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rc → Judy Bini

Dr. Kirkland Jones
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New Mexico Health and Environment Department
1190 Harold Runnels Building
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Mr. Matthew Hale
Deputy Director
Office of Solid Waste (OS-341)
U.S. Environmental Protection Agency
401 M Street, SW
Washington, D.C. 20460

Dear Messrs. Jones and Hale:

Enclosed for your review is the Department of Energy (DOE) position paper regarding compliance with the waste characterization requirements for the Waste Isolation Pilot Plant No-Migration Determination (WIPP-NMD). This position paper focuses only on those conditions associated with the waste characterization requirements in the NMD. The purpose of this paper is to provide the details of DOE's approach to demonstrate compliance with these requirements. The paper includes a discussion of the requirements, background information, and DOE's compliance approach.

DOE would like to request a meeting with the Environmental Protection Agency-Office of Solid Waste on May 9, 1991, to discuss the planned quality assurance/quality control measures associated with compliance with the NMD. This position paper will be incorporated into Revision 1.0 of the Quality Assurance Program Plan for WIPP due for external review in June 1991.

If you have any questions concerning the position paper or the proposed meeting, please contact Mark Duff of my staff at 301-353-7206.

Mark W Frei

Mark Frei
Headquarters WIPP Task Force
Office of Environmental Restoration
and Waste Management

Attachment

cc w/o attachment:
J. Lytle, EM-30
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DEPARTMENT OF ENERGY
POSITION PAPER REGARDING COMPLIANCE WITH THE WASTE CHARACTERIZATION REQUIREMENTS FOR THE WIPP NO-MIGRATION DETERMINATION

April 30, 1991

DEPARTMENT OF ENERGY
POSITION PAPER REGARDING COMPLIANCE WITH THE WASTE CHARACTERIZATION REQUIREMENTS FOR THE WIPP NO-MIGRATION DETERMINATION

1.0 INTRODUCTION

In response to the Department of Energy's (DOE) No-Migration Variance Petition (the Petition) for the Waste Isolation Pilot Plant (WIPP), the Environmental Protection Agency, Office of Solid Waste (EPA) published its notice of the final No-Migration Determination (NMD) for the WIPP on November 14, 1990 (USEPA, 1990). As a result of this NMD, DOE may place a limited amount of untreated transuranic (TRU) waste subject to the land disposal restrictions of the Resource Conservation and Recovery Act (RCRA) in the WIPP for the purposes of testing and experimentation. The NMD imposes several conditions on such placement and is for a maximum of ten years.

This position paper focuses only on those conditions associated with the waste characterization requirements imposed by EPA. The purpose of this paper is to provide EPA with the details of DOE's proposed approach to demonstrate compliance with these requirements. This paper includes a discussion of the requirements, background information, and DOE's compliance approach. It will serve as the basis for future discussions with EPA to address any questions and finalize the protocols necessary to ensure that the wastes received at the WIPP are adequately characterized in accordance with EPA requirements. Based on the discussions with EPA, the quality assurance/quality control measures necessary to demonstrate compliance will be incorporated into the <u>Quality Assurance Program Plan (QAPP) for the WIPP Experimental-Waste Characterization Program</u> (USDOE, 1991a). Compliance with the other conditions of the NMD (e.g., the air monitoring requirements) are addressed in the WIPP Part B permit application (USDOE, 1991b).

Figure 1 provides a schematic of the overall waste characterization approach for compliance with the NMD. Specific requirements and the compliance approach are described based on the sequence of events and amount of data required to obtain the necessary waste characterization information.

<u>Data Quality Objectives</u>

The following data quality objectives (DQOs) have been established for demonstrating compliance with the conditions in EPA's NMD associated with waste characterization:

Comparability - To demonstrate that the headspace concentrations of volatile organic compounds (VOCs) listed in Table 1 do not exceed two times the maximum concentrations reported in DOE's Petition at a confidence level of 80 percent.

No-Migration Demonstration - To demonstrate that the headspace concentrations of VOCs listed in Table 2 do not exceed ten times the mean concentrations reported in DOE's Petition at a confidence level of 80 percent.

Flammability - Prior to waste container emplacement in the WIPP, it must be demonstrated that: (1) the headspace concentrations of flammable VOCs listed in Table 3 do not exceed 500 ppmv at a confidence level of 80 percent, and that if a mixture of flammable VOCs exceeds 500 ppmv, then to demonstrate using an explicit "flame test" that the mixture is nonflammable; and (2) To demonstrate that the concentrations of hydrogen and methane in a binary mixture do not exceed 50% of the theoretical LEL using the Le Chatelier formula at a confidence level of 80%.

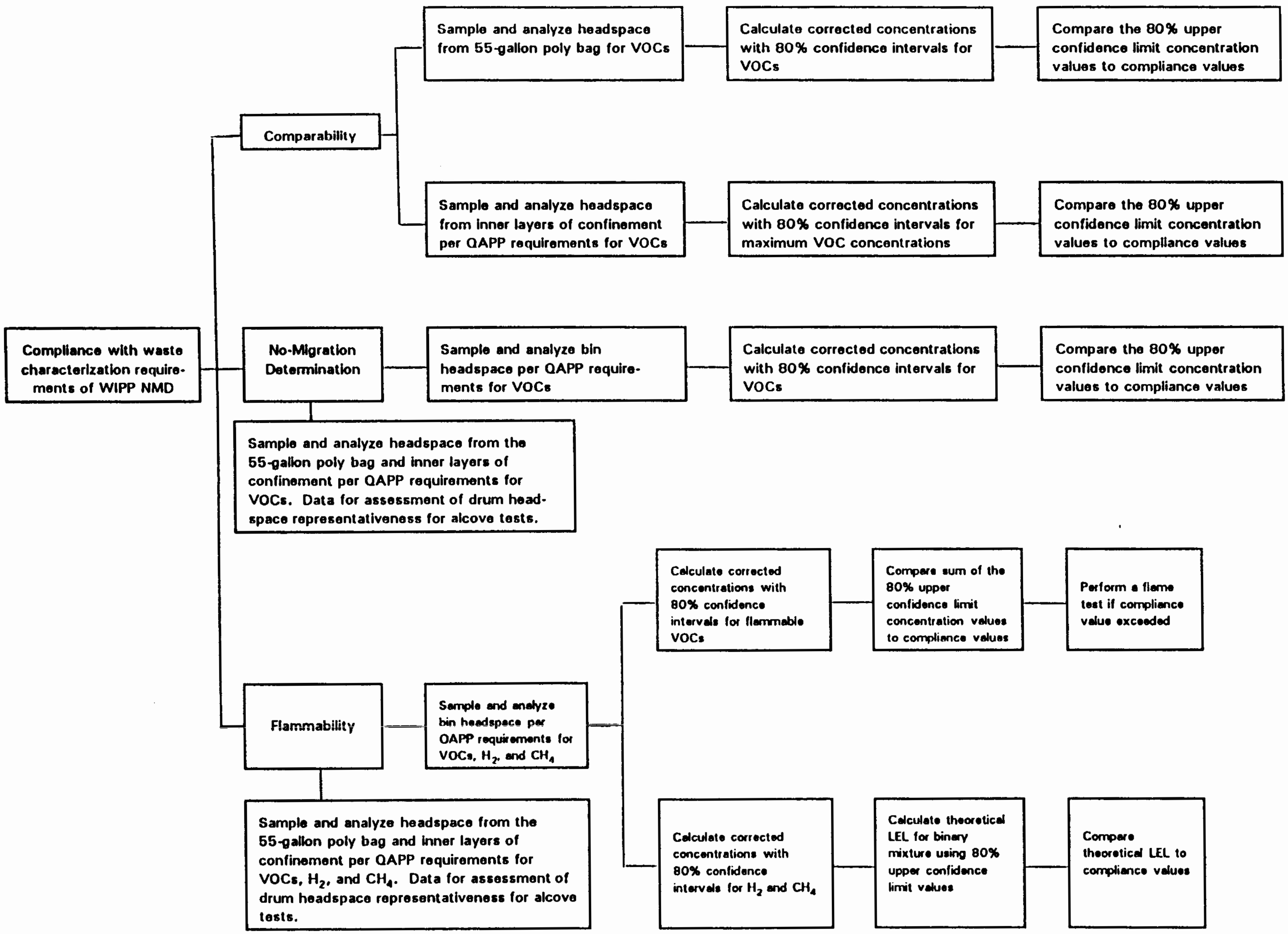

Figure 1. Overall Approach to Compliance With WIPP No-Migration Determination

Table 1. Maximum Allowable Volatile Organic Headspace Concentrations (Volume Percent) by Waste Type[a,b]

Constituent	Type I	Type II	Type III	Type IV
Carbon tetrachloride	0.08	0.18	0.58	8.18
Methylene chloride	0.44	0.84	0.50	1.42
1,1,1-Trichloroethane	1.88	5.68	2.12	14.96
Trichloroethylene	0.08	0.34	0.28	0.28
1,1,2-Trichloro-1,2,2-trifluoroethane	0.05	1.62	5.74	20.80

[a]Waste types are identified in USDOE, 1989.
[b]Concentration values from the No-Migration Determination (USEPA, 1990). These concentrations are obtained by multiplying the maximum VOC headspace concentrations reported in the Petition by two.

Table 2. Allowable Mean Volatile Organic Headspace Concentrations (Volume Percent) by Waste Type[a,b]

Constituent	Type I	Type II	Type III	Type IV
Carbon tetrachloride	0.24	0.26	0.30	6.90
Methylene chloride	0.39	0.42	0.33	0.93
Trichloroethylene	0.25	0.28	0.29	0.38

[a]Waste types are identified in USDOE, 1989.
[b]Concentration values from the No-Migration Determination (USEPA, 1990). These concentration values are obtained by multiplying the mean VOC headspace concentrations reported in the Petition by ten.

Table 3. Flammable Volatile Organic Compounds (VOCs) and Their Lower Explosive Limit (LEL) Values[a,b]

VOCs	LEL (v/v%)
Acetone	2.5
Benzene	1.3
n-Butanol	1.4
2-Butanone	1.4
Chlorobenzene	1.3
Cyclohexane	1.3
1,1-Dichloroethane	5.6
1,2-Dichloroethane	6.2
1,1-Dichloroethene	6.5
cis-1,2-Dichloroethene	5.6
Ethyl benzene	1.0
Diethyl ether	1.9
Methanol	6.0
4-Methyl-2-petanone	1.2
Toluene	1.2
o-Xylene	1.0
m-Xylene	1.1
p-Xylene	1.1

[a]The lower explosive limit is also referred to as the lower flammable limit (ASTM, 1989; NFPA, 1986).

[b]Only the most conservative lower explosive limit values are reprinted (NFPA, 1986; De Renzo, 1986).

2.0 STATISTICAL PROCEDURES FOR ASSESSING COMPLIANCE WITH NMD REQUIREMENTS

REQUIREMENT

Statistical procedures are needed to assess compliance with NMD requirements for potential waste headspace gas flammability, waste comparability, and the no-migration finding. These procedures must be applied to laboratory analytical data prior to comparing these data with the regulatory limits specified in the NMD.

BACKGROUND

Statistical procedures are employed to determine compliance with limits imposed upon environmental programs. Statistical procedures are selected and developed from established statistical techniques based on sampling constraints, population distributions, and other controlling factors. Compliance limits and sampling constraints for this program will be given and discussed in subsequent sections of this paper.

COMPLIANCE APPROACH

A single statistical procedure has been developed to assess compliance with all the regulatory limits established in the NMD. The statistical procedure developed has taken sampling constraints and sample homogeneity into consideration. Sampling headspace from innermost layers of confinement limits sample acquisition to a single sample. This sample may be collected into several SUMMA® canisters simultaneously due to the homogenous nature of the sample matrix. The statistical procedure assumes there is some non-quantifiable error associated with the sampling procedure. This error is introduced when the needle assembly (Section 4.0) is inserted into the innermost layers of confinement (i.e., plastic bags). Due to the nature of the sample and unknown sampling error, the procedure assumes that the majority of the sampling and measurement error is due to laboratory error.

In the absence of replicate sample precision and accuracy data, precision and accuracy data from laboratory procedure performance studies can be used in conjunction with data obtained on individual samples to assess compliance with regulatory limits. Procedure performance data can be used to estimate the precision and accuracy of individual sample analyses if 30 replicates have been analyzed to establish procedure performance precision and accuracy. The statistical procedure developed for this program uses precision and accuracy data obtained from procedure performance studies in conjunction with Z-values, obtained from normal distribution tables, to calculate the values (concentration or LEL) at the upper confidence limit at a specified level of significance. These upper confidence level values are then compared to regulatory limits to determine compliance. The following equations are used to determine compliance with all regulatory limits specified in the NMD:

$$X_{UL} = \sum a_i x_{ci} + \sum a_i s_i Z_{\alpha=0.2} \tag{1}$$

$$\textit{where} \quad X_{ci} = \frac{100 X_{mci}}{\%R_i} \tag{2}$$

$$s_i = \frac{(\%RSD_i)\ X_{mci}}{\%R_i} \tag{3}$$

where

X_{UL} = Upper confidence limit concentration value at the 80% confidence level

a_i = Independent variable [for flammability calculations, this is the reciprocal of the lower explosive limit (LEL); for comparability and no-migration finding, the variable is one]

X_{ci} = Recovery corrected measured concentration of compound i

s_i = Standard deviation of compound i

$Z_{\alpha=0.2}$ = Z-value at 80% confidence level (two-tailed) is 1.29

$\%RSD_i$ = Percent relative standard deviation of compound i (obtained from method performance data)

$\%R_i$ = Percent recovery of compound i (obtained from method performance data)

X_{mci} = Experimentally measured concentration of compound i.

Equation 1 will be used to determine compliance with regulatory limits at the 80% (two-tailed) confidence level using measured concentrations and procedure performance data. A confidence level of 80% is typically used for the purpose of evaluating solid wastes (USEPA, 1989). Analytical methods described in the QAPP, Revision 0 will be used to analyze all samples. A value of one-half the method detection limit will be used when compounds are not detected.

Each laboratory participating in this program will be required to initially analyze 30 replicates to establish procedure performance precision and accuracy. After the initial demonstration, each laboratory will be required to analyze a minimum of seven replicates semi-annually. The precision and accuracy from the continuing procedure performance studies will be compared to the initial data and will be used to revise and update these data.

Initial procedure performance data indicate that typical precision and accuracy values for VOCs are approximately 5% relative standard deviation and 85% recovery, and for H_2 and CH_4 are approximately 3% relative standard deviation and 95% recovery, respectively. These values will be used for the example calculations included in this paper.

3.0 CRITERIA FOR INNERMOST LAYERS OF CONFINEMENT

REQUIREMENT

EPA is requiring that headspace sampling be representative of the entire void space of each waste container emplaced in the WIPP. Until DOE can demonstrate to the EPA, based on data collected, that the headspace sampling of all waste confinement layers is unnecessary, all innermost layers of confinement in a container must be sampled and analyzed.

BACKGROUND

Waste packaging methods are reported in the TRUPACT-II Content Codes (TRUCON) (USDOE,1989). Packaging methods are selected based upon the physical, chemical, and radiological properties of the waste. In addition, operational considerations may influence the waste packaging method selected. Waste packaging configurations are distinguished primarily by the types and quantities of waste confinement layers and the mechanism for bag closure.

COMPLIANCE APPROACH

The bounding conditions for the headspace sampling of the innermost layers of confinement are as follows:

- The innermost layer of confinement is defined as that layer which contains actual waste. In other words, for waste that is packaged within multiple individual plastic bags, only the headspace within the innermost bag containing the waste will be sampled.

- To ensure the representativeness of the headspace sample collected, the innermost layers of confinement headspace sampling should not remove more than 10% of the headspace gas.

- A minimum of one liter of estimated available headspace must be present within the innermost layer of confinement for a representative sample to be obtained. This volume is dictated by (1) the analytical sample size requirement of 100 ml, and (2) the objective of not removing more than 10% of the available headspace gas.

- Based on the waste configuration and packaging, it is anticipated that the total estimated size of the innermost layer of confinement must be 4 liters to ensure the presence of at least 1 liter of available headspace gas.

- The headspace gas within rigid innermost layers of confinement (e.g., glass, metal, and plastic containers) will not be sampled. Dilution of the headspace gas from intrusion of ambient air would preclude obtaining a representative sample. However, waste operations personnel will document the type and size of each rigid innermost layer of confinement and provide a visual description of its contents.

  Bin headspace gas sampling will ensure that VOC sources that may be present within sealed rigid innermost layers of confinement will be identified. This is based on the Sandia National Laboratories' Bin-Scale Test Plan, Addendum 1 (Molecke and Lappin, 1990), which requires that all innermost layers of confinement greater than 60 ml in volume must be breached or opened prior to bin closure and subsequent shipment.

- No field duplicates will be collected from innermost layers of confinement due to the limited available headspace.

- During pretest waste characterization activities, participating DOE generator/storage sites must have standard operating procedures (SOPs) that address requirements to document any non-routine events or occurrences (e.g., the condition of the innermost layers of confinement) that may affect the quality of the headspace sample collected.

4.0 HEADSPACE SAMPLING OF INNERMOST LAYERS OF CONFINEMENT

REQUIREMENT

To evaluate TRU wastes in terms of comparability, DOE must obtain a representative sample of gases and VOCs from the waste containers to be emplaced in the WIPP.

BACKGROUND

The TRU wastes to be emplaced in WIPP as part of the Test Phase are packaged in 55-gallon drums and can contain several waste items individually packaged in layers of plastic. Depending on the operation, waste may be packaged in one or more plastic bags. Pretest waste characterization for the bin-scale tests will include sampling and analyzing gases and VOCs from three areas within drums of TRU waste. These areas include (1) the drum headspace (i.e., the headspace directly under the drum lid), (2) the 55-gallon poly bag headspace, and (3) the innermost layers of confinement headspace. Drum headspace sampling will be included in Revision 2 of the QAPP. In addition, bin headspace gas samples will be obtained (Section 5.0). In order to use the results obtained from the sampling and analysis of drum headspace gases and VOCs to demonstrate compliance in the future when drums could be directly emplaced in the WIPP, DOE must demonstrate to EPA's satisfaction that a drum headspace gas sample is representative of the gases and VOCs within the entire drum.

COMPLIANCE APPROACH

DOE will address EPA's requirement that headspace samples from TRU waste drums be representative of the entire void space within a drum by sampling all of the inner layers of confinement that meet the criteria specified in Section 3.0. All samples will be analyzed for hydrogen, methane, and VOCs. Data obtained from waste characterization for innermost layers of confinement of wastes included in the bin-scale tests will be evaluated to determine whether additional information is needed for wastes included in the alcove tests. To accomplish innermost layer confinement sampling, DOE has developed two SUMMA® canister-based headspace sampling systems, a direct canister system, and a low-volume headspace sampling manifold. Both are described below.

Description of the Direct Canister Sampling Equipment

Figure 2 illustrates the direct canister sampling equipment for innermost bag sampling. Samples are collected using the direct canister sampling equipment by free expansion of innermost layer of confinement headspace gas into an evacuated SUMMA® canister. Figure 2 shows a stainless steel needle fitted into a Swagelok® reducer, a Nupro® 0.5 μm filter, and a port connector that allows the filter to be connected to the 1/4-inch Swagelok® port of the SUMMA® canister's Nupro® valve. Both the port connector and the reducer are made of stainless steel and have Swagelok® fittings. The port connector and the reducer both have internal volumes of approximately 0.5 ml.

The needle, used to puncture the innermost layer of confinement during headspace sampling, is 1/8-inch stainless steel tubing, approximately 5 inches long and sharpened at the end. It has an inner diameter of approximately 0.1 inch with an estimated internal volume of approximately 0.2 ml.

The filter is a Nupro® particulate filter. It has a 0.5 μm sintered stainless steel fritt and has 1/4-inch Swagelok® fittings on both its inlet and outlet. The filter housing is made of stainless steel and is estimated to have an internal volume of approximately 4 ml.

The combined internal volume of these components is approximately 5 ml. This low internal volume, approximately 2 percent of the sample volume, should not significantly affect the quality of the headspace sample being collected.

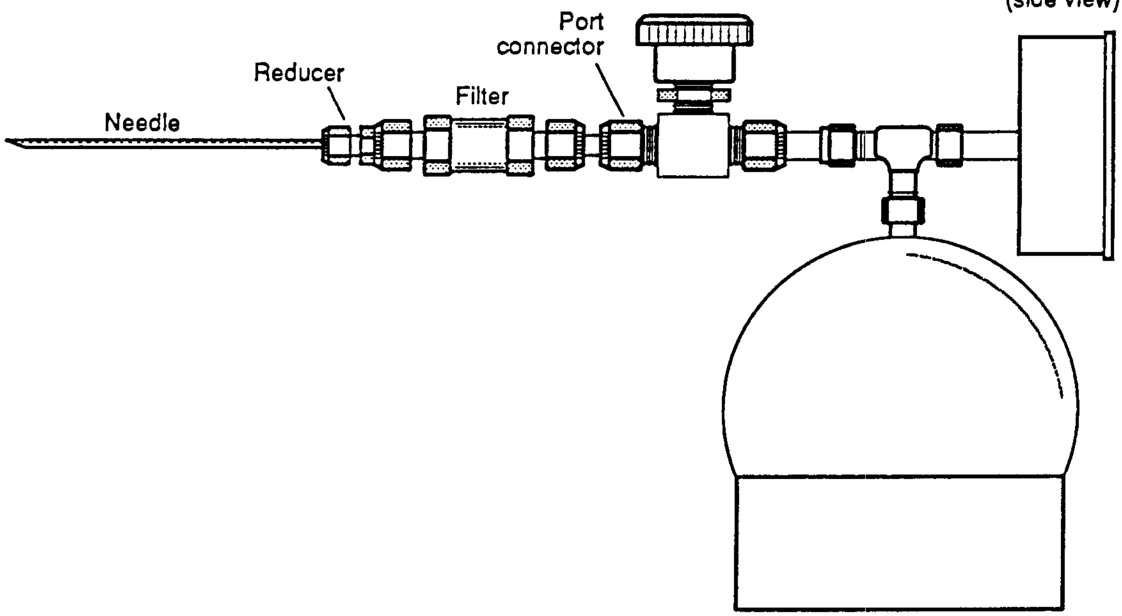

Figure 2. Schematic Diagram of Direct Canister Sampling Equipment

Quality Control Measures for Direct Canister Sampling

- To prevent cross contamination, the needle, adaptors and filter will be disposed of or, if reused, cleaned between sample collections.

- Field blanks and sampling equipment blanks, as well as field reference standards will be collected as QC checks using the sampling equipment to evaluate cleanliness and overall accuracy, respectively.

- The low internal volume of the needle and filter attached to the SUMMA® canister will minimize VOC sample dilution.

- The needle and filter should be purged with zero air or helium and capped for storage to prevent sample contamination by VOCs present in the ambient air.

Description of the Low Volume Manifold Sampling Equipment

The equipment, operation, and QA/QC requirements for low volume manifold sampling are essentially the same as those for 55-gallon poly bag sampling as described in the QAPP, Revision 0. Only minor modifications of the 55-gallon poly bag sampling equipment will be necessary to reduce its overall internal volume. These modifications will include reducing the length and possibly the inner diameter of most pneumatic lines.

5.0 HEADSPACE SAMPLING OF EXPERIMENTAL BINS

REQUIREMENT

DOE must ensure that no container of waste to be emplaced in the WIPP contains potentially flammable mixtures of gases and VOCs, and that the mean concentrations of methylene chloride, trichloroethylene, and carbon tetrachloride do not exceed ten times the mean values reported in its Petition.

BACKGROUND

A container is defined in 40 CFR §260.10 as any portable device in which a material is stored, transported, treated, disposed of, or otherwise handled. During the WIPP Test Phase, DOE plans to conduct bin-scale experiments in the WIPP to assess the rates and potential for gas generation that may influence the long-term integrity of the repository. Four to six drums of TRU wastes will be emptied into test bins and placed in WIPP standard waste boxes (SWBs) for shipment to the WIPP. The experimental bin will be sampled at the generator/storage sites to demonstrate compliance with certain conditions specified in the NMD (Sections 7.0 and 8.0).

COMPLIANCE APPROACH

The design of the bin sampling equipment is a modification of a system used for ambient air sampling for EPA Method TO-14 (USEPA, 1988). The ambient air system from which the bin sampling equipment is adapted has been used by EPA, Office of Radiation Programs, to collect samples of the air in the WIPP repository. As a bin sampling device, the equipment is used to collect a headspace sample for flammability testing (ASTM Designation E681-85). The remainder of the sample is analyzed for the the other program-required analytes.

Description of the Bin Sampling Equipment

The bin headspace sampling equipment, shown in Figure 3, consists of a portable metal box (not shown) containing a pump, flow controlling devices, an electronic timer/controller, a flow meter, filters, valves, pneumatic lines, sample canisters, and other equipment. The metal box houses and protects the electronic and pneumatic equipment and allows the bin headspace sampling equipment to be easily transported. The pump and flow controlling devices are used to recirculate and homogenize bin headspace gas at a preset flow rate for a programmed length of time, thereby making the collection of a representative headspace sample possible. The flow rate and time will be a function of waste type and packging configuration.

The bin headspace sample is automatically collected by the bin sampling equipment after the programmed recirculation time has elapsed. The pre-programmed timer/controller simultaneously closes the solenoid valve at the system outlet and switches the two three-way solenoid valves to direct flow into the canister(s). Since the solenoid valve at the system outlet has been closed, the canister(s) collect bin headspace gas across the pneumatic flow controller until the canister(s) reaches a pressure of approximately 15 psig.

Once the canister(s) is pressurized, recirculation flow through the sampling equipment continues; however, the bin headspace gas is now diverted entirely through the pressure regulating valve on the pump head. The equipment continues to operate in this manner for several minutes to ensure that the canister(s) is properly filled. The pre-programmed timer/controller then switches the three-way solenoid valves and outlet solenoid valve back to the initial recirculate position. The equipment continues to recirculate bin headspace gas until sampling technicians close the canister's manually operated bellows valves and turn off the pump.

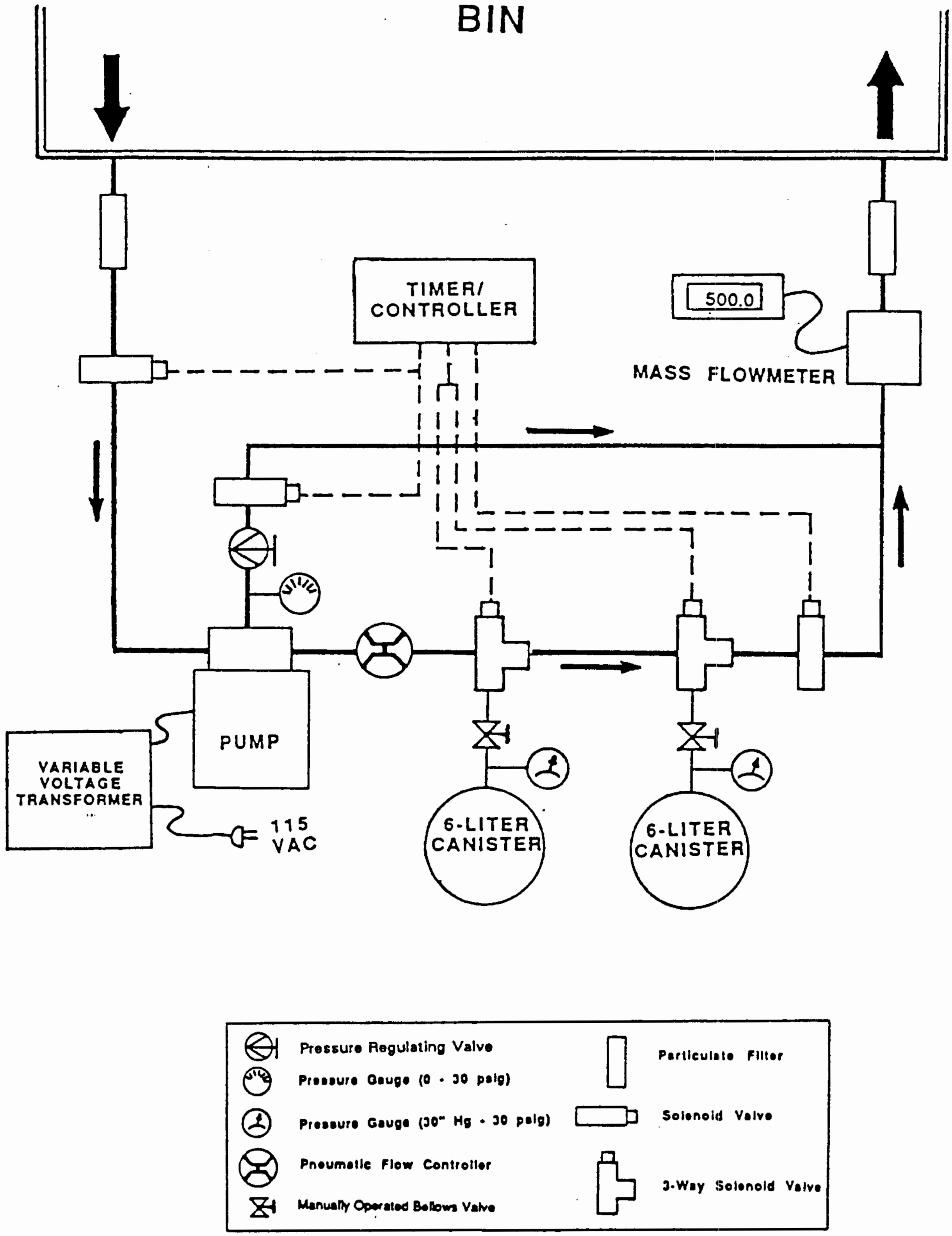

Figure 3. Schematic Diagram of Bin Sampling Equipment

Quality Control Measures

Measures include cleaning and leak checking the bin headspace sampling equipment. In the laboratory, the bin sampling equipment is cleaned by purging with humidified zero air. After purging, a sample of zero air is collected through the bin sampling equipment and analyzed for the program-required analytes. Bin sampling equipment cleanliness may also be checked by purging with zero air and monitoring the zero air with an optional photoionization detector.

The bin sampling equipment is also checked for leaks after each cleaning. This is performed by pressurizing the bin sampling equipment to two atmospheres with zero air.

In the laboratory, field reference standard gas (pressurized cylinder gas containing known analytes at known concentrations) is also circulated through the bin sampling equipment and a field reference standard sample is collected in the same manner as a bin headspace sample. The results of this sample indicate the efficiency of sampling and analytical recovery.

Field duplicates may be collected if sufficient bin headspace is available.

6.0 DEMONSTRATION OF COMPARABILITY

REQUIREMENT

Prior to receiving waste at the WIPP for bin-scale and alcove testing, DOE must demonstrate, by waste type, that the composition of hazardous constituents in the headspace of containers is similar to those concentrations reported in the Petition. The headspace concentrations of the five major hazardous constituents reported by DOE must be compared to the maximum allowable concentrations in EPA's NMD (Table 1). No drum of waste containing in excess of these maximum concentrations may be sent to the WIPP without prior treatment or modification to reduce the headspace concentrations to below the maximum levels.

BACKGROUND

In accordance with 40 CFR §268.6(a)(1), a no-migration demonstration must include an identification of the specific waste(s) for which the demonstration is made. Therefore, EPA is requiring that the DOE demonstrate, by analyzing representative headspace samples, that the wastes included as part of the WIPP Test Phase are similar to those described in the Petition.

COMPLIANCE APPROACH

In order to comply with the maximum concentration comparability conditions of the NMD, DOE will collect and analyze a sequence of headspace samples from the innermost layers of confinement within waste drums (Section 4.0). Headspace samples will be collected from within the drum 55-gallon poly bag and from within all innermost layers of confinement which meet the criteria specified in Section 3.0. The 55-gallon poly bag will be sampled in accordance with procedures and requirements specified in the QAPP, Revision 0. The procedures and requirements for sampling innermost layers of confinement will be included in Revision 1 of the QAPP. A preliminary discussion of innermost layers of confinement sampling is presented in Section 4.0.

Samples from within the 55-gallon poly bag and from the innermost layers of confinement will be used to determine the headspace concentrations of carbon tetrachloride (CCl_4), methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) (Figure 4). Once determined, the maximum headspace concentration found in the innermost layers of confinement of each of these five major constituents will be compared at the 80% confidence level to the compliance values listed in Table 1. For example, in a given drum of a particular waste type, the concentration of CCl_4 in each innermost layer of confinement will be determined and the maximum value identified. It is the highest concentration of CCl_4 at the upper confidence limit that will be compared to the maximum allowable concentration in Table 1 (See example calculation).

The 55-gallon poly bag headspace gas concentration at the upper confidence limit of each of the five major hazardous constituents will also be compared to the maximum allowable concentrations in Table 1. If this comparison and the one described above indicate that the maximum concentrations of each of the five major hazardous constituents are less than the maximum allowable concentrations specified in Table 1, then DOE may place the contents of the drum being tested into a bin for inclusion in the WIPP test program.

Example Calculation

As an example, Table 4 presents hypothetical concentrations of VOCs from the innermost layers of confinement of a drum of TRU waste. Consider CCl_4 in the innermost layers of confinement. The maximum measured concentration of CCl_4 is 0.052 volume % in innermost layer of confinement number 5. According to Section 2.0, the recovery corrected measured concentration, X_c, of CCl_4 is given by Equation 2.

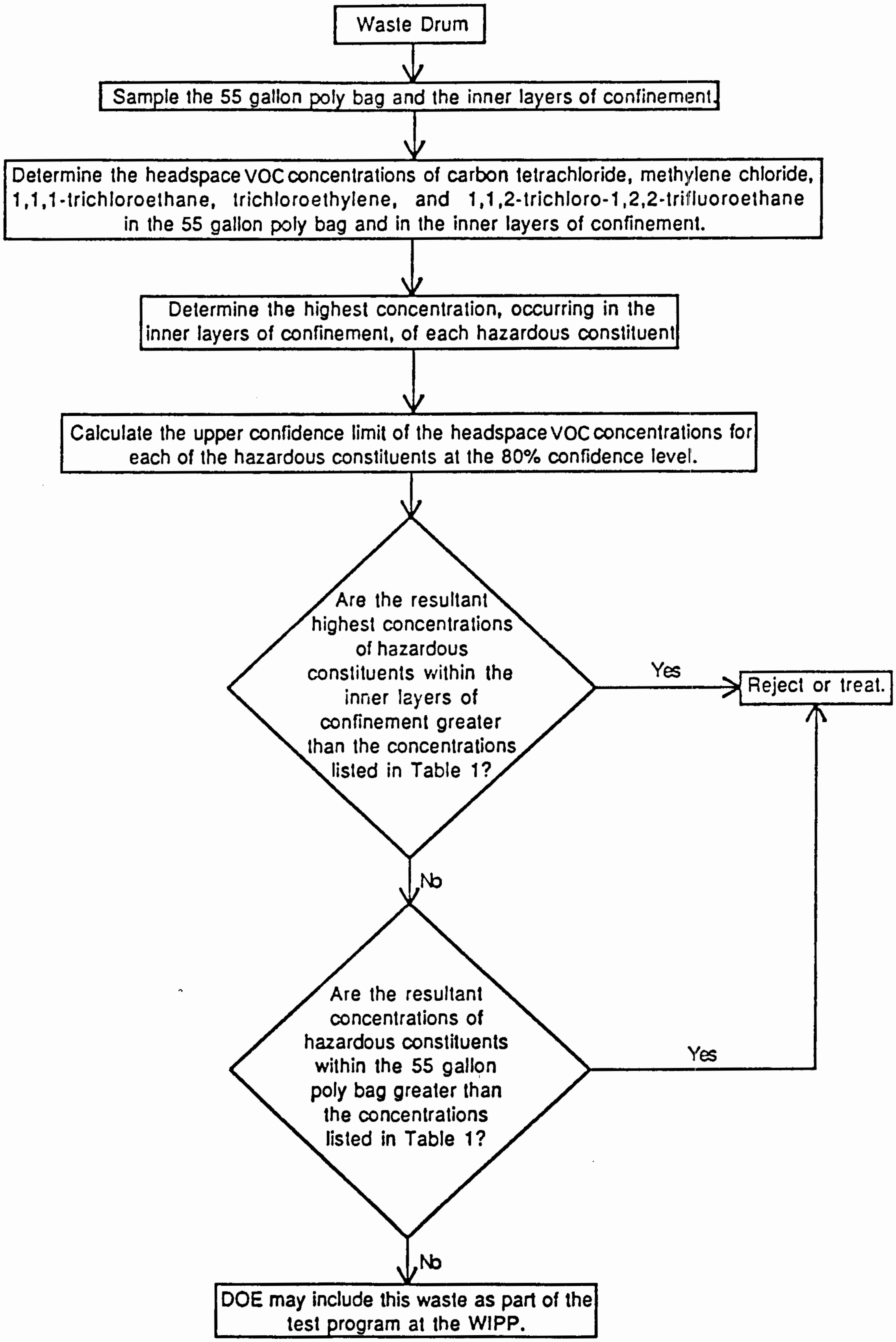

Figure 4. Comparability Flowchart

Table 4. Hypothetical Concentration Data From a Drum of Waste Type I (volume percent)

Inner Layer of Confinement	CCl_4	CH_2Cl_2	TCA	TCE	Freon-113
55-gallon bag	0.032	0.18	1.0	0.032	0.014
1	0.040	0.21	1.2	0.022	0.0060
2	0.0090	0.18	0.82	0.060	0.009
3	0.022	0.090	1.3	0.0090	0.021
4	0.035	0.11	0.71	0.040	0.014
5	0.052	0.32	1.0	0.035	0.019

Where X_{mc} is the measured concentration of CCl_4 and %R is the percent recovery of CCl_4. Assuming %R equals 85%, the recovery corrected measured concentration of CCl_4 in innermost layer of confinement 5, is 0.061 volume percent (Table 5). Now assuming the relative standard deviation of this value is equal to 5%, the standard deviation, s, is given by Equation 3. In this example, s = 0.0031.

Finally, the concentration at the upper confidence limit, X_{UL}, at the 80% confidence level can be calculated according to Equation 1. For CCl_4 in innermost layer of confinement 5, the concentration at the upper confidence limit is 0.065 volume percent. Similarly, the results of this calculation for the maximum concentrations of the other VOCs of interest in the innermost layers of confinement are summarized in Table 5. In all cases, including the 55-gallon poly bag, the maximum concentrations at the upper confidence limit at the 80% confidence level are less than the compliance values listed in Table 1. Therefore, the waste in this drum may be included as part of the WIPP test program.

Table 5. Results From Example Calculations (volume percent)

Constituent	X_{mc}	X_c	s	X_{UL}
CCl_4	0.052	0.061	0.0031	0.065
CH_2Cl_2	0.32	0.38	0.019	0.40
TCA	1.3	1.5	0.076	1.6
TCE	0.060	0.071	0.0035	0.076
Freon-113	0.021	0.025	0.0012	0.027

7.0 DEMONSTRATION OF NO-MIGRATION

REQUIREMENT

Prior to shipment of waste to the WIPP, DOE must ensure that the no-migration finding by EPA remains valid by demonstrating that for each container of waste to be sent to the WIPP (drum or bin), the mean headspace concentrations of three of the hazardous constituents reported in the Petition are less than or equal to the mean headspace concentrations included in the NMD (Table 2).

BACKGROUND

In accordance with 40 CFR §268.6, DOE, in its Petition, demonstrated that the concentrations of hazardous constituents in air would not exceed health-based limits at the WIPP unit boundary. EPA's no-migration finding for air releases is based upon the mean headspace concentrations for volatile organic constituents reported by DOE in its Petition. Therefore, EPA is requiring that this assessment of the mean headspace concentrations associated with experimental wastes be evaluated to ensure that the no-migration finding remains valid.

COMPLIANCE APPROACH

In order to comply with this condition of the NMD during the bin-scale tests, DOE will collect a headspace sample from within each experimental bin. The procedures and requirements for sampling experimental bins will be included in Revision 1 of the QAPP. A preliminary discussion of experimental bin sampling is presented in Section 5.0. Based on the data obtained from the bins and innermost layers of confinement within the drums, DOE will evaluate the need to obtain additional information on the concentrations of hazardous constituents within drums that will be emplaced in the WIPP during the alcove tests.

Headspace samples from the experimental bins will be used to determine the concentration of CCl_4, CH_2Cl_2, and TCE (Figure 5). Once determined, the headspace concentrations of each of these hazardous constituents will be compared at the 80% confidence level to the allowable concentrations specified in Table 2 (see example calculation). If this comparison indicates that the headspace concentrations of each of the three hazardous constituents are less than those specified, the DOE may emplace the bin in the WIPP as part of the test program.

Example Calculation

As an example, Table 6 presents hypothetical concentrations, recovery corrected measured concentrations, standard deviations, and upper confidence limit concentrations for the three VOCs of interest. According to Section 2.0, the recovery corrected measured concentration, X_c, of CCl_4 is given by Equation 2. Where X_{mc} is the measured concentration of CCl_4 and %R is the percent recovery of CCl_4. Assuming %R equals 85, the recovery corrected measured concentration of CCl_4 in this example bin is 0.020 volume percent. Assuming the relative standard deviation of this value is equal to 5%, the standard deviation, s, is given by Equation 3. In this example, s = 0.0010.

Finally, the concentration at the upper confidence limit, X_{UL}, at the 80% level can be calculated according to Equation 1. For CCl_4, in this example, the concentration at the upper confidence limit is 0.021 volume percent. For all three hazardous constituents, concentrations at the upper confidence limit at the 80% confidence level, X_{UL} are less than the compliance values in Table 2. Therefore, DOE may emplace this bin in the WIPP as part of the test program.

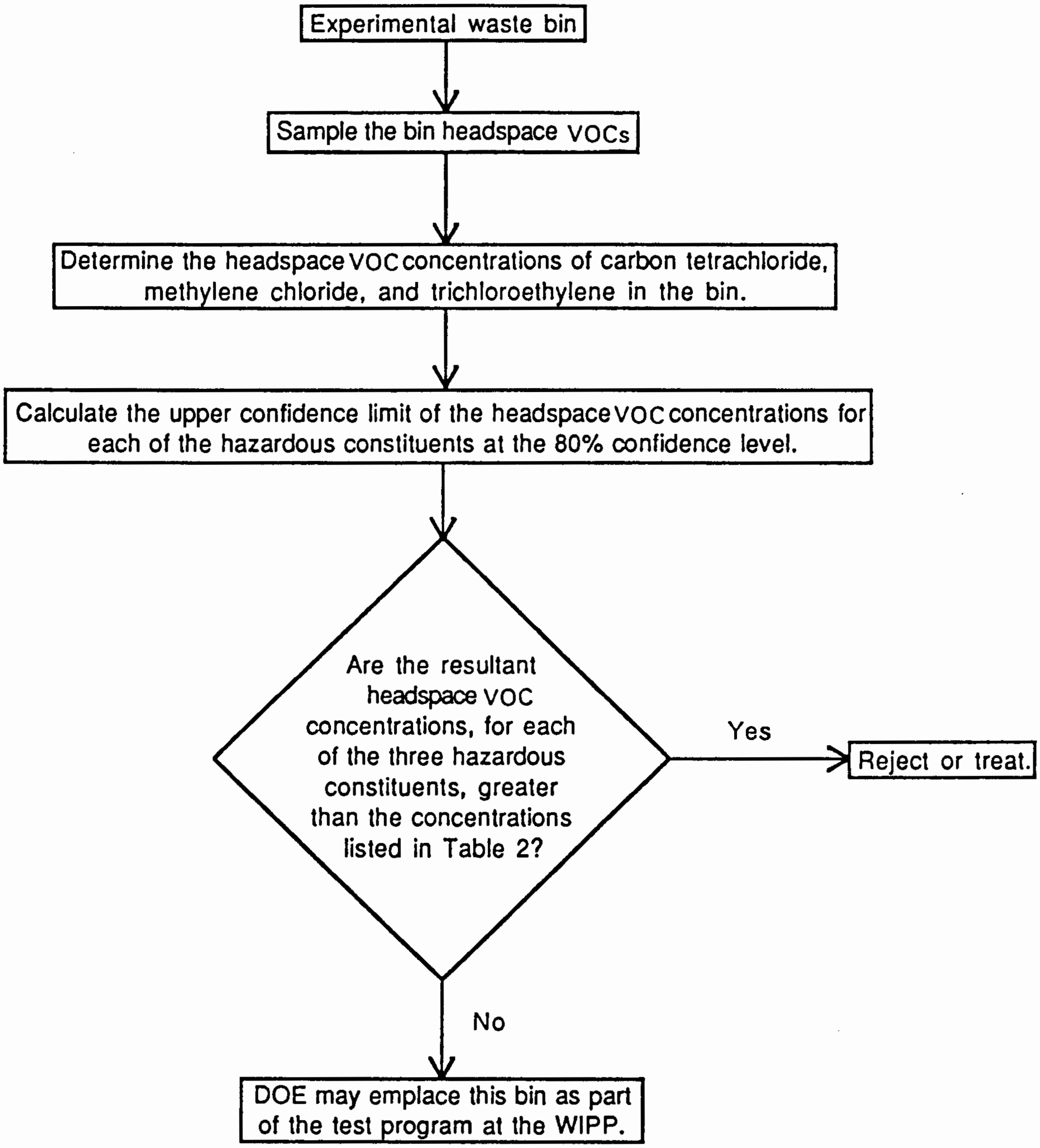

Figure 5. No-Migration Demonstration Flowchart

Table 6. Results of Example Calculations for No-Migration Demonstration (volume percent)

Constituent	X_{mc}	X_c	s	X_{UL}
CCl_4	0.017	0.020	0.0010	0.021
CH_2Cl_2	0.032	0.038	0.0019	0.040
TCE	0.029	0.034	0.0017	0.036

8.0 DETERMINATION OF FLAMMABILITY

REQUIREMENT

DOE must ensure that each waste container emplaced underground at the WIPP has no layer of confinement containing flammable mixtures of gases and vapors or mixtures of gases and vapors that could become flammable when mixed with air. EPA believes that the potential for fire or explosion exists during waste handling activities prior to final waste emplacement, when credible accident scenarios are possible. The following four requirements must be met to demonstrate compliance:

a. DOE must test each drum or individual container for hydrogen, methane, and flammable volatile organic compounds (VOCs).

b. If the measured concentration of flammable VOCs (excluding methane) exceeds 500 ppmv in the sample, then an explicit flame test must be performed.

c. The concentration values of hydrogen and methane from all headspace samples will be evaluated using the Le Chatelier formula (Coward and Jones, 1952) to determine if the binary mixture exceeds 50% of the theoretical LEL.

d. DOE must determine the length of time during waste handling activities in which the mixture of gases and VOCs will remain below 50% of the theoretical LEL, and emplace the waste prior to exceeding that time limit. Theoretically determined hydrogen concentrations will be verified.

BACKGROUND

EPA stated in the preamble to the final rule that if a fire or explosion occurred as a result of accidental ignition of flammable gases or vapors in waste containers, retrieval, if necessary, could be much more difficult and the possibility of a release of hazardous constituents above health-based limits would be increased. To assure a sufficient margin of safety, EPA defined any mixture of gases that exceeds 50% of the LEL of the mixture in air as potentially flammable.

COMPLIANCE APPROACH

Figure 6 shows the overall approach to compliance with the flammability testing requirements. Each of the four requirements above are addressed separately for clarity in the compliance approach. The sampling requirements to address 8a have been previously addressed in Section 5.0 of this document. The analytical methods for determining the concentrations of hydrogen, methane, and VOCs have been described in the QAPP, Revision 0, provided to EPA for its review. Therefore, this document focuses on requirements 8b through 8d.

8.a. The compliance approach to bin headspace sampling, which was discussed in Section 5.0, is also valid for flammability determinations. Data from the testing of drum innermost layers of confinement for hydrogen, methane, and VOCs will be used to assess compliance for alcove tests.

8.b. The analytical results from bin headspace samples will be evaluated to determine if significant levels of flammable VOCs are present in the bins included in the WIPP test program. Significant levels of flammable VOCs (Table 3) are defined as measured concentrations (excluding methane) of 500 ppmv or greater. To perform the evaluation,

1. Correct measured analyte concentrations for recovery using Equation 2, Section 2.

2. Calculate analyte standard deviations using analyte recovery corrected measured concentrations and analyte relative standard deviation values using Equation 3, Section 2.

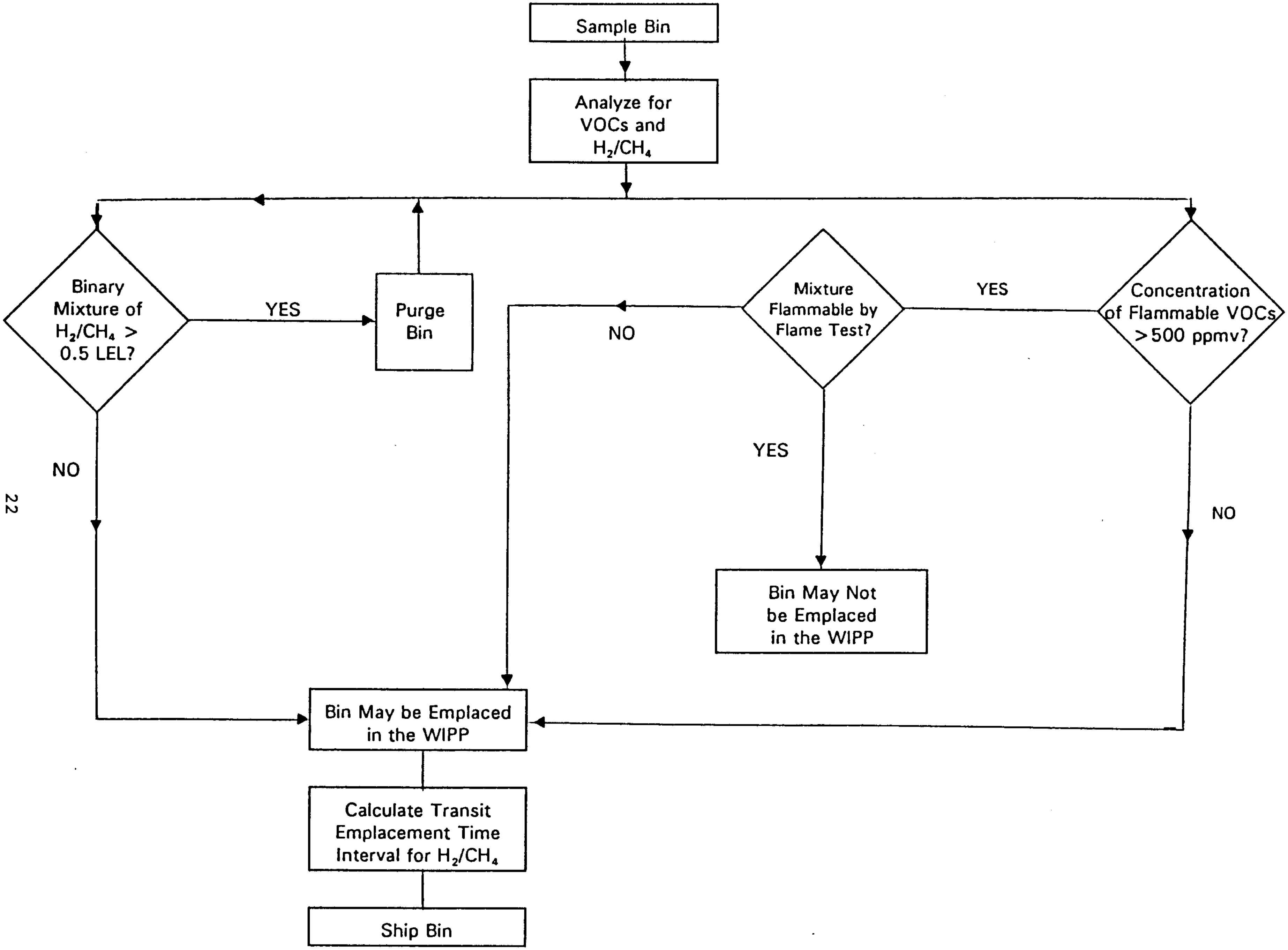

Figure 6. Compliance With Flammability Testing Requirements

3. Sum the upper confidence limit concentrations of all analytes using Equation 1, Section 2. If the summed value exceeds 500 ppmv at an 80% confidence level, then the flammability of the headspace sample will be determined by the flame test.

The flammability of a headspace vapor mixture will be evaluated using a modified version of ASTM Method E 681-85 when the sum the upper confidence limit concentrations of flammable VOCs in the mixture exceeds 500 ppmv. A headspace vapor mixture is considered flammable if, under the specified conditions of the test, the mixture propagates a flame from the ignition source to the test vessel walls. The determination of flame propagation from an ignition source to the test vessel wall is qualitative. Since qualitative determinations do not lend themselves to statistical error analysis, the accuracy of flame test determinations will be assured by using standardized apparatus, procedures, and operator qualifications. DOE is currently developing a standardized flame test apparatus and procedure based on ASTM Method E 681-85.

As an example, Table 7 presents hypothetical concentrations, recovery corrected concentrations, standard devaitions, and upper confidence limit concentrations for three flammable VOCs. Using these data, the sum of the upper confidence limit concentrations is equal to 510 ppmv. Since 510 ppmv exceeds the action limit, a flame test of the mixture must be performed. If, under the conditions of the flame test, the mixture propagates a flame from the ignition source to the test vessel walls it is flammable. Otherwise, it is not.

Table 7. Simulated Data and the Results of
Sample Calculations on Three Flammable VOCs (in ppmv)

Flammable VOC	X_{mc}	X_c	s	X_{UL}
Benzene	120	140	7.1	150
Diethyl ether	120	140	7.1	150
Cyclohexane	170	200	10	210

8.c. The Le Chatelier formula (Coward and Jones, 1952) will be used to determine if a headspace gas mixture exceeds 50% of the lower explosive limit (LEL) for binary mixtures of hydrogen and methane. The Le Chatelier formula is generated when the reciprocal of the LEL is substituted for the independent variable "a" in Equation 1. A binary gas mixture that exceeds 50% of the theoretical LEL is flammable. To perform the Le Chatelier determination,

1. Correct measured analyte concentrations for recovery using Equation 2, Section 2.

2. Calculate analyte standard deviations using analyte recovery corrected concentrations and analyte relative standard deviation values using Equation 3, Section 2.

3. Calculate a value using the Le Chatelier formula expressed as Equation 1, Section 2. The mixture exceeds 50% of the theoretical LEL if the calculated value exceeds 0.5 with an 80% degree of confidence.

As an example, Table 8 presents hypothetical concentrations, recovery corrected concentrations, standard devaitions, upper confidence limit concentrations, and LEL values for a binary mixture. The LEL values are those reported by the NFPA for hydrogen and methane. Using these data, the calculated Le Chatelier formula value is 0.48, which is less than 0.5. The binary mixture does not exceed 50% of the theoretical LEL at an 80% degree of confidence and is therefore non-flammable.

Table 8. Simulated Data and the Results of Sample Calculations for the Gases of a Binary Mixture (in v/v%)

Gas	X_{mc}	X_c	s	X_{UL}	LEL	X_{UL}/LEL
H_2	1.1	1.2	0.036	1.2	4.0	0.030
CH_4	0.82	0.86	0.026	0.90	5.0	0.18

8.d As an example of generating predictive formulas for bin headspace hydrogen concentrations as a function of time, it is assumed that the contents of six drums are emptied into a bin and the loaded bin is then placed in a SWB. The SWB containing the bin remains at the site for a period of time, and hydrogen mass balances are applied to each container (bin, SWB) as follows:

1. The equation (Brodkey and Hershey, 1988) describing the build-up of hydrogen inside the bin during this site storage time is stated as "the accumulation of hydrogen (dX_{bin}/dt) within a bin is equal to the generation (G/V_{bin}) inside the bin, minus the outflow [R_1 (X_{bin} - X_{swb})] from the bin," or mathematically,

$$\frac{dX_{bin}}{dt} = (G \; / \; V_{bin}) \; - \; (R_1 \; / \; V_{bin}) \; (X_{bin} \; - \; X_{swb}) \tag{4}$$

where

X_{bin} = the hydrogen volume fraction in the bin [(X_{bin} - X_{swb}) is the gradient across the bin filters]

X_{swb} = the hydrogen volume fraction in SWB (outside the bin)

G = the hydrogen gas generation rate term inside the bin (liters/sec) [Note: methane generation is accounted for in the rate term used for applicable waste types (NuPac, 1989)]

R_1 = the effective release rate of hydrogen across the bin liners and bin filters (liters/sec)

t = time (sec)

V_{bin} = void volume in a bin (liters).

2. Similarly, the equation describing the hydrogen build-up inside the SWB, but outside the bin, during this site storage time is,

$$\frac{dX_{swb}}{dt} = (R_1 / V_{swb})(X_{bin} - X_{swb}) - (R_2 / V_{swb}) X_{swb} \qquad (5)$$

where

V_{swb} = void volume in an SWB (outside the bin) (liters)

R_2 = the effective release rate of hydrogen across the SWB filters (liters/sec).

The simultaneous solution of Equations 4 and 5 provides expressions for X_{bin} and X_{swb}, the hydrogen concentrations inside the bin and SWB containers during site storage.

3. The equations describing the system after the loaded SWB is placed in the TRUPACT-II shipping container are written as,

$$\frac{dX_{bin}}{dt} = (G / V_{bin}) - (R_1 / V_{bin})(X_{bin} - X_{swb}) \qquad \text{(inside the bin) (6)}$$

$$\frac{dX_{swb}}{dt} = (R_1 / V_{swb})(X_{bin} - X_{swb}) - (R_2 / V_{swb})(X_{swb} - X_{Tru}) \qquad \text{(inside the SWB) (7)}$$

$$\frac{dX_{Tru}}{dt} = (R_2 / V_{Tru})(X_{swb} - X_{Tru}) \qquad \text{(inside the TRUPACT-II) (8)}$$

where

X_{Tru} = the hydrogen volume fraction inside the TRUPACT-II (outside the SWB)

Equations 6, 7, and 8 are solved using numerical methods (Reklaitis et al., 1983; Press et al., 1986) to obtain solutions for hydrogen concentrations, as a function of time, inside the three void volumes during shipment and emplacement.

4. A data plot is made of time versus discrete values of bin headspace concentration and a polynomial is fit to the data. This gives an equation to calculate the time remaining before 50% of the LEL is exceeded, based upon either a headspace sample and/or knowledge of storage time. In using the time remaining under the conservative assumptions of maximum generation and minimum release conditions, compliance under anticipated actual conditions can be expected.

The general procedure is summarized as follows:

- An initial value for bin headspace hydrogen concentration is obtained.

- Based on the initial sample value, the number of days remaining until 50% of the LEL is exceeded is determined from the data plot of calculated concentrations versus time. The data plot will make allowance for a three-day shipping period.

- If the sampling method is not used, the data plot can be used to determine remaining time below LEL, given knowledge of the time since the containers were loaded.

Using the sampling method allows maximization of the amount of time a bin may be stored, and thereby avoids unnecessary storage restrictions.

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