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May 2, 1996

Mr. Steve Zappe
New Mexico Environment Department
Hazardous & Radioactive Materials Bureau
2044 A Galisteo Street
Santa Fe, N.M. 87502

Dear Mr. Zappe:

Enclosed are responses to comments made on the Transuranic Waste Characterization Sampling and Analysis Methods Manual, Revision 0, and two copies of Revision 1 of this document. Revision 1 of the Methods Manual was generated in response to the comments which were attached to the Notice of Deficiency comments on the Waste Isolation Pilot Plant Resource Conservation and Recovery Act Part B Permit Application.

If you have any questions regarding the Methods Manual, or require additional information, please contact Mr. Craig Snider at (505) 234-7452.

Sincerely,

James A. Mewhinney
for Michael H. McFadden
Assistant Manager
Office of Regulatory Compliance

Enclosures

cc w/enclosures:
S. Narasimbachari, A.T. Kearney
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REVIEW COMMENTS
TRANSURANIC WASTE CHARACTERIZATION
SAMPLING AND ANALYSES METHODS MANUAL
REVISION 0, MAY 1995

GENERAL COMMENTS

1) Overall, detail concerning corrective action measures for analytical procedures is lacking. For example, Method 430.2, Section 8.5.2 states that "If the percent difference (%D) criterion is not met, corrective action must be taken." However, there is no guidance for the analyst on what corrective action may be necessary. Although the reader is referred to the Quality Assurance Program Plan (QAPP) for corrective action, this information should be included in the Transuranic Waste Characterization Sampling and Analyses Methods Manual (Manual). Additional detail regarding corrective action measures is required for all procedures outlined in the Manual.

Response

The Methods Manual has been revised to reference a new section that has been added to the WAP that specifies the corrective action process associated with nonconformances. This WAP section (Section C8-13) is consistent with QAPP Section 2.1.2.1. All of the analytical procedures in the Methods Manual now reference both the QAPP Section 2.1.2.1 and WAP Section C8-13 for corrective action. In addition, Methods Manual procedures that directly reference SW-846 methods have been revised to reference SW-846 with respect to required corrective action if acceptance criteria are not met.

2) Some of the Quality Control (QC) criteria outlined in the Manual are less stringent than the SW-846 standards. For example, percent relative standard deviation (%RSD) for VOCs in Method 430.2 (Table 3 and Section 8.5.1.2) is stated to be less than 35%, but SW-846 requires less than 30%. It is understood that the Manual is "based" on SW-846 methods and the methods have been modified for DOE. However, when QC requirements are less stringent than those in SW-846, justification for the modifications is required to demonstrate that the integrity of the methods has not been compromised.

Response

Methods Manual Procedure 430.2 is for the analysis of headspace gas samples. Although based on SW-846 Methods 8240 and 8260, no equivalent analytical method is included in SW-846. This procedure is similar to the SW-846 methods with respect to calibration requirements and quality control, but the QAOs are based on the requirements of the program. The acceptance criterion of %RSD < 35 is adequate for the determination of the headspace gas analytes. The headspace gas analytical methods were developed by DOE specifically for TRU Waste Characterization. The stability and integrity of these methods have been demonstrated during original method development and over the course of sampling and analyzing TRU waste headspace gas for the past five years.

3) The Manual frequently references other documents such as the QAPP and the PDP for information. For example, Section 1.1 of Method 110.1 states that "The quality assurance requirements for this procedures are described in the *Transuranic Waste Characterization Quality Assurance Program Plan*" and Section 8.1 of Method 120.1 indicates that the "Headspace gas

collection in accordance with the requirements specified in the QAPP may be necessary...". Since laboratory personnel will rely on the Manual for project-specific analytical requirements, and must be able to readily access this information, it would prove more useful if Manual were more "stand-alone" by including referenced information (except for SW-846.)

Response

A document hierarchy has been added to the WAP. In addition, the Methods Manual has been revised to reference applicable portions of the WAP. DOE has developed the Methods Manual for use in conjunction with the WAP and the QAPP. Any site that characterizes waste for WIPP must meet the requirements of many documents, including the QAPP, PDP Plans, and WAP. The Methods Manual (as well as the QAPP or the PDP Plans) were never intended to be "stand alone." To incorporate into the Methods Manual all applicable requirements of the QAPP and PDP Plans would result in a very large and complex document. DOE believes it is more efficient and effective to separate appropriate quality assurance, performance demonstration, and sampling/analytical requirements into unique documents. EPA follows this same strategy by issuing separate documents that contain sampling and analytical requirements (SW-846), quality assurance (QAMS documents), and their appropriate performance demonstration programs.

4) The Manual frequently states that the analytical procedures and equipment should operated by "experienced" analysts. For example, Method 510.1, Section 1.1 states that the procedure is "restricted to use by, or under supervision of, analysts experienced in the use of Mass Spectrometry (MS) and skilled in the interpretation of mass spectra." However, level of expertise that DOE requires for these analysts is not specified. The Manual should include an overview of these criteria, and reference where the detailed experience requirements are presented.

Response

The program-required minimum training and expertise for key analytical personnel has been included in Appendix C8 of the WAP, consistent with the QAPP. Procedures that specify unique training requirements have been revised to indicate minimum training and qualification requirements are included in the WAP.

