of Gas Chromatographic Procedure for chlorinated pesticides, Method 8080 (7.2)

The GC analyses are carried out using a glass capillary column and programmed oven temperature. GC conditions are as follows:

Instrument: HP 5890 GC with Electron Capture Detector
Automatic Sampler: HP 7672 or HP 7673
Data System: HP 1000; LAS.

GC Column: A 60 meter, 0.75 mm I.D. glass column coated with 1.0 um. SPB-5.

WRITER: NAME/DATE		
Neal Dirk 6-9-87		R A Magee 6/20/87
ACTIVITY MGR: NAME/DATE	NAME/DATE	NAME/DATE
Larry Wolfe 6-16-87	Fred Shore 6/17/87	Y.G. Fishman 6-18-87

4.0 QUALITY CONTROL

The appropriate quality control procedures described in Method 8080 section 8.0, should be carried out. In addition, the analyst should refer to SOPs 321-SP-001 and 321-CH-001 for additional information and directions on proper quality control.

4.1 Preparation of Standards

Primary standards for most of the pesticides are EPA solutions of 5000 ug/mL. If these are not available, a solution is prepared from the neat material by accurately weighing 50 mg and dissolving in 10 mL of methanol.

A working standard is prepared by adding 100 uL of each of the primary standards to a 100 mL volumetric flask. This solution will contain 10 ng/uL. Further serial dilutions of this standard are required to prepare injection standards in the calibration range of the instrument: from 50 pg/uL to 5000 pg/uL.

4.2 Calibration

The external standard method of calibration is used with the Hewlett Packard LAS system. Initial calibration is done using at least three injection standards: 50 pg/uL, 500 pg/uL and 5000 pg/uL. The detector should be linear over this range.

The response factors of each pesticide at 500 pg/uL should be calculated daily. Figure 1 is an example of a daily QC chart for this assay. The LAS method for Appendix IX pesticides is stored as PESTX, where X = the number of the latest revision. Figure 2 is a copy of this method with typical response factors for each pesticide. See the SOP on the LAS for more information on response factors.

4.3 Surrogate Standards

The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference then GC/MS, a secondary surrogate is to be used when sample interference is apparent. Dibutylchlorendate (DBC) is also subject to acid and base degradation. Therefore, two surrogate standard are added to each sample; however, only one need be calculated for recovery. DBC is the primary surrogate and should be used whenever possible. However, if DBC recovery is low or compounds interfere with DBC, then 2,4,5,6-tetrachloro-meta-xylene should be evaluated for acceptance. Proceed with corrective action when both surrogates are out of limits for a sample indicating the proper procedure for preparing these surrogates.

1D/R3/1469B

TABLE 1. ELUTION ORDER OF CHLORINATED PESTICIDES ON A 60M SPB-5 MEGABORE CAPILLARY COLUMN

Compound	Retention Time (minutes)
α -BHC	10.9
PCB 1232	11.0[a]
PCB 1221	11.1[a]
β -BHC	12.2
Lindane	12.5
δ -BHC	13.8
Aroclor 1016	15.7[a]
PCB 1242	15.9[a]
Heptachlor	16.6
Aldrin	18.9
Heptachlor epoxide	21.6
PCB 1248	22.4[a]
Chlordane	23.5
Endosulfan I	24.3
p,p'-DDE	26.1
Dieldrin	26.2
PCB 1254	26.9[a]
Endrin	27.9
Endosulfan II	28.6
p,p'-DDD	29.3
Toxaphene	29.8[a]
Endrin aldehyde	30.3
Kepone	30.7
p,p'-DDT	32.3
Methoxychlor	37.1
PCB 1260	38.3[a]

[a]Multiple peaks - this is R.T. of the largest peak.

TABLE 3. PESTICIDE RECOVERIES WITH FLORISIL[a]

Compound	% Recovery
Heptachlor	99
Aldrin	87
Heptachlor epoxide	94
p,p'-DDE	95
Dieldrin	71
p,p'-DDD	92
p,p'-DDT	87

[a]Data obtained at Radian during method validation study for samples spiked at 1 ug/L, extracted and cleaned up using Florisil.

```
MAY 21, 1986     3:57
METHOD: PEST3      ON CPN LS                CREATED:  16:13 ON MAR  5, 1986
CHANNEL  0                                  MODIFIED: 10:59 ON MAY  7, 1986

1. DATA INPUT

 RUNTM    #PKS
  55.00, -300

 MV/MIN    DELAY    MIN-AR    BUNCH
   .500,    6.00,     1000,    NO

 INTEGRATOR EVENTS
     TIME    EVENT
 1      .10,  W
 2    /E

 CONTROL EVENTS
     TIME    EVENT  ECM  RLY
 1   60.00, CY
 2    /E

2. DATA ANALYSIS

 PROC  RPRT  SUP-UNK
 ESTD,  EX,   NO

 UNITS   TITLE
 PG/UL . APPNDX VIII

 REF-RTW  %RTW   PF-UNK        ID-LVL     DVT
   .250,  3.000, 0.0000E+ 0,    1100,    0.00

 CALIBRATION PEAKS       CALIBRATED: 11:55 ON MAY  7, 1986
     TIME      AMOUNT       FACTOR      NAME
 1    11.76, 5.0000E+ 2, 5.2777E- 4, A-BHC
 2    13.05, 5.0000E+ 2, 1.2712E- 3, B-BHC
 3    13.42, 5.0000E+ 2, 5.9154E- 4, #LINDANE
 4    14.70, 5.0000E+ 2, 6.5413E- 4, D-BHC
 5    17.67, 5.0000E+ 2, 6.3700E- 4, HEPTACHLOR
 6    19.96, 5.0000E+ 2, 5.7308E- 4, ALDRIN
 7    22.73, 5.0000E+ 2, 6.8241E- 4, #HEPT-EPOX
 8    25.41, 5.0000E+ 2, 7.4433E- 4, A-ENDOSULF
 9    27.12, 5.0000E+ 2, 7.2410E- 4, PP-DDE
10    27.33, 5.0000E+ 2, 6.2146E- 4, DIELDRIN
11    29.00, 5.0000E+ 2, 1.0591E- 3, ENDRIN
12    29.81, 5.0000E+ 2, 8.7697E- 4, B-ENDOSULF
13    30.47, 5.0000E+ 2, 1.0410E- 3, PP-DDD
14    31.32, 5.0000E+ 1, 1.8348E- 3, ENDRIN ALDH
15    33.44, 5.0000E+ 2, 9.5855E- 4, #PP-DDT
16    38.23, 5.0000E+ 2, 1.9603E- 3, METHOXYCHLOR
17    60.00, 5.0000E+ 2, 1.0000E+ 0, #NOTHING
18    /E

7. USER PROGRAMS

 POST--NAL  DIALG-PRG  PARAM-FILE
```

Figure 2. Method for LAS Analysis of Appendix IX Chlorinated Pesticides

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCBs

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a halogen-specific detector (HSD).

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, toluene, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature is set at 200°C isothermal. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature held isothermal at 200°C. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow so that 4,4'-DDT has a retention time of approximately 12 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-level standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

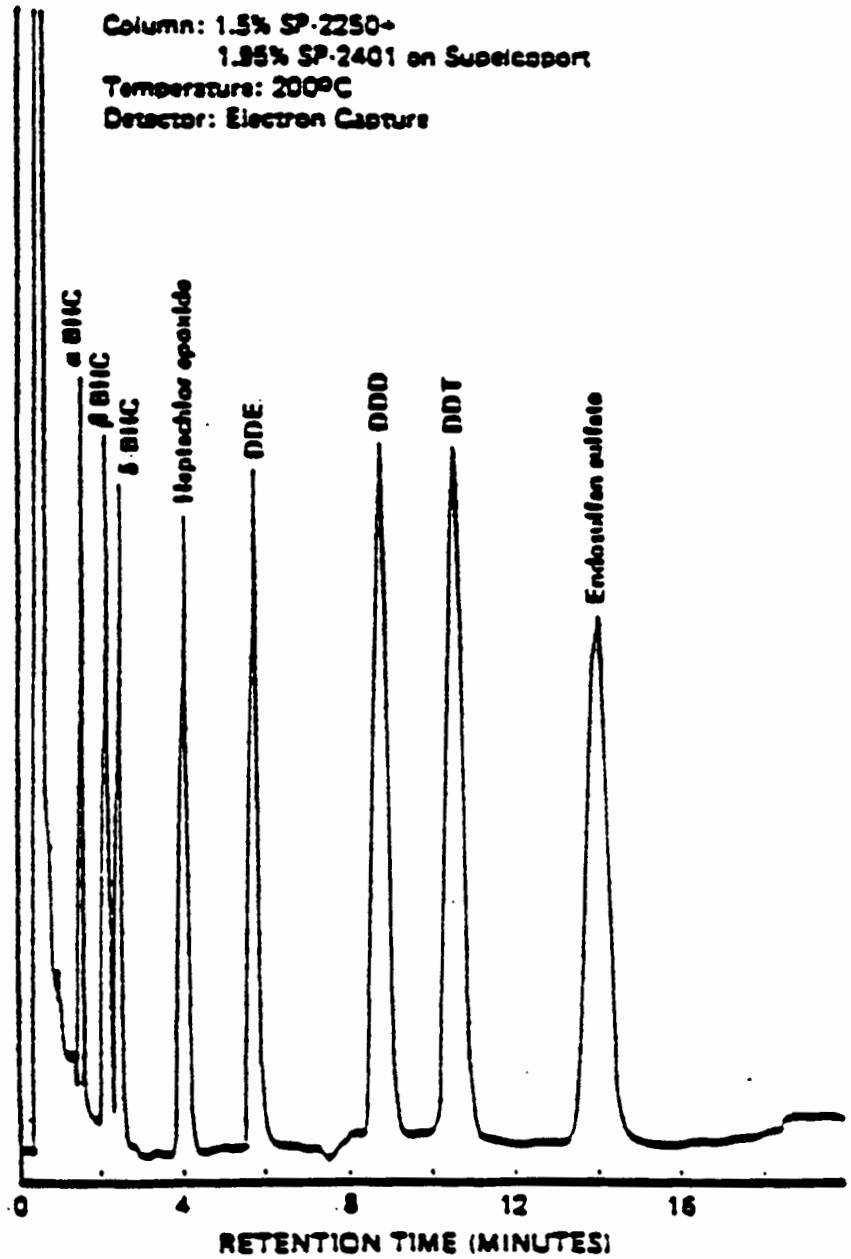


Figure 1. Gas chromatogram of pesticides.

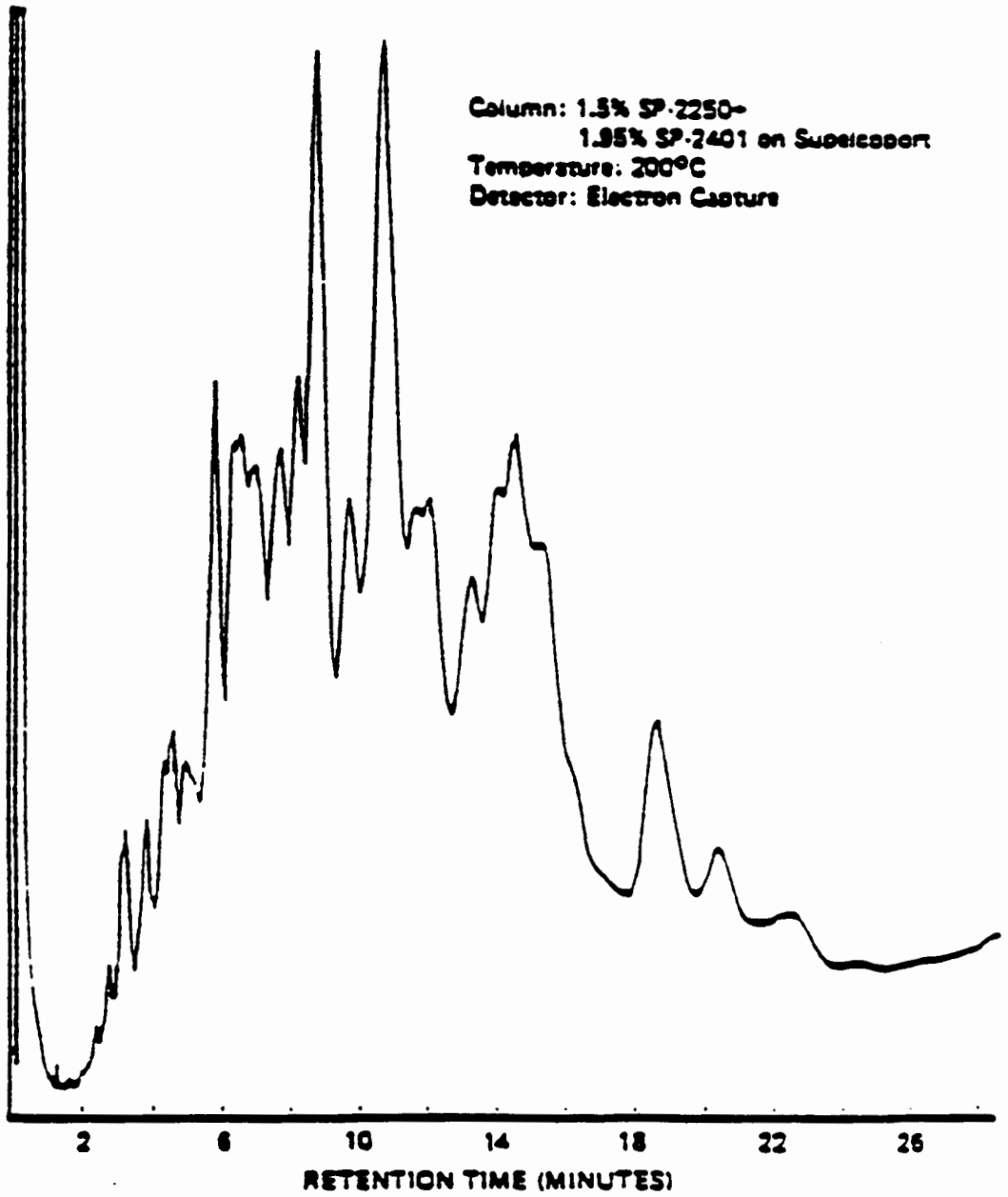


Figure 3. Gas chromatogram of toxaphene.

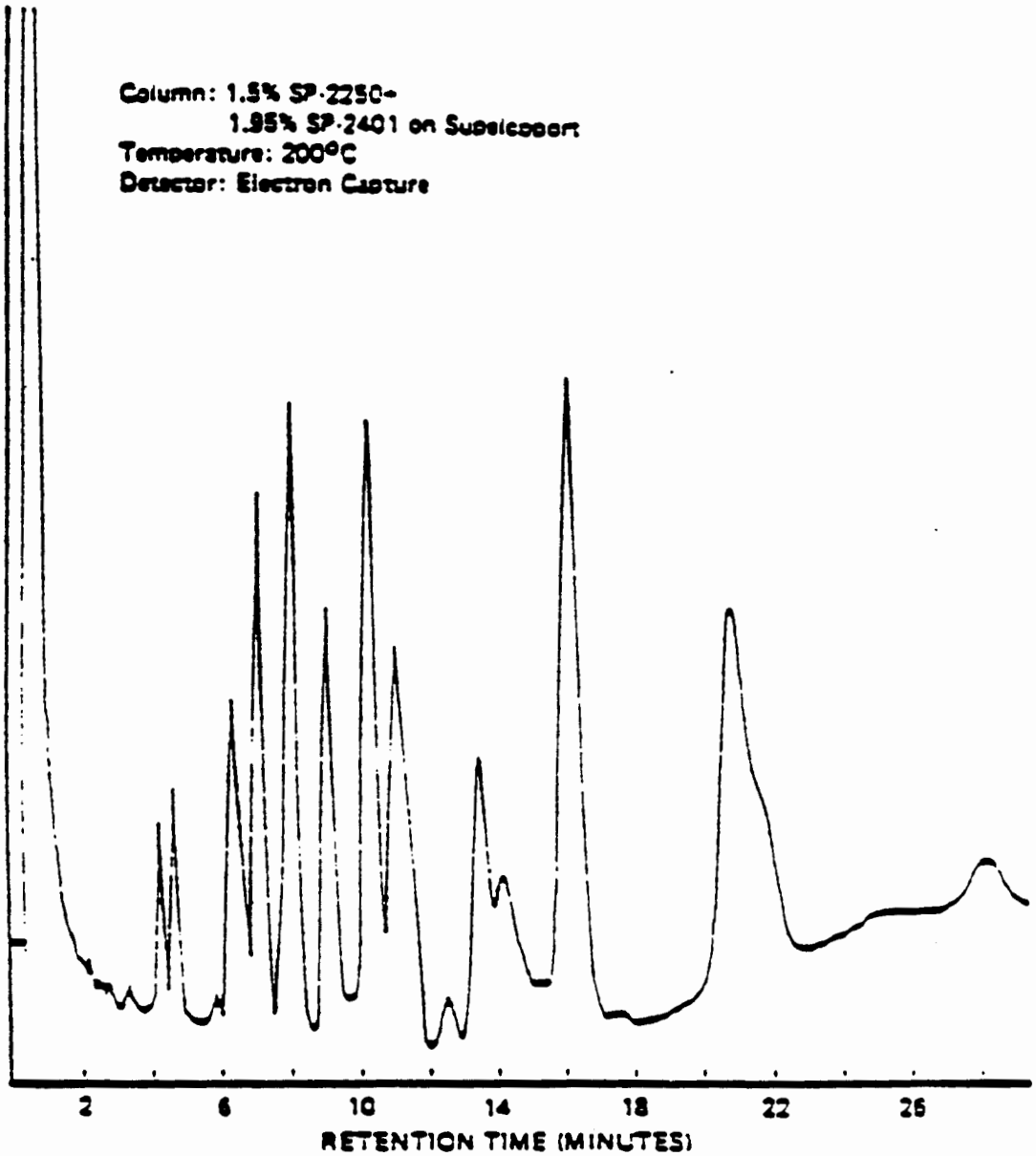
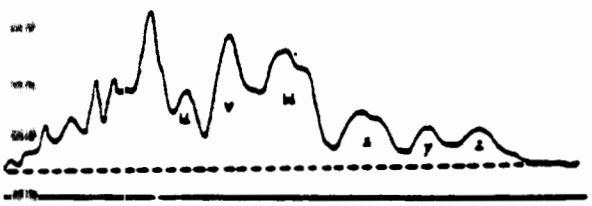
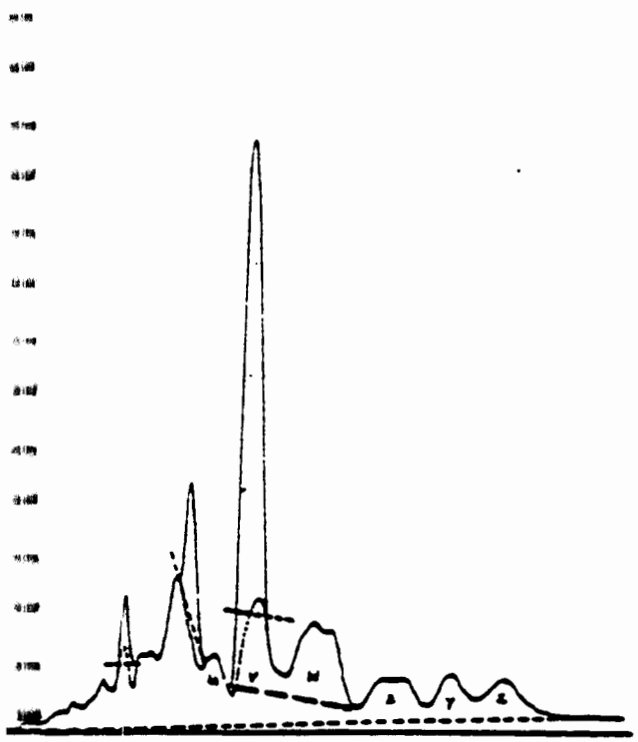


Figure 5. Gas chromatogram of PCB-1260.



...ne construction for multiple residues with standard toxaphene.



...line construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

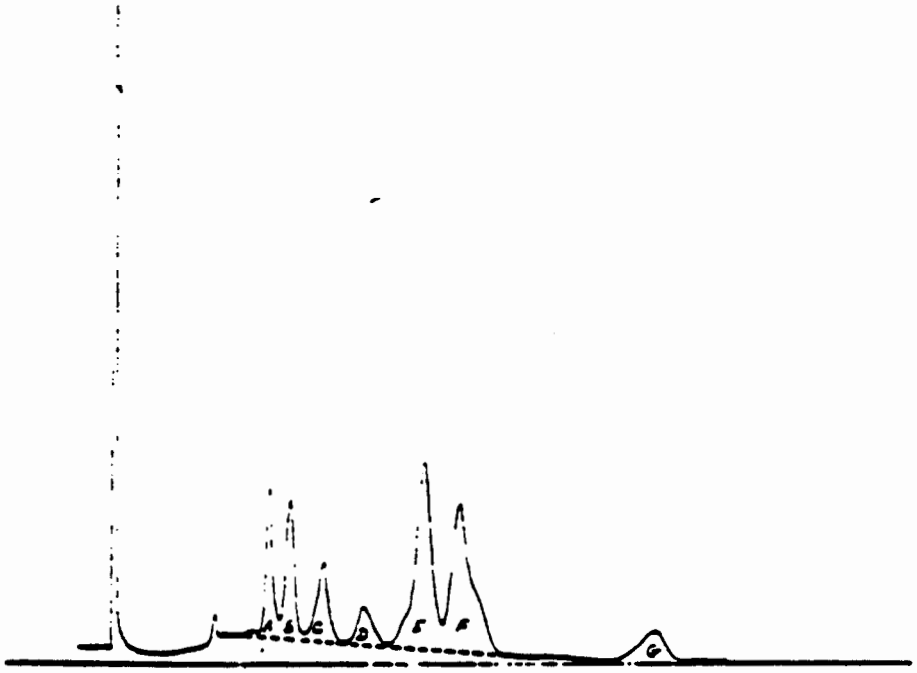


Fig. 9a—Baseline construction for multiple residues: standard chlordane.

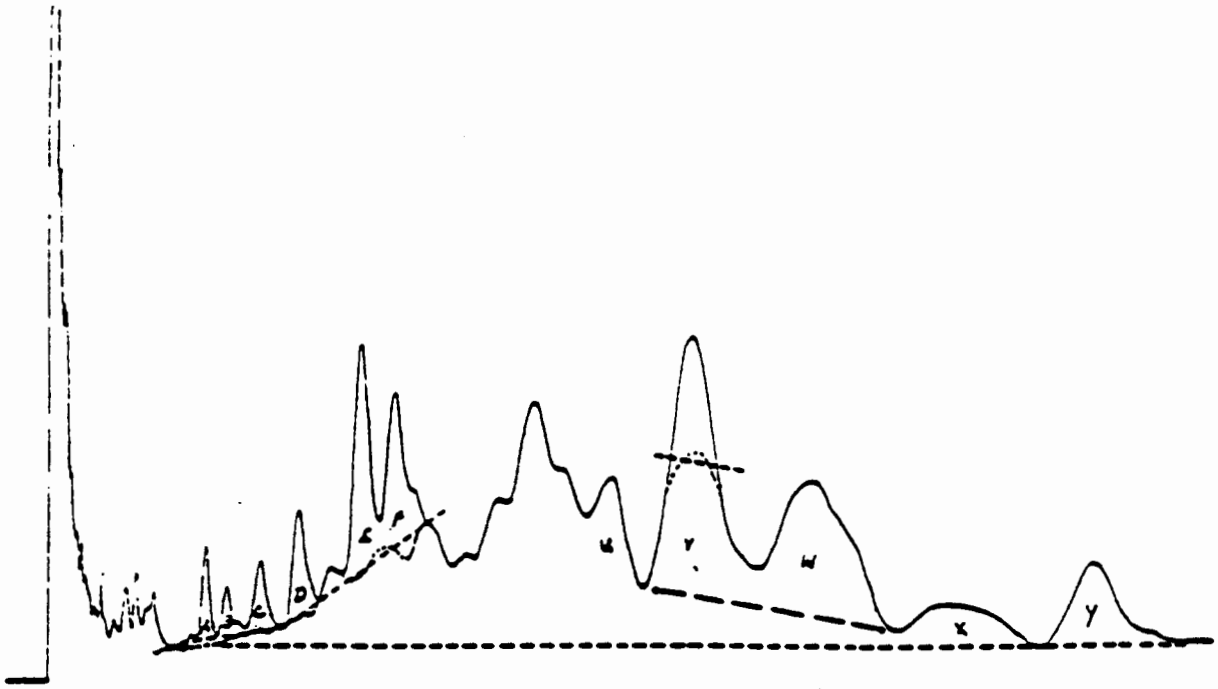


Fig. 9b—Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.

D, a chlordane analog; G, coelution of cis-nonachlor and "Compound K," a chlordane isomer. The right "shoulder" of peak F is caused by trans-nonachlor.

7.6.4.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane; plant and/or animal metabolities; and products of degradation caused by exposure to environmental factors such as water and sunlight. Only limited information is available on which residue GC patterns are likely to occur in which samples types, and even this information may not be applicable to a situation where the route of exposure is unusual. For example, fish exposed to a recent spill of technical chlordane will contain a residue drastically different from a fish whose chlordane residue was accumulated by ingestion of smaller fish or of vegetation, which in turn had accumulated residues because chlordane was in the water from agricultural runoff.

7.6.4.2 Because of this inability to predict a chlordane residue GC pattern, it is not possible to prescribe a single method for the quantitation of chlordane residues. The analyst must judge whether or not the residue's GC pattern is sufficiently similar to that of a technical chlordane reference material to use the latter as a reference standard for quantitation.

7.6.4.3 When the chlordane residue does <u>not</u> resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate each peak separately against the appropriate reference materials and report the individual residues. (Reference materials are available for at least 11 chlordane constituents, metabolites or degradation products which may occur in the residue.)

7.6.4.4 When the GC pattern of the residue resembles that of technical chlordane, quantitate chlordane residues by comparing the total area of the chlordane chromatogram from peaks A through F (Figure 9a) in the sample versus the same part of the standard chromatogram. Peak G may be obscured in a sample by the presence of other pesticides. If G is not obscured, include it in the measurement for both standard and sample. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion as in Figure 6j, calculate these separately and subtract their areas from total area to give a corrected chlordane area. (Note that octachlor epoxide, metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.5.3 Quantitate PCB residues by comparing total area or height of residue peaks to total area of height of peaks from appropriate Aroclor(s) reference materials. Measure total area or height response from common baseline under all peaks. Use only those peaks from sample that can be attributed to chlorobiphenyls. These peaks must also be present in chromatogram of reference materials. Mixture of Aroclors may be required to provide best match of GC patterns of sample and reference.

7.6.6 **DDT:** DDT found in samples often consists of both o,p'- and p,p'-DDT. Residues of DDE and TDE are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such.

7.6.7 **Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride):** Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

7.6.7.1 Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the α-, γ-, and δ-isomers and 14 weeks for the β-isomer. Thus it may be possible to have any combination of the various isomers in different food commodities. BHC found in dairy products usually has a large percentage of β-isomer.

7.6.7.2 Individual isomers (α, β, γ, and δ) were injected into gas chromatographs equipped with flame ionization, microcoulometric, and electron capture detectors. Response for the four isomers is very nearly the same whether flame ionization or microcoulometric GLC is used. The α-, γ-, and δ-isomers show equal electron affinity. β-BHC shows a much weaker electron affinity compared to the others isomers.

7.6.7.3 Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer, using a GC column which separates all the isomers from one another.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 ug/L for single-component pesticides and from 8.5 to 400 ug/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

1. U.S. EPA, "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 10: Pesticides and PCBs," Report for EPA Contract 68-03-2605.

2. U.S. EPA, "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, October 1980.

3. Pressley, T.A., and J.E. Longbottom, "The Determination of Organohalide Pesticides and PCBs in Industrial and Municipal Wastewater: Method 617," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-84-006, 1982.

4. "Determination of Pesticides and PCB's in Industrial and Municipal Wastewaters, U.S. Environmental Protection Agency," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, EPA-600/4-82-023, June 1982.

5. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9, 1971.

6. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

7. Webb, R.G. and A.C. McCall, "Quantitative PCB Standards for Electron Capture Gas Chromatography," Journal of Chromatographic Science, 11, 366, 1973.

8. Millar, J.D., R.E. Thomas and H.J. Schattenberg, "EPA Method Study 18, Method 608: Organochlorine Pesticides and PCBs," U.S. EPA/EMSL, Research Triangle Park, NC, EPA-600/4-84-061, 1984.

9. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

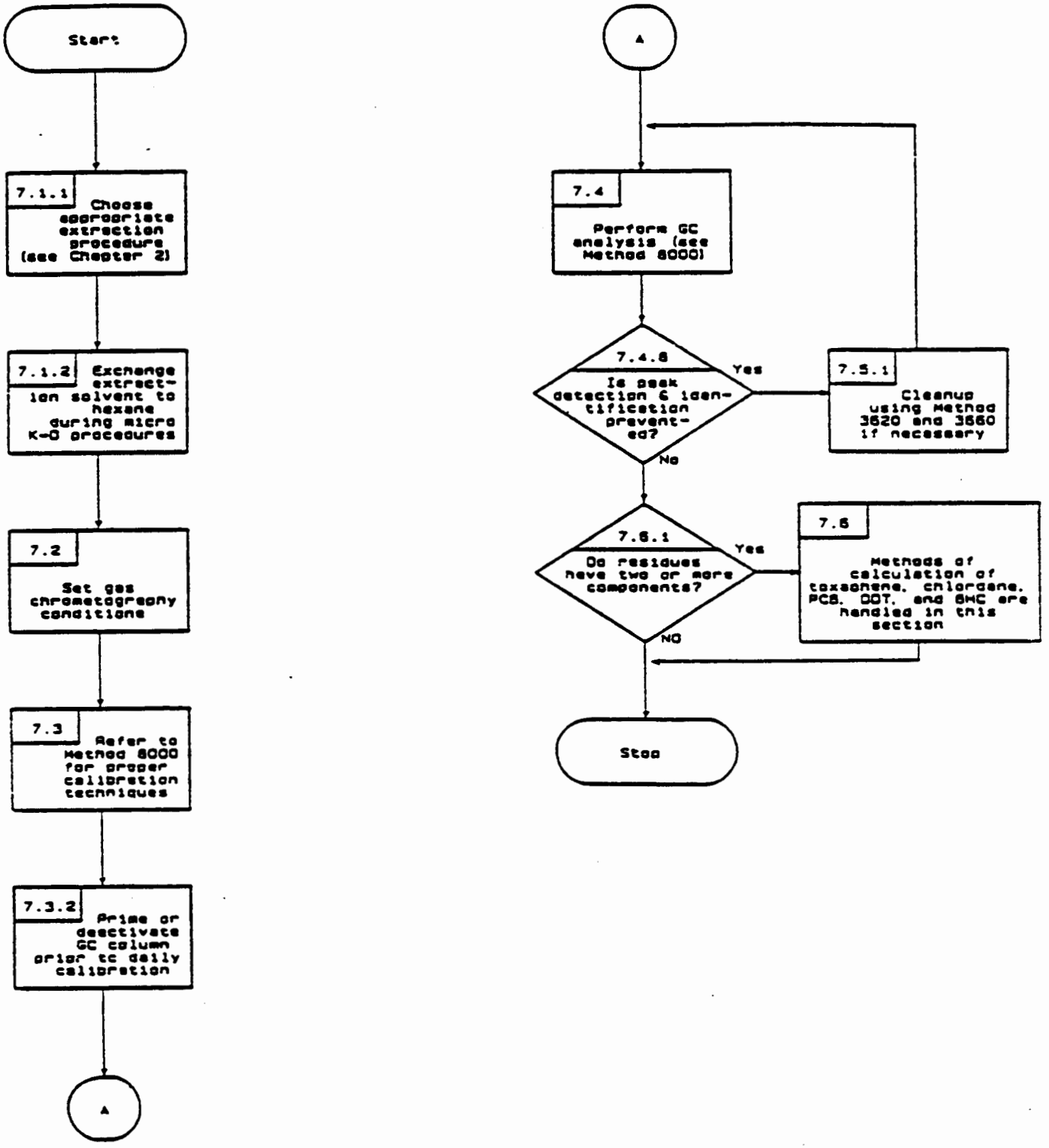
P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

METHOD 8080

ORGANOCHLORINE PESTICIDES & PCBs



Revision 0
Date September 1986

RADIAN CORPORATION

CONFIDENTIAL

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: GC/MS	PROCEDURE NO: 321-MS-009	PAGE: 1 of 46
TITLE: Analysis of Purgeable Volatile Appendix VIII Compounds Using USEPA SW-846 Method 8240	REVISION NO: 0	EFFECTIVE DATE: 9/24/86 JUN 3 1987
	SUPERCEDES:	

RADIAN DOCUMENT

REFERENCES: 321-MS-003, 321-MS-004, 321-SP-001 , 321-MS-001

SATELLITE FILES: 1-101

REASON FOR REVISION:

None

1.0 PURPOSE

The purpose of this SOP is to outline the extraction and analysis procedures used in analyzing Appendix VIII volatile organic compounds by GC/MS.

2.0 SCOPE

This SOP discusses the proper extraction procedures for a variety of matrices and the methodology involved in analyzing for volatile organics. Also discussed is a specific list of the compounds of interest as well as the proper quality control and safety procedures involved in handling volatile organic compounds.

3.0 EXTRACTION SUMMARY

For liquid samples, the direct purge-and-trap method (Method 8240) is used. The headspace analysis method (5020) is an alternate method. Solid samples are mixed with tetraglyme, and then a portion of the tetraglyme is added to water and analyzed by the purge-and-trap method. Specifics for these methods may be found in the Test Methods for Evaluating Solid Waste, USEPA, SW-846, 2nd Edition, July 1982 for Method 8240 referenced in Appendix A. Table 3-1 lists the compounds of interest as well as their detection limits.

WRITER: NAME/DATE		
P.G. Schumacher 6/02/87		V.A. Fishman 6-3-87
ACTIVITY MGR: NAME/DATE	NAME/DATE	NAME/DATE
Patricia W. Mathur 6/2/87	Fred Shore 6/2/87	R.A. Magee 6/3/87

10/83/14698

TABLE 3-1. RETENTION TIME ORDER AND DETECTION LIMITS FOR THE REVISED 8240 COMPOUND LIST (Continued)

Compound	Retention Time (min)	Primary Ion (m/z)	Instrument Detection Limit (ng)	Method Detection Limit (ug/L)
1,1,1,2-Tetrachloroethane	18.06	131	10	2
4-Methyl-2-Pentanone (MIBK)	18.20	43	10	2
2-Hexanone	19.50	43	10	2
1,2,3-Trichloropropene	19.52	75	25	5
1,1,2,2-Tetrachloroethane	20.10	83	10	2
Toluene-d_8 (I.S.)	21.06	98	NA	NA
Ethyl methacrylate	21.16	69	10	2
Toluene	21.18	91	10	2
Chlorobenzene	22.22	112	10	2
Ethyl benzene-d_5 (I.S.)	23.58	96	NA	NA

[a]Column conditions for reported retention times: Carbopack B (60/80 mesh) coated with 1% SP-1000 packed in a 6 ft by 2 mm ID glass column with helium carrier gas at a flow rate of 30 ml/min. Initial oven temperature of 35°C, held for 2.5 minutes and then ramp at 8°C/min to 220°C and held for 15 minutes.
[b]MDL assumes a 5 mL sample.
[c](I.S.) Designates an internal standard.
[d]NA = Not applicable.

1,2-DBTFE, fluorobenzene, m-BBTF and BFB. The calibration curve should contain a minimum of 3 points, with a separate standard demonstrating the lower limit of quantitation. The remaining standards on the curve should define the linear range of the instrument. Total Volatile Content (TVC) is not required for purgeables and Section 7.3.1 and 7.3.2 of Appendix A may be skipped.

The GC conditions for the volatile organic analysis are essentially the same as those described in Section 7.3.5 with a slight change in the initial temperature. The column and conditions used are as follows:

Column: 6 ft x 2 mm ID glass column of 1% SP-1000 on Carbopack B (60/80 mesh)

Temperature Program: Initial temperature 36°C for 2.5 min., then ramp at 8°C/min to 220°C and hold at 220°C for 15 minutes.

8.0 QUALITY CONTROL

The appropriate quality control as described in Appendix A, Section 8.0, should be followed. Ion confirmation and ion abundance should be checked daily prior to running any standards or samples. The tuning compound for volatile analysis should be 4-bromofluorobenzene (BFB). The specific tuning criteria for BFB are found in Table 2 of Appendix A.

After tuning, a three point calibration curve should be run and a separate standard analyzed to demonstrate the IDL. After running, or checking, the calibration curve, a surrogate standard should be run to determine surrogate response factors. A quality control chart displaying response factor versus time should be updated once

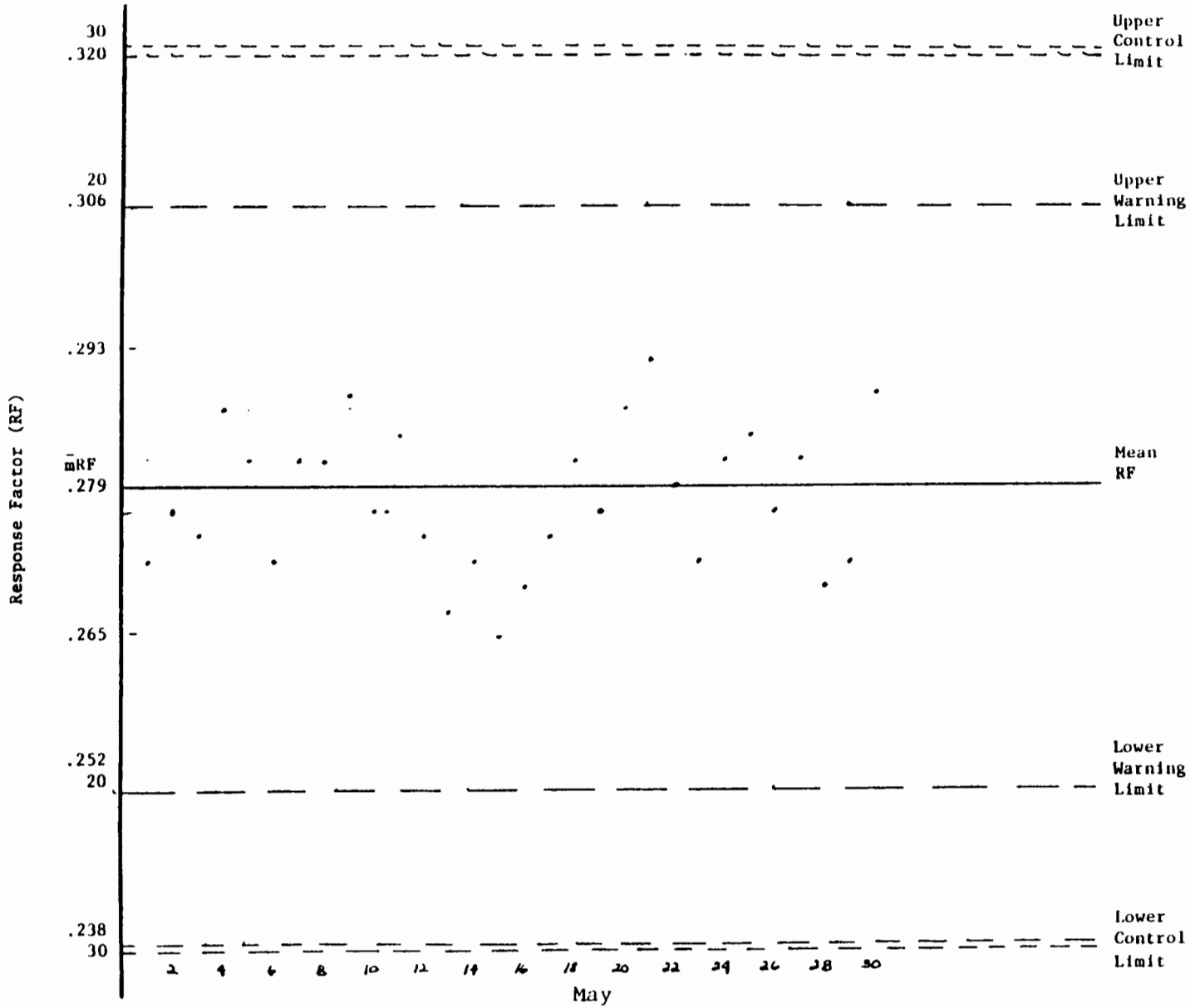


Figure 8-1. Daily Response Factors for Fluorobenzene Surrogate for the Month of May

2 / ORGANIC ANALYTICAL METHODS - GC/MS

2.4 Table 1 lists detection limits that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min) Column 1[a]	Method detection limit (µg/l)
Chloromethane	2.3	ND
Bromomethane	3.1	ND
Vinyl chloride	3.8	ND
Chloroethane	4.6	ND
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	ND
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
trans-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
cis-1,3-Dichloropropene	17.2	ND
2-Chloroethylvinyl ether	18.6	ND
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	ND
1,2-Dichlorobenzene	35.0	ND
1,4-Dichlorobenzene	35.4	ND

ND = not determined.

[a]Column conditions: Carbopack B (60/80 mesh) coated with 1% SP-1000 packed in a 6-ft by 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature is isothermal at 45° C for 3 min, then programmed at 8° C per minute to 220° and held for 15 min.

4 / ORGANIC ANALYTICAL METHODS - GC/MS

4.2.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 2.5 mm. The trap must be packed to contain the following minimum lengths-of-adsorbents: 1.0 cm of methyl-silicone-coated packing (Section 5.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 5.3.1), and 8 cm of silica gel (Section 5.3.3). The minimum specifications for the trap are illustrated in Figure 2.

4.2.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec. The polymer section of the trap should not be heated higher than 180° C and the remaining sections should not exceed 220° C. The desorber design, illustrated in Figure 2, meets these criteria.

4.2.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

4.3 Gas chromatograph/mass spectrometer system

4.3.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Column: 2-m x 2-mm I.D. stainless steel or glass, packed with 1% SP-1000 on 60/80 mesh Carbopack B or equivalent.

4.3.3 Mass spectrometer: Capable of scanning from 40 to 250 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet or introduced in the purge-and-trap mode.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Section 9) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

6 / ORGANIC ANALYTICAL METHODS - GC/MS

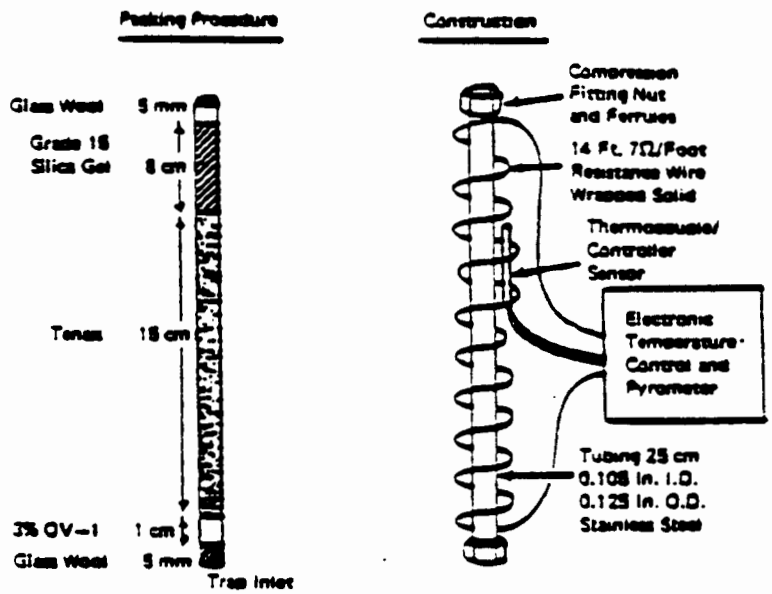


Figure 2. Trap packings and construction to include desorb capability.

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Hardware and software must be available to transform the data into a compatible format. These generally consist of a 9-inch, 800-bpi tape drive and the associated software.

4.4 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle or no needle attached. Samples should be introduced into the syringe by (1) removing the plunger from the syringe, (2) pouring the sample into the barrel, and (3) replacing the barrel and inverting the syringe to remove any air trapped in the syringe. Do not draw the sample up into the syringe. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the closed end of the barrel of a glass hypodermic syringe.

TABLE 2. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 100% of mass 174
177	5 to 9% of mass 176

10 / ORGANIC ANALYTICAL METHODS - GC/MS

5.1.4 Reagent water may also be purchased under the name "HPLC water" from several manufacturers (Burdick and Jackson, Baker and Waters, Inc.).

5.2 Reagent PEG: Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest.

5.2.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

5.3 Trap materials

5.3.1 2,6-Diphenylene oxide polymer: 60/80-mesh Tenax, chromatographic grade or equivalent.

5.3.2 Methyl silicone packing: 3 percent OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.3.3 Silica gel, Davison Chemical (35/60 mesh), grade-15 or equivalent.

5.3.4 Prepared trapping columns may be purchased from several chromatography suppliers.

5.4 Methanol: Distilled-in-glass quality or equivalent.

5.5 Calibration standards; stock solutions (2 mg/ml): Stock solutions of calibration standards may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions of individual compounds in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn by analysts when handling high concentrations of these materials.

5.5.1 Place about 9.8 ml of methanol in a 10-ml ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

concentrations prepared and the amount of solution added to each sample should be those required to give an amount of each surrogate in the purging device that is equal to the amount of each internal standard added, assuming a 100% recovery of the surrogate standards.

5.8 Internal standards: In this method, internal standards are employed during analysis of all samples and during all calibration procedures. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. However, for general use, D_4-1,2-dichloroethane, D_6-benzene, and D_5-ethylbenzene are recommended as internal standards covering a wide boiling point range.

5.9 4-Bromofluorobenzene (BFB): BFB is added to the internal standard solution or analyzed alone to permit the mass spectrometer tuning for each GC/MS run to be checked.

5.10 Internal standard solution: Using the procedures described in Sections 5.5 and 5.6, prepare a methanolic solution containing each internal standard at a concentration of 12.5 µg/ml.

5.11 Sodium monohydrogen phosphate: 2.0 µ in distilled water.

5.12 n-Nonane and n-dodecane, 98+% purity.

5.13 N-Hexadecane, distilled-in-glass (Burdick and Jackson, or equivalent).

6.0 Sample Collection, Handling, and Preservation

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples must be stored in Teflon-lined screw cap vials. Sample containers should be filled as completely as possible so as to minimize headspace or void space. Vials containing liquid sample should be stored in an inverted position.

6.3 All samples must be iced or refrigerated from the time of collection to the time of analysis, and should be protected from light.

including the internal standards. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/A_{is} C_s)$$

where:

A_s = Area of the primary characteristic ion for the compound to be measured

A_{is} = Area of the primary characteristic ion of the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the compound to be measured.

The internal standard selected for the calculation of the RF of a compound and subsequent quantification of the compound is generally the internal standard that has a retention time closest to that of the compound. It is assumed that a linear calibration plot will be obtained over the range of concentrations used. If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, versus RF.

7.1.3.4 The RF must be verified on each working day. The concentrations selected should be near the midpoint of the working range. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within ±20% of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for BFB (see Table 2).

7.2.2 The BFB performance test requires the following instrumental parameters:

Electron Energy:	70 volts (nominal)
Mass Range:	40 to 250 amu
Scan Time:	to give approximately 6 scans per peak but not to exceed 3 sec per scan.

during the shaking process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate phase separation.

7.3.2.4 Analyze a 2-µl aliquot of the n-hexadecane supernatant using the conditions described in Section 7.3.2.1. Determine the total area response of all components eluting prior to the retention time of n-dodecane and subtract the corresponding area of an n-hexadecane blank. Using the area response factor determined for n-nonane in Section 7.3.2.2, calculate the TVC as follows:

$$TVC = \frac{TAR_{sample} - TAR_{blank}}{\text{n-Nonane Area Response Factor}} \times 20$$

where:

TVC = total volatile content of the sample in mg/g

TAR_{sample} = total area response obtained for the sample

TAR_{blank} = total area response obtained for a blank.

7.3.3 The transfer of an aliquot of the sample for extraction with methanol or PEG should be made as quickly as possible to minimize loss of volatiles from the sample.

7.3.3.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent methanol or PEG. Weigh the capped centrifuge tube and methanol or PEG on an analytical balance.

7.3.3.2 Using an appropriate implement (see Section 4.4), transfer approximately 2 g of sample to the methanol or PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the methanol or PEG as quickly as possible. Take care not to touch the sample-transfer implement to the methanol or PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.3.3.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

18 / ORGANIC ANALYTICAL METHODS - GC/MS

7.3.5.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column: 6-ft x 2-mm I.D. glass column of 1% SP-1000 on Carbo-pack B (60-80 mesh).

Temperature: Isothermal at 45° C for 3 min, then increased at 8° C/min to 220° C, and maintained at 220° C for 15 min.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180° C while backflushing the trap with helium at a flow rate of 30 ml/min for 4 min. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30° C or lower during the 4-min desorb step and starting the GC program after the desorb step.

7.3.5.3 Return the purge-and-trap device to the purge mode and continue acquiring GC/MS data.

7.3.5.4 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution and distilled water, and then dried at 105° C.

7.3.5.5 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected when the trap is heated to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.3.6 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 7.3.2.3.

7.4 Qualitative identification

7.4.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.4.1.1 The characteristic ions of each compound of interest must maximize in the same or within one scan of each other.

20 / ORGANIC ANALYTICAL METHODS - GC/MS

8.2.1 Analyze four aliquots of the unspiked check sample according to the method in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methanol at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples by adding the spiking solution to the PEG used for the extraction. Analyze the spiked aliquots according to the method in Section 7.3.

8.2.4 Calculate the average percent recovery, R, and the standard deviation of the percent recovery, s, for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery, s/R x 100, must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standards to monitor spike recoveries. The spiking level used should be that which will give an amount in the purge apparatus that is equal to the amount of the internal standard assuming a 100% recovery of the surrogate standards. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be

22 / ORGANIC ANALYTICAL METHODS - GC/MS

TABLE 3. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

Parameter	Reagent Water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Benzene	99	9	98	10
Bromodichloromethane	102	12	103	10
Bromoform	104	14	105	16
Bromomethane	100	20	88	23
Carbon tetrachloride	102	16	104	15
Chlorobenzene	100	7	102	9
Chloroethane	97	22	103	31
2-Chloroethyl vinyl ether	101	13	95	17
Chloroform	101	10	101	12
Chloromethane	99	19	99	24
Dibromochloromethane	103	11	104	14
1,1-Dichloroethane	101	10	104	15
1,2-Dichloroethane	100	8	102	10
1,1-Dichloroethene	102	17	99	15
trans-1,2-Dichloroethene	99	12	101	10
1,2-Dichloropropane	102	8	103	12
cis-1,3-Dichloropropene	105	15	102	19
trans-1,3-Dichloropropene	104	11	100	18
Ethyl benzene	100	8	103	10
Methylene chloride	96	16	89	28
1,1,2,2-Tetrachloroethane	102	9	104	14
Tetrachloroethene	101	9	100	11
Toluene	101	9	98	14
1,1,1-Trichloroethane	101	11	102	16
1,1,2-Trichloroethane	101	10	104	15
Trichloroethene	101	9	100	12
Trichlorofluoromethane	103	11	107	19
Vinyl chloride	100	13	98	25

Samples were spiked between 10 and 1000 µg/l.

2 / SAMPLE INTRODUCTION TECHNIQUES

4.6 Crimper: Hand (Pierce #13212, or equivalent).

5.0 Reagents

5.1 Refer to Methods 8010, 8015, 8020, or 8030.

6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Methods 8010, 8015, 8020, or 8030.

7.0 Procedure

7.1 Place 10.0 g each of the well-mixed waste sample into three separate 125-ml septum seal vials.

7.2 Dose one sample vial through the septum with 200 µl of a 50-ng/µl methanolic standard of the compounds of interest. Label this "1-ppm spike."

7.3 Dose a separate (empty) 125-ml septum seal vial with 200 µl of the 50 ng/µl standard methanol solution. Label this "1-ppm standard."

7.4 Place the sample, 1-ppm-spike, and 1-ppm-standard vials into a 90° C water bath for 1 hr. Store the remaining sample vial at 4.0° C for possible future analysis.

7.5 While maintaining the vials at 90° C, withdraw 2 ml of the headspace gas with a gas-tight syringe and analyze by injecting into a GC, operating under the appropriate conditions for the GC measurement method being used (8010, 8015, 8020, or 8030).

7.6 Analyze the 1-ppm standard and adjust instrument sensitivity to give a minimum response of at least 2x the background. Record retention times (RT) and peak areas of compounds of interest.

7.7 Analyze the 1-ppm spiked sample in the same manner. Record RT's and peak areas.

7.8 Analyze the undosed sample as in Section 7.7.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a

2 / SAMPLE INTRODUCTION TECHNIQUES

3.0 Interferences

3.1 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.3.

3.2 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.4 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water (PEG or methanol solution) to check for cross contamination. After each use, the purging chamber is cleaned as described in Section 7.12. The trap and other parts of the system are also subject to contamination; therefore, frequent additional bakeout and purging or the entire system may be required.

4.0 Apparatus and Materials

4.1 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are commercially available.

4.1.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.1.2 The sorbent trap consists of a 1/8-in. O.D. (0.105-in. I.D.) x 25-cm-long stainless steel tube packed with the appropriate absorbents as described in Table 1 (see Figures 2 and 3).

4.1.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec.

5030 / 3

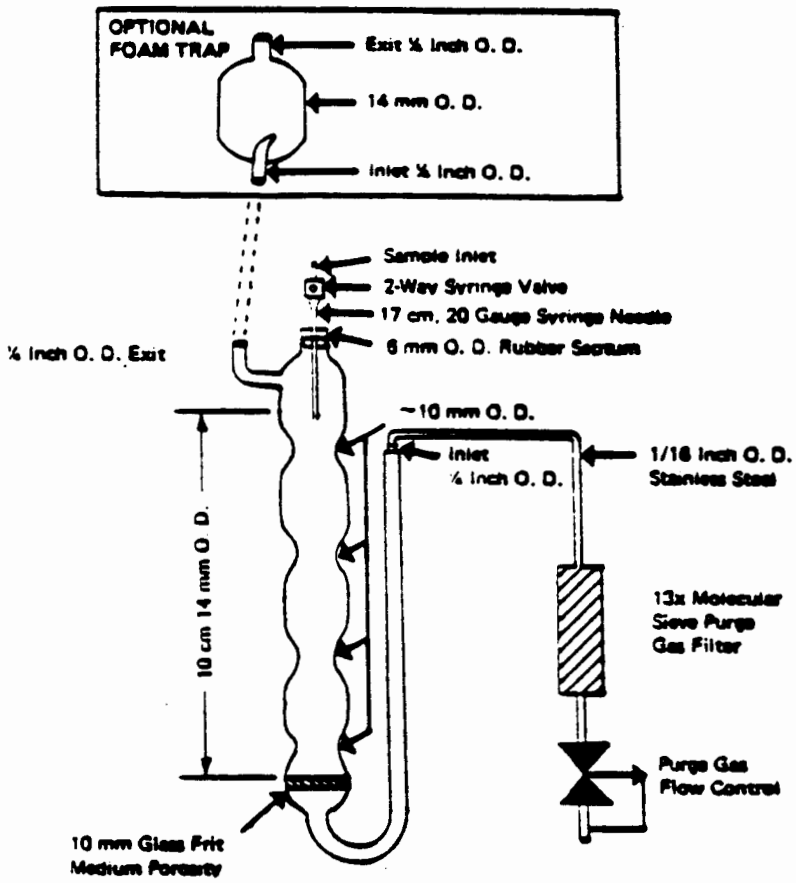


Figure 1. Purging chamber.

5030 / 5

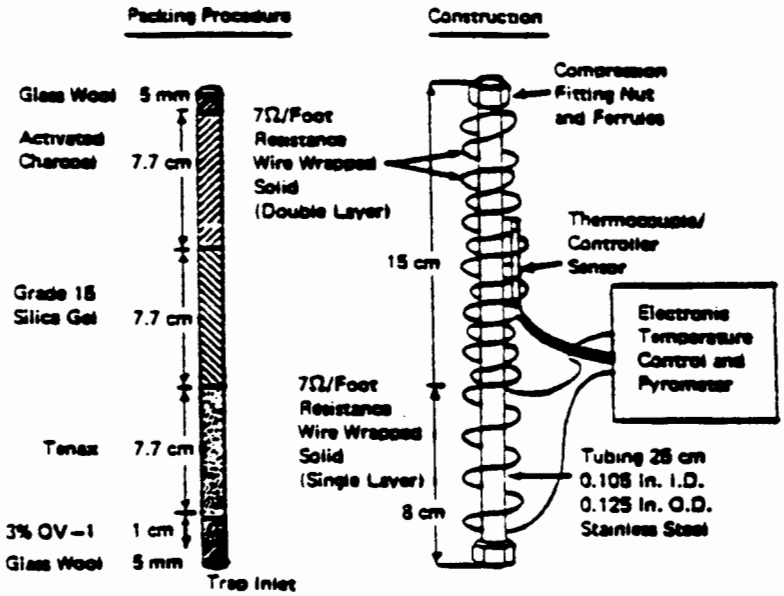


Figure 2. Trap packings and construction for Method 8010.

4.1.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 4 through 6.

4.2 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.3 Micro syringes: 10 µl, 25 µl, 100 µl, 250 µl, 500 µl, and 1,000 µl. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.4 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation (Kimble #46212 or equivalent).

4.5 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.6 Syringe valve: 2-way, with Luer ends (2 each; Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting or equivalent).

4.7 Syringe: 5-ml, gas-tight with shutoff valve.

4.8 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.9 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.10 Rotary evaporator: Equipped with Teflon-coated seals (Buchi Rotavapor R-110 or equivalent).

4.11 Vacuum pump: Mechanical, two-stage.

5.0 Reagents

5.1 Trap materials (see Table 1 and Figures 2 and 3 for configuration).

5.1.1 2,6-Diphenylene oxide polymer: 60/80 mesh Tenax, chromatographic grade or equivalent.

5.1.2 Methyl silicone packing: 3% OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.1.3 Silica gel, Davison Chemical (35/60 mesh), grade 15 or equivalent.

5030 / 9

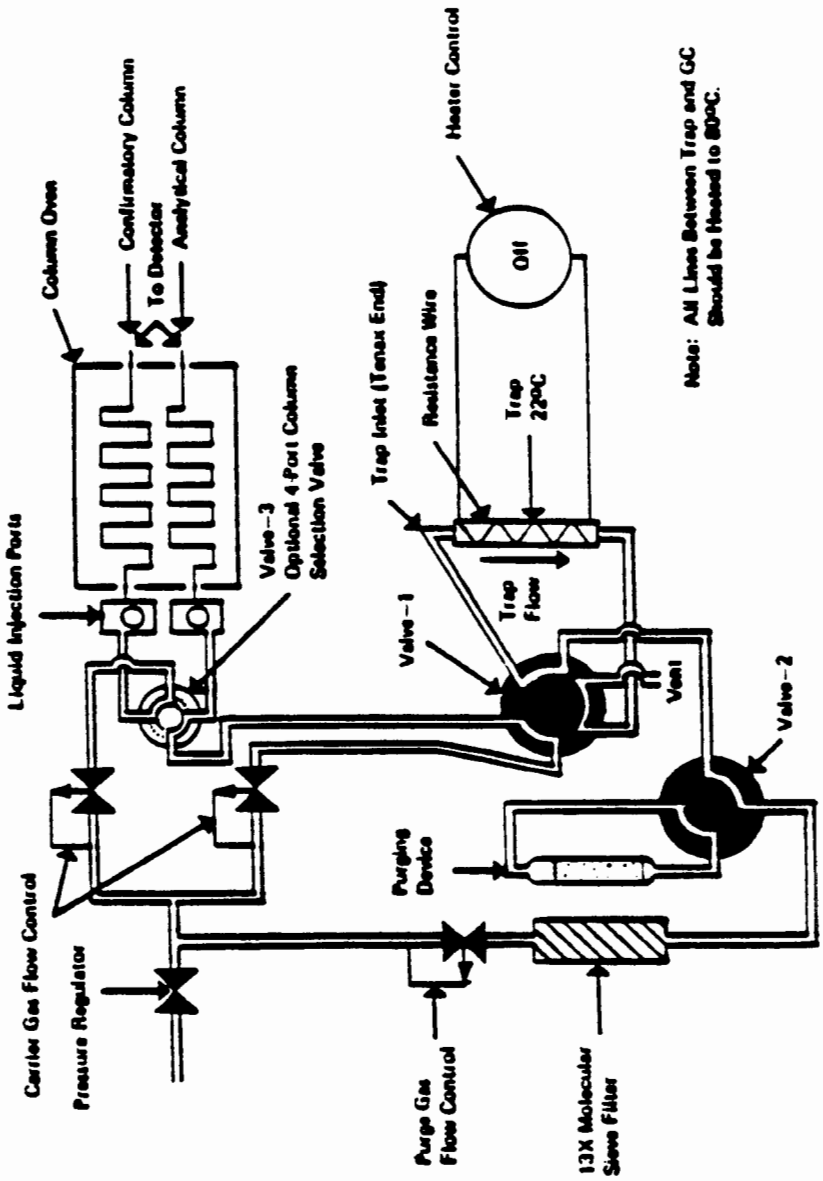


Figure 6. Purge and trap system, trap dry mode, for Methods 8020 and 8030.

5.2 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.2.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.3 Reagent PEG (polyethylene glycol; for solid samples): Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest. Methanol which has been distilled in glass can be used as a substitute for PEG.

5.3.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.3.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Method 8010, 8020, or 8030 for pertinent information.

7.0 Procedures

7.1 Assemble the purge-and-trap device (see Figures 4 through 6). Purge parameters to be used depend on the compounds being analyzed for; see Table 1. Pack the trap as shown in Figure 2 or 3 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the trap for 10 min by backflushing at 180° C.

7.8 Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the liquid samples for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data.

7.9 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber. Close both valves and purge the sample for the time specified in Table 1. If Method 8020 will be used for analysis of the sample, dry the trap by maintaining a flow rate of 40 ml/min dry purge for 4 min.

7.10 Attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to the backflush temperature indicated in Table 1, while backflushing the trap with an inert carrier gas at 20 to 60 ml/min for 4 min. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30° C (or subambient, if problems persist) instead of the initial program temperature of 45° or 50° C.

7.11 Return the purge trap device to the purge mode.

7.12 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution, and distilled water and drying at 105° C.

7.13 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected by heating the trap to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.14 The analysis of blanks is most important in the purge-and-trap technique since the purging device and the trap can become contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water. Blanks should be sealed, stored at 4° C, and analyzed with each group of samples.

GROUP OR LABORATORY: Sample Preparation	PROCEDURE NO: 321-SP-008	PAGE: 1 of 4
TITLE: Operation of the Ultratip Probe Sonication System	REVISION NO: 1	EFFECTIVE DATE: 10/26/87
	SUPERCEDES: 3/22/86	

REFERENCES: 321-SP-001

SATELLITE FILES: 1-118

REASON FOR REVISION: Revise section 3.3

1.0 PURPOSE

1.1 The purpose of this section is to provide a guideline for operation and maintenance of the Ultratip Probe WW-201 System.

2.0 SCOPE

2.1 This document covers the correct handling requirements for using the Ultratip Probe WW-201 System.

3.0 OPERATION

3.1 Place the Ultratip generator on a secure flat surface, which allows adequate ventilation on either side and back of the generator. It is extremely important that ventilation be provided for the Ultratip generator to avoid overheating of the system.

3.2 Use a large clamp to support the motor transducer and horn on a ring-stand. The tip of the horn should be immersed in liquid

WRITER: NAME/DATE Kevin P. Kelly 10-21-87		
ACTIVITY MGR: NAME/DATE SK Martens	NAME/DATE F. S. Shore 10/26/87	NAME/DATE RA Magee 10/26/87

4.0 SAFETY

4.1 Since aerosols are produced from the solvents used, the motor transducer and horn assembly must be used in the hood.

4.2 The ultrasonic tip is designed to disrupt cells. DO NOT TOUCH the tip while the probe is in operation or immerse any fingers into the solution.

4.3 Never use carbon tetrachloride in conjunction with ultrasonics as it decomposes into the toxic phosgene gas.

4.4 The noise output from sonication will vary depending on the volume of substance being sonicated, power level and type of tip being used. Ear protection will be available to the user and should be worn whenever the noise level is irritating or for prolonged time periods.

5.0 MAINTENANCE

5.1 The horn is equipped with a replaceable (ES) tip, and satisfactory results will be obtained only if the tip is properly installed. A loose tip will produce localized heating and substantially reduce power. A 1/2 inch box wrench is used for the ES tip. When installing the tip, wrap a one inch length of Teflon plumber's "Tape Dope" clockwise around its threads and tighten until firm. The manufacturer states that 80 inch pounds of torque should not be exceeded. Tightening beyond this limit may fracture the tip so caution should be exercised in tightening. A silicone grease should not be used because of its interaction with the solvents used.

5.2 If the micro-tip is required for small sample sizes, use a 7/16 inch open-end wrench to install it.

CONFIDENTIAL

RADIAN

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation	PROCEDURE NO: 321-SP-020	PAGE: 1 of 15
TITLE: Sonication Extraction by EPA Method SW-846-3550	REVISION NO: 1 / EFFECTIVE DATE: 8/12/88	
	SUPERSEDES: 3/22/86	
REFERENCES: 321-SP-001, -004, -008		
SATELLITE FILES: 1-118		
REASON FOR REVISION: New Edition of SW-846		

1.0 PURPOSE

The purpose of this document is to establish a guideline for procedural adaptations of the EPA-OSW SW-846 "Method 3550 Sonication Extraction".

2.0 PROCEDURE

The modifications of Method 3550 (Method attached) normally applied in the Sample Preparation Laboratory are outlined as follows:

2.1 Section 4.0 of Method 3550 is modified in the following section:

4.15 Drying column: Funnel, packed with a plug of silanized glass wool and 3.5 cm of adsorbent (approximately 80 grams).

2.2 Section 5.0 of Method 3550 is modified in the following section:

5.2 Methylene chloride will be the solvent for all extractions unless otherwise specified in the extraction workplan.

2.3 Section 7.0 of Method 3550 is modified in the following sections:

7.1.1 If a water layer is murky or not well separated from sediment, it may be necessary to homogenize a wet sediment/soil. Ask the lab manager or project sponsor for guidance when in doubt.

WRITER: NAME/DATE: Kevin O'Kelly, 7/15/88		
ACTIVITY MGR: NAME/DATE: A. Medeiros 7/22/88	NAME/DATE: T. Shore 8/11/88	NAME/DATE: R. Magee 8/12/88

7-87-27815

7.4.8 The concentration step will not necessarily take 15-20 minutes. The time required depends on the volume of solvent that needs to be removed, and the bath temperature that is specified (if any).

7.4.9 If a solvent exchange is required (as indicated in Table 1), begin adding the exchange solvent through the top of the Snyder column when the volume of the extract has been reduced to about 25 mL. Add the exchange solvent in portions (of less than 10 mL each), at a rate that does not cause the boiling of the extract to cease. Wait between portions for the balls of the Snyder column to resume chattering before adding the next portion. Concentrate the extract, as described in Paragraph 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.4.11 If a final extract volume appreciably less than 10 mL is required, it is necessary to further concentrate the extract using a micro-Snyder column. In cases where bumping or severe foaming of the sample liquid would be expected, nitrogen evaporation may be substituted for the micro-Snyder technique.

7.5.1 The standard sample size for a matrix containing high levels of analytes (e.g. waste feed) is 2 grams; however, a larger or smaller sample may be used, depending on expected analyte concentrations or target detection limits. Record sample weight to nearest 0.01 g or better.

7.5.2 More sodium sulfate may be required if a larger sample size is used or the sample is very wet. Use at least 2 g.

7.5.3 The amount of spiking solutions used depends on sample size and expected level of analytes. Use the amounts that are given on the workplan.

4.0 SAFETY

Normal laboratory procedures as described in SOP 321-SP-004 must be followed. The sonication and concentration must be done in a working fume hood. Ear protection should be worn if necessary (see 321-SP-008).

5.0 QUALITY CONTROL

Duplicates, spikes, blanks, and other quality control samples will be prepared in accordance with SOP 321-SP-001. Other QA/QC considerations pertinent to the project must be detailed in the project work plan.

4.2 Sonication: A horn-type sonicator equipped with a titanium tip should be used. The following sonicator, or an equivalent brand and model, is recommended:

Ultrasonic cell disrupter: Heat Systems - Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent (Power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapered microtip probe.

4.3 Sonabox: Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent moisture:

4.4.1 Oven: Drying.

4.4.2 Desiccator.

4.4.3 Crucibles: Porcelain.

4.5 Pasteur glass pipets: Disposable, 1-mL.

4.6 Beakers: 400-mL.

4.7 Vacuum filtration apparatus:

4.7.1 Buchner funnel.

4.7.2 Filter paper: Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 Concentrator tube: 10-mL graduated (Kontes K-570050-1025 or equivalent).

4.8.2 Evaporator flask: 500-mL (Kontes K-570001-0500 or equivalent).

4.8.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

7.1.3 Dry waste samples amenable to grinding: Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \%\ \text{moisture}$$

7.3 Determination of pH (if required): Transfer 50 g of sample to a 100-mL beaker. Add 50 mL of water and stir for 1 hr. Determine the pH of sample with glass electrode and pH meter while stirring. Discard this portion of sample.

7.4 Extraction method for samples expected to contain low concentrations of organics and pesticides ($\lesssim$20 mg/kg):

7.4.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g. Non-porous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Add 1 mL of surrogate standards to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.4.2 Place the bottom surface of the tip of the #207 3/4 in. disruptor horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.4.3 Sonicate for 3 min, with output control knob set at 10 and with mode switch on Pulse and percent-duty cycle knob set at 50%. Do NOT use microtip probe.

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a]To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b]Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c]The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

5.0 mL in a concentrator tube if further concentration is required. Follow Paragraphs 7.4.6 through 7.4.12 for details on concentration. Normally, the 5.0 mL extract is concentrated to 1.0 mL.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subject to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

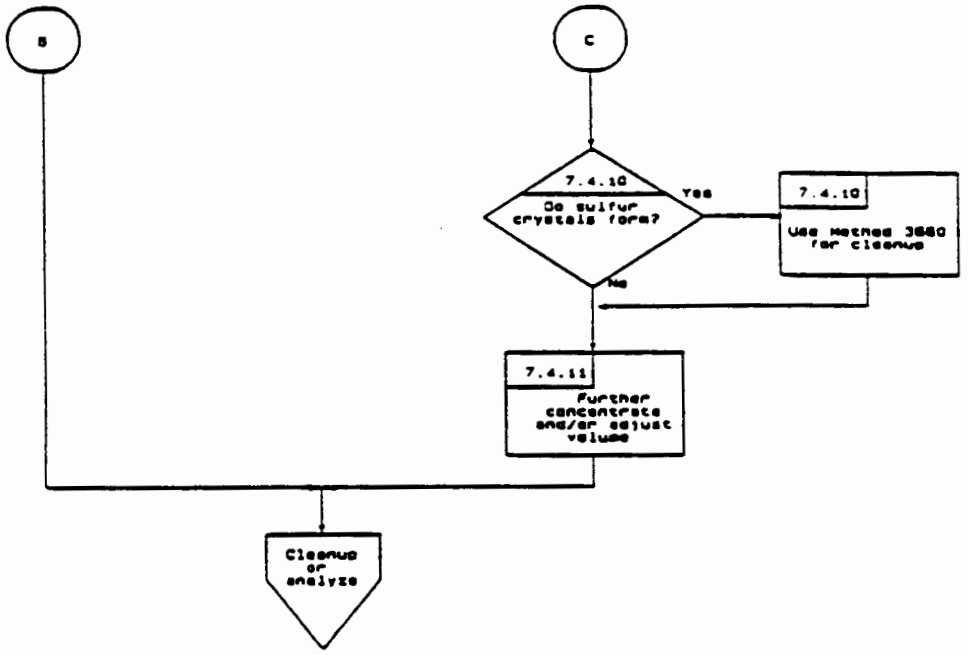
10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

METHOD 3550

SONICATION EXTRACTION
(Continued)



CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Inorganic Metals Laboratory	PROCEDURE NO: 325-AA-003	PAGE: 1 of 5
TITLE: ANALYSIS OF SELENIUM BY GRAPHITE FURNACE	REVISION NO: Original	EFFECTIVE DATE: 5/27/88
	SUPERSEDES: N/A	

REFERENCES: EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 270.2

SATELLITE FILES:

REASON FOR REVISION:

Original

1.0 SCOPE AND APPLICATION

Selenium in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require digesting to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper digestion. Selenium may also be analyzed by hydride AA or ICP. Detection limits and matrices are considerations when choosing the best method for analyzing the sample.

2.0 SUMMARY OF METHOD

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor. Because the tube area is small, the vaporized atoms are more concentrated allowing for lower limits of detection.

3.0 INTERFERENCES

3.1 This technique is subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. These effects must be taken into consideration in the analysis of each different matrix encountered. Known chemical interferences are chlorides (>800 ppm) and sulphates (>200 ppm).

3.2 Nitric acid is preferable for any digestion or solubilization step. If another acid is required in addition to HNO_3, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

WRITER: NAME/DATE: Diana M. Conway 5/10/88		
ACTIVITY MGR: NAME/DATE 5/10/88	NAME/DATE 5/23/88	NAME /DATE 5/27/88

7-87-27815

5.4 Working Standards

Dilute 1 mL of 1000 ppm stock to 1 L with deionized water containing 1% HNO_3. Dilute 0, 2, 4, 6 mL of this intermediate solution to 100 mL with deionized water. This will prepare 0, 20, 40, and 60 ppb standards for use in the calibration procedure below.

6.0 CALIBRATION PROCEDURES

6.1 Calibration standards are analyzed beginning with the blank and proceeding to the highest standard. Each is analyzed in duplicate. Linear regression is used to define the calibration curve. The regression line is constructed using concentration as the X-value and mean response as the Y-variable. The blank is included as X=0.

6.2 The correlation coefficient of the standard curve must be $\geq$0.995 for the analysis to continue. If not, the analyst will correct the problem, remaking standards as necessary before the analysis will continue.

7.0 QUALITY CONTROL

7.1 This is Radian's standard quality control protocol. In the areas of QC check samples, duplicates, and spikes, it meets or exceeds the requirements set forth in SW-846, 3rd Ed. Method 7740. It is not, however, a strict SW-846 protocol and should not be construed as such.

7.2 Quality Control Check Samples

In addition to calibration standards, quality control (QC) check samples are to be analyzed initially to verify the calibration curve and at a frequency of one in ten throughout the analysis. If the QC recovery is within acceptable limits (85-115%), the analysis may proceed. If any QC sample falls outside these limits, the analysis must be stopped and any of the following performed to bring the standard into control:

- Check instrument operating parameters (e.g., gas pressure),
- Recalibration,
- Re-make of QC standard, or
- Check with lab supervisor.

After the problem is addressed, analyses may commence, including all samples analyzed since the last acceptable QC standard.

7.3 Duplicates

Duplicates are to be performed at a rate of one in ten samples. A duplicate is defined as a sample which is split and treated as two independent samples and carried throughout the entire protocol (digestion, interference modifier solution, analysis). Duplicates should agree within 20 percent.

9.0 REPORTING

Reporting requirements include:

- Instrument usage log,
- Instrument maintenance log,
- Analysis bench sheet,
- QC summary sheet,
- Print out, and
- Any lab notebook pages relevant to the data.

9.1 Each instrument has a corresponding log book requesting pertinent information relevant to the analysis to be performed. This log book must be filled out prior to completion of analysis to document standard conditions and response of the instrument.

9.2 The instrument maintenance log provides information regarding <u>any</u> maintenance performed before, during, or after the analysis.

9.3 The analysis and QC summary sheet should be filled out completely following instruction provided on each bench sheet.

9.4 All entries must be in black ink with corrections made by making one horizontal mark through the incorrect data and the correct data placed beside it. The correction is to be dated and initialed.

9.5 When using AA bench, the analyst will make hard copies of the AA bench equivalent of the analysis bench sheet and the QC summary sheet. Instructions for preparing the documents are in the AA Bench Users Guide.

10.0 SAFETY

10.1 Safety glasses and laboratory coat must be worn to prevent accidental injury due to the corrosivity of some of the reagents.

10.2 Because standards and samples contain nitric acid, they must be disposed of in the safety containers located in the lab.

GROUP OR LABORATORY: Inorganic Laboratory	PROCEDURE NO: 325-IN-001	PAGE: 1 of 8
TITLE: EQUIPMENT MAINTENANCE	REVISION NO: Original	EFFECTIVE DATE: 5/31/88
	SUPERSEDES: N/A	

REFERENCES: Radian SOP #325-IN-002

SATELLITE FILES:

REASON FOR REVISION:

Original

1.0 INTRODUCTION

The purpose of the performance and documentation of equipment maintenance procedures is to help insure quality analyses in the laboratory and aid in quickly identifying chronic problems.

2.0 SCOPE

This document addresses instrument maintenance in the individual laboratories and computer hardware maintenance in Sample Control.

3.0 ATOMIC SPECTROSCOPY LABORATORY

3.1 Atomic Absorption Spectrometers

Maintenance procedures performed by the analyst according to the Preventative Maintenance Schedule (Attachment A) are documented in the instrument logbooks. The logbooks are discussed further in the analytical methods themselves. When repair by a service technician is deemed necessary, a description of all procedures is kept on file by the lab manager for quick reference. All of the atomic absorption spectrometers are covered by service contracts. Copies of service contracts are kept by the lab manager.

3.2 Inductively Coupled Argon Plasma Emission Spectrometer (ICPES)

3.2.1 Daily Log

A daily log is generated by the ICPES analyst before calibration of the instrument each day. This log provides a status report of fourteen electronics and spectrometer parameter readings. Additional readings pertaining to the RF generator and argon source are determined by the analyst. Acceptable value ranges for all of

WRITER: NAME/DATE: 5/9/88		
ACTIVITY MGR: NAME/DATE 5/9/88	NAME/DATE 5/31/88	NAME /DATE 5/31/88

7.0 SAFETY

Normal safety practices should be followed. This includes lab coats and safety glasses being worn at all times in the lab areas. For a more extensive discussion of saftey in the lab, please refer to the inorganic lab safety S.O.P (#325-IN-002).

Daily Log for ICP 34000 - 291

Electronics Reading		Value		Range
-1000 VDC Supply	=	-1020	TO	-960
-100 VDC Supply	=	-101	TO	-99
-15 VDC Supply	=	-15.3	TO	-14.5
-10 VDC Reference	=	9.9	TO	10.2
-1 VDC Reference	=	.99	TO	1.01
-0.1 VDC Reference	=	.096	TO	.104
Ground Reference	=	.001	TO	.005
+5 VDC Supply	=	4.5	TO	5.5
+15 VDC Supply	=	14.7	TO	15.3
+24 VDC Supply	=	22.2	TO	26.4
Line Voltage (AC)	=	198	TO	242
Cabinet Temperature	=	20	TO	40

RF Generator Readings	Value
Incident Power	_____
Reflected Power	_____
Plate Current (<0.65 AMP)	_____
P.A. Filament Voltage (7.5 $^{+}$ 0.4 Volts)	_____
P.A. Voltage (<4800 Volts)	_____
P.A. Grid Current (<0.4 AMP)	_____

Spectrometer Conditions		Value		Range
Spectrometer Vacuum	=	0	TO	75
Spectrometer Temp.	=	30	TO	40

ICP Source Parameters

Coolant Argon Meter Reading (PSI)	_____
Plasma Argon Meter Reading (PSI)	_____
Nebulizer Argon Meter Reading (PSI)	_____
Nebulizer Uptake Rate (ML/MIN)	_____

ATTACHMENT D

Conductivity Deionized Water

	Mon.	Tues.	Wed.	Thurs.	Fri.	
Indicator, 4-149						Comments:
Indicator, 4-144						
Reading, umho/cm						
Checked by						
Date						
Verification						

RADIAN CORPORATION

7-87-27793a

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation	PROCEDURE NO: 321-SP-024	PAGE: 1 of 4
TITLE: Special Procedures When Preparing Samples For GC/ECD Analyses	REVISION NO: Original	EFFECTIVE DATE: 3/10/88
	SUPERSEDES: N/A	

REFERENCES: 321-SP-001, -004 , -008, -010, -012, -013, -018, -020, -022

SATELLITE FILES: 1-119

REASON FOR REVISION: Original

1.0 SCOPE AND APPLICATION

This document covers all phases of sample preparation for GC analyses using the electron capture detector (GC/ECD). It contains recommendations for reagents and procedures that will avoid contamination of samples and blanks.

Methods to which this material applies include EPA SW-846, 3rd ed., Method 8080 (Organochlorine Pesticides and PCBs), and Method 8150 (Chlorinated Herbicides, see also 321-SP-019). It also applies to Method 8040 when the analytes are chlorinated phenols (such as pentachlorophenol).

Refer to SW-846 manual and the appropriate SOP for details regarding separatory funnel extraction (Method 3510, 321-SP-010), continuous liquid/liquid extraction (Method 3520, 321-SP-012), Soxhlet extraction (Method 3540, 321-SP-013), sonication (Method 3550, 321-SP-020 and 321-SP-008), and waste dilution (Method 3580, 321-SP-022).

2.0 SUMMARY

GC/ECD analyses are very sensitive to contamination from substances that will capture electrons in the detector, particularly PLASTI-

WRITER: NAME/DATE: Kevin T. Kelly 2/4/88		
ACTIVITY MGR: NAME/DATE: J K Mertens 2/8/88	NAME/DATE: T J Shaw 3/3/88	NAME /DATE: R A Magee 3/10/88

7-87-27815

3.6 Solvents: Avoid commercial grade acetone when drying glassware to be used for GC/ECD analyses. All solvents must be pesticide grade or equivalent.

3.7 Soxhlet thimbles: Preextracted with the extraction solvent in Soxhlet extractor, for at least two hours, and oven dried in a clean, glass container.

3.8 Teflon sleeves for glass joints: Clean using the procedure outlined above for cleaning needles. Use enough solvent to completely cover the sleeves. Remove the clean sleeves with tongs and mount them in the joint; don't wait for them to dry.

3.9 Reagent water: HPLC grade (e.g. Burdick & Jackson) water should be used for blanks, and to prepare all reagent solutions needed (e.g. acid and base neutralizing solutions).

4.0 PROCEDURE

4.1 Maintain an awareness of all incidents where your hands or gloves touch any implements or containers that will be in contact with the sample or solvent. If an item becomes accidentally contaminated, stop and rinse it with solvent before proceeding.

4.2 Avoid placing your hands near the mouth of any container that will contact sample, solvent, or extract. Grasp all containers from the bottom. Keep hands away from standard taper (ground glass) joints.

4.3 Keep rubber hoses away from the mouths of condensers and extractors.

CONFIDENTIAL

RADIAN

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Inorganic Metals Laboratory	PROCEDURE NO: 325-AA-004	PAGE: 1 of 5
TITLE: ANALYSIS OF LEAD BY GRAPHITE FURNACE	REVISION NO: Original	EFFECTIVE DATE: 11/23/88
	SUPERSEDES: NA	

REFERENCES: EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 239.2

SATELLITE FILES: 4-154, 4-135

REASON FOR REVISION:

NA

1.0 SCOPE AND APPLICATION

Lead in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require digesting to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper digestion. Lead may also be analyzed by hydride AA or ICP. Detection limits and matrices are considerations when choosing the best method for analyzing the sample.

2.0 SUMMARY OF METHOD

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor. Because the tube area is small, the vaporized atoms are more concentrated allowing for lower limits of detection.

3.0 INTERFERENCES

3.1 This technique is subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. These effects must be taken into consideration in the analysis of each different matrix encountered.

3.2 Nitric acid is preferable for any digestion or solubilization step. If another acid is required in addition to HNO_3, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

WRITER: NAME/DATE: Robert R. Brook		
ACTIVITY MGR: NAME/DATE 11/18/88	NAME/DATE T. L. Shore 11/23/88	NAME/DATE Robert A. Magee 11/23/88

7-87-27815

5.4 Matrix Modifier Working Solution

Pipette 2.0 mL of the ammonium phosphate solution into the matrix modifier cup. Add 1 mL of the magnesium nitrate solution and dilute with deionized water to 4 mL. Mix well. This solution is added to the graphite furnace by the autosampler after each injection of sample is made into the furnace.

5.5 Working Standards

Dilute 1 mL of 1000 ppm stock to 1 L with deionized water containing 1% HNO_3. Dilute 0, 2, 4, 6 mL of this intermediate solution to 100 mL with deionized water. This will prepare 0, 20, 40, and 60 ppb standards for use in the calibration procedure below.

6. CALIBRATION PROCEDURES

6.1 Calibration standards are analyzed beginning with the blank and proceeding to the highest standard. Each is analyzed in duplicate. Linear regression is used to define the calibration curve. The regression line is constructed using concentration as the X-value and mean response as the Y-variable. The blank is included as X=0.

6.2 The correlation coefficient of the standard curve must be $\geq$0.995 for the analysis to continue. If not, the analyst will correct the problem, remaking standards as necessary before the analysis will continue.

7. QUALITY CONTROL

7.1 This is Radian's standard quality control protocol. In the areas of QC check samples, duplicates, and spikes, it meets or exceeds the requirements set forth in SW-846, 3rd Ed. Method 7740.

7.2 Quality Control Check Samples

In addition to calibration standards, quality control (QC) check samples are to be analyzed initially to verify the calibration curve and at a frequency of one in ten throughout the analysis. If the QC recovery is within acceptable limits (90-110%), the analysis may proceed. If any QC sample falls outside these limits, the analysis must be stopped and any of the following performed to bring the standard into control:

- Check instrument operating parameters (e.g., gas pressure),
- Recalibration,
- Re-make of QC standard, or
- Check with lab supervisor.

After the problem is addressed, analyses may commence, including all samples analyzed since the last acceptable QC standard.

8.0 SETUP

Lamp:	Lead HCL
Wavelength:	283.3
Dry °C/Sec:	140/35
Char °C/Sec:	650/30
Atomizer °C/Sec:	2100/5
Purge Gas:	Argon
Background Correction:	Yes
Injection Volume:	25 uL (20 uL on Zeeman AA)

9.0 REPORTING

Reporting requirements include:

- Instrument usage log,
- Instrument maintenance log,
- Analysis bench sheet,
- QC summary sheet,
- Print out, and
- Any lab notebook pages relevant to the data.

9.1 Each instrument has a corresponding log book requesting pertinent information relevant to the analysis to be performed. This log book must be filled out prior to completion of analysis to document standard conditions and response of the instrument.

9.2 The instrument maintenance log provides information regarding <u>any</u> maintenance performed before, during, or after the analysis.

9.3 The analysis and QC summary sheet should be filled out completely following instruction provided on each bench sheet.

9.4 All entries must be in black ink with corrections made by making one horizontal mark through the incorrect data and the correct data placed beside it. The correction is to be dated and initialed.

9.5 When using AA bench, the analyst will make hard copies of the AA bench equivalent of the analysis bench sheet and the QC summary sheet. Instructions for preparing the documents are in the AA Bench Users Guide.

10.0 SAFETY

10.1 Safety glasses and laboratory coat must be worn to prevent accidental injury due to the corrosivity of some of the reagents.

10.2 Because standards and samples contain nitric acid, they must be disposed of in the safety containers located in the lab.

GROUP OR LABORATORY: GC/MS	PROCEDURE NO: 321-MS-010	PAGE: 1 of 49
TITLE: Analysis of Appendix IX Semivolatile Compounds by EPA Method SW-846-8270	REVISION NO: 1	EFFECTIVE DATE: 1-30-89
	SUPERSEDES:	

REFERENCES: 321-MS-001, -003, -004, 321-SP-010, -012

SATELLITE FILES: 1-101

REASON FOR REVISION:

New Edition of SW-846

1.0 PURPOSE

The purpose of this SOP is to provide an outline for the GC/MS analysis of semivolatile organic compounds.

2.0 SCOPE

This SOP outlines in detail the GC/MS procedures and associated QA/QC for the analysis of Appendix IX semivolatile compounds extracted from all types of solid waste matrices, soils, and groundwaters. This method is taken from U.S. EPA SW-846 Method 8270, Test Methods for Evaluating Solid Waste, 3rd Edition, September 1986. Method 8270 must be read and understood by the GC/MS analyst before beginning any semivolatiles work.

3.0 INSTRUMENTATION

A GC/MS instrument which has the performance capabilities outlined in Section 4.0 of Method 8270 must be used. At Radian, the HP-5985/87 and HP-5970 are used for Method 8270 semivolatiles work. A list of instrument operating conditions for these two instruments is shown on Tables 3-1 and 3-2.

WRITER: NAME/DATE: Dwayne Hardin 1/30/89		
ACTIVITY MGR: NAME/DATE Michael C. Shepherd 1/30/89	NAME/DATE T. Shore 1/30/89	NAME/DATE Richard A. Magee 1/30/89

4.0 TARGET LIST IDENTIFICATION AND QUANTITATION

Most of Radian's GC/MS semivolatiles work involves identification and quantitation of Appendix IX analytes. The "Appendix IX" target list is a list of known and suspected toxic compounds identified by the EPA and outlined in the Federal Register.

4.1 Compound Identification

Table 4-1 shows the Appendix IX target list in elution order. Also shown are the primary quantitating ions and instrument detection limits for each analyte.

For positive identification two criteria must be met: the sample component must have the same relative retention time (RRT) as the standard component, and the sample component must have the same mass spectrum as the standard component. A sample component is considered to have the same mass spectrum as a standard when all ions greater than 10% in the standard mass spectrum are present, and when the three major sample component ions have intensities within ±20% of those in the standard spectrum.

4.2 Quantitation

When a compound has been identified, it is quantitated based on the ratio of the primary ion intensity to that of the nearest internal standard. The calculation is as follows:

$$\text{Conc} = \frac{A_x \bullet C_{is} \bullet \text{Vol} \bullet \text{DF}}{A_{is} \bullet \text{Rf} \bullet \text{S}}$$

TABLE 4-1. APPENDIX IX COMPOUNDS FOR METHOD 8270 ANALYSIS DISPLAYING RETENTION TIMES, PRIMARY IONS AND DETECTION LIMITS (Continued)

Compound	Retention Time[a] (min)	Primary Ion (m/z)	Instrument Detection Limit (ng)
Hexachlorocyclopentadiene	18.37	237	5
2,4,6-Trichlorophenol	18.48	196	5
2-Fluorobiphenyl (Surr.)	19.17	172	NA
2-Chloronaphthalene	19.21	162	2
1-Chloronaphthalene	19.30	162	2
1,4-Naphthoquinone	19.48	158	5
Dimethyl phthalate	20.09	163	2
m-Dinitrobenzene	20.15	168	5
2,6-Dinitrotoluene	20.21	165	5
Acenaphthalene	20.32	152	2
Acenaphthene	21.03	154	2
2,4-Dinitrophenol	21.10	184	50
2,4-Dinitrotoluene	21.27	165	5
Pentachlorobenzene	21.31	250	5
1-Naphthyl amine	21.40	143	5
2,3,4,5-Tetrachlorophenol	21.46	232	10
2,3,5,6-Tetrachlorophenol	21.46	232	10
2,3,4,6-Tetrachlorophenol	21.54	232	10
Diethyl phthalate	22.06	149	2
4-Chlorophenyl phenyl ether	22.22	204	10
Fluorene	22.25	166	2
4,6-Dinitro-o-cresol	22.36	198	10
Thiuram	22.39	88	5
N-Nitroso-diphenylamine	22.40	169	5
1,2-Diphenyl hydrazine	22.47	77	2
2,4,6-Tribromophenol (Surr.)	23.01	332	NA
4-Bromophenyl phenyl ether	23.43	141	2
Hexachlorobenzene	24.12	284	2
4-Aminobiphenyl	24.27	169	5
Pronamide	24.38	173	10
Pentachlorophenol	24.39	266	5
Benzidine	24.46	184	10
Pentachloronitrobenzene	24.52	237	5
Phenanthrene-d_{10} (I.S.)	25.03	188	NA
Phenanthrene	25.06	178	2
Anthracene	25.14	178	2
Dibutylphthalate	26.35	278	2
Fluoranthene	28.28	202	2
Pyrene	29.07	202	2
p-Terphenyl-d_{14} (Surr.)	29.27	244	NA
p-Dimethylamino azobenzene	29.51	120	5
Butyl benzyl phthalate	30.46	149	2
Bis(2-ethylhexyl)phthalate	32.22	228	2

(Continued)

where:

Conc = concentration in the sample

Ax = area of compound quantitating ion

Ais = area of internal standard major ion

Cis = concentration of internal standard

Rf = response factor from standard curve

Vol = final extract volume

Df = dilution factor

S = initial sample size extracted (mL or L for liquids, g or Kg for solids)

4.3 Reporting

The Radian Appendix IX SAM report form is shown on Table 4-2. Compounds are listed in alphabetical order and method detection limits (MDL) are given. The MDL corresponds to the lowest level on the calibration curve adjusted for sample size and extract volume. When additional compounds are required and a standard is unavailable, an N/A is reported. When reporting data to the client use "less than the MDL" (e.g. <10), not "ND" for not detected. An ND may be used only for compounds not in the standards mixture and only if a library search was performed and the compound in question was not found.

5.0 QUALITY CONTROL

A summary of all the QA/QC procedures associated with Method 8270 is shown on Table 5-1.

5.1 Instrument Tuning

The mass spectrometer must be tuned properly using PFTBA before beginning any work. To verify this, a spectrum of DFTPP must be recorded which passes the criteria shown on Table 3 of Method 8270. Acceptable chromatography must also be demonstrated by recording the peak shape of

EPA METHOD 8270

RESULTS IN ug/L

CAS #	COMPOUND	01A
122-09-8	2,2-Dimethylphenethylamine	<25
105-67-9	2,4-Dimethylphenol	<10
131-11-3	Dimethylphthalate	<10
99-65-0	1,3-Dinitrobenzene	<100
584-52-1	4,6-Dinitro-o-cresol	<50
51-28-5	2,4-Dinitrophenol	<50
121-14-2	2,4-Dinitrotoluene	<10
806-20-2	2,6-Dinitrotoluene	<10
84-74-2	Di-n-butylphthalate	<10
117-84-0	Di-n-octylphthalate	<10
621-64-7	Di-n-propylnitrosamine	<10
122-39-4	Diphenylamine	<10
62-50-0	Ethyl methanesulfonate	<10
206-44-0	Fluoranthene	<10
86-73-7	Fluorene	<10
118-74-1	Hexachlorobenzene	<10
87-68-3	Hexachlorobutadiene	<10
77-47-4	Hexachlorocyclopentadiene	<10
67-72-1	Hexachloroethane	<10
70-30-4	Hexachlorophene	<10
1888-71-7	Hexachloropropene	<10
193-39-5	Indeno(1,2,3-c,d)pyrene	<10
78-59-1	Isophorone	<10
120-58-1	Isosafrole	<100
91-80-5	Methapyrilene	<10
56-49-5	3-Methylcholanthrene	<100
66-27-3	Methyl methanesulfonate	<20
91-57-6	2-Methylnaphthalene	<10
91-20-3	Naphthalene	<10
130-15-4	1,4-Naphthoquinone	<200
134-32-7	1-Naphthylamine	<100
91-59-8	2-Naphthylamine	<100
88-74-4	2-Nitroaniline	<50
99-09-2	3-Nitroaniline	<50
100-01-6	4-Nitroaniline	<50
98-95-3	Nitrobenzene	<10
88-75-5	2-Nitrophenol	<50
100-02-7	4-Nitrophenol	<50
56-57-5	4-Nitroquinoline-1-oxide	<50
924-16-3	N-Nitrosodi-n-butylamine	<50
55-18-5	N-Nitrosodiethylamine	<50
62-75-9	N-Nitrosodimethylamine	<50
86-30-6	N-Nitrosodiphenylamine	<50
10595-95-6	N-Nitrosomethylethylamine	<50

TABLE 5-1. QA/QC SUMMARY

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Semivolatilew	8270 (GC/MS)	Mass scale calibration using PFTBA	Daily prior to sample analyses	Refer to method	Repeat calibration
		Check of mass spectral ion intensities using DFTPP	Daily prior to sample analyses	Refer to method	Retune instrument Repeat DFTPP analysis
		Chromatography check	Daily with DFTPP solution	Refer to method	Cut head of column, replace column
		Systems performance check compounds	Every 12 hours	RF $\geq$0.050	1) Evaluate system 2) Repeat calibration
		Calibration check compounds	Every 12 hours	% Difference <30%	1) Evaluate system 2) Take corrective action
		Surrogate spikes	Every sample	Refer to method	1) Evaluate system 2) Recalculate data and/or reanalyze extract 3) Reextract and re-analyze sample or flag data
		Internal standards	Every sample	Refer to method	Flag data
		Extraction blank	5%	<5 X MDL	1) Run solvent blank 2) Evaluate system
		Matrix spike analysis	5%	Refer to method	1) Run check standard 2) Correct problem 3) Flag data
		Matrix spike duplicate samples	5%	RPD <50%	Evaluate system
		QC check compound analysis	With each new standard prep-aration or client request	See Table 6 Method 8270	Make up new stan-dards or retune instrument

Also, the following system performance check compounds (SPCCs) must have response factors of greater than 0.05 using the 50 ug/mL calibration standard:

- N-Nitrosodi-n-propylamine,
- hexachlorocyclopentadiene,
- 2,4-dichlorophenol, and
- 4-nitrophenol.

5.3 Daily Calibration

Every 12 hours the midrange calibration standard must be reanalyzed. As with the initial calibration, all SPCCs must show a response factor of greater than 0.05. Also, each CCC must show a response factor within ±30% of the response factor generated from the five-point calibration. If these criteria are not met, corrective action must be taken. If, after corrective action, these criteria are not met, then the instrument must be recalibrated and a new five-point calibration performed.

5.4 Surrogate Recoveries

Before extraction, each sample is spiked with a mixture of the following surrogates:

- 2-fluorophenol,
- phenol-d_5,
- nitrobenzene-d_5,
- 2-fluorobiphenyl,
- 2,4,6-tribromophenol, and
- terphenyl-d_{14}.

Response factors for the surrogates are generated from a single injection of the surrogate solution used for spiking. Recoveries of the surrogates

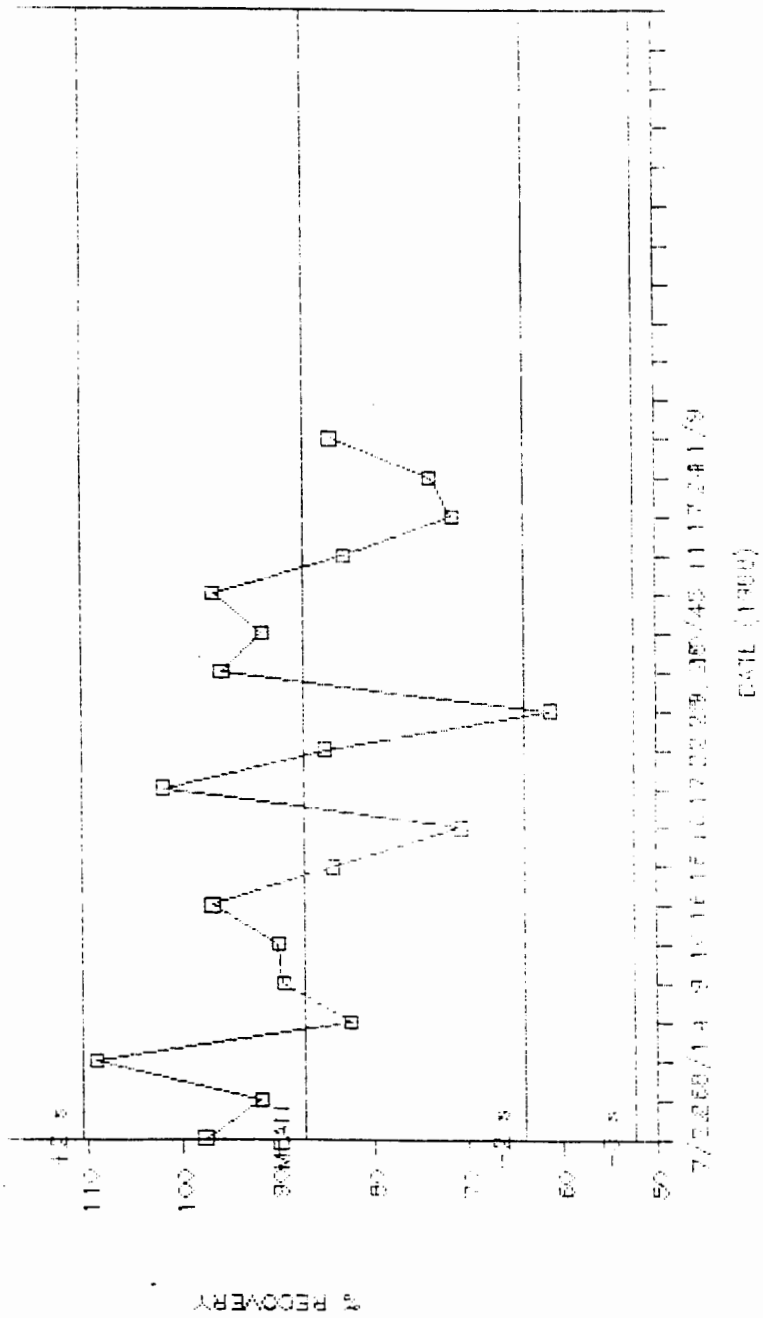


Figure 5-1

METHOD 8270

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The practical quantitation limit (PQL) of Method 8270 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 ug/L for ground water samples (see Table 2). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
4,4'-DDT	--	235	237, 165
Dibenz(a,j)acridine	32.55[a]	279	280, 277
Dibenz(a,h)anthracene	39.82	278	139, 279
Dibenzofuran	15.63	168	139
Di-n-butylphthalate	21.78	149	150, 104
1,3-Dichlorobenzene	6.27	146	148, 111
1,4-Dichlorobenzene	6.40	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	6.35	152	150, 115
1,2-Dichlorobenzene	6.85	146	148, 111
3,3'-Dichlorobenzidine	27.88	252	254, 126
2,4-Dichlorophenol	9.48	162	164, 98
2,6-Dichlorophenol	10.05[a]	162	164, 98
Dieldrin	--	79	263, 279
Diethylphthalate	16.70	149	177, 150
p-Dimethylaminoazobenzene	24.48[a]	120	225, 77
7,12-Dimethylbenz(a)anthracene	29.54[a]	256	241, 257
α-,α-Dimethylphenethylamine	9.51[a]	58	91, 42
2,4-Dimethylphenol	9.03	122	107, 121
Dimethylphthalate	14.48	163	194, 164
4,6-Dinitro-2-methylphenol	17.05	198	51, 105
2,4-Dinitrophenol	15.35	184	63, 154
2,4-Dinitrotoluene	15.80	165	63, 89
2,6-Dinitrotoluene	14.62	165	63, 89
Diphenylamine	17.54[a]	169	168, 167
1,2-Diphenylhydrazine	--	77	105, 182
Di-n-octylphthalate	30.48	149	167, 43
Endosulfan I	--	195	339, 341
Endosulfan II	--	337	339, 341
Endosulfan sulfate	--	272	387, 422
Endrin	--	263	82, 81
Endrin aldehyde	--	67	345, 250
Endrin ketone	--	317	67, 319
Ethyl methanesulfonate	5.33[a]	79	109, 97
Fluoranthene	23.33	202	101, 203
Fluorene	16.70	166	165, 167
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64
Heptachlor	--	100	272, 274
Heptachlor epoxide	--	353	355, 351
Hexachlorobenzene	18.65	284	142, 249
Hexachlorobutadiene	10.43	225	223, 227
Hexachlorocyclopentadiene	12.60	237	235, 272
Hexachloroethane	7.65	117	201, 199
Indeno(1,2,3-cd)pyrene	39.52	276	138, 227

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS**

Semivolatiles	CAS Number	Practical Quantitation Limits* Ground Water ug/L	Low Soil/Sediment[1] ug/Kg
Phenol	108-95-2	10	660
bis(2-Chloroethyl) ether	111-44-4	10	660
2-Chlorophenol	95-57-8	10	660
1,3-Dichlorobenzene	541-73-1	10	660
1,4-Dichlorobenzene	106-46-7	10	660
Benzyl Alcohol	100-51-6	20	1300
1,2-Dichlorobenzene	95-50-1	10	660
2-Methylphenol	95-48-7	10	660
bis(2-Chloroisopropyl) ether	39638-32-9	10	660
4-Methylphenol	106-44-5	10	660
N-Nitroso-Di-N-propylamine	621-64-7	10	660
Hexachloroethane	67-72-1	10	660
Nitrobenzene	98-95-3	10	660
Isophorone	78-59-1	10	660
2-Nitrophenol	88-75-5	10	660
2,4-Dimethylphenol	105-67-9	10	660
Benzoic Acid	65-85-0	50	3300
bis(2-Chloroethoxy) methane	111-91-1	10	660
2,4-Dichlorophenol	120-83-2	10	660
1,2,4-Trichlorobenzene	120-82-1	10	660
Naphthalene	91-20-3	10	660
4-Chloroaniline	106-47-8	20	1300
Hexachlorobutadiene	87-68-3	10	660
4-Chloro-3-methylphenol	59-50-7	20	1300
2-Methylnaphthalene	91-57-6	10	660
Hexachlorocyclopentadiene	77-47-4	10	660
2,4,6-Trichlorophenol	88-06-2	10	660
2,4,5-Trichlorophenol	95-95-4	10	660

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS**
(Continued)

		Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
Semi-Volatiles	CAS Number	ug/L	ug/Kg
Chrysene	218-01-9	10	660
Di-n-octyl phthalate	117-84-0	10	660
Benzo(b)fluoranthene	205-99-2	10	660
Benzo(k)fluoranthene	207-08-9	10	660
Benzo(a)pyrene	50-32-8	10	660
Indeno(1,2,3-cd)pyrene	193-39-5	10	660
Dibenz(a,h)anthracene	53-70-3	10	660
Benzo(g,h,i)perylene	191-24-2	10	660

*PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis, therefore, PQLs will be higher based on the % moisture in each sample. This is based on a 30-g sample and gel permeation chromatography cleanup.

**Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable.

Other Matrices	Factor[1]
Medium-level soil and sludges by sonicator	7.5
Non-water-miscible waste	75

[1]PQL = [PQL for Ground Water (Table 2)] X [Factor].

software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe: 10-uL.

5.0 REAGENTS

5.1 Stock standard solutions (1.00 ug/uL): Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.1.3 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

5.2 Internal standard solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Paragraph 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/uL. Each 1-mL sample extract undergoing analysis should be spiked with 10 uL of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard. Store at 4°C or less when not being used.

5.3 GC/MS tuning standard: A methylene chloride solution containing 50 ng/uL of decafluorotriphenylphosphine (DFTPP) should be prepared. The

7.1.1 Direct injection: In very limited applications direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted where concentrations in excess of 10,000 ug/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorous pesticides	3620, 3640
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration: The recommended GC/MS operating conditions:

Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40°C for 4 min
Column temperature program: 40-270°C at 10°C/min
Final column temperature hold: 270°C (until benzo[g,h,i]perylene has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 uL
Carrier gas: Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

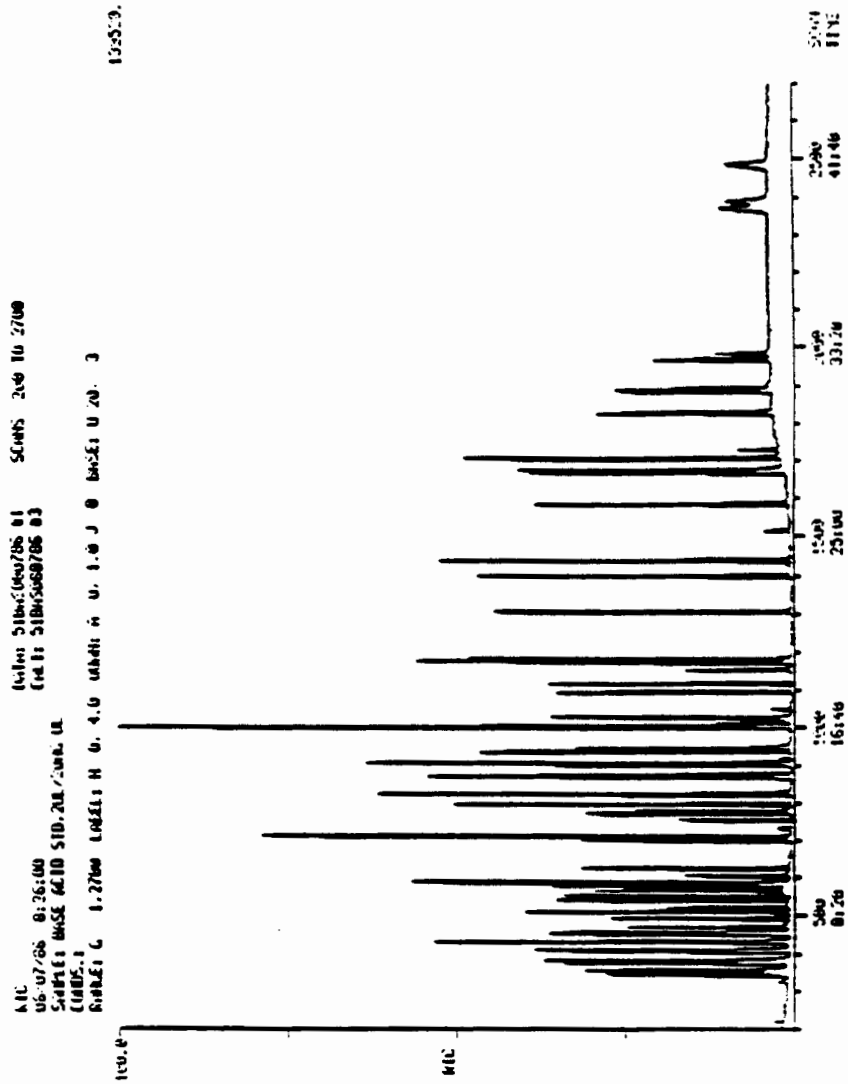


Figure 1. Gas chromatogram of base/neutral and acid calibration standard.

3270 - 14

Revision 0
Date September 1986

7.4 Daily GC/MS calibration:

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12-hr shift.

7.4.2 A calibration standard(s) at mid-level concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12-hr during analysis. Compare the response factor data from the standards every 12-hr with the average response factor from the initial calibration for a specific instrument as per the SPCC (Paragraph 7.4.3) and CCC (Paragraph 7.4.4) criteria.

7.4.3 System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hr shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_c}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_c = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Paragraph 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethylphenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr.)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr.) = surrogate

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7.6.2.5 Quantitation of multicomponent compounds (e.g., Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

TABLE 6. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike duplicate/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 ug/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte:

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.96C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.06	0.26X-0.54
Aldrin	0.78C+1.66	0.27X-1.28	0.43X+1.13
Anthracene	0.80C+0.68	0.21X-0.32	0.27X-0.64
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22X+0.43	0.29X+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X+1.03	0.35X+0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18X+0.94	0.53X+0.92
β-BHC	0.87C-0.94	0.20X-0.58	0.30X+1.94
δ-BHC	0.29C-1.09	0.34X+0.86	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.99	0.35X+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X+1.34	0.26X+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X+0.28	0.25X+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X+0.73	0.36X+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X+0.66	0.16X+0.66
2-Chloronaphthalene	0.89C+0.01	0.07X+0.52	0.13X+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20X-0.94	0.30X-0.46
Chrysene	0.93C-1.00	0.28X+0.13	0.33X-0.09
4,4'-DDD	0.56C-0.40	0.29X-0.32	0.66X-0.96
4,4'-DDE	0.70C-0.54	0.26X-1.17	0.39X-1.04
4,4'-DDT	0.79C-3.28	0.42X+0.19	0.65X-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30X+8.51	0.59X+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13X+1.16	0.39X+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20X+0.47	0.24X+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25X+0.68	0.41X+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X+0.23	0.29X+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28X+7.33	0.47X+3.45
Dieldrin	0.82C-0.16	0.20X-0.16	0.26X-0.07
Diethyl phthalate	0.43C+1.00	0.28X+1.44	0.52X+0.22
Dimethyl phthalate	0.20C+1.03	0.54X+0.19	1.05X-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12X+1.06	0.21X+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14X+1.26	0.19X+0.35
Di-n-octylphthalate	0.76C-0.79	0.21X+1.19	0.37X+1.19
Endosulfan sulfate	0.39C+0.41	0.12X+2.47	0.63X-1.03
Endrin aldehyde	0.76C-3.86	0.18X+3.91	0.73X-0.62
Fluoranthene	0.81C+1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X+0.26	0.13X+0.61
Heptachlor	0.87C-2.97	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.33X-0.46	0.28X+0.64
Hexachlorobenzene	0.74C+0.66	0.18X-0.10	0.43X-0.52
Hexachlorobutadiene	0.71C-1.01	0.19X+0.92	0.26X+0.49
Hexachloroethane	0.73C-0.83	0.17X+0.67	0.17X+0.80

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 ug/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 625," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

4. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

5. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

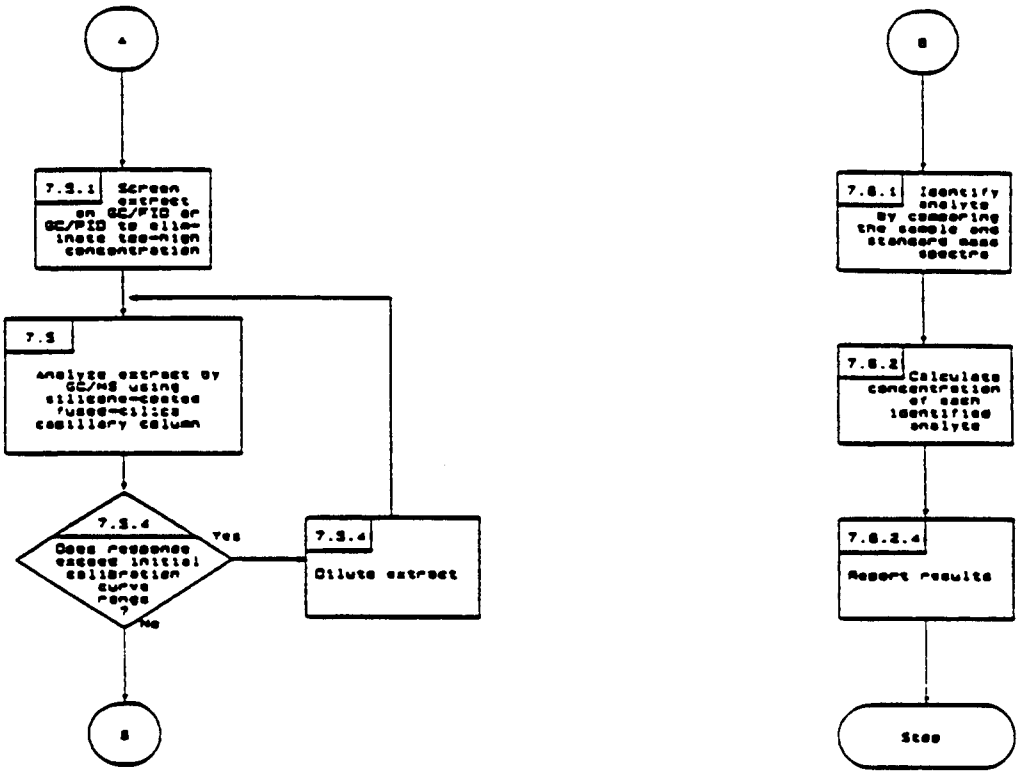
6. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

METHOD 8270

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS:

CAPILLARY COLUMN TECHNIQUE
(Continued)



2. Check that the standby (SB) and fatigue (FAT) lights are lit and the HV power switch is ON then check that the argon tank main valve is open and the tank is not empty.

3. Check that the pressure is 50 psi (350 kPa). If the pressure is not correct, adjust it by turning the regulator valve handle. Turn on the plasma work coil coolant water and exhaust vents.

4. Check that the drain tube is inserted into a plastic water bottle containing at least 8 inches of water. Insure that no dips develop in the tube. Waste solution can collect in them, impeding drainage.

5. Check that the BLUE "R.F. OFF" lamp on the generator control panel is illuminated. This lamp comes on automatically about 5 minutes after the generator is switched on, PROVIDED ALL INTERLOCKS ARE CLOSED. If this lamp is OFF, check water and argon for adequate supply pressure and check that the plasma chamber door is properly closed.

6. Turn on the Torch and Auxiliary gas toggle switches. If the center of the bead in the Torch line flowmeter does not read 18, adjust to this value using the control knob located behind the side door of the torch compartment (near the rear pressure gauge).

7. Turn the Sample gas control knob until the bead in the Sample line flowmeter reaches a value of 0.6.

8. ORGANICS ONLY - Turn knob of the Auxiliary flow control until the flowmeter reads 1.5.

a. Return forward power to zero.

b. If the OL light is lit, then turn the forward power rheostat fully counterclockwise and press the OL button. Turn up forward power to 0.5 kW, and turn the tuning dial slightly to try to reignite.

16. Observe the color of the excited gas, it should be white. Orange or red tinges indicate torch overheating. If you see colored light, open the front access door. This breaks the load circuit, and extinguishes the plasma. If the torch is glowing red, it is overheating. Reasons for overheating are as follows:

a. The gas flow is inadequate to maintain the position of the plasma. Either the gauges are malfunctioning, the pressures are not set correctly, the rates of flow are not set correctly, or a leak has developed. To recover, set the valves correctly of replace faulty equipment. Replacement requires a nightly shutdown.

b. The torch is not positioned correctly with respect to the coil. The torch may be too far up in the coil. Recover by repositioning the torch so the bottom of the coil is 2-3 mm from the nozzle of the sample line conduit.

Turn the forward power rheostat fully counterclockwise and close the front access door.

17. Once the plasma is lit, rotate the forward power rheostat knob until the forward power meter reading is 1.0 - 1.1 kW for aqueous solutions or 1.5 - 2.0 kW for organic solutions.

4.3. If your sample contains high dissolved solids, clean the nebulizer. In some severe cases it may also be necessary to remove the torch and clean it in the same manner to prevent solidification of solids at the sample orifice tip.

4.4. Reduce the rate of argon flow. Two alternative procedures exist: total gas shutdown and partial gas shutdown. Use the total shutdown for spectrometers without a vacuum system and for vacuum systems when you have decided to turn off the POPS line flow. Partial shutdown must be selected when the POPS purge remains on.

a. Total Shutdown: Turn off the gas at the tank while the toggle switches are still open. When both gauges on the tank read 0, turn OFF the toggle valves.

b. Partial Shutdown: Since the POPS requires more gas to re-purge the system than to maintain the inert atmosphere, partial shutdown is recommended for vacuum systems. For partial shutdown, turn OFF the torch gases at the gas panel, but leave ON the gas tank and the purge toggle switch.

4.6. Turn off the torch coolant water either at the tap or at the user-installed supply apparatus.

4.6. Turn off any user installed exhaust systems.

5.0 COMPUTER START-UP

5.1 The thermo SPEC software is resident on the computers hard disk. The software will be automatically loaded as soon as the computer is turned on. The thermo SPEC software is a comprehensive series of interwoven programs designed to carry out all

refractor plate micrometer screw or turns the knob of the optical monitoring system and observes the profile meter. The setting of maximum intensity is the correct one. To improve precision, use the average of the two settings at 75% intensity on either side of the observed maximum. Note that a vacuum spectrometer must be profiled for daily use only when air pressure in the chamber is low enough for operation. Of course, you would not be using the spectrometer for daily analysis unless that were the case.

6.6 Profiling should be performed at least twice a day to compensate for diurnal changes. In the air spectrometer, the air pressure can change, resulting in a slight change in the index of refraction. If temperature, pressure, and humidity are controlled, profiling twice a day will be more than adequate. If the atmosphere and the climate is such that daily changes are extreme, profiling every few hours is suggested.

7.0 ENTERING PROFILE

7.1 Profile may be entered from a number of points within the ThermoSPEC software. Entry points are available from ANALYSIS, CALIBRATION, and both WAVELENGTH and TIME SCANS in addition to pressing <Profile> from the Operation menu. However, in normal daily operation, the entry path will be from the ANALYSIS Menu. In each case, Profile is entered by pressing <Profile>. The default line is shown on the screen, together with options for Manual or Automatic Profile, or selecting a line. Select the desired option and follow the instructions which will appear on the screen. Additional instructions are available by pressing <HELP>. Manual profiling is usually more accurate and should be performed as the first profile of the day. Subsequently, Automatic Profile may be used as a check. In general, if an automatic profile results in a displacement of the refractor

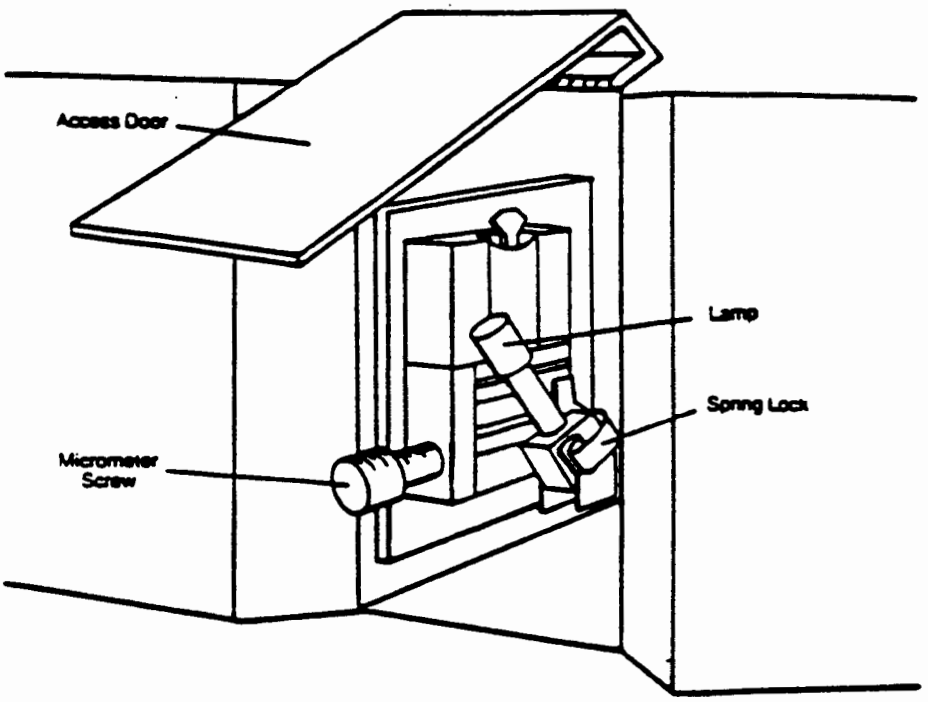


Figure 7-3: Air Spectrometer Mercury Lamp

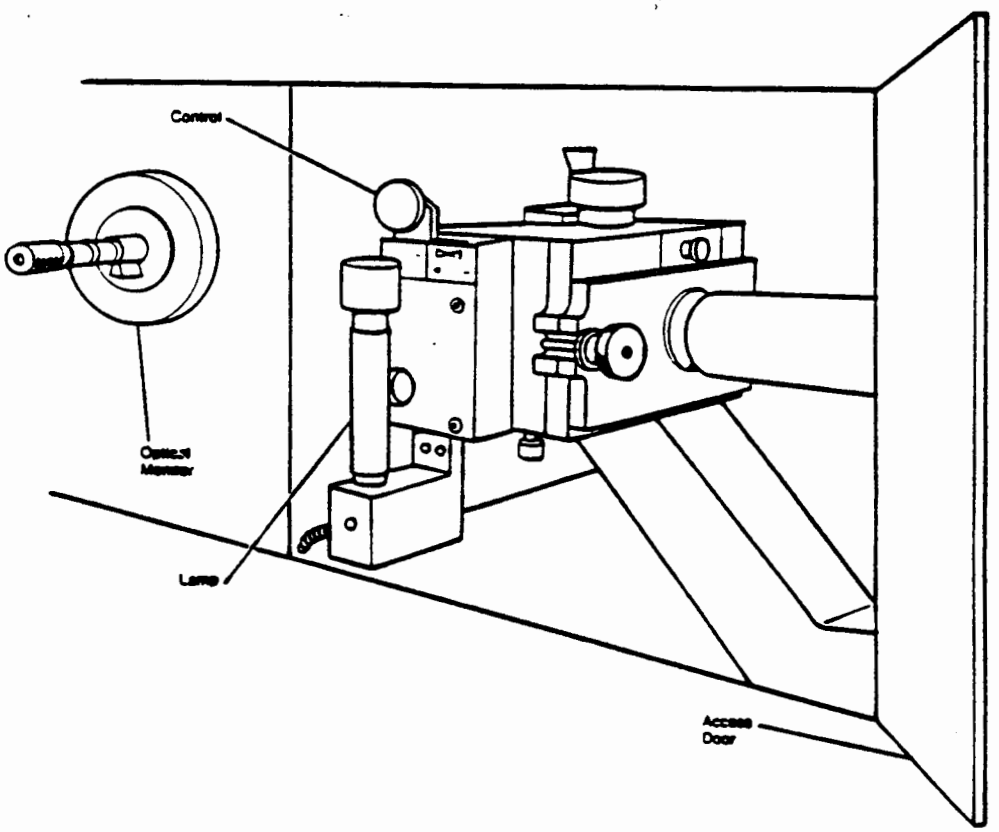


Figure 7-4: Vacuum Spectrometer Mercury Lamp

8.4. Press <Manual> to select Manual Profile. Full directions will be provided on the screen for carrying out the profiling function. Carefully turn the micrometer screw in the direction specified in the instructions which appear on the screen. The micrometers used on the air and vacuum systems are shown schematically in Figures 7-6 and 7-7 respectively. When profiling is complete, press <Done/Keep> to accept the profile, and return the mercury lamp to its original position in the air spectrometer, or turn the shutter control to the closed position on the vacuum spectrometer.

9.0 STANDARDIZATION

9.1 Standardization is that process of correcting the system to the original calibration to account for small differences in instrument parameters. Plasma standardization always uses two point standardization, with the reagent blank as the low standard. The high standard should be at least 1,000 x the detection limits. The frequency of standardization depends on machine drift and how much accuracy you desire.

a. <u>Standardize</u>

When you first turn on the computer, the ICP software will load automatically. The first screen that appears will be the instrument function screen.

<u>Operations</u> <u>Methods</u> <u>IMS</u> <u>System</u> <u>Exit</u>

All profiling, standardizing and analysis take place in the operations mode.

After all the standards have been run, a standardization report is displayed. If all data is acceptable press <F9> = Done/Keep. The ICP is now standardized and ready to analyze samples.

The calibration standards used are custom blend standard concentrates from SPEX. Currently three mixed standards (xRAD-1, xRAD-2, and xRAD-3) are being used. To make working standards we make one to twenty (5 mL in a 100 mL volumetrically) dilutions of the concentrates. The table below lists the standards and the working concentrations.

xRAD-1	ug/L	xRAD-2	ug/L	xRAD-3	ug/L
B	5	CA	100	Ag	5
P	5	NA	100	AS	5
Mo	5	K	100	BA	5
Sb	5	AL	50	BE	5
Si	5	Mg	50	Cd	5
SN	5			Co	5
				CU	5
				FE	5
				MN	5
				Ni	5
				Pb	5
				SE	5
				TL	5
				V	5
				ZN	5
				SR	5

The fourth standard is the blank. For optimum results the blank, standards, and samples should contain the same type and concentration of acid.

b. Analysis

This module contains the procedures used every day to analyze samples. These procedures include profiling,

standardization, and sample analysis. Daily operation assumes the instrument has been optimized for the analysis in question and, if necessary, calibrated.

The Analysis module is entered by selecting Operation from the Main Menu, followed by selecting Analysis from the Operation Menu. Immediately upon selecting Analysis, a Method Name will be requested. You may supply this by typing it or by pressing <List> and choosing from the list of available Method names. Once the Method name is supplied, it will be displayed. This will be the assumed starting point for all procedures described in this section.

```
Example of the Main Menu  - - - - -  Getting Next Action

                                     Analysis / Operation / Main Menu
NEWMTD
Command:                             F1 = Analyze     F2 = QC Stndrd
                                     F3 = Stndrdize   F4 = Blank
Press a Function Key, or             F5 = Profile     F6 =
Enter Command and press <Return>     F7 =             F8 = ALT Opts
<Page> keys active                   F9 = Autosmplr   F10 = HELP
```

c. Beginning Analysis

From the Analysis screen the following procedures may be carried out (in addition to Profile and Standardization). Additional operating instructions are available at every stage by pressing <HELP>.

Three types of samples may be identified; unknowns, QC Check Samples and blanks. While analysis of each is

analysis will be reported based on the Output parameters in the "Analysis".

4. Whenever <Analyze> is pressed, the screen shown below appears.

```
Getting Sample Information / Analysis / Operation / Main Menu
NEWMTD    Unknown

Output Mode = Concentration
Background Correction = Yes    Blank Subtraction = No
Limit Check Table = LCTAB      Limit Checking = No
Override Print Limits? = No    Override Significant Figures? = No

Sample Name    :
Comment        :
Operator ID    :
Corr. Factor   :
Cust. ID       :
Cust. Samp. ID:
Lab. ID        :

Introduce Unknown and Press <RUN>
                              F1 = RUN      F2 = OUTPUT
                              F3 =          F4 =
Enter Sample Name             F5 =          F6 =
(up to 20 characters)         F7 =          F8 =
<Arrow> keys active           F9 =          F10 = HELP
```

e. <u>Editing Sample Information</u>

At this point you may type in sample information using the arrow keys to select the information field.

10.0 GENERATING A REPORT

1. Press <ESC> twice to get to DOS window. To exit to DOS, line up cursor to DOS symbol and press enter.

11.0 Maintenance

11.1 CLEANING AIR FILTERS

R.F. Generator Filters

The washable air filter for the axial fan at the top rear of the instrument should be cleaned every three weeks. This depends on the use of the R.F. generator, cleanliness of the room, and position of the generator.

Warning

There are LETHAL VOLTAGES within the R.F. generator. Never touch anything within it, without first UNPLUGGING the power cord, and GROUNDING the capacitors using the ground wand provided.

1. Remove the four filter screws and slide the filter sideways out of the mounting rails.
2. Vacuum both sides of the filter.
3. If grease or oily dirt remain on the filter, flush it through hot, soapy water.
4. Rinse thoroughly so that no soap film remains.
5. Dry the filter with a vacuum cleaner or other air source.
6. Recoat the filter with air filter oil to restore its dust removal properties.
7. Replace the filter and tighten the four screws.

Computer Filter

The filter on the back panel of the computer's keyboard compartment must be cleaned every three weeks or as necessary.

1. Pull down the back panel of the keyboard compartment box. There are magnets that hold the back panel in place so you have to pull hard.
2. Slide out the square filter located on the lower left of the panel.
3. Clean the filter with mild soap in warm water.
4. Rinse and dry the filter thoroughly before replacing it.
5. Slide the filter into its mounting rails and close the back panel.

11.2 REPLACING A PLASMA TORCH

Removing the Plasma Torch

1. Remove the joint clamp that connects the torch to the mixing chamber.
2. Unscrew the collar screw and remove the left

side of the collar.

3. Carefully slide out the torch by lowering it downward through the work coil.

4. Disconnect the tubing for the torch and auxiliary argon inlets and the tesla coil connection located on the torch.

Installing and Aligning the Plasma Torch

1. Reconnect all the tubings and the tesla coil connection. (Coil connection goes to top coolant gas tube).

2. Insert the torch by sliding it upward through the work coil.

3. Replace the joint clamp so it clamps the torch to the mixing chamber.

4. Screw on the left side of the collar.

5. Adjust and center the torch in the work coil so there is 2 mm between the bottom of the work coil and the top of the inner tube of the torch.

6. Check that the work coil is 0.5 inches in overall height. If not carefully expand or compress the coil.

7. Center the torch in the work coil by releasing the two screws on the chamber mount slowly moving the mixing chamber back and forth.

8. Tighten the chamber mount screws when the torch is in correct position.

Removing the Mixing Chamber and Drain

There may be a time when removing the mixing chamber and drain is required. Below are the instructions:

1. Follow the directions for removing the plasma torch in the previous section Removing the Plasma Torch.

2. Remove the two short thumb screws located on the chamber mount.

3. Slide off the top part of the chamber mount.

4. Disconnect the nebulizer from the mixing chamber.

5. Remove the drain by carefully raising the mixing chamber and pulling the drain out.

6. Slide out the mixing chamber.

11.3 CLEANING THE NEBULIZER

Occasionally the capillary in the nebulizer becomes plugged with lint, dust, or suspended solids in the sample causing a decrease in analytical sensitivity or no signal at all. This can be checked by measuring the sample uptake rate in ml/min.

1. Disconnect the peristaltic pump tubing if applicable.

2. Disconnect the argon line to the nebulizer.

3. Remove the nebulizer from the mixing chamber.

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Gas Chromatography Laboratory	PROCEDURE NO: 325-GC-005	PAGE: 1 of 34
TITLE: DOCUMENTATION AND DATA REVIEW	REVISION NO: Original	EFFECTIVE DATE:
	SUPERSEDES: N/A	

REFERENCES: EPA Method 8000, SW846, 3rd Ed.

SATELLITE FILES: 4-134

REASON FOR REVISION: N/A

1.0 PURPOSE

1.1 This SOP supplements EPA Method 8000, SW846, 3rd Ed.

1.2 This SOP describes the documentation necessary for sample analyses.

1.3 This SOP explains the steps necessary to generate a report from the GC lab data.

2.0 SAMPLE CONTROL

2.1 The steps for handling samples between Sample Control and the GC lab can be found in the Sample Control SOP # 325-GC-006.

2.2 Sample Control (Sam®) will generate the necessary worksheets for each work order. These will include the following information: client, tests required, date sample collected, and worksheets for data.

2.3 Each Sam work order is logged into the client logbook (see Figure 1). Each client will have a page. Each page includes the work order, the number of samples, the matrix spikes (MS), and the matrix spike duplicates (MSD) to be run. When the work order is completed, the correct number of MS/MSD's is entered and the work order is marked "Complete."

2.4 A file folder is made for each Sam work order. The label will have the Sam number, client, tests, number of samples, and hold time expiration date.

3.0 DOCUMENTATION

3.1 For a detailed description of any of the following documentation, see the appropriate method SOP.

WRITER: NAME/DATE: Lauri Allica 9/21/89		
ACTIVITY MGR: NAME/DATE Marilyn Melton 10/12/89	NAME/DATE Fred Shore 3/21/90	NAME /DATE G A Magee 3/23/90

7-87-27815

4.7 A quality traveler is filled out and sent to Document Control with each report before it is finalized (see Figure 7). This serves as a final check of all details of the report before it is sent to the client.

5.0 DATA REVIEW

5.1 A copy of the chromatograms of the system blank, EPA QC check, calibration standard, and reagent blank should accompany each set of samples for a chromatograms work order.

5.2 The necessary MS/MSD results will also accompany the work orders. The data from the MS/MSD are transferred to the appropriate spike form (see Figures 8 and 9).

5.3 The following considerations need to be made during the review process:

5.3.1 The system blank should be clean. If it is not, it should be rerun until the system is clean.

5.3.2 The reagent blank should contain no analytes at a concentration greater than the detection limit. If it was a methanol reagent blank, it is possible there may be some contamination. If there is contamination in the methanol reagent blank, it is reported in Sam. Any samples run based on that reagent blank will have the data found in the reagent blank flagged with a B. This indicates that the analyte was also found in the reagent blank.

5.3.3 The concentration determined of all compounds in the QC samples must be within the acceptance limits. If not, the QC must be rerun. If it was rerun and a compound was still out, the compound needs to be flagged with a Q on all related runs. For example, if toluene was out on the QC, the data for the reagent blank and all the samples must have a Q next to the toluene results.

5.3.4 The surrogate recovery for each run should be within control limits. If an out-of-control result was caused by a matrix effect, the result should be flagged with a Q. If it is not due to a matrix effect, the sample should be rerun.

5.3.5 Quantitation of an analyte should be within the calibration range. If it is out of range, the sample must be run at a different dilution. Results for one sample may need to be reported from two different dilutions. If so, the compound from the different dilution needs to be flagged with a "D."

5.3.6 Recoveries of spiked analyte in the MS/MSD should be within acceptance limits. Any recoveries outside limits are flagged with a Q. The relative per cent difference between the MS and MSD recoveries should be ≤ 25. If the RPD is >25, the analyte is flagged with a Q on the sample that was spiked.

SECTION 7.1

Appendix 1

METHOD 8000

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The gas chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of reagent water to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^{*}}{\text{Mass injected (in nanograms)}}$$

*For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than +15%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 Internal standard calibration procedure:

7.4.3.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent.

standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse products (i.e., PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis:

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multilevel calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 Direct Injection: Inject 2-5 uL of the sample extract using the solvent flush technique. Smaller (1.0-uL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the resulting peak size in area units or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.7.2 **Capillary columns:** Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.7.3 **Metal injector body:** Turn off the oven and remove the analytical column when oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.3.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catching the rinsate in the beaker.

7.7.3.2 Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

7.8 Calculations:

7.8.1 **External standard calibration:** The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Paragraph 7.4.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples:

$$\text{Concentration (ug/L)} = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(V_s)]$$

where:

A_x = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of extract injected, uL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.5 <u>Required instrument QC</u>:

8.5.1 Section 7.4 requires that the %RSD vary by <20% when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Section 7.4 sets a limit of ±15% difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual X̄ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.6.2.

8.6.6.2 Beginning with Section 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.6.2.

8.7 The laboratory must, on an ongoing basis, spike at least one sample per analytical batch (maximum of 20 samples per batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.7.1 The concentration of the spike in the sample should be determined as follows:

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC check sample (8.6.2) or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g., maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC check sample concentration (Section 8.6.2).

complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method must be measured in the sample in Section 8.7, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 **Preparation of the QC check standard:** For volatile organics, add 10 uL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 5 mL of reagent water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.7. Prepare the QC check standard for analysis following the guidelines given in Method 3500 (e.g., purge-and-trap, extraction, etc.).

8.8.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Section 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.9 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix type) as in Section 8.7, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.10 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.10.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.10.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

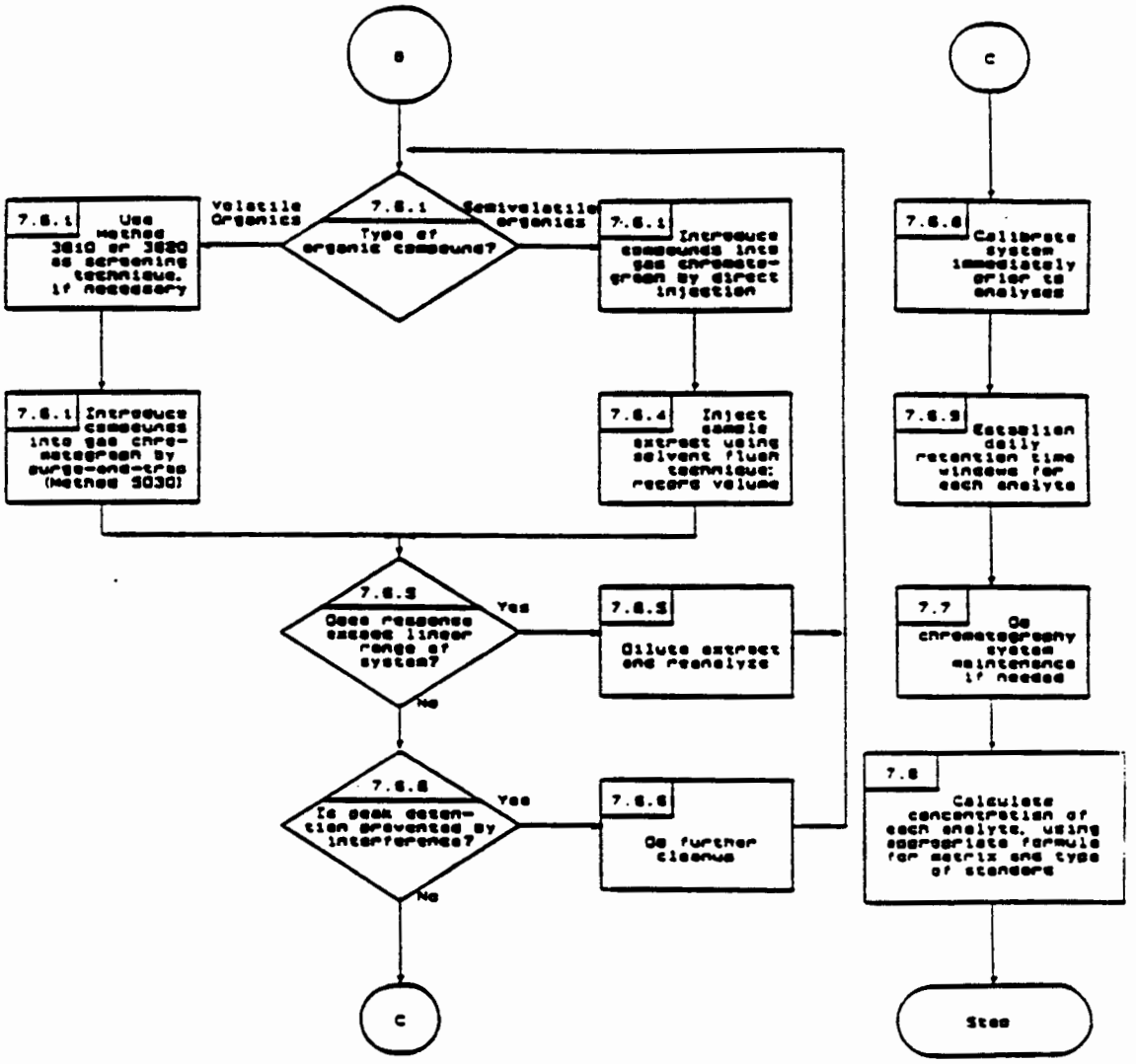
10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA 40 CFR Part 136, Appendix B. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

METHOD 8000
GAS CHROMATOGRAPH
(Continued)



SECTION 7.3

Figure 2

DAILY QUALITY CONTROL

(BENTONE)

DATE: _____ INSTRUMENT: _____

EPA QC WP879 Conc. 1				
Compound	True Value (ug/L)	95% Confidence Interval	Analyzed Value (ug/L)	% Recovery
Benzene	30.7	13.5-36.7		
Toluene	4.1	1.6- 7.7		
Ethylbenzene	11.5	7.2-12.9		
P-xylene	19.1	12.4-28.8		
M-xylene	42.6	33.5-60.5		
O-xylene	10.6	7.7-17.1		

EPA QC WP879 Conc. 2				
Benzene	12.3	9.6-12.7		
Toluene	37.1	19.1-40.7		
Ethylbenzene	32.9	24.9-36.3		
P-xylene	7.6	5.3- 9.8		
M-xylene	19.2	14.5-25.4		
O-xylene	30.2	21.5-42.8		

EPA QC WP882 (IV) #2				
P-xylene	11.1			
M-xylene	10.2			
O-xylene	12.1			

SECTION 7.5

Figure 4

DAILY QUALITY CONTROL
(SP1000)

DATE: _____ INSTRUMENT: _____

EPA QC WP781 (II)				
Compound	True Value (ug/L)	Acceptable Range	Analyzed Value (ug/L)	% Recovery
Methylene Chloride	9.2	6.4-12.0		
1,1-Dichloroethene	10.0	7.0-13.0		
T-1,2-Dichloroethene	5.4	3.2- 7.6		
1.2-Dichloroethane	5.4	3.2- 7.6		
Carbon Tetrachloride	10.0	7.0-13.0		
1.2-Dichloropropane	8.0	5.6-10.4		
Trichloroethene	10.2	7.1-13.3		
Dibromochloromethane	6.0	3.6- 8.4		
1,1,2,2-Tetrachloroethane	10.0	7.0-13.0		
Chlorobenzene	8.2	5.7-11.0		

EPA QC WS484				
Compound	True Value	95% Confidence Interval	Analyzed Value	% Recovery
Chloroform	10.0	5.3-13.1		
Bromodichloromethane	10.1	5.0-14.2		
Dibromochloromethane	9.6	4.2-14.8		
Bromoform	9.8	3.4-15.2		

EPA QC WP483 Conc.1				
Compound	True Value	95% Confidence Interval	Analyzed Value	% Recovery
Chloroform	12.0	6.7-14.9		
1,2-Dichloroethane	2.0	MDL- 4.5		
1,1,1-Trichloroethane	1.4	MDL- 2.3		
Carbon Tetrachloride	2.6	0.7- 4.3		
Bromodichloromethane	2.0	0.6- 3.2		
Trichloroethene	2.9	0.4- 5.2		
Dibromochloromethane	2.6	0.9 - 4.1		
BROMOFORM	2.9	1.1 - 4.5		
TETRACHLOROETHENE	1.6	0.5 - 2.5		

SECTION 7.7

Figure 6

DAILY CALIBRATION CHECK STANDARD

602/8020

Instrument: _____ Date of Curve: _____

Date: _____

Compound	Standard	10 ug/L Standard Analyzed Value	Acceptable Value* ug/L	Acceptable Value* % Rec.	Pass or Fail?
Benzene	602M		3.9-15	39-150	
Toluene	602M		4.6-15	46-148	
Ethyl Benzene	602M		3.2-16	32-160	
Chlorobenzene +	602M		5.5-14	55-135	
1,4-Dichlorobenzene	602M		4.2-14	42-143	
1,3-Dichlorobenzene	602M		5-14	50-141	
1,2-Dichlorobenzene	602M		3.7-15	37-154	
P-Xylene + #	EPA QC #		15.4-28.8	65-151	
M-Xylene #	EPA QC #		33.5-60.5	79-142	
O-Xylene #	EPA QC #		7.7-17.1	73-161	

* Federal Register, 40 CFR Part 136

+ Coelute

EPA QC WP879 conc. 1 - 95% confidence limit

Comments:

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2 / n\right]$$

$$S = (S^2)^{1/2}$$

where:

X_i; i=1 to n, = are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha=.99)} (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the others into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

APPENDIX A **APPENDICES**

STATISTICAL INFORMATION

Table B

t Scores

(For Checking Only Upper or Lower Limits)

Degrees of Freedom (df)	Level of Certainty 90%	95%	99%	99.5%
1	3.078	6.314	31.821	63.657
2	1.886	2.920	6.965	9.925
3	1.638	2.353	4.541	5.841
4	1.533	2.132	3.747	4.604
5	1.476	2.015	3.365	4.032
6	1.440	1.943	3.143	3.707
7	1.415	1.895	2.998	3.499
8	1.397	1.860	2.896	3.355
9	1.383	1.833	2.821	3.250
10	1.372	1.812	2.764	3.169
11	1.363	1.796	2.718	3.106
12	1.356	1.782	2.681	3.055
13	1.350	1.771	2.650	3.012
14	1.345	1.761	2.624	2.977
15	1.341	1.753	2.602	2.947
16	1.337	1.746	2.583	2.921
17	1.333	1.740	2.567	2.898
18	1.330	1.734	2.552	2.878
19	1.328	1.729	2.539	2.861
20	1.325	1.725	2.528	2.845
21	1.323	1.721	2.518	2.831
22	1.321	1.717	2.508	2.819
23	1.319	1.714	2.500	2.807
24	1.318	1.711	2.492	2.797
25	1.316	1.708	2.485	2.787
26	1.315	1.706	2.479	2.779
27	1.314	1.703	2.473	2.771
28	1.313	1.701	2.467	2.763
29	1.311	1.699	2.462	2.756
30	1.310	1.697	2.457	2.750
40	1.303	1.684	2.423	2.704
60	1.296	1.671	2.390	2.660
120	1.289	1.658	2.358	2.617
∞	1.282	1.645	2.326	2.576

Table C

t

(For Checking Bot

Degrees of Freedom (df)	80%	90%
1	3.078	6.314
2	1.886	2.920
3	1.638	2.353
4	1.533	2.132
5	1.476	2.015
6	1.440	1.943
7	1.415	1.895
8	1.397	1.860
9	1.383	1.833
10	1.372	1.812
11	1.363	1.796
12	1.356	1.782
13	1.350	1.771
14	1.345	1.761
15	1.341	1.753
16	1.337	1.746
17	1.333	1.740
18	1.330	1.734
19	1.328	1.729
20	1.325	1.725
21	1.323	1.721
22	1.321	1.717
23	1.319	1.714
24	1.318	1.711
25	1.316	1.708
26	1.315	1.706
27	1.314	1.703
28	1.313	1.701
29	1.311	1.699
30	1.310	1.697
40	1.303	1.684
60	1.296	1.671
120	1.289	1.658
∞	1.282	1.645

SECTION 7.10

Figure 8

VOA SPIKE RESULTS

LAB #_____

SAMPLE ID_____

METHOD_____

UNITS_____

COMPOUND	SPIKED SAMPLE RESULT (SSR)	SAMPLE RESULT (SR)	SPIKE ADDED (SA)	% R
Benzene				
Toluene				
Ethyl benzene				
Chlorobenzene				
1,4-Dichlorobenzene				
1,3-Dichlorobenzene				
1,2-Dichlorobenzene				
P-Xylene				
M-Xylene				
O-Xylene				

% R = [(SSR-SR)/SA] x 100

DRAFT

California Department of Health Services
Hazardous Materials Laboratory

SOP No.: 338
Revision No.: 0
Date: 09-09-87
Page 1 of 8
Approved by:

Method Status: Draft

(HML Chief)

(Section Supervisor)

HML METHOD 338

Determination of Organic Lead Compounds by Flame Atomic Absorption Spectrometry

1.0 Scope and Application

This method is used to determine the sum of organic lead compounds ("organolead") in liquids, solids or sludges. The method detection limit for a 50 g sample is 0.1 ug/g (as Pb).

The method is based on a procedure originally developed in the Du Pont Petroleum Laboratory for the determination of organic lead in leaded gasoline tank sludge (1).

2.0 Summary of Method

Organolead is separated from the sample matrix by extraction with xylene. The organolead in the extract is reacted with Aliquat 336 and iodine and the solution is made up to volume with MIBK. Lead contained in this mixture is determined by flame atomic absorption spectrometry. If the original sample is completely soluble in xylene, the extraction step is omitted.

3.0 Safety

Some organic lead compounds are volatile and toxic. Therefore, samples must be processed in a well ventilated hood. Antiknock lead compounds are particularly poisonous and must not be inhaled, ingested, or come into contact with the skin; they should never be exposed to elevated temperatures (above 50 °C) or to acids and oxidizing agents. Whenever organic lead compounds are handled outside of a well ventilated hood, protective respiratory equipment, protective clothing and rubber gloves must be worn. The material safety data sheets (MSDS) for organolead standards should be read.

6.2 Methyl isobutyl ketone (MIBK, 4-methyl-2-pentanone).

6.3 Iodine solution: Dissolve 3.0 g of elemental iodine in toluene and make up to 100 ml with the same solvent. Store in a brown bottle in a refrigerator.

6.4 Aliquat 336 (Tri-capryl methyl ammonium chloride), available Aldrich, Milwaukee, WI, or from McKesson Co., Minneapolis, MN. Note: Aliquat is a registered trademark of Henkel Corporation.

Prepare two solutions, one containing 10 % (w/v) and one containing 1 % (w/v) in MIBK. Store in a refrigerator.

6.5 Anhydrous sodium sulfate, crystals.

6.6 Lead chloride, crystals; dry at 105 °C for 3 h before use.

6.6.1 Prepare a stock solution containing 1000 mg/l of Pb by dissolving 0.3356 g of lead chloride in 10 % Aliquat 336 in MIBK and dilute to 250 ml. Store in a brown bottle in a refrigerator.

6.6.2 Prepare an intermediate Pb standard by pipetting 10 ml of the stock standard into a volumetric flask and diluting to 100 ml with a 40 % (v/v) solution of xylene in MIBK. Store in a brown bottle in a refrigerator.

7.0 Sample Collection, Preservation, and Handling

7.1 The safety precautions see section 3.0.

7.2 Liquid samples should be collected in glass bottles (preferably 500 ml size) with ground glass stoppers without leaving any headspace. During sampling, contact of the sample with air should be minimized.

7.3 Solid samples should be collected in glass jars (preferably 250 ml size) with airtight, Teflon-lined lids. The jars should be filled as much to capacity as possible.

7.4 All samples should be transported and stored at refrigerator temperature (about 5 °C).

NOTE: If less than 220 ml of sample is available, the miscibility with xylene may be tested with a smaller aliquot.

8.2.2 If a single liquid phase is obtained, i.e., if the sample is completely soluble in xylene, discard the sample/xylene mixture and pipet 20 ml of neat sample into a 50 ml volumetric flask, add 20 ml of MIBK, mix, and continue as described in step 8.1.4 above.

8.2.3 If an emulsion is obtained which requires more time for phase separation, add about 5 g of NaCl to the separatory funnel, shake briefly, and let the mixture settle for 20 min.

8.2.4 After separation of the xylene phase from the sample solvent phase (e.g., water), drain off the lower phase into a second separatory funnel and collect the xylene extract in a 100 ml flask with ground glass stopper.

8.2.5 Add 25 ml of xylene to the sample solvent phase, shake for 1 - 2 min and allow 5 -10 min for phase separation.

8.2.6 Repeat step 8.2.4, adding the xylene phase to the first extract. Then repeat steps 8.2.5 and 8.2.4 with another 25 ml of xylene.

8.2.7 Filter the combined extract through filter paper holding about 10 g of anhydrous sodium sulfate.

8.2.8 Pipet 20 ml of MIBK and 20 ml of the filtered extract into a 50 ml volumetric flask and mix. Continue as described in step 8.1.4 above.

8.3 <u>Standard and Blank Preparation</u>

Prepare a blank and a minimum of three appropriate working standards from the intermediate organolead standard containing 100 mg/l as Pb.

8.3.1 Place 40 ml of xylene into a 100 ml volumetric flask and add the correct amount of the 100 mg/l standard to prepare the desired concentration.

8.3.2 Immediately add 0.2 ml of iodine solution and mix well.

standards consistent

blank NDS
remove fuel - QC check
QC before & after
± 20%

8.4.5 If sample readings fall outside the calibrated range, the solutions to be aspirated into the nebulizer must be diluted with a 40 % (v/v) solution of xylene in MIBK and analyzed again.

9.0 Calculations

Depending on the type of sample analyzed and the method of sample preparation, one of the following three formulas is used to calculate the concentration of organolead in the sample:

9.1 Solid Samples

$$\text{Conc (ug/g)} = \text{AA-Result (mg/l)} \times \frac{100\text{ml}}{W\text{ (g)}} \times \frac{50\text{ml}}{20\text{ml}} \times F$$

where W (g) is the sample mass in grams and F is the dilution factor.

9.2 Liquid Samples not Soluble in Xylene

$$\text{Conc (mg/l)} = \text{AA-Result (mg/l)} \times \frac{100\text{ml}}{V\text{(ml)}} \times \frac{50\text{ml}}{20\text{ml}} \times F$$

where V (ml) is the sample volume in ml (usually 200 ml) and F is the dilution factor.

9.3 Xylene-Soluble Liquid Samples

$$\text{Conc (mg/l)} = \text{AA-Result (mg/l)} \times \frac{100\text{ml}}{V\text{(ml)}} \times \frac{50\text{ml}}{20\text{ml}} \times F$$

where V (ml) is the sample volume in ml (usually 20 ml) grams and F is the dilution factor.

10.0 Quality Control

10.1 Analyze a method blank along with each batch of ten samples (or less). If the blank indicates a significant contamination (more than twice the method detection limit), repeat all procedures with samples and blank.

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation		PROCEDURE NO: 321-SP-013	PAGE: 1 of 10
TITLE: Soxhlet Extraction by EPA Method SW-846-3540, 3rd Edition.		REVISION NO: 1	EFFECTIVE DATE:
		SUPERSEDES: 3/22/86	
REFERENCES: 321-SP-001, -004, -009			
SATELLITE FILES: 1-118			
REASON FOR REVISION: New Edition of SW-846.			

INFORMATION COPY FOR INTERNAL PURPOSES ONLY

1.0 PURPOSE

The purpose of this document is to establish a guideline for procedural adaptations of the EPA-OSW SW-846 "Method 3540 Soxhlet Extraction".

2.0 PROCEDURE

The modifications of Method 3540 (Method attached) normally applied in the Sample Preparation Laboratory are outlined as follows:

2.1 Section 4.0 of Method 3540 is modified in the following sections:

4.1 Soxhlet extractor: size required may vary with sample volume.

4.2 Drying Column: funnel, 100 mm diameters packed with a plug of silanized glass wool and 3.5 cm of adsorbent (approximately 80 grams).

2.3 Section 5.0 of Method 3540 is modified in the following section:

5.3.1 Delete.

5.3.2 Shall apply to all samples.

WRITER: NAME/DATE: Kevin P. Kelly 4-1-88		
ACTIVITY MGR: NAME/DATE: [illegible] 4/13/88	NAME/DATE: J L Shore 4/15/88	NAME /DATE: RA Magee 4/19/88

7-87-27815

7.6 Delete

7.7 Delete

7.8 The concentration step will not necessarily take 15-20 minutes. The time required depends on the volume of solvent that needs to be removed, and the bath temperature that is specified (if any).

7.9 If a solvent exchange is required (as indicated in Table 1), begin adding the exchange solvent through the top of the Snyder column when the volume of the extract has been reduced to about 25 mL. Add the exchange solvent in portions (of less than 10 mL each), at a rate that does not cause the boiling of the extract to cease. Wait between portions for the balls of the Snyder column to resume chattering before adding the next portion. Concentrate the extract, as described in Paragraph 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10 If a final extract volume appreciably less than 10 mL is required, it is necessary to further concentrate the extract using a micro-Snyder column. In cases where bumping of the sample liquid would be expected, nitrogen evaporation may be substituted for the micro-Snyder technique.

3.0 SAFETY

Normal laboratory procedures as described in SOP 321-SP-004 must be followed. If necessary, the extractions can be done in a working fume hood. Extract concentrations will be done in a working fume hood.

METHOD 3540

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor: 40-mm I.D., with 500-mL round-bottom flask.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

10/83/14698

5.3.1.1 Toluene/Methanol: 10:1 (v/v), pesticide quality or equivalent.

5.3.1.2 Acetone/Hexane: 1:1 (v/v), pesticide quality or equivalent.

5.3.2 Other samples shall be extracted using the following:

5.3.2.1 Methylene chloride: pesticide quality or equivalent.

5.4 Exchange solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling:

7.1.1 **Sediment/soil samples:** Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 **Waste samples:** Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 **Dry waste samples amenable to grinding:** Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \%\ \text{moisture}$$

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a]To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b]Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c]The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

10/83/14698

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation		PROCEDURE NO: 321-SP-026	PAGE: 1 of 22
TITLE: Method 8280 for Analysis of Dioxins and Furans		REVISION NO: Original	EFFECTIVE DATE: 5/26/88
		SUPERSEDES: N/A	
REFERENCES: 321-SP-001, -008; 321-HM-004, -028, -034, -040, -041			
SATELLITE FILES: 1-119			
REASON FOR REVISION: Original			

INFORMATION COPY FOR INFORMATIONAL PURPOSES ONLY

1.0 PURPOSE

The purpose of this document is to establish a guideline for procedural adaptations of the EPA-OSW SW-846, Method 8280 "The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans."

2.0 SCOPE

This document outlines the required adaptations made to EPA OSW-846 Method 8280. Most of the changes are in the sections outlining soil extractions, and are adapted from the EPA Region VII Method.

3.0 PROCEDURE

The modifications of Method 8280 (method attached) normally applied in the Sample Preparation Laboratory are outlined as follows:

3.1 Section 4.00 of Method 8280 is modified in the following sections:

4.19 Carbon Column (gravity flow): Prepare carbon/silica gel packing material by mixing 5 percent by weight active carbon AX-21 (Anderson Development Co., Adrain, MI), pre-washed with methanol and dried in a vacuum oven at 100°C and 95 percent (by weight) silica gel (Type 60, EM Reagent 70-230 Mesh, CMS #393-066) followed by activation of the mixture at 130°C for 6 hours. Prepare 10 mL disposable serological pipet column by cutting off

WRITER: NAME/DATE: 5/23/88		
ACTIVITY MGR: NAME/DATE 5/25/88	NAME/DATE 5/26/88	NAME/DATE 5/26/88

7-87-27815

9.7 Gravity column: Disposable serological pipet (10 mL). Pack a solvent-rinsed 10 mL disposable serological pipet in the following manner:

Insert a glass wool plug into the bottom of the pipet. Add a one-half inch layer of sodium sulfate. Add a 4 g layer of Woelm Super 1 neutral alumina. Tap the top of the column gently. Add a one-half inch layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane. Discard the eluant. Do not allow column to go dry, if necessary add more hexane.

9.8 Dissolve the residue from 9.2.5 in 2 mL hexane and apply the hexane solution to the top of the column. If the residue does not disperse well in the hexane, place the flask containing the residue and hexane in the ultrasonic bath for 30 seconds to 2 minutes to ensure that transfer of residue can be complete. Elute with enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluant.

9.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane. Discard the eluant.

9.8.2 Elute the PCDDs and PCDFs from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this in a disposable 20 x 150 mm culture tube (ASP TI29-10A or equivalent).

9.8.3 Prepare a carbon column as in 3.1. Using a stream of nitrogen, concentrate the 60% fraction to 2-3 mL. Rinse the column with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column. Elute with 10 mL of

At least one sample per set of 20 must be run in duplicate to determine intralaboratory precision. Field duplicates (individual samples taken from the same location of the same time) should be analyzed periodically to determine the total precision (field and lab). Where appropriate, "field blanks" will be provided to monitor for possible cross-contamination of samples in the field.

The performance of the alumina and carbon columns are verified each time a good blank is obtained. However, if poor blank surrogate recoveries are obtained, a series of calibration standards (surrogates) will be put through the column procedure to validate elution patterns and the absence of interferents from reagents. If poor surrogate recoveries are obtained on a sample and reanalysis is done, check the 8% methylene chloride/hexane eluate* from the alumina column for presence of target analytes.

*NOTE: This fraction is intended to contain a high level of interferents and analysis near the detection limit may not be possible.

METHOD 8280

THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

1.0 SCOPE AND APPLICATION

1.1 This method is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) in chemical wastes including still bottoms, fuel oils, sludges, fly ash, reactor residues, soil and water.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposed quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water. Actual values have been shown to vary by homologous series and, to a lesser degree, by individual isomer. The total detection limit for each CDD/CDF homologous series is determined by multiplying the detection limit of a given isomer within that series by the number of peaks which can be resolved under the gas chromatographic conditions.

1.3 Certain 2,3,7,8-substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Special instructions are included which measure 2,3,7,8-substituted congeners.

1.4 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.5 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. A laboratory planning to use these compounds should prepare a disposal plan to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450). Additional safety instructions are outlined in Appendix B.

2.0 SUMMARY OF THE METHOD

2.1 This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) techniques.

2.2 If interferents are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

0/83/14698

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 6-3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit (Section 11.6) stated in Table 8.

3.4 High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers.

3.5 Aqueous samples cannot be aliquoted from sample containers. The entire sample must be used and the sample container washed/rinsed out with the extracting solvent.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment for discrete or composite sampling:

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be acid washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil, used with the shiny side toward the sample, may be substituted for Teflon if the sample is not corrosive. Apply tape around cap to completely seal cap to bottom.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

is defined as an Selected Ion Current Profile (SICP). Software must also be able to integrate the abundance, in any SICP, between specified time or scan number limits.

4.4 Pipets-Disposable, Pasteur, 150-mm long x 5-mm I.D. (Fisher Scientific Company, No. 13-678-6A, or equivalent).

4.4.1 Pipet, disposable, serological 10-mL (American Scientific Products No. P4644-10, or equivalent) for preparation of the carbon column specified in Paragraph 4.19.

4.5 Amber glass bottle (500-mL, Teflon-lined screw-cap).

4.6 Reacti-vial 2-mL, amber glass (Pierce Chemical Company). These should be silanized prior to use.

4.7 500-mL Erlenmeyer flask (American Scientific Products Cat. No. f4205 500f0) fitted with Teflon stoppers (ASP No. s9058-8, or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049, or equivalent).

4.9 125-mL and 2-L Separatory Funnels (Fisher Scientific Company, No. 10-437-5b, or equivalent).

4.10 500-mL Kuderna-Danish fitted with a 10-mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02, or equivalent).

4.11 Teflon boiling chips (Berghof/American Inc., Main St., Raymond, New Hampshire 03077, No. 15021-450, or equivalent). Wash with hexane prior to use.

4.12 300-mm x 10.5-mm glass chromatographic column fitted with Teflon stopcock.

4.13 15-mL conical concentrator tubes (Kontes No. K-288250, or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20, or equivalent).

4.15 Nitrogen blowdown apparatus (N-Evap (reg. trademark) Analytical Evaporator Model 111, Organomation Associates Inc., Northborough, Massachusetts or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.16 Microflex conical vials 2.0-mL (Kontes K-749000, or equivalent).

4.17 Filter paper (Whatman No. 54, or equivalent). Glass fiber filters or glass wool plugs are also recommended.

4.18 Solvent reservoir (125-mL) Kontes: (special order item) 12.5-cm diameter, compatible with gravity carbon column.

0/83/14698

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade): Extracted by manual shaking with several portions of hexane and dried at 100°C.

5.8 Sodium chloride - (analytical reagent), 5 percent (w/v) in distilled water.

6.0 CALIBRATION

6.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. The other type, routine calibration, consists of analyzing the column performance check solution and a concentration calibration solution of 500 ng/mL (Paragraph 6.2). No samples are to be analyzed until acceptable calibration as described in Paragraphs 6.3 and 6.6 is demonstrated and documented.

6.2 Initial calibration:

6.2.1 Prepare multi-level calibration standards[2] keeping one of the recovery standards and the internal standard at fixed concentrations (500 ng/mL). Additional internal standards ($^{13}C_{12}$-OCDD 1,000 ng/mL) are recommended when quantification of the hepta- and octa-isomers is required. The use of separate internal standards for the PCDF's is also recommended. Each calibration standard should contain the following compounds:

2,3,7,8-TCDD,		
1,2,3,7,8-PeCDD	or any available	2,3,7,8,X-PeCDD isomer,
1,2,3,4,7,8-HxCDD	or any available	2,3,7,8,X,Y-HxCDD isomer,
1,2,3,4,6,7,8-HpCDD	or any available	2,3,7,8,X,Y,Z-HpCDD isomer,
2,3,7,8-TCDF		
1,2,3,7,8,PeCDF	or any available	2,3,7,8,X-PeCDF isomer,
1,2,3,4,7,8-HxCDF	or any available	2,3,7,8,X,Y,HxCDF isomer,
1,2,3,4,6,7,8-HpCDF	or any available	2,3,7,8,X,Y,Z-HpCDF isomer,

OCDD, OCDF, $^{13}C_{12}$-2,3,7,8-TCDD, $_{13}C_{12}$-1,2,3,4-TCDD and $_{13}C_{12}$-OCDD.

---

2 $^{13}C_{12}$-labeled analytes are available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper quantification requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required consistent with the technique of isotopic dilution.

It is the responsibility of the laboratory to verify the conditions suitable for maximum resolution of 2,3,7,8-TCDD from all other TCDD isomers. The peak representing 2,3,7,8-TCDD should be labeled and identified as such on all chromatograms.

6.4 Acceptable SIM sensitivity is verified by achieving a minimum signal-to-noise ratio of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/mL calibration standard.

6.5 From injections of the 5 calibration standards, calculate the relative response factors (RRF's) of analytes vs. the appropriate internal standards, as described in Paragraph 11.1.2. Relative response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards.

6.6 For each analyte calculate the mean relative response factor (RRF), the standard deviation, and the percent relative standard deviation from triplicate determinations of relative response factors for each calibration standard solution.

6.7 The percent relative standard deviations (based on triplicate analysis) of the relative response factors for each calibration standard solution should not exceed 15 percent. If this condition is not satisfied, remedial action should be taken.

6.8 The Laboratory must not proceed with analysis of samples before determining and documenting acceptable calibration with the criteria specified in Paragraphs 6.3 and 6.7.

6.9 Routine calibration:

6.9.1 Inject a 2-uL aliquot of the column performance check mixture. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the ions being monitored.

NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution. The column performance check solution must be run at the beginning and end of a 12 hr period. If the contractor laboratory operates during consecutive 12-hr periods (shifts), analysis of the performance check solution at the beginning of each 12-hr period and at the end of the final 12-hr period is sufficient.

Determine and document acceptable column performance as described in Paragraph 6.3.

6.9.2 Inject a 2-uL aliquot of the calibration standard solution at 500 ng/mL at the beginning of a 2-hr period. Determine and document acceptable calibration as specified in Paragraph 6.3, i.e., SIM sensitivity and relative ion abundance criteria. The measured RRF's of

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing, other potential sources of contamination which may absorb the target analytes.

8.2 All samples must be stored at 4°C, extracted within 30 days and completely analyzed within 45 days of collection.

9.0 EXTRACTION AND CLEANUP PROCEDURES

9.1 Internal standard addition. Use a sample aliquot of 1 g to 1,000 mL (typical sample size requirements for each type of matrix are provided in Paragraph 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD, and any other material which is to be used as an internal standard, (Paragraph 6.2). All samples should be spiked with at least one internal standard, for example, $^{13}C_{12}$-2,3,7,8-TCDD, to give a concentration of 500 ng/mL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 uL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD, assuming 100% recovery. Adoption of different calibration solution sets (as needed to achieve different quantification limits for different congeners) will require a change in the fortification level. Individual concentration levels for each homologous series must be specified.

9.2 Extraction

9.2.1 Sludge/fuel oil. Extract aqueous sludge samples by refluxing a sample (e.g. 2 g) with 50 mL of toluene (benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through a fiber filter, or equivalent, into a 100-mL round bottom flask. Rinse the filter with 10 mL of toluene, combine the extract and rinsate. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Step 9.2.4.

9.2.2 Still bottom. Extract still bottom samples by mixing a sample (e.g., 1.0 g) with 10 mL of toluene (benzene) in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50-mL round bottom flask. Rinse the beaker and filter with 10 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C while connected to a water aspirator. Proceed with Step 9.2.4.

0/83/14698

Pour the entire sample (approximately 1-L) into a 2-L separatory funnel. Proceed with Step 9.2.6.1.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 sec to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL of methylene chloride to the distilling flask; add sufficient reagent water to ensure proper operation, and extract for 24 hr. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Paragraphs 9.2.6.1 and 9.2.6.2. Proceed with Paragraph 9.2.6.3.

9.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 sec to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500-mL Kuderna-Danish concentrator (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

9.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Paragraph 9.3.

9.3 In a 250-mL Separatory funnel, partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 min.

9.9 Carbon column cleanup:

Prepare a carbon column as described in Paragraph 4.18.

9.9.1 Using a carefully regulated stream of nitrogen (Paragraph 4.15), concentrate the 8 percent fraction from the alumina column (Paragraph 9.8.1) to about 1 mL. Wash the sides of the tube with a small volume of hexane (1 to 2 mL) and reconcentrate to about 1 mL. Save this 8 percent concentrate for GC/MS analysis to check for breakthrough of PCDD's and PCDF's. Concentrate the 60 percent fraction (Paragraph 9.8.2) to about 2 to 3 mL. Rinse the carbon with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 mL of cyclohexane/methylene chloride (50:50 v/v) and 5 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine (this fraction may be used as a check on column efficiency). Now turn the column over and in the direction of forward flow elute the PCDD/PCDF fraction with 20 mL toluene.

NOTE: Be sure no carbon fines are present in the eluant.

9.9.2 Alternate carbon column cleanup. Proceed as in Section 9.9.1 to obtain the 60 percent fraction re-concentrated to 400 uL which is transferred to an HPLC injector loop (1 mL). The injector loop is connected to the optional column described in Paragraph 4.18. Rinse the centrifuge tube with 500 uL of hexane and add this rinsate to the injector loop. Load the combined concentrate and rinsate onto the column. Elute the column at 2 mL/min, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard the eluant. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is then discarded and 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through a new column to prepare it for the next sample.

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0-mL Reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of N_2. The final volume should be 100 uL for soil samples and 500 uL for sludge, still bottom, and fly ash samples; this is provided for guidance, the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted. Gently swirl the solvent on the lower portion of the vessel to ensure complete dissolution of the PCDD's and PCDF's.

9.10 Approximately 1 hr before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial (Paragraph 4.16). Add to this sufficient recovery standard ($^{13}C_{12}$1,2,3,4-TCDD) to give a concentration of 500 ng/mL. (Example: 36 uL aliquot of extract and 4 uL of recovery standard solution. Remember to adjust the final result to correct for this dilution. Inject an appropriate aliquot (1 or 2 uL) of the sample into the GC/MS instrument.

10/83/14698

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation	**PROCEDURE NO:** 325-SP-018	**PAGE:** 1 of 7
TITLE: Sample Preparation for Chlorinated Herbicides in Sludge or Solid Matrices	**REVISION NO:** Original	**EFFECTIVE DATE:** 8/27/91
	SUPERSEDES: N/A	
REFERENCES: 325-SP-001, -004, -006, -007, -013, -019, -020, -022, -024		
SATELLITE FILES: 1-119		
REASON FOR REVISION: original FLC		

INFORMATION COPY
FOR INFORMATIONAL PURPOSES ONLY

1.0 PURPOSE

The purpose of this SOP is to establish a guideline for the extraction of sludge or solid samples for free acid herbicide analysis.

2.0 SCOPE AND APPLICABILITY

2.1 Scope

This document describes the procedure used to extract, hydrolyze, and concentrate sludge or solid samples for SW-846 Method 8150. It contains recommendations for all reagents and procedures. Refer to SW-846 and the appropriate SOP for details regarding Soxhlet extraction (Method 3540, 325-SP-013).

2.2 Applicability

These modifications contained in this SOP are applicable in Austin Sample Preparation Lab for preparation of sludge and solid samples for Method 8150.

WRITER: NAME/DATE Mary A. Delaunistan 3/21/91	R. Kaldwell 3/21/91	Malcolm A. Beeler 3/24/91
ACTIVITY MGR: NAME/DATE Michael C. Slupski 6/21/91	**NAME/DATE** T. J. Shore 6/25/91	**NAME/DATE** FCS 8/27/91

7-87-27815

6.1.2 Separatory funnel: 500-mL, acid-rinsed and solvent-washed.

6.1.3 Vials: 12 mL glass, with screw-top cap and Teflon septum, acid-rinsed and solvent-washed.

6.1.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.2 Apparatus

6.2.1 Kuderna-Danish (K-D) apparatus:

- Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

- Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

- Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

- Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.2 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

6.2.3 Balance: Analytical, capable of accurately weighting to the nearest 0.0001 g.

6.2.4 Nitrogen blowdown, apparatus: with stainless steel needles and water bath.

7.6 Phosphoric acid: 85%, reagent

7.7 Potassium hydroxide solution: 37% (w/v), in reagent water.

8.0 PROCEDURE

8.1 See SOP 325-SP-024, Special Procedures When Preparing Samples for GC/ECD Analyses, for special and important considerations regarding prevention of contamination.

8.2 Solid samples should be acidified to pH <2, by treatment with 1 mL or more of 1:1 sulfuric acid/reagent water, followed by drying with sodium sulfate. This will convert the salts to acids and help ensure recovery of analytes, since they will be in the carboxylic acid form.

8.3 Prepare an extract of the sample using an appropriate method (see SW-846, Method 3540, 3550, or 3580, and SOP's 325-SP-013, -020, or -022), extract with methylene chloride. Adjust volume of the extract to about 60 mL in a Kuderna-Danish apparatus. Add 5 mL of 37% aqueous potassium hydroxide, 40 mL of methanol, and a fresh boiling chip (if needed).

8.4 Adjust the water bath temperature to 140-150°F, which should cause the methylene chloride to reflux gently. Heat the solution for 90 minutes to complete the hydrolysis. CAUTION: once hydrolysis is complete, remove the mixture from the K-D apparatus if storage is necessary. Strong alkali can corrode the ground glass connections.

8.5 Pour the contents of the K-D apparatus into a separatory funnel; rinse the K-D apparatus twice with reagent water and twice with methylene chloride, combining these rinses into the separatory funnel, also; add 50 mL deionized water and 50 mL of methylene chloride. Shake well for 1 minute, and vent often; allow the layers to separate for at least 10 minutes, and drain the solvent layer into an Erlenmeyer flask. Add two more 50 mL portions of methylene chloride, shaking and draining after

12.0 DOCUMENTATION

All workplans/travelers shall be in accordance with Documentation SOPs.

13.0 PUBLISHED REFERENCES

EAP SW-846, Method 8150, 3rd Edition.

14.0 APPENDICES

See Attachment 1.

METHOD 8150

CHLORINATED HERBICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.3 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.4 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 4-mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.1.2 Column 2: 1.8-m x 4-mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.1.3 Column 3: 1.98-m x 2-mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopack C or equivalent.

4.1.2 **Detector:** Electron capture (ECD).

4.2 Erlenmeyer flasks: 250- and 500-mL Pyrex, with 24/40 ground-glass joint.

4.3 Beaker: 500-mL.

4.4 Diazomethane generator: Refer to Section 7.3 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 **Diazald kit:** recommended for the generation of diazomethane using the procedure given in Section 7.3.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150-mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Section 7.3.3.

4.5 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw cap.

4.6 Separatory funnel: 2-L, 125-mL, and 60-mL.

4.7 Drying column: 400-mm x 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.8.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.8.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.11 Microsyringe: 10-uL.

4.12 Wrist shaker: Burrell Model 75 or equivalent.

4.13 Glass wool: Pyrex, acid washed.

4.14 Balance: Analytical, capable of accurately weighting to the nearest 0.0001 g.

4.15 Syringe: 5-mL.

4.16 Glass rod.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commerically prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.10.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

5.11 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.12 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.12.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.11.

5.12.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with diethyl ether.

5.12.3 Analyze each calibration standard according to Section 7.0.

5.13 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

7.1.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125-mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.3 **Solvent cleanup:**

7.1.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.1.3.2 Combine ether extracts in a 125-mL Erlenmeyer flask containing 1.0 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

7.1.3.3 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.1.3.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the

7.2.3 **Solvent cleanup:**

7.2.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into a 250-mL Erlenmeyer flask, and pour the organic layer into a 125-mL Erlenmeyer flask containing about 0.5 g of acidified sodium sulfate. Repeat the extraction twice more with 10-mL aliquots of diethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.2.3.2 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.3 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.2.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.2.3.5 Determine the original sample volume by refilling the sample bottle to the mark with water and transferring to a 1-liter graduated cylinder. Record the sample volume to the nearest 5 mL.

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation	PROCEDURE NO: 325-SP-039	PAGE: 1 of 6
TITLE: Sulfur Cleanup by SW-846, Method 3660	REVISION NO: Original	EFFECTIVE DATE:
	SUPERSEDES: N/A	

REFERENCES: None

SATELLITE FILES: 1-119

REASON FOR REVISION: Original

INFORMATION COPY FOR INFORMATIONAL PURPOSES ONLY

1.0 PURPOSE

This document contains procedural guidelines and adaptations for the removal of sulfur from organic extracts per SW-846 3rd Edition, Method 3660.

2.0 SCOPE AND APPLICABILITY

2.1 Scope

Sulfur interference follows along with organophosphorous and organochlorine pesticides. Three techniques for the elimination of sulfur are detailed in this method: a) copper powder; b) mercury and c) tetrabutylammonium (TBA)-sulfite.

2.2 Applicability

These techniques are applicable to the Sample Preparation Lab. TBA-sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper and mercury may degrade organophosphorous and some organochlorine pesticides.

3.0 SUMMARY OF METHOD

The sample extract is mixed with the cleanup reagent, shaken, and the extract is then removed from the sulfur cleanup reagent.

WRITER: NAME/DATE		
Gary M Dickinson 6/26/91	Malcolm A. Barker 6/26/91	
ACTIVITY MGR: NAME/DATE	NAME/DATE	NAME /DATE
Michael C Sugden 6/26/91	7/3/91	FLS 8/27/91

7-87-27815

6.1 Materials

6.1.1 Pipets, disposable, Pasteur.

6.1.2 Centrifuge: 12 mL, calibrated.

6.1.3 Glass bottles or vials: 10 mL and 50 mL, with Teflon-lined screw caps.

6.2 Apparatus

Mechanical shaker/mixer: such as Vortex Genie.

7.0 CHEMICALS AND REAGENTS

7.1 Reagent water: defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

7.2 Nitric acid: dilute.

7.3 Acetone, hexane, 2-propanol: pesticide quality or equivalent.

7.4 Copper powder: remove oxides by treating with dilute nitric acid, rinsing with reagent water to remove all traces of acid, rinse with acetone, dry under stream of nitrogen. (Copper, fine granular, Mallinckrodt 4649 or equivalent).

7.5 Mercury: triple distilled.

8.2 Removal of sulfur using TBA-sulfite:

8.2.1 Concentrate sample to 5.0 mL [1.0] and quantitatively transfer to 25 mL glass bottle.

8.2.2 Add 1.0 mL TBA-sulfite reagent and 2 mL 2-propanol, seal bottle with Teflon or foil-lined cap. Shake for 1 minute, if clear crystals are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add 100 mg portions of crystalline sodium sulfite until a residue remains after shaking.

8.2.3 Add 5 mL reagent water and shake 1 minute. Allow to separate 5-10 minutes. Transfer hexane (top layer) to concentrator tube and concentrate to required method volume.

8.3 Removal of sulfur using copper:

8.3.1 Concentrate extract to 5.0 mL [1.0 mL for 8140].

8.3.2 Quantatively transfer extract to a centrifuge tube, calibrated to 5.0 mL and 0.5 mL [1.0 mL & 0.5 mL for 8140].

8.3.3 Add approximately 2 gm copper (0.5 mL mark) to centrifuge tube. Mechanically mix for 1 minute.

8.3.4 Transfer the extract, by dispo pipet, to solvent rinsed vial. The volume remaining represents a 5.0 mL [1.0 mL for 8140] sample.

9.0 SHORTHAND PROCEDURE

None.

ATTACHMENT 1

4.3 Centrifuge tubes: Calibrated, 12-mL.

4.4 Glass bottles or vials: 10-mL and 50-mL, with Teflon-lined screw-caps.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Nitric acid: Dilute.

5.3 Acetone, hexane, 2-propanol: Pesticide quality or equivalent.

5.4 Copper powder: Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen. (Copper, fine granular Mallinckrodt 4649 or equivalent).

5.5 Mercury: Triple distilled.

5.6 Tetrabutylammonium (TBA)-sulfite reagent: Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL reagent water. To remove impurities, extract this solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw-cap. This solution can be stored at room temperature for at least one month.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Removal of sulfur using copper:

7.1.1 Concentrate the sample to exactly 1.0-mL in the Kuderna-Danish tube.

7.1.2 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the K-D tube. Transfer the extract to a calibrated centrifuge tube.

7.1.3 Add approximately 2 g of cleaned copper powder (to the 0.5 mL mark) to the centrifuge tube. Mix for at least 1 min on the mechanical shaker.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 All reagents should be checked prior to use to verify that interferences do not exist.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the effect of using copper and mercury to remove sulfur on the recovery of certain pesticides.

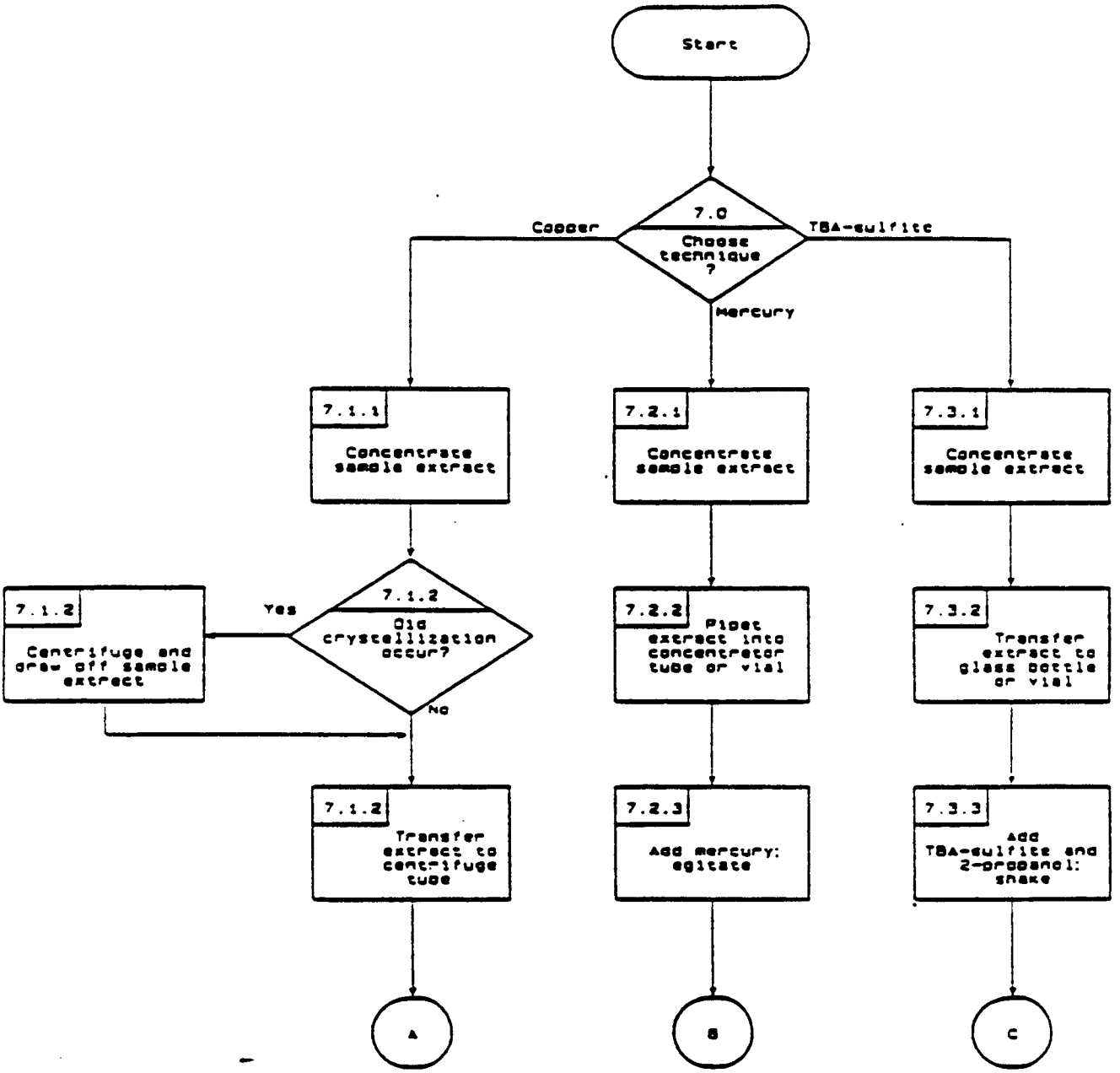
10.0 REFERENCES

1. Loy, E.W., private communication.

2. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).

3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

METHOD 3660
SULFUR CLEANUP



CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation	PROCEDURE NO: 325-SP-014	PAGE: 1 of 8
TITLE: Alumina Column Cleanup - Method SW-846, 3611, 3rd Edition	REVISION NO: 1	EFFECTIVE DATE: 5/27/91
	SUPERSEDES: 11/13/87	
REFERENCES: 325-SP-001, -004, -010		
SATELLITE FILES: 1-119		
REASON FOR REVISION: General Revisions		

INFORMATION COPY FOR INFORMATIONAL PURPOSES ONLY

1.0 PURPOSE

The purpose of this document is to establish guidelines for procedural adaptations of the EPA SW-846 Method 3611 Alumina Column Cleanup.

2.0 SCOPE AND APPLICABILITY

2.1 Scope

This SOP covers all steps or their modifications for the cleanup of samples containing high levels of interfering aliphatic hydrocarbons.

2.2 Applicability

This SOP is applicable, in Sample Preparation Lab, for the separation of aliphatic and aromatic compounds by applying this procedure to the base/neutral fraction obtained from the acid-base separation technique.

3.0 METHOD SUMMARY

An appropriate amount of the base/neutral sample extract to be used is determined gravimetrically. Extract is solvent-exchanged into hexane. Wet pack column with neutral alumina. Load sample extract and sequentially elute column with hexane (to remove aliphatics) and methylene chloride (for aromatic

WRITER: NAME/DATE: Gary M. Milbrister 6/11/91	Malcolm A. Butler 6/12/91	
ACTIVITY MGR: NAME/DATE Michael C. Shepherd 6/18/91	NAME/DATE F. L. Shore 6/21/91	NAME /DATE FLS 8/27/91

7-87-27815

6.2 Apparatus

6.2.1 Muffle furnace.

6.2.2 Kuderna-Danish (K-D) apparatus:

6.2.2.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

6.2.2.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

6.2.2.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.2.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.3 Water bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

7.0 CHEMICALS AND REAGENTS

7.1 Sodium sulfate: (ACS) Granular, anhydrous; purified by heating at 400°C for 4 hours in a shallow tray, stored in a glass, sealable container.

7.2 Eluting solvents: Methanol, hexane, methylene chloride (pesticide quality or equivalent).

7.3 Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 130°C prior to use.

8.3.2 Heat the K-D apparatus on a water bath until the sample is concentrated to a volume of less than 5 mL.

8.3.3 After cooling, remove the Snyder column, rinse the K-D with a small amount of hexane and allow it to drain. Use nitrogen to reduce the volume of the concentrate to less than 2 mL.

8.4 Column Clean-Up

8.4.1 To pack the column, weigh out 10 gm of alumina and add it to a chromatographic column that contains a small plug of glasswool above the stopcock and that is at least two-thirds filled with hexane. Pouring alumina into hexane will produce less channeling than a dry-packed column per Method 3611. Add about 1 cm of anhydrous sodium sulfate to the top of the alumina. Open the stopcock on the column and let the hexane flow slowly while the alumina particles settle to the bottom. Allow the solvent to flow until the head of the liquid in the column is about 0.5 cm above the sodium sulfate layer, then stop the flow.

8.4.2 Quantitatively transfer the sample extract, in hexane, to the column. If extract is particularly dirty, agitate it for a minute, using the ultrasonic bath, to homogenize the concentrate. Drain the hexane level to the top of the sodium sulfate. Transfer the concentrate to the column and drain the level to the top of the sodium sulfate. Rinse the concentrator tube with a small amount of hexane (<1 mL) and transfer to column and drain the level to the top of the sodium sulfate, again. (SAVE concentrator tube for step 8.4.5).

8.4.3 Start the flow in the column and elute with 13 mL of hexane. Add the hexane carefully so that the adsorbant bed is not distrubed.

NOTE: Flow rate for all elutions is 2 mL/minute.

8.5.3 Transfer the base/neutral aromatic extract to a calibrated 10 mL vial with several rinsings of the concentrator tube with solvent and adjust the final volume to 10 mL.

8.6 Post-Clean Up Gravimetric Determination

A post-clean up gravimetric determination similar to that described in Section 6.1 may be performed as a check on cleanup efficiency if desired.

8.7 Post-Clean Up Analysis

Reduce final volume of the column eluate to 1 mL, or to the volume required by the analysis. Acid and base/neutral portions may be combined prior to final concentration if desired.

9.0 SHORTHAND PROCEDURE

See Attachment 1.

10.0 CALCULATIONS

None.

11.0 QUALITY CONTROL

Duplicates, spikes, blanks and other quality control samples will be prepared in accordance with QA/QC SOP. Other QA/QC considerations pertinent to the project must be detailed in the project workplan.

12.0 DOCUMENTATION

Documentation will be noted on the sample traveler as neutral alumina cleanup (or inclusive in Oily Waste Cleanup) and in accordance with Documentation SOPs.

ATTACHMENT 1

ATTACHMENT 2

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Caution must be taken to prevent overloading of the chromatographic column. As the column loading for any of these types of wastes approaches 300 mg of extractable organics, separation recoveries will suffer. If overloading is suspected, an aliquot of the base-neutral extract prior to cleanup may be weighed and then evaporated to dryness. A gravimetric determination on the aliquot will indicate the weight of extractable organics in the sample.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300-mm x 10-mm I.D., with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500-mL.

4.3 Reagent bottle: 500-mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

4.5.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.5.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.5.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.6 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

7.6 Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 1 mL of hexane was used as a rinse, then 13 mL of additional hexane should be used. Collect the effluent in a 50-mL flask and label this fraction "base/neutral aliphatics." Adjust the flow rate to 2 mL/min.

7.7 Elute the column with 100 mL of methylene chloride and collect the effluent in a 250-mL flask. Label this fraction "base/neutral aromatics."

7.8 Elute the column with 100 mL of methanol and collect the effluent in a 250-mL flask. Label this fraction "base/neutral polars."

7.9 Concentrate the extracts by the standard K-D technique to whatever volume is required (1-10 mL) in the appropriate determinative method (Section 4.3 of this chapter). Analyze whichever fractions contain the analytes of interest.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 A rag oil sample was analyzed by a number of laboratories according to the procedure outlined in this method. The results of these analyses for selected components in the rag oil are presented in Table 1. Reconstructed ion chromatograms from the GC/MS analyses are included as Figures 1 and 2.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation	PROCEDURE NO: 325-SP-011	PAGE: 1 of 7
TITLE: Acid-Base Cleanup Extraction-EPA Method SW-846-3650, 3rd Edition	REVISION NO: 2	EFFECTIVE DATE: 5/27/91
	SUPERSEDES: 321-SP-011	
REFERENCES: 325-SP-001, -004, -010		
SATELLITE FILES: 1-119		
REASON FOR REVISION: General Revisions		

INFORMATION COPY
FOR INFORMATIONAL PURPOSES ONLY

1.0 PURPOSE

The purpose of this document is to establish guidelines for procedural adaptations of the EPA SW-846 Method 3650 Acid-Base Cleanup Extraction.

2.0 SCOPE AND APPLICABILITY

2.1 Scope

This SOP covers all steps or their modifications for acid-base partitioning of analytes using pH adjustment.

2.2 Applicability

This SOP is applicable, in Austin Sample Preparation lab, for the liquid-liquid partioning of acid analytes from base/neutrals for the cleanup of petroleum wastes.

3.0 METHOD SUMMARY

Load sample (approximate volume, 200 mL) into separatory funnel. Extract organic layer three times with 0.1N NaOH, save organic phase containing base/neutral analytes. Load aqueous phase into separatory funnel, adjust pH<2, and extract three times with methylene chloride to recover acid analytes. Proceed with additional cleanup of base/neutrals and/or concentrate as required.

WRITER: NAME/DATE		
Gary M Dubrinsson 3/1/91	Malcolm A. Beeler 3/12/91	R Bobbitt 3/19/91
ACTIVITY MGR: NAME/DATE	NAME/DATE	NAME /DATE
Michael C. Stupl 6/3/91	L Shaw 6/14/91	FCS 8/27/91

7-87-27815

6.2 Apparatus

6.2.1 Kuderna-Danish (K-D) Apparatus:

- Concentrator tube: 10-mL, graduated (Kontes K5700-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.
- Evaporation flask: 500-mL (K-570001-0500 or equivalent). Attach to concentrator tube with springs.
- Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).
- Snyder column: Two-ball micro (Kontes K569001-0219 or equivalent).

6.2.2 Water Bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

6.2.3 Zymark TurboVap

7.0 CHEMICALS AND REAGENTS

7.1 Reagent-Water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

7.2 Sodium hydroxide, 0.1N: Solution with a pH >12 should be prepared using a 8.33 : 100 dilution of 12N NaOH (which is made from ACS grade NaOH pellets and organic-free water) into organic free water which has been saturated with ACS grade NaCl (in order to help minimize emulsion problems during the extraction).

8.6 Re-extract the organic layer twice more with 50 mL portions of 0.1N sodium hydroxide solution. If less than 100 mL of aqueous portions has been recovered, perform a fourth extraction and allow extra time for separation of layers.

8.7 Save both the base/neutral species in the organic phase and the acid species in the aqueous phase.

8.8 Adjust the pH of the acid species in the aqueous phase to less than 2 with 2:1 sulfuric acid solution.

8.9 Transfer the acidified aqueous phase to the separatory funnel that was used for step 8.3.

8.10 Add 75 mL of solvent to the separatory funnel. After shaking, check that the pH is still less than 2 and collect the solvent in a 250 mL Erlenmeyer flask. Avoid collecting any of the aqueous layer with it. Perform a second and third extraction, 75 mL each, in the same manner, combining the extracts in the Erlenmeyer.

8.11 If the acid and base/neutral fractions are to be analyzed together, it may be advantageous to save the acid extracts and concentrate them in combination with the base/neutral extracts, after the base/neutral portion has received any additional cleanup (such as Method 3611) that is necessary.

8.12 If possible, do not use any drying agent to treat the acid extract. Loss of acid surrogates may be experienced, if drying agent is used. If drying is necessary, use acidified sodium sulfate.

13.0 PUBLISHED REFERENCES

EPA SW-846, Method 3650, 3rd Edition.

14.0 APPENDICES

See Attachment 2.

Oily waste clean-up: Acid/Base Partition of
8270's (See SOP 325-SP-011, -014)

1) Gravimetrically determine appropriate sample volume to use and dilute to 200 mL with $MeCl_2$.

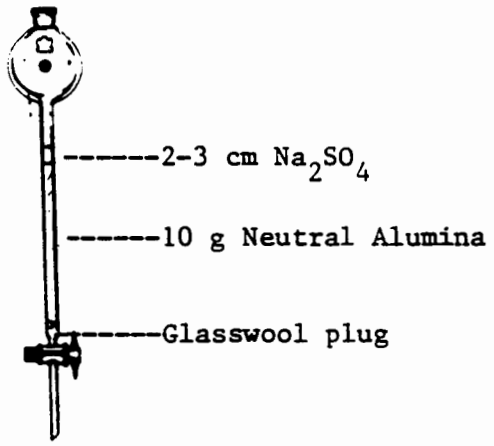
2) Wash 3 times with 50 mL portions of 0.1N NaOH (shake 1-2 min. each time in a small sep-funnel with periodic venting). Save the aqueous portion for acid wash. Be sure pH is maintained at ≥ 12 and do a 4th wash if <100 mL of aqueous solution is recovered.

3) Collect the organic layer in a 250 mL Erlenmeyer and KD to 3.5 mL, with hexane exchange. Save this portion for neutral alumina column clean-up. (Base/Neutral fraction)

4) To the 100-150 mL aqueous portion in Step 2, add 2:1 H_2SO_4:H_2O to pH ≤ 2, transfer to sep-funnel, and add 75 mL $MeCl_2$. Shake and mark "acid" portion.

5) Neutral Alumina Column Clean-up:
   a) Wet pack 1 cm column with 10 g baked neutral alumina.
   b) Add 1 cm Na_2SO_4 & elute solvent to just above the sulfate layer.
   c) Quantitatively transfer sample to column, rinse the receiver, and drain to the top of the sulfate layer.
   d) Start the flow and elute with 13 mL of hexane (approx. 2 mL/min.). This 15 mL fraction is the aliphatics portion and should be collected in a 20 mL vial and stored in the refrigerator. (Save the receiver for a $MeCl_2$ rinse).
   e) Elute the column with 100 mL $MeCl_2$ after rinsing the receiver 2 or 3 times. Collect the eluate in an Erlenmeyer flask or KD.
   f) If polar analytes are of interest, follow with a second elution of 100 mL of MeOH, after rinsing receiver. Collect eluate in a separate Erlenmeyer flask.

6) Combine B/N fraction with acid fraction and KD to 1.0 mL.



METHOD 3650

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 was formally Method 3530 in the second edition of this manual.

1.2 This is a liquid-liquid partitioning method to separate acid analytes from base/neutral analytes using pH adjustment. It may be used for cleanup of petroleum waste prior to alumina cleanup.

2.0 SUMMARY OF METHOD

2.1 The solvent extract is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and then ready for analysis for the acid analytes.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compound of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel: 125-mL, with Teflon stopcock.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 Concentrator tube: 10-mL, graduated (Kontes K5700-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

7.2 Add 20 mL of methylene chloride to the separatory funnel.

7.3 Add 20 mL of reagent water and adjust the pH to 12-13 with sodium hydroxide.

7.4 Seal and shake the separatory funnel for 1-2 min with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third of the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

7.6 Separate the aqueous phase and transfer it to a 125-mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL portions of reagent water pH 12-13. Combine the aqueous extracts.

7.7 At this point the analytes will be in the organic and/or in the aqueous phase. Organic acids and phenols will be in the aqueous phase, whereas, base/neutral analytes will be in the organic solvent. If the analytes are in the aqueous phase only, discard the organic phase and proceed to Paragraph 7.8. If the analytes are in the organic phase, discard the aqueous phase and proceed to Paragraph 7.10.

7.8 Transfer the aqueous phase to a clean separatory funnel. Adjust the aqueous layer to a pH of 1-2 with sulfuric acid. Add 20 mL of methylene chloride to the separatory funnel and shake for 2 min. Allow the solvent to separate from the aqueous phase and collect the solvent in an Erlenmeyer flask.

7.9 Add a second 20 mL volume of methylene chloride to the separatory funnel and re-extract at pH 1-2 a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

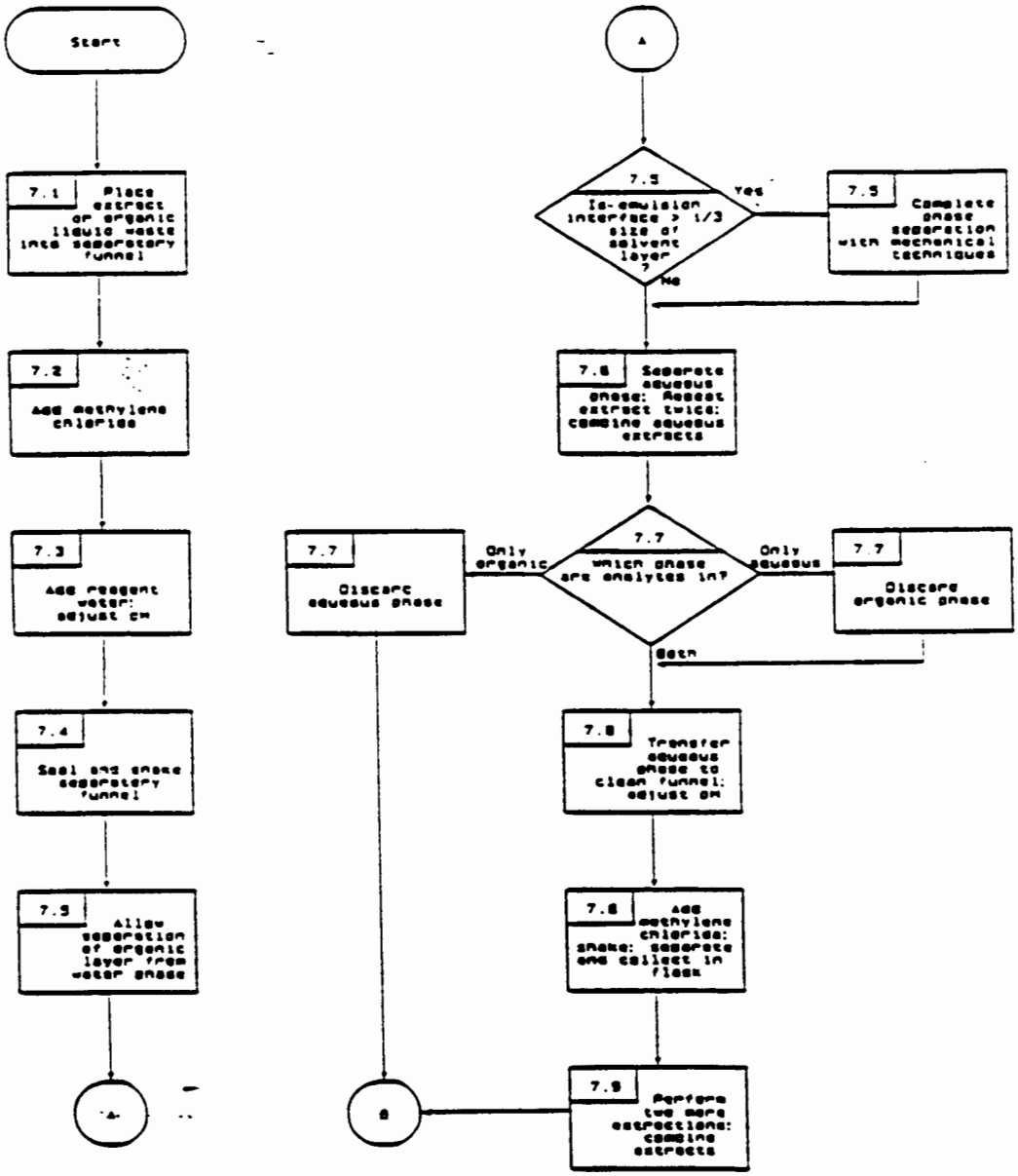
7.10 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11 Dry the extracts by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Rinse the Erlenmeyer flask which contained the solvent extract and the column with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 Add one or two boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot

METHOD 3650

ACID-BASE PARTITION CLEANUP



Revision 0
Date September 1986

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation		PROCEDURE NO: 325-SP-034	PAGE: 1 of 14
TITLE: Silica Gel Cleanup for Analysis of PNA's		REVISION NO: Original	EFFECTIVE DATE: 2/25/91
		SUPERSEDES:	
REFERENCES: 325-SP-001, -003, -004, -006, -007, -014			
SATELLITE FILES: 1-119			
REASON FOR REVISION:			

INFORMATION COPY
FOR INFORMATIONAL
PURPOSES ONLY

1.0 PURPOSE

The purpose of this document is to establish guidelines for the preparation, quality control, and use of silica gel for cleanup of sample extracts containing polynuclear aromatic hydrocarbons.

2.0 SCOPE AND APPLICABILITY

2.1 Silica gel is an adsorbent of amorphous silica with weakly acidic properties. Silica gel is used for column chromatography and separates the analytes of interest from interfering compounds of a different polarity.

2.2 Specific applications: This method includes guidance for cleanup of sample extracts containing polynuclear aromatic hydrocarbons.

3.0 SUMMARY OF METHOD

3.1 The column is packed with the 10 grams of silica gel, topped with 1-2 cm anhydrous sodium sulfate and, and then loaded with the sample to be analyzed. Elution of analytes is effected first with hexane, then 2:3 mixture of methylene chloride and hexane leaving the interfering compounds on the column. The second eluate (2:3 mixture) is then concentrated.

WRITER: NAME/DATE: Gary M. DeBruckner 8/17/90	Fred Shore 3/1/91	R.H. Babb 3/4/91
ACTIVITY MGR: NAME/DATE Patricia L. Babbitt 8/28/90	NAME/DATE Malcolm G. Butler 2/21/91	NAME/DATE Michael C. Shepherd 2/25/91

7-87-27815

6.5 Reagent bottle: 500 mL.

6.6 Water bath: Heated with concentric ring cover, capable of temperature control (+5 degrees). The bath should be used in fume hood.

6.7 Boiling chips: Pre-extracted, approximately 10/40 mesh Teflon.

6.8 Erlenmeyer flask: 50-250 mL.

7.0 CHEMICALS AND REAGENTS

7.1 Silica gel: 70-230 mesh (Aldrich Chem. 28, 862-4 or equivalent). Extracted with methylene chloride, then activated >16 hours at 130°C, in clean loosely covered glass tray. Following activation, the silica gel is immediately transferred to a clean, glass, sealable container with a Teflon lid liner.

7.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating in a muffle furnace at 400°C for 4 hours in shallow tray). Following purification, the anhydrous sodium sulfate is cooled to approximately 100°C then immediately transferred into a clean, glass, sealable container with a Teflon lid liner.

7.3 Eluting solvents: Hexane, methylene chloride (pesticide quality or equivalent).

8.0 PROCEDURE

8.1 Perform gravimetric analysis on extract if column cleanup appears to be warranted. See SW-846 Method 3611 instructions (oily-waste cleanup with alumina) and SOP 325-SP-014 for the gravimetric procedure. Adjust the amount of extract aliquot to be cleaned so that the aliquot contains no more than 200-300 mg of extractable material.

SILICA GEL CLEANUP (for PNA's)

1) Place glasswool plug in bottom of 2 cm column and fill 1/2 way with hexane.

2) Weigh out 10 gm of silica gel into 100 mL beaker and add enough hexane to cover the silica gel. Swirl the silica gel and hexane to make a slurry.

3) Pour slurry into the column, rinsing beaker with hexane to effectively transfer all the silica gel into the column.

4) After the slurry has settled into the column, by tapping gently and rinsing, add a 3 cm layer of sodium sulfate.

5) Elute the column @ 2 mL/min. until the solvent level is just above the sulfate level.

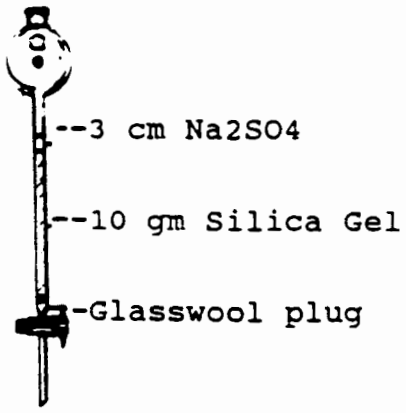
6) Transfer extract to column and rinse receiver with 2 mL hexane.

7) Elute (2 mL/min.) with 25 mL hexane and discard.

8) Elute (2 mL/min.) with 25 mL 2:3 methylene chloride:hexane (10 mL : 15 mL).

9) Concentrate by N2 blowdown to 1.0 mL.

10) Exchange solvent with acetonitrile, final volume 1.0 mL.



ATTACHMENT 1

13.0 PUBLISHED REFERENCES

SW-846, Method 8310 and 3630.

14.0 APPENDICES

14.1 See Attachment 2, SW-846 Method 3630.

may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500-mL.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Silica gel: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr at 130°C in a shallow glass tray, loosely covered with foil.

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents: Cyclohexane, hexane, 2-propanol, toluene, methylene chloride, pentane (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

Indeno(1,2,3-cd)pyrene
Napnthalene
Phenanthrene
Pyrene

7.2 Derivatized phenols:

7.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040.

7.2.2 Place 4.0 g of activated silica gel into a 10-mm I.D. chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.3 Preelute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.4 Elute the column, in order, with: 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using this method.

TABLE 1. SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

Parameter	Percent Recovery by Fraction[1]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

1 Eluant composition:

Fraction 1-15% toluene in hexane.
Fraction 2-40% toluene in hexane.
Fraction 3-75% toluene in hexane.
Fraction 4-15% 2-propanol in toluene.

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Sample Preparation	PROCEDURE NO: 325-SP-038	PAGE: 1 of 5
TITLE: Florisil Column Cleanup	REVISION NO: Original	EFFECTIVE DATE: 8/27/91 JLC
	SUPERSEDES: N/A JLC	
REFERENCES: 325-SP-001, -003, -004, -006, -007, -014		
SATELLITE FILES: 1-119		
REASON FOR REVISION: original JLC		

INFORMATION COPY
FOR INFORMATIONAL
PURPOSES ONLY

1.0 PURPOSE

The purpose of this document is to establish guidelines for the preparation, quality control, and the use of Florisil for cleanup of sample extracts containing pesticides and/or PCBs, or for organophosphorous pesticides.

2.0 SCOPE AND APPLICATION

2.1 Scope

This SOP documents guidelines and modifications for extract cleanup by SW-846, Method 3620, for pesticide/PCB or organophosphorous pesticide samples.

2.2 Applicability

This SOPs guidelines and modifications are applicable to the Sample Preparation Laboratory.

3.0 SUMMARY OF METHOD

The columns are packed with 20 grams of Florisil, topped with 1-2 cm anhydrous sodium sulfate and then loaded with the sample to be analyzed. Elution of analytes is effected with ether:hexane, leaving the interfering compounds on the column. The combined eluates are then concentrated and delivered for analysis.

WRITER: NAME/DATE: Gary M. Dalmann 6/25/91	Malcolm A. Beeler 6/26/91	
ACTIVITY MGR: NAME/DATE Michael C. Shepherd 6/26/91	NAME/DATE Fred Shore 7/24/91	NAME /DATE FLS 8/27/91

7-87-27815

6.5 Reagent bottle: 500 mL.

6.6 Water bath: heated with concentric ring cover, capable of temperature control (+5 degrees). The bath should be used in fume hood.

6.7 Boiling chips: Pre-extracted, approximately 10/40 mesh Teflon.

6.8 Erlenmeyer flask: 50-250 mL.

7.0 CHEMICALS AND REAGENTS

7.1 Florisil: pesticide residue (PR) grade (60/100 mesh). Extracted with methylene chloride, then activated >16 hours at 130°C, in a loosely covered glass tray. Following activation, the Florisil is immediately transferred to a clean, sealable container with a Teflon lid liner.

7.2 Sodium sulfate (ACS): granular, anhydrous (purified by heating in muffle furnace or kiln, at 400°C for 4 hours in shallow tray). Following purification, the anhydrous sodium sulfate is cooled to approximately 100°C then immediately transferred into a clean, sealable container with Teflon lid liner.

7.3 Eluting solvents: hexane, diethyl ether (pesticide quality or equivalent). Diethyl ether must be free of peroxides as indicated by EM Quant test strips. Procedures recommended for removal of peroxides are provided with the test strips.

8.0 PROCEDURE

8.1 Perform gravimetric analysis on extract if column cleanup appears to be warranted. See SW-846 Method 3611 instructions (oily-waste cleanup with alumina) and SOP 325-SP-014 for the gravimetric procedure. Adjust the amount of extract aliquot to be cleaned so that the aliquot contains no more than 200-300 mg of extractable material.

10.0 CALCULATIONS

Not applicable.

11.0 QUALITY CONTROL

11.1 New batches of pre-extracted, activated florisil will be quality tested before use, by testing a blank sample in the following manner:

11.1.1 Procedures 8.3, 8.4, 8.5 will be followed with the exception that, no sample or spike will be transferred to the column.

11.1.2 Analyze for Total Chromatographical Organics via GC/ECD.

12.0 DOCUMENTATION

12.1 Preparation of new batches of florisil will be logged into the Sample Preparation REAGENTS NOTEBOOK.

12.2 A QC number will be assigned and a quality control sample will be performed via GC/ECD with results kept in the QC FILE.

12.3 All other documentation will be in accordance with SOPs 325-SP-006, -007.

13.0 PUBLISHED REFERENCES

SW-846, 3rd Edition.

14.0 APPENDICES

See Attachment 2 of SW-846, Method 3611.

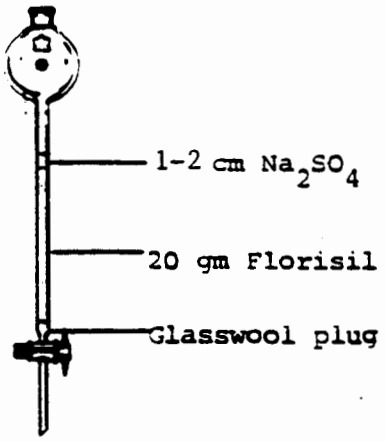
Florisil Column Clean-up for 8080/8140

1. Make sure that the Florisil has been pre-extracted and baked.
2. Put a plug of glasswool in the bottom of 2 cm column, then fill column about 3/4ths full with hexane (about 40 mL).
3. Add 20 gm of Florisil and settle column bed by tapping gently.
4. Add layer of sodium sulfate, 1 to 2 cm deep, to the top of the column.
5. Pre-elute with 40 mL of hexane to rinse the sodium sulfate & Florisil.
6. Elute column until the solvent level is just above the sulfate layer.
7. Adjust the extract volume to 10 mL, with hexane, and transfer to the the column. Rinse receiver two times with 1 mL hexane, add to column.
8. Required elution fractions are:

   8080 for PCBs - Fractions 1 & 2

   8080 for Pest./PCBs - Fractions 1, 2, & 3

   8140 - Fractions 1, 2, 3, & 4
9. Prepare batches of ether/hexane consisting of Fraction 1 (6% ether), Fraction 2 (15% ether), Fraction 3 (50% ether), and Fraction 4 is 100% ether.
10. Place a 1 L Erlenmeyer flask under the column and lower the extract level to just above the sulfate layer.
11. Begin elution with Fraction 1, 200 mL, at 5 mL/minute. Follow with other fractions per 8. DO NOT LET COLUMN BED GO DRY!!!
12. Collect and combine fraction eluates. Concentrate the eluates to 5.0 mL for 8080 or 1.0 mL for 8140.



ATTACHMENT 2

METHOD 3620

FLORISIL COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered tradename of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; nitrosamines; organochlorine pesticides; nitroaromatics; haloethers; chlorinated hydrocarbons; and organophosphorous pesticides.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Beaker: 500-mL.

4.2 Chromatographic column: 300-mm long x 10-mm I.D. or 400-mm long x 20-mm I.D., to be specified in Paragraph 7.0; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits

(Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g (Mills).)

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents:

5.3.1 **Diethyl ether:** Pesticide quality or equivalent.

5.3.1.1 Must be free of peroxides as indicated by EM Quant test strips (available from EM Laboratories Inc., 500 Executive Boulevard, Elmsford, NY 10523).

5.3.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.3.2 **Acetone; hexane; methylene chloride; pentane; petroleum ether** (boiling range 30-60°C): Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place 10 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.3.2 Add a weight of Florisil (nominally 20 g), predetermined by calibration, to a 20-mm I.D. chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

7.3.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 mL hexane, adding each rinse to the column.

7.3.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (v/v) (Fraction 1) using a drip rate of about 5 mL/min. All of the haloethers are in this fraction. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (v/v) (Fraction 2), into a second K-D flask. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v) (Fraction 3), and a final elution with 200 mL of 100% ethyl ether (Fraction 4), into separate K-D flasks.

7.3.5 Concentrate the eluates by standard K-D techniques using the water bath at about 85°C (75°C for Fraction 4). Adjust the final volume to whatever volume is required (1-10 mL). Analyze by gas chromatography.

7.4 Nitroaromatics and isophorone:

7.4.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.4.2 Prepare a slurry of 10 g activated Florisil in methylene chloride/hexane (1:9) (v/v) and place the Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top. Adjust the elution rate to about 2 mL/min.

7.4.3 Just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1:9) (v/v) and continue the elution of the column. Discard the eluate.

7.4.4 Next, elute the column with 30 mL of acetone/methylene chloride (1:9) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction, while exchanging the solvent to hexane. To exchange the solvent, reduce the elution solvent to about 10 mL. Add 50 mL of hexane, a fresh boiling chip, and return the reassembled K-D apparatus to the hot water bath. Adjust the

TABLE 2

DISTRIBUTION OF ORGANOPHOSPHOROUS PESTICIDES INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
Azinophos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

[a]Eluant composition: Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery information presented) (U.S. FDA).
NR = Not recovered (U.S. FDA).
V = Variable recovery (U.S. FDA).
ND = Not determined.

SOURCE: U.S. EPA and FDA data.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the distribution of chlorinated pesticides, PCB's, and haloethers in various Florisil column fractions.

9.2 Table 2 indicates the distribution of organophosphorous pesticides in various Florisil column fractions.

10.0 REFERENCES

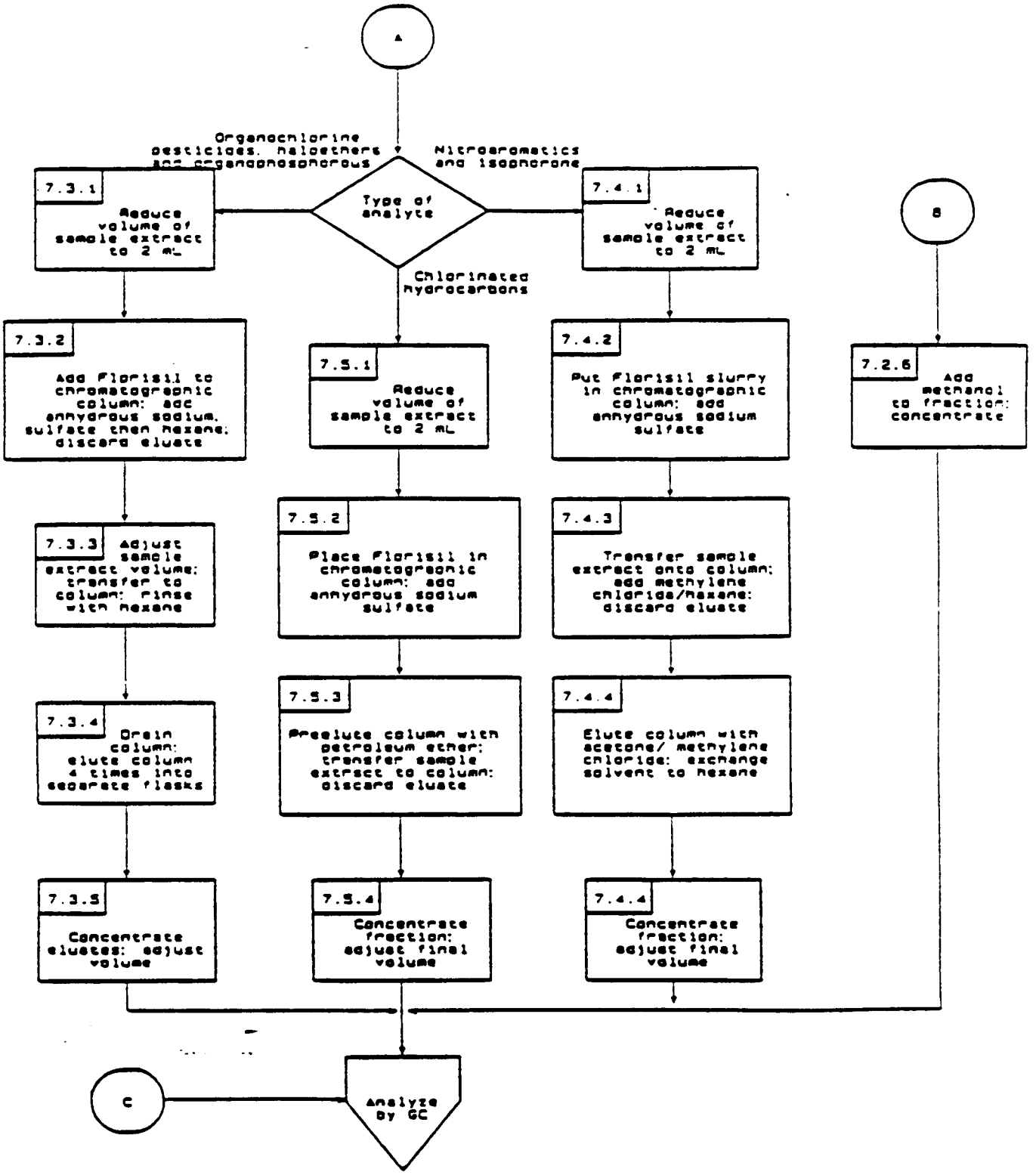
1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. Floridin of ITT System, Florisil: Properties, Application, Bibliography, Pittsburgh, Pennsylvania, 5M381DW.

3. Mills, P.A., "Variation of Florisil Activity; Simple Method for Measuring Absorbent Capacity and its use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29, 1968.

4. U.S. Food and Drug Association, Pesticides Analytical Manual (Volume 1), July 1985.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.


A
Organochlorine pesticides, haloethers and organophosphorous
Nitroaromatics and isophorone
Type of analyte
Chlorinated hydrocarbons
7.3.1 Reduce volume of sample extract to 2 mL
7.3.2 Add Florisil to chromatographic column; add anhydrous sodium sulfate then hexane; discard eluate
7.3.3 Adjust sample extract volume; transfer to column; rinse with hexane
7.3.4 Drain column; elute column 4 times into separate flasks
7.3.5 Concentrate eluates; adjust volume
7.5.1 Reduce volume of sample extract to 2 mL
7.5.2 Place Florisil in chromatographic column; add anhydrous sodium sulfate
7.5.3 Preelute column with petroleum ether; transfer sample extract to column; discard eluate
7.5.4 Concentrate fraction; adjust final volume
7.4.1 Reduce volume of sample extract to 2 mL
7.4.2 Put Florisil slurry in chromatographic column; add anhydrous sodium sulfate
7.4.3 Transfer sample extract onto column; add methylene chloride/hexane; discard eluate
7.4.4 Elute column with acetone/ methylene chloride; exchange solvent to hexane
7.4.4 Concentrate fraction; adjust final volume
B
7.2.6 Add methanol to fraction; concentrate
C
Analyze by GC

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: GC/MS	PROCEDURE NO: 321-MS-011	PAGE: 1 of 13
TITLE: GC/MS PCDD/PCDF Analysis	REVISION NO: Original	EFFECTIVE DATE: 10/27/87
	SUPERSEDES: N/A	
REFERENCES: SW-846 3rd Ed. Method 8280		
SATELLITE FILES: 1-101		
REASON FOR REVISION: Original		

INFORMATION COPY FOR INFORMATIONAL PURPOSES ONLY

1.0 PURPOSE

This document describes the Radian procedure for polychlorinated dibenzodioxin/polychlorinated dibenzofuran (PCDD/PCDF) analysis.

2.0 SCOPE

This SOP covers calibration, QA/QC, isomer class totals quantitation, and toxic isomers quantitation. Most of this SOP is taken from SW-846 Method 8280.

3.0 INITIAL CALIBRATION

For isomer class totals using the J&W DB-5 column, a five-point calibration must be performed in triplicate and the average isomer class response factor is used for quantitation. The % RSD between the three calibration runs must be less than 15% for all analytes. The standards used and their concentrations are shown on Table 1. The standards must be remade and the calibration reperformed once a year.

WRITER: NAME/DATE: Duane Jordan 10/19/87		
ACTIVITY MGR: NAME/DATE Patrick W Meehan 10/21/87	NAME/DATE T. L. Shore 10/22/87	NAME /DATE G A Magee 10/27/87

7-87-27815

5.0 SAMPLE PREPARATION

After all the daily calibrations are performed, samples may be analyzed. An amount of $^{13}C_{12}$-1,2,3,4-TCDD equal to the nominal surrogate amount is added to each extract. Ten uL of the $^{13}C_{12}$-1,2,3,4-TCDD internal standard solution will provide 50 ng of I.S. More benzene may be added if necessary to dissolve all of the residue, but additional solvent will raise the method detection limit. Occasionally, an extremely dirty extract will require dilution using the PCDD/PCDF surrogate solution as the solvent.

6.0 IDENTIFICATION OF PCDD/PCDF

Two ions for each internal standard and four from each PCDD/PCDF isomer group are monitored for identification and quantitation purposes. For positive identification, the relative intensities of the two major chlorine isotope cluster ions must agree within ±15% with those shown on Table 3 of Method 8280 and a COCL loss peak must be present. Peak maxima must agree within ±2 scans. Our procedure calls for three chlorine isotope peaks to be monitored (Method 8280 calls for two). This third peak, although not required, can be used for identification purposes and detection limit calculations and is helpful with extremely dirty samples. The loss of COCl <u>must</u> be present to positively identify a peak as PCDD or PCDF.

7.0 QUANTITATION

Quantitation is performed using response factors and isotopic dilution. To determine PCDD/PCDF concentrations use the following

purpose. This column can resolve 2,3,4,8-TCDF and 2,3,7,8-TCDF to about 75% valley. 1,2,3,4,8-PeCDF and 1,2,3,7,8-PeCDF coelute on this column, however. If desired, these two PeCDFs can be resolved on DB-5. The SP-2331 column is only partially cross-linked, and special precautions must be taken: samples must be taken up in dodecane, do not temperature program the column past 275°C, do not heat or cool the column more than 20°C/min. and always use a one meter deactivated fused silica guard column.

With the Supelco SP-2331, a single-point calibration is used for toxic isomers quantitation. A standard solution in dodecane containing our usual surrogates and all of the toxic isomers is used to generate relative retention times and response factors.

A retention time standard in dodecane is used to determine isomer group windows on the SP-2331 column. Since we are not looking for all PCDD/PCDFs, however, the toxic isomers standard can be used to define the SIM retention time windows.

10.0 QA/QC

Due to the sensitive nature of PCDD/PCDF results, all QA/QC procedures must be thoroughly followed and documented. Before beginning any work, the mass spectrometer tune and mass assignments must be verified between 198-443 amu by DFTPP injection. For each project, the daily response factor calibration check (Figure 1), the retention time window analysis (Figure 2), the chromatography check, and the surrogate response factor determination (Figure 3) should be documented and filed with the master file.

TABLE 1. 5 PT. DIOXIN CALIBRATION STANDARDS

	5ppm std.	2.5ppm std.	1ppm std.	0.5ppm std.	0.2ppm std.
13C-2378 TCDD	1ppm	1ppm	1ppm	1ppm	1ppm
13C-2378 TCDF	1ppm	1ppm	1ppm	1ppm	1ppm
13C-12378 PeCDD	1ppm	1ppm	1ppm	1ppm	1ppm
13-12378 PeCDF	1ppm	1ppm	1ppm	1ppm	1ppm
13C-123678 HxCDD	1ppm	1ppm	1ppm	1ppm	1ppm
13C-123478 HxCDF	1ppm	1ppm	1ppm	1ppm	1ppm
13C-1234678 HpCDD	1ppm	1ppm	1ppm	1ppm	1ppm
13C-1234678 HpCDF	1ppm	1ppm	1ppm	1ppm	1ppm
13C-OCDD	1ppm	1ppm	1ppm	1ppm	1ppm
13C-OCDF	1ppm	1ppm	1ppm	1ppm	1ppm
2378 TCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
12378 PeCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
12347 PeCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
123478 HxCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
123678 HxCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
123789 HxCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
1234578 HpCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
2378 TCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
12378 PeCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
23478 PeCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
123478 HxCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
123678 HxCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
123789 HxCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
234678 HxCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
1234678 HpCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
1234789 HpCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
OCDD	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm
OCDF	5ppm	2.5ppm	1ppm	0.5ppm	0.2ppm

Solvent: Benzene/Nonane
Final Concentration as indicated in table
Prepared 5/87 MDR/SJC

FIGURE 1

DATE:_____ FRN:_____

DAILY RESPONSE FACTOR CALIBRATION CHECK

Isomer Group	Average Determined Response Factor	Average RF from Triplicate 5-pt.	Percent Difference
TCDD	_____	_____	_____
TCDF	_____	_____	_____
PeCDD	_____	_____	_____
PeCDF	_____	_____	_____
HxCDD	_____	_____	_____
HxCDF	_____	_____	_____
HpCDD	_____	_____	_____
HpCDF	_____	_____	_____
OCDD	_____	_____	_____
OCDF	_____	_____	_____

FIGURE 3

PCDD/PCDF SURROGATE RESPONSE FACTORS

DATE:_____ FRN:_____

	Area	Retention Time	Relative Response Factor
$^{13}C_{12}$-1,2,3,4-TCDD (I.S.)			
$^{13}C_{12}$-2,3,7,8-TCDD			
$^{13}C_{12}$-2,3,7,8-TCDF			
$^{13}C_{12}$-1,2,3,7,8-PeCDD			
$^{13}C_{12}$-1,2,3,7,8-PeCDF			
$^{13}C_{12}$-HxCDD			
$^{13}C_{12}$-HxCDF			
$^{13}C_{12}$-HpCDD			
$^{13}C_{12}$-HpCDF			
$^{13}C_{12}$-OCDD			
$^{13}C_{12}$-OCDF			

FIGURE 5

Sample _____ FRN: _____

TOXIC ISOMERS QA/QC SUMMARY SHEET

Toxic Isomer	Retention Time	RRT	Area	Amount (ng)	Conc. (ng/g)
2,3,7,8-TCDD					
1,2,3,7,8-PeCDD					
1,2,3,4,7,8-HxCDD					
1,2,3,6,7,8-HxCDD					
1,2,3,7,8,9-HxCDD					
1,2,3,4,6,7,8-HpCDD					
2,3,7,8-TCDF					
1,2,3,7,8-PeCDF*					
2,3,4,7,8-PeCDF					
1,2,3,4,7,8-HxCDF**					
1,2,3,6,7,8-HxCDF					
1,2,3,7,8,9-HxCDF					
2,3,4,6,7,8-HxCDF					
1,2,3,4,6,7,8-HpCDF					
1,2,3,4,7,8,9-HpCDF					

* Coelutes with 1,2,3,4,8-PeCDF on SP-2331.

** Coelutes with 1,2,3,4,7,9-HxCDF on SP-2331.

CONFIDENTIAL

RADIAN CORPORATION

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Inorganic Metals Laboratory	PROCEDURE NO: 325-AA-005	PAGE: 1 of 5
TITLE: ANALYSIS OF THALLIUM BY GRAPHITE FURNACE	REVISION NO: Original	EFFECTIVE DATE: 11/23/88
	SUPERSEDES: NA	

REFERENCES: EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 279.2

SATELLITE FILES: 4-154, 4-135

REASON FOR REVISION: NA

INFORMATIONAL COPY FOR INFORMATION ONLY

1.0 SCOPE AND APPLICATION

Thallium in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require digesting to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper digestion. Thallium may also be analyzed by hydride AA or ICP. Detection limits and matrices are considerations when choosing the best method for analyzing the sample.

2.0 SUMMARY OF METHOD

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor. Because the tube area is small, the vaporized atoms are more concentrated allowing for lower limits of detection.

3.0 INTERFERENCES

3.1 This technique is subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. These effects must be taken into consideration in the analysis of each different matrix encountered. Known chemical interferences are hydrochloric acid or excessive chloride concentrations.

3.2 Nitric acid is preferable for any digestion or solubilization step. If another acid is required in addition to HNO_3, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

WRITER: NAME/DATE		
ACTIVITY MGR: NAME/DATE 11/18/88	NAME/DATE 11/23/88	NAME/DATE 11/23/88

7-87-27815

6.0 CALIBRATION PROCEDURES

6.1 Calibration standards are analyzed beginning with the blank and proceeding to the highest standard. Each is analyzed in duplicate. Linear regression is used to define the calibration curve. The regression line is constructed using concentration as the X-value and mean response as the Y-variable. The blank is included as X=0.

6.2 The correlation coefficient of the standard curve must be $\geq$0.995 for the analysis to continue. If not, the analyst will correct the problem, remaking standards as necessary before the analysis will continue.

7.0 QUALITY CONTROL

7.1 This is Radian's standard quality control protocol. In the areas of QC check samples, duplicates, and spikes, it meets or exceeds the requirements set forth in SW-846, 3rd Ed. Method 7740.

7.2 Quality Control Check Samples

In addition to calibration standards, quality control (QC) check samples are to be analyzed initially to verify the calibration curve and at a frequency of one in ten throughout the analysis. If the QC recovery is within acceptable limits (90-110%), the analysis may proceed. If any QC sample falls outside these limits, the analysis must be stopped and any of the following performed to bring the standard into control:

- Check instrument operating parameters (e.g., gas pressure),
- Recalibration,
- Re-make of QC standard, or
- Check with lab supervisor.

After the problem is addressed, analyses may commence, including all samples analyzed since the last acceptable QC standard.

7.3 Duplicates

Duplicates are to be performed at a rate of one in ten samples. A duplicate is defined as a sample which is split and treated as two independent samples and carried throughout the entire protocol (digestion, interference modifier solution, analysis). Duplicates should agree within 20 percent.

$$RPD = \frac{S-D}{M} \times 100$$

where S = sample
D = duplicate result
M = mean

If this is not the case, analyses must be terminated and the problem identified and corrected.

9.1 Each instrument has a corresponding log book requesting pertinent information relevant to the analysis to be performed. This log book must be filled out prior to completion of analysis to document standard conditions and response of the instrument.

9.2 The instrument maintenance log provides information regarding <u>any</u> maintenance performed before, during, or after the analysis.

9.3 The analysis and QC summary sheet should be filled out completely following instruction provided on each bench sheet.

9.4 All entries must be in black ink with corrections made by making one horizontal mark through the incorrect data and the correct data placed beside it. The correction is to be dated and initialed.

9.5 When using AA bench, the analyst will make hard copies of the AA bench equivalent of the analysis bench sheet and the QC summary sheet. Instructions for preparing the documents are in the AA Bench Users Guide.

10.0 SAFETY

10.1 Safety glasses and laboratory coat must be worn to prevent accidental injury due to the corrosivity of some of the reagents.

10.2 Because standards and samples contain nitric acid, they must be disposed of in the safety containers located in the lab.

GROUP OR LABORATORY: Inorganic Metals	PROCEDURE NO: 325-AA-001	PAGE: 1 of 5
TITLE: ANALYSIS OF ARSENIC BY GRAPHITE FURNACE	REVISION NO: Original	EFFECTIVE DATE: 11/23/88
	SUPERSEDES: NA	

REFERENCES: SOP 325-AA-007
EPA Methods for Chemical Analysis of Water and Wastes, 1979, Method 206.2

SATELLITE FILES: 4-154, 4-135

REASON FOR REVISION: NA

INFORMATION COPY FOR INFORMATIONAL PURPOSES ONLY

1.0 SCOPE AND APPLICATION

Arsenic in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require digesting to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper digestion. Arsenic may also be analyzed by hydride AA or ICP. Detection limits and matrices are considerations when choosing the best method for analyzing the sample.

2.0 SUMMARY OF METHOD

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor. Because the tube area is small, the vaporized atoms are more concentrated allowing for lower limits of detection.

3.0 INTERFERENCES

3.1 This technique is subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. These effects must be taken into consideration in the analysis of each different matrix encountered. Known chemical interferences are chlorides (>800 ppm) and sulphates (>200 ppm).

3.2 Nitric acid is preferable for any digestion or solubilization step. If another acid is required in addition to HNO_3, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

WRITER: NAME/DATE: Robert Wood		
ACTIVITY MGR: NAME/DATE: 11/18/88	NAME/DATE: 11/23/88	NAME/DATE: 11/23/88

5.4 Working Standards

Dilute 1 mL of 1000 ppm stock to 1 L with deionized water containing 1% HNO_3. Dilute 0, 2, 4, 6 mL of this intermediate solution to 100 mL with deionized water. This will prepare 0, 20, 40, and 60 ppb standards for use in the calibration procedure below.

6.0 CALIBRATION PROCEDURES

6.1 Calibration standards are analyzed beginning with the blank and proceeding to the highest standard. Each is analyzed in duplicate. Linear regression is used to define the calibration curve. The regression line is constructed using concentration as the X-value and mean response as the Y-variable. The blank is included as X=0.

6.2 The correlation coefficient of the standard curve must be $\geq$0.995 for the analysis to continue. If not, the analyst will correct the problem, remaking standards as necessary before the analysis will continue.

7.0 QUALITY CONTROL

7.1 This is Radian's standard quality control protocol. In the areas of QC check samples, duplicates, and spikes, it meets or exceeds the requirements set forth in SW-846, 3rd Ed. Method 7740.

7.2 Quality Control Check Samples

In addition to calibration standards, quality control (QC) check samples are to be analyzed initially to verify the calibration curve and at a frequency of one in ten throughout the analysis. If the QC recovery is within acceptable limits (90-110%), the analysis may proceed. If any QC sample falls outside these limits, the analysis must be stopped and any of the following performed to bring the standard into control:

- Check instrument operating parameters (e.g., gas pressure),
- Recalibration,
- Re-make of QC standard, or
- Check with lab supervisor.

After the problem is addressed, analyses may commence, including all samples analyzed since the last acceptable QC standard.

7.3 Duplicates

Duplicates are to be performed at a rate of one in ten samples. A duplicate is defined as a sample which is split and treated as two independent samples and carried throughout the entire protocol (digestion, interference modifier solution, analysis). Duplicates should agree within 20 percent.

9.0 REPORTING

Reporting requirements include:

- Instrument usage log,
- Instrument maintenance log,
- Analysis bench sheet,
- QC summary sheet,
- Print out, and
- Any lab notebook pages relevant to the data.

9.1 Each instrument has a corresponding log book requesting pertinent information relevant to the analysis to be performed. This log book must be filled out prior to completion of analysis to document standard conditions and response of the instrument.

9.2 The instrument maintenance log provides information regarding <u>any</u> maintenance performed before, during, or after the analysis.

9.3 The analysis and QC summary sheet should be filled out completely following instruction provided on each bench sheet.

9.4 All entries must be in black ink with corrections made by making one horizontal mark through the incorrect data and the correct data placed beside it. The correction is to be dated and initialed.

9.5 When using AA bench, the analyst will make hard copies of the AA bench equivalent of the analysis bench sheet and the QC summary sheet. Instructions for preparing the documents are in the AA Bench Users Guide.

10.0 SAFETY

10.1 Safety glasses and laboratory coat must be worn to prevent accidental injury due to the corrosivity of some of the reagents.

10.2 Because standards and samples contain nitric acid, they must be disposed of in the safety containers located in the lab.