5) The Manual frequently states that certain procedures or information must be "implemented with the site-specific standard operating procedures." For example, Section 10.0 of Methods 430.1 through 650.7 indicates that "each laboratory must have standard operating procedures (SOPs) documenting and describing activities involved in using this procedure." To ensure consistency among all sites relative to the sampling and analysis procedures outlined in the Manual, provide more detail on the required content of these SOPs.

Response

The Methods Manual procedures have been revised to state (in Section 1.0, "Scope and Application") that site specific SOPs must include all of the elements found in Methods Manual procedures.

6) Section 6.0 of Methods 110.1 through 310.2 states that "Studies to characterize TRU waste require careful planning to prepare facilities, develop written documentation, secure laboratory support, and evaluate data." The meaning of this statement is unclear. Clarify this assertion with regard to the sampling methods presented in the Manual. If the laboratory is required to conduct

such studies, then provide a detailed outline that addresses requirements for preparation of facilities, documentation development, laboratory support, and data evaluation.

Response

The Methods Manual has been revised as, "The activities specified in this procedure...".

7) Several of the methods state that if criteria are not met, the data should be flagged. For example, Section 10.6 of Method 640.1 states that "Duplicates which do not meet these criteria should be flagged." To ensure that each laboratory is using the same flags on the data packages, provide a list of the appropriate lab qualifiers along with the corresponding definitions.

Response

The WAP has been revised to include data qualifying flags, and definitions, for use if laboratory QC samples reported with the data do not meet the acceptance criteria. The waste characterization program already has flags for qualifying blanks, dilutions, and low or no-detect samples. These flags are included in the analytical sections of the QAPP. A new flag has been added to the WAP, 'Z' which indicates that the data is estimated because one or more QC samples did not meet the acceptance criteria. These flags and definitions have also been added to the Methods Manual Preface. Each of the analytical procedures (Quality Control Section 10.1 or 10.2) have been revised as, "Data qualifying flags are included in the preface of this Methods Manual."

8) The Manual does not adequately address analysis for formaldehyde and hydrazine in all instances. For example, Tables 4 of Procedures 430.1 and 430.2 do not include the characteristic ions for the compounds, and Tables 5 of the methods state that "Sites required to analyze samples for formaldehyde and hydrazine must determine the appropriate internal standard for each." To obtain consistent and comparable data, clearly outline the information necessary (e.g., characteristic ions, internal standards)to analyze these compounds in the Manual.

Response

Only select sites are required to analyze samples for formaldehyde and hydrazine (i.e., Oak Ridge National Laboratory, Los Alamos National Laboratory, Savannah River Site). This is stated in the headspace gas VOC and solidified VOC analytical Procedures and appropriate sections of the WAP. Sites required to analyze samples for these constituents must develop analytical methods (including characteristic ions and internal standard requirements) and submit this information for approval in accordance with Appendix C7 of the WAP. The Methods Manual has been revised as, "This procedure is not currently approved for the analysis of formaldehyde and hydrazine. Sites required to analyze samples for these compounds must develop analytical methods and submit them for review and approval in accordance with Appendix C7 of the WIPP Waste Analysis Plan. For convenience, Appendix C7 of the WIPP Waste Analysis Plan has been reprinted in the preface of this Methods Manual."

9) The Manual should be revised to be consistent with the Part B permit application Waste Analysis Plan (WAP). Some of the discrepancies are noted in specific comments, but forthcoming revisions of the manual should be revised, as appropriate, to be consistent with the WAP.

Response

Appropriate revisions to the Methods Manual have been submitted to NMED for review with the revised WIPP Part B Permit Application. The Methods Manual has been made consistent with the WAP and has been revised to address NMED comments. However, it should be noted that certain portions of the Methods Manual do not apply to the WAP. For example, the analysis of hydrogen and methane is not addressed in the WAP.

10) It as assumed the Rev. 0. is the most recent version of the Manual, as this was the document provided by DOE when NMED requested the most updated version. If Rev. 0. is not the most recent version of the Manual, the latest version should be provided.

Response

Revision 0 of the Methods Manual was the most current version at the time of WIPP Part B Permit Application submittal. Revisions to the Methods Manual to address NMED comments have been submitted for review and approval with the revised WIPP Part B Permit Application per Appendix C7 of the WAP.

REVIEW COMMENTS
TRANSURANIC WASTE CHARACTERIZATION
SAMPLING AND ANALYSES METHODS MANUAL
REVISION 0, MAY 1995

SPECIFIC COMMENTS

Preface

Purpose of the Manual, page v: The following concerns regarding language in the Preface should be addressed:

1. The first paragraph states that the Manual is a "unified" source of sampling and analysis information which enables facilities to comply the current requirements of the QAPP and the WIPP TRU Waste Characterization Program. However, the document does not indicate that requirements of the WAP must also be met. Since the Manual is a key source of information that is heavily referenced throughout the WAP and since the WAP drives all other waste analysis and waste characterization documents, revise the Manual to state that compliance with the WAP must also be met.

   Response

   The Preface of the Methods Manual has been revised as, "...implementing the Program requirements specified in the QAPP and the WIPP Waste Analysis Plan."

2. The Manual indicates that each site is required to document procedures for those methods where only guidance, rather than step-by-step procedures, is offered from DOE (e.g., non-destructive characterization). The last sentence of the second paragraph on this page states that each DOE site must "demonstrate the efficacy of such procedures". Discuss the elements and level of detail that is required from each site to fulfill this requirement.

   Response

   By meeting all of the QC requirements (e.g., training), consistency will be ensured. The text has been revised as, "Sites must meet all of the specified quality control requirements of the applicable procedure."

3. The last paragraph of the Preface states that "Future revisions of this Methods Manual will be published to reflect requirements in future QAPP revisions." Since the Manual is heavily referenced in the Part B permit application's WAP, any Manual revisions should also be dependent on permit application revisions. The Manual should be revised to indicate this.

   Response

   The Methods Manual has been revised as, "Any changes to the Methods Manual must be submitted for review and approval in accordance with Appendix C7 of the WIPP Waste Analysis Plan." In addition, Appendix C7 of the WAP has been re-printed in the Preface of the Methods Manual.

4. The Manual also states that for any procedures to be included in the Manual, the procedures must "satisfy all of the programmatic requirements and quality assurance objectives identified in the QAPP" and must undergo a "technical review". Indicate the title and qualifications of personnel who will perform this technical review to determine if the programmatic requirements and quality assurance objectives (QAOs) have been met prior to acceptance of methods in the Manual.

Response

Appendix C7 of the WAP outlines the process for submission and approval of new testing, sampling, and analytical methods. The Methods Manual has been revised to reference Appendix C7 for the requirements of new method submission, review, and approval. In addition, Appendix C7 of the WAP has been re-printed in the Preface of the Methods Manual.

5. The last paragraph on page v states that the Manual is dependent only on CAO approval. However, the permit application indicates that NMED approval will also be required. The Manual should be revised to clarify this to ensure that the NMED is involved with all revisions to the Manual.

Response

The Methods Manual has been revised as, "Any changes to the Methods Manual will be submitted for review and approval in accordance with Appendix C7 of the WIPP Waste Analysis Plan." In addition, Appendix C7 of the WAP has been re-printed in the Preface of the Methods Manual.

Procedure 110.1

6. **Section 5.4, Pressure and Temperature Measurement Apparatus, page 110.1-4**: This section of the method states that the sampling manifold pressure and the ambient temperature must be monitored and recorded. Indicate the frequency of these readings.

Response

The Methods Manual indicates recording of pressure and temperature readings for every sample (see Section 8.2.1).

7. **Table 2, Headspace Gas Target Analyte List, page 110.1-8**: The target analyte list presented in Table 2 is not consistent with the analytes identified in Table C-8 of the permit application. Table C-8 includes formaldehyde and hydrazine, which are not included in Table 2 of the Manual. However, Table 2 includes hydrogen, methane, and m, o, and p-xylene, which are not included on Table C-8. Address this discrepancy. This comment also applies to Table 2 on page 110.2-8.

Response

The Methods Manual has been revised to include formaldehyde and hydrazine on Table 2 of Procedures 110.1 and 110.2, with a footnote that states only samples collected for analysis of these constituents must be associated with equipment blanks analyzed for these constituents. The WAP does not address flammability of headspace gas, but the QAPP does. Therefore, the sampling and analytical methods included in the Methods Manual include hydrogen and methane, while the WAP does not. m-, o-, and p-Xylenes are included collectively as "Xylenes" in Table C-8 of the WAP.

8. **Section 8.2.1, Step 3, Headspace Gas Sample Collection, page 110.1-11**: This section of the method discusses inner bag sampling. Discuss how inner bag sampling will be performed if the poly bag is torn or breached. Clarify whether there is an alternative headspace gas sampling location relative to the deteriorated areas (e.g., next to the tear, opposite side of the poly bag).

Response

DOE has performed a study that shows the analytes present in drum headspace are representative of analytes present in all inner layers of confinement. The title of the report containing the results of this study is: *Position for Determining Gas Phase Volatile Organic Compound Concentrations in Transuranic Waste Containers* (INEL-95/0109, Revision 1, August 1995).

9. **Section 9.1, Quality Control, page 110.1-16**: This section of the manual outlines the quality control procedures in place to ensure representative sampling. The third and fourth bullets in this section state that "low internal volume sampling apparatus" and "small sample volume" will be taken. Clarify what are considered "low" and "small" volume measurements.

Response

The WAP (Appendix C8) states that sites must determine and document internal volume of sampling equipment and collect no more than 10% of available headspace when an estimate can be made. This helps ensure a representative sample of headspace gas is collected. The Methods Manual has been revised to clarify this requirement in the headspace gas sampling procedures.

10. **Section 9.2, Quality Control for Pressure and Temperature Measurement, page 110.1-16**: Discuss the calibration procedures documentation for all of the pressure and temperature measurement apparatus listed in this section of the method.

Response

Appendix C4 of the WAP specifies that pressure and temperature readings, as well as other sampling information, must be recorded in field log books. The Methods Manual has been revised AS, "...is recorded in field logbooks."

11. **Figure 1, page 110.1-23**: Figure C4-1 within the permit application indicates that some sample is diverted to the purge assembly prior to the sample canisters. However, this is not apparent upon Figure 1. Address this apparent discrepancy.

Response

Figure C4-1 of the WAP is a schematic diagram of a sampling manifold. It is meant to show that a flexible hose must be used for sampling so that the sampling head can be hooked up to a purge assembly for cleaning. The original figure should show this flexible hose hooked up to the purge assembly as a dotted line indicating a separate, temporary position for the hose. This figure in the WAP will be revised to better indicate this situation.

12. **Section 5.3, Pressure and Temperature Measurement Apparatus, page 110.2-2**: This section of the method states that the sampling manifold pressure and the ambient temperature must be monitored and recorded. Indicate the frequency of these readings.

Response

See Response #6, above.

13. **Section 8.2.1, Step 3, Headspace Gas Sample Collection, page 110.2-6**: This section of the method presents inner bag sampling. Discuss how inner bag sampling will be performed if the poly bag is torn or breached. Clarify whether there is an alternative headspace gas sampling location relative to the deteriorated areas (e.g., next to the tear, opposite side of the poly bag).

Response

See Response #8, above.

14. **Section 8.2.4, Sampling Equipment Blank Collection, page 110.2-7**: The second sentence of this section states that "A field blank may be used in lieu of the equipment blank if the analytes listed in Table 2 are not expected to be present at or above, the method detection limits." However, footnotes b and e of Table 3 on page 110.2-12, indicate that an equipment blank must be analyzed to certify cleanliness of the sampling equipment prior to use. Clarify this discrepancy. Also clarify how the anticipated headspace gas concentration will be determined prior to sampling.

Response

Procedure 110.2 is for direct canister sampling. The Methods Manual has been revised as, "A field blank is a sample of ambient air collected through the needle assembly and sampling head into an evacuated canister. An equipment blank can be a sample of either humid zero air, nitrogen, or ambient air collected through the needle assembly and sampling head into an evacuated canister. Therefore, for this sampling method, an equipment blank and a field blank are essentially the same." Furthermore, Table 3 (footnote b) has been revised as, "A field blank may be used to meet this requirement."

15. **Section 9.1, Quality Control, page 110.2-10**: This section of the manual outlines the quality control procedures in place to ensure representative sampling. The third and fourth bullets in this section state that "low internal volume sampling apparatus" and "small sample volume" will be taken. Clarify what is considered "low" and "small" volume measurements.

Response

See Response #9, above.

16. **Section 9.2, Quality Control for Pressure and Temperature Measurement, page 110.2-11**: Discuss the calibration procedures documentation for all of the pressure and temperature measurement apparatus listed in this section of the method.

Response

See Response #10, above.

Methods 110.3 and 110.4

17. **Section 8.1, Procedure, Page 110.3-2 and 110.4-6**: Section 8.1 of the method(s) states that the collection of the samples may be performed by either "Procedure 110.1" or "Procedure 110.2"; however, Section 8.2 of the method only references Method 110.1. If Method 110.2 may also be used, revise the method to include the appropriate references to that sampling method.

Response

Section 8.2 of these procedures reference Procedure 110.1 for the appropriate steps using the manifold system. The Methods Manual has been revised as, "... described below for the sampling manifold system."

Method 120.1

18. **Section 2.1, Summary of Procedure, page 120.1-1**: The method states that this "procedure is based on sampling methods are similar to those approved by EPA for solid waste and soil sampling contained in SW-846, Third Edition, Final Update I, and Final Update II.." Clearly identify which SW-846 Methods are referenced in this paragraph. Since the methods are "similar", discuss the sampling method differences and demonstrate that these differences do not compromise the integrity of the method.

Response

The Methods Manual has been revised as, "This procedure is based, generally, on SW-846 Chapters One and Nine, as well as the referenced EPA methods."

19. **Table 5, page 120.1-15**: Clarify what will happen if the percentages required for analysis, as listed in Table 5, are not sampled.

Response

Table 5 is provided only for guidance on the amounts and volumes of various waste types needed to provide enough sample for analysis. The Methods Manual has been revised as, "This table is provided for guidance only, and adequate sample size should be determined by site personnel prior to or during sampling operations. Sample amounts must be adequate to meet PRQLs, but must also address sample disposal issues."

20. **Table 6, page 120.1-18**: Table 6 lists the acceptance limits for equipment blanks collected for VOCs and SVOCs. However, it is unclear why the limits are presented in mg/kg, when the equipment blanks are liquid samples.

Response

The Methods Manual has been revised to state acceptance criteria for equipment blanks in units of mg/L.

Method 210.1

21. **Section 8.2, Procedure, page 210.1-4**: Specify the documentation procedures required to certify cleanliness of the canisters.

Response

The Methods Manual has been revised as, "Facilities performing canister cleaning operations must maintain on file the results of the equipment blank described in Section 9.0. This information documents the certification of canister cleanliness."

Method 310.1

22. **Section 3.0, Limitations and Interferences, page 310.1-1**: Discuss how waste containers that are configured with lead liner will be examined. If radiography cannot be performed for a lead-lined container, then the Manual must be revised to discuss how identification of contents, including free liquids, will then be determined.

Response

The Methods Manual has been revised as, "Sites that are unable to radiographically examine a waste container due to the presence of a lead liner must visually examine the contents of these waste containers to determine the matrix parameter category and waste material parameter weights."

23. **Section 8.0, Procedure, page 310.1-3**: The procedures described do not include information regarding determination of percentage of free liquids within a container. Step 9 of this section states that "Table 3 is provided as a reference to aid in determining liquid quantities." Table 3 includes information regarding volume conversions. However, it is unclear how these measurements will be used to determine the quantity of free liquids (to ensure $< 1\%$ readings or "1 inch", as per the WAC) within the containers. Provide this information.

Response

Table 3 is provided to assist radiography operators in the determination of volumes of variously sized and shaped containers, both empty and liquid filled. The $< 1\%$ free liquid limit is based on the volume of containers. Sites are required to develop procedures that outline and document the determination of free liquid quantities. For clarity, the Methods Manual has been revised as follows:

- Step 3: "...so that the volume of the container and the volume utilization percentage can be determined. Table [3] provides guidance on determining volumes of containers."
- Step 4: "Describe the location, container, and estimated volume (as a percent of the container volume and depth of liquid within the container) of any liquids detected. Table [3] provides guidance on determining volumes of containers."

24. **Section 9.2, Quality Control, page 310.1-4**: The method states that "It is the responsibility of each participating site to determine the criteria by which an operator is considered qualified." This is insufficient. DOE must provide guidance and required criteria that must be met before an operator is considered "qualified".

Response

The WAP outlines training requirements for radiography operators. The Methods Manual has been revised to include these requirements as part of the Quality Control Section of this procedure.

Method 310.2

25. **Section 1.1, Scope and Application, page 310.2-1**: The Manual states that visual examination will be used as a quality control check for radiography. However, the permit application states that visual examination may be used in lieu of radiography. Clarify this apparent discrepancy.

Response

The Methods Manual has been revised as, "Sites may choose to perform visual examination on waste packages instead of radiography."

26. **Section 3.0, Limitations and Interferences, page 310.2-1**: The Manual indicates that opening of non-transparent inner bags is up to "technical experts" and may be based on process knowledge. This is unacceptably vague, and should be discussed more comprehensively.

Response

The Methods Manual has been revised as, "In these cases documented acceptable knowledge may be used to identify the matrix parameter category and estimate waste material parameter weights. Visual examination experts should assess the need to open the bags/packages..."

27. **Section 8.0, Procedure, page 310.2-3**: The first paragraph of this section states that "If the available information is judged by a technical expert to be comprehensive.." Specify the qualifications of the "technical expert" and explain what is considered to be "comprehensive". Also, the last sentence of this paragraph states that "In some cases, a decision to open all bags/packages....may be made in advance." Clarify the title and qualifications of those who make these decisions and how such determinations are made. Also, item 4 on this page requires clarification regarding how technical experts will decide when a bag should be opened and the titles of those considered to be experts. For clarity, also specify when, during this process, any inner bag headspace gas sampling will be performed.

Response

The Methods Manual has been revised in Section 8.0 of the Procedure as,

"If the available information is judged by the visual examination expert to be comprehensive..."

"The training and qualifications of the visual examination expert are included in Section 9.0, 'Quality Control.'"

"These decisions will be made by the visual examination expert based on documented acceptable knowledge, or data from previous visual examinations of the waste, regarding the type of waste material parameters and packaging configurations associated with the waste. The basis of these decisions must be documented."

Note: Any required headspace gas sampling must be performed prior to opening waste containers or bags within waste containers (as applicable). Refer to Procedures 110.1 through 110.4 for headspace gas sampling requirements."

in Step 4, all references to 'technical experts' have been revised to 'visual examination experts.'

The WAP describes minimum training and qualification requirements for the visual examination expert. The Methods Manual has been revised to include the duties of the visual examination expert.

28. **Section 9.1, Quality Control, page 310.2-6**: This section presents visual examiner training, but this discussion is too vague and does not reference specific requirements that could be contained in other documents. Address this concern.

Response

The Methods Manual has been revised to include the minimum training and qualification requirements for visual examination personnel, consistent with the WAP, in the Quality Control Section of this procedure.

29. **Section 9.2, Quality Control, page 310.2-6**: This section discusses standard error calculation procedures that have been developed and goes on to state that "Participating sites would coordinate these efforts to assure maximum consistency." This is insufficient. DOE should include this information in the Manual to ensure that all generator sites produce consistent and comparable data. Revise the document to provide more detail on the standard error calculation procedures referenced. Also, indicate the replicate precision acceptance limits referenced in Section 9.3.

Response

The WAP has been revised to indicate that radiography and visual examination are for the purpose of determining the waste matrix code and waste matrix code group only. The determination of waste material parameters is for the purpose of Performance Assessment. The Methods Manual has also been revised as, "Upon completion of the performance assessment, Sandia National Laboratories will determine the relative importance (i.e., sensitivity) of each waste material parameter to compliance with the long term performance standards. If any of the waste material parameters are found to significantly impact long term performance, Sandia National Laboratories will develop standard error calculations for use by the sites."

30. **Section 9.6, Quality Control, page 310.2-6**: This section of the method should be revised to indicate the actions taken if two operators do not concur with the results of a visual exam.

Response

The Methods Manual has been revised as, "The visual examination expert will resolve any discrepancies between visual examination personnel."

Method 430.1

31. **Section 1.3, Scope and Application, page 430.1-1**: Table 1 includes several compounds that are not included in either of the referenced SW-846 Methods. For example, the following are listed in

Table 1 and not in SW-846 Methods 8240A: cyclohexane, cis-1,2-dichloroethylene, ethyl ether, formaldehyde, hydrazine, 1,1,2-trichloro-1,2,2,-trifluoroethane, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, butanol and methanol. Justify inclusion of these analytes that are not included in the 8240A target compound list and ensure that the methods are able to detect these compounds. Also, provide data to ensure that acceptable detection limit studies have been performed on these compounds for inclusion in the method.

Also, as indicate in the footnotes to Table 1, two of the compounds, formaldehyde and hydrazine, are required for homogenous solids and soils/gravels matrices from only two facilities (not all facilities). Clarify the inclusion of these compounds on the target analyte list. Revise Table 1 of Method 430.1 to include only the analytes to be analyzed for waste container headspace. To avoid confusion, each method should only contain the required information for the specific method.

Response

Procedure 430.1 is based primarily on EPA Compendium Method TO-14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis," as stated in Section 1.1 of the procedure. Method TO-14 includes cis-1,2-dichloroethylene, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene in its target analyte list. Furthermore, Section 4.5 of Method TO-14 states that this method can be applied to VOCs and goes on to state VOCs are generally classified as those organics having saturated vapor pressures at 25° C at 10^{-1} mm Hg. SW-846 Methods 8240B and 8260A allow the analysis of most volatile organic compounds with a boiling point below 200 degrees centigrade and that are insoluble or slightly soluble in water.

Procedure 430.1 was developed specifically for the analysis of headspace gas in TRU waste containers. The headspace gas performance demonstration program provides ongoing assurance that the method is capable of detecting all analytes listed in Table 1 and at the detection limits specified. Tables 9 and 10 of the procedure provide results of samples run at the detection limit. Laboratories are required to demonstrate acceptable method performance prior to analyzing any field samples (see Section 10.2).

The Methods Manual has been revised as, "Required only for samples of headspace gas from containers of homogenous solids and soil/gravel..."

32. **Section 1.3, Scope and Application, page 430.1-1**: Section 1.3, states that "EPA has not determined the stability of alcohols and ketones when stored in pressurized or sub-ambient pressure SUMMA canisters." The text goes on to state that "It is anticipated that no adverse problems will be encountered with these types of VOCs when stored in SUMMA canisters..." It is unclear how DOE has made this determination. Provide the data available to support this claim.

Response

EPA Compendium Method TO-14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis" uses SUMMA canisters for the collection and storage of gaseous volatile organic compound samples. SUMMA canister based sampling methods have been developed specifically for the analysis of headspace gas in TRU waste containers. These methods have been used extensively for headspace gas sampling and the stability and integrity of these methods have been proven over

the five years of headspace gas sampling and analysis at DOE facilities. The headspace gas performance demonstration program provides ongoing assurance that headspace gas target analytes (including alcohols and ketones) are stable when stored in SUMMA canisters.

The Performance Demonstration Program (PDP) for analysis of headspace gases consists of regular distribution (approximately every 26 weeks) of single blind audit samples to laboratories analyzing headspace gas samples from TRU waste containers. The samples contains program analytes in the concentration ranges expected in field samples. PDP samples must be analyzed by the same methods used for field samples. Only methods actually used in the PDP will be considered acceptable to support the analysis of headspace samples from containers of TRU waste destined for WIPP. PDP results are available and will be forwarded for review.

33. **Section 6.0, Reagents, page 430.1-7**: This section of the method must be revised to include preparation of surrogate and matrix spike standards. Both of these standards and analyses are required by SW-846 Method 8240A, as well as the QAPP. It appears from the procedures described within the method that these QC checks will not be performed for these analyses. Revise the procedures to includes these analyses and to include all of the QC criteria acceptance limits for surrogates and matrix spike/matrix spike duplicate (MS/MSD).

Response

Procedure 430.1 is for the analysis of headspace gas samples, not samples of solidified waste. The preparation and analysis of surrogate standards, matrix spikes and matrix spike duplicates is not appropriate or necessary for the analysis of headspace gas samples. Surrogates, matrix spikes, and matrix spike duplicates are for determination of matrix interferences. Matrix interferences are not found in headspace gas samples because air is a non-interfering matrix.

34. **Table 4, page 430.1-19**: The table lists several incorrect secondary ions for several of the compounds. The table should be revised to reflect the following corrections:

- Benzene: The secondary ions should be 52, 71 not 52, 77;
- Methanol, Cyclohexane: The table does not list the secondary ions. Revise the Table to include this information;
- Methyl ethyl ketone: The secondary ions should be 43, 72, not 57, 43; and,
- 1,1,2,2-Tetrachloroethane: The secondary ions should be 85, 131, 133 not 85, 131, 166.

Response

The Methods Manual has been revised to specify the appropriate secondary ions from the most current version of SW-846. Cyclohexane and methanol are not included in SW-846 Method 8240B or 8260A. The Methods Manual has been revised as, "Analysts are required to determine the most appropriate secondary ions for cyclohexane and methanol."

35. **Tables 7, 8, 9, 10, pages 430.1-29 through 430.1-32**: The performance demonstration (PDP) information provided in these tables does not include all of the samples or chemical compound classifications included in the target compound list. For example, formaldehyde and hydrazine are not included. If the data in these tables were used to determine precision and accuracy for each analyte, it is unclear how the precision and accuracy for compounds not included on the tables are determined. Provide this information.

Response

The PDP has not included formaldehyde and hydrazine in blind audit samples as yet because the sites required to analyze their samples for these compounds have not developed headspace gas sampling/analysis programs. As this information becomes available, the Methods Manual will include it in the next revision.

Method 430.2

36. **Section 1.1, Scope and Application, page 430.2-1**: The procedure states that the method is a modification of Methods 8240 and 8260 in the SW-846 Third Edition, Final Update I (EPA 1995). The Final Update I includes 8240A not 8240. Method 8240 is included in the November 1986 SW-846 Third Edition. Ensure that the correct method is referenced.

Response

Procedure 430.2 has been revised to reference SW-846 Methods 8240B and 8260A.

37. **Section 1.1, Scope and Application, page 430.2-1**: Table 1 includes several compounds that are not included in either of the referenced SW-846 Methods. For example, the following are listed in Table 1 and not in SW-846 Methods 8240 or 8260: cyclohexane, ethyl ether, formaldehyde, hydrazine, 1,1,2-trichloro-1,2,2,-trifluoroethane, butanol and methanol. Justify inclusion of these analytes that are not included in the 8240/8260 target compound list and ensure that the methods are able to detect these compounds. Also, provide data to ensure that acceptable detection limit studies have been performed on these compounds for inclusion in the method.

Also, as indicate in the footnotes to Table 1, two of the compounds, formaldehyde and hydrazine, are required for homogenous solids and soils/gravels matrices from only two facilities (not all facilities). Revise Table 1 of Method 430.2 to include only the analytes to be analyzed for waste container headspace. To avoid confusion, each method should only contain the required information for the specific method.

Response

See Response #31, above.

38. **Section 1.3, Scope and Application, page 430.2-1**: Section 1.3, states that "EPA has not determined the stability of alcohols and ketones when stored in pressurized or sub-ambient pressure SUMMA canisters." The text goes on to state that "It is anticipated that no adverse problems will be encountered with these types of VOCs when stored in SUMMA canisters...". It is unclear how DOE has made this determination. Provide data to support this claim.

Response

See Response #32, above.

39. **Section 6.0, Reagents, page 430.2-4**: This section of the method must be revised to include preparation of surrogate and matrix spike standards. Both of these standards and analyses are required by SW-846 Methods 8240A, and 8260, as well as the QAPP. It appears from the procedures described within the method that these QC checks will not be performed for these

analyses. Revise the procedures to includes these analyses and include all of the QC criteria acceptance limits for surrogates and MS/MSD.

Response

See Response #33, above.

40. **Section 6.1, Methanol or Propanol, page 430.2-4**: Revise the text to state that these solvents (methanol and propanol) should be stored apart from other chemicals.

Response

The Methods Manual has been revised as, "Solvents should be stored separately."

41. **Section 6.9, Calibration Standards, page 430.2-5**: Revise the text to ensure that the calibration standards will be prepared daily.

Response

The Methods Manual (Procedure 430.2, Section 6.9) has been revised as, "Calibration standards prepared in water must be prepared daily."

42. **Table 3, page 430.2-8**: Revise Table 3 to include the minimum acceptable relative retention factor (RRF) for the compounds (0.300 for all compounds and 0.250 for bromoform).

Response

Procedure 430.2 was developed specifically for the analysis of headspace gas in TRU waste containers. It has been determined that SPCCs are not necessary for the determination of headspace gas VOCs because SPCCs are used to assess system performance when interfering matrices are present in samples. Because air is a non-interfering matrix, SPCCs are not necessary in the course of headspace gas analysis. This method has been used extensively for headspace gas analysis and the stability and integrity of this method has been proven over the five years of headspace gas sampling and analysis at DOE facilities. The headspace gas performance demonstration program provides ongoing assurance that the method is capable of detecting all analytes listed in Table 1 and at the detection limits specified. Performance demonstration data will be forwarded for review.

43. **Table 4, page 430.2-9**: The table lists several incorrect secondary ions for several of the compounds. Revise the table to reflect the following corrections:

- Benzene: The secondary ions should be 52, 71 not 52, 77;
- Methanol, Cyclohexane: The table does not list the secondary ions. Revise the Table to include this information;
- Methyl ethyl ketone: The secondary ions should be 43, 72 not 57, 43; and,
- 1,1,2,2-Tetrachloroethane: The secondary ions should be 85, 131, 133 not 85, 131, 166.

Response

See Response #34, above.

44. **Tables 7, 8, 9, pages 430.2-19 and 430.2-20**: The PDP information provided in these tables does not include all of the samples or chemical compound classifications included in the target compound list. For example, formaldehyde and hydrazine are not included. If the data in these tables were used to determine precision and accuracy for each analyte, it is unclear how the precision and accuracy for compounds not included on the tables are determined. Revise the Manual to include this information.

Response

See Response #35, above.

Methods 430.3 and 430.4

45. **Table 1, page 430.3-2 and 430.4-2**: Table 1 includes several compounds that are not included in the referenced SW-846 Method. For example the following are listed in Table 1 and not in SW-846 Methods 8240B: 1,4-dichlorobenzene, ortho-dichlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, butanol, ethyl ether, formaldehyde, hydrazine, methyl ethyl ketone and pyridine. Justify inclusion of these analytes that are not included in the 8240B target compound list and ensure that the methods are able to detect these compounds. Also, provide data to ensure that acceptable detection limit studies have been performed on these compounds for inclusion in the method.

Response

Table C12-2 in the WAP addresses the inclusion of the compounds discussed in the NMED comment. The analyte list in Table 1 of Procedure 430.3 is a subset of that found in SW-846 Method 8240B except for 1,4-dichlorobenzene, ortho-dichlorobenzene, and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). SW-846 Method 8240B allows the analysis of most volatile organic compounds with a boiling point below 200 degrees centigrade and that are insoluble or slightly soluble in water. The dichlorobenzenes fit this description, but can also be analyzed as semi-volatile organic compounds as specified in Table 1. Freon 113 is very similar to other freon compounds included in SW-846 Method 8240B. SW-846 Method 8240B is capable of quantitating at Procedure 430.3 method detection limit. Participating analytical facilities must prepare and analyze method performance samples prior to the analysis of any waste samples. The analysis of method performance samples includes the determination of method detection limit.

46. **Section 8.0, Procedure, page 430.3-3 and 430.4-3**: The method states that each site/analyst is free to select the preparation methods. It is unclear what preparation methods may be needed for VOCs analysis since any preparation is included within the method itself. If the text is referencing screening methods, which are used to provide guidance on whether sample dilution is necessary, then this must be clarified.

Response

The Methods Manual has been revised as, "Extraction or sample preparation methods must be submitted for review and approval in accordance with Appendix C7 of the WIPP Waste Analysis Plan. For convenience, Appendix C7 of the WIPP Waste Analysis Plan has been re-printed in the preface of this Methods Manual."

Methods 430.5 and 430.6

47. **Section 1.1, Scope and Application, pages 430.5-1 and 430.6-1**: Table 1 includes several compounds that are not included in either of the referenced SW-846 Methods. For example the following are listed in Table 1 and not in SW-846 Methods 8250A or 8270B: cresols, 1,4-dichlorobenzene, ortho-dichlorobenzene, and pyridine. Justify inclusion of these analytes that are not included in the method target compound list and ensure that the methods are able to detect these compounds. Also, provide data to ensure that acceptable detection limit studies have been performed on these compounds for inclusion in the method.

Response

Tables C12-4 and C12-5 in the WAP address the inclusion of the compounds discussed in the NMED comment. The analyte list in Table 1 of Procedures 430.5 and 430.6 are subsets of the analyte lists in SW-846 Methods 8250A and 8270B, respectively. Cresols are the same as methylphenols and ortho-dichlorobenzene is the same as 1,2-dichlorobenzene. The SW-846 methods do not include pyridine in the analyte lists, but allow for it in Subsection 1.2. SW-846 Methods 8250A and 8270B are capable of quantitating at the Methods Manual method detection limit. Participating analytical facilities must prepare and analyze method performance samples prior to the analysis of any waste samples. The analysis of method performance samples includes the determination of method detection limit.

48. **Section 8.0, pages 430.5-3 and 430.6-3**: The methods indicate that each site/analyst may select the preparation methods. However, no guidance is provided regarding which methods may chosen. The Manual should either include the necessary information, or reference the appropriate SW-846 section. For example, Section 7.1 of SW-846 Method 8250A states that "Samples must be prepared by one of the following methods prior to GC/MS analysis" (SW-846 continues listing several preparation methods). To ensure comparable data between generator sites, this information must be provided in the Manual and must not be left to individual analysts/sites to determine.

Response

The Methods Manual has been revised to reference SW-846 (Method 8250A or 8270B) for sample preparation and cleanup methods.

Method 440.1

49. **Section 1.3, Scope and Application, page 440.1-1**: Section 1.3, states that "EPA has not determined the stability of alcohols and ketones when stored in pressurized or sub-ambient pressure SUMMA canisters." The text goes on to state that "It is anticipated that no adverse problems will be encountered with these types of VOCs when stored in SUMMA canisters..." It is unclear how DOE has made this determination. Provide the data that support this claim.

Response

See Response #32, above.

Method 440.2

50. **Section 1.2, Scope and Application, page 440.2-1**: The method states that the procedure is based on "DOE Method OGO15R (DOE 1994)." To properly evaluate Method 440.2, this referenced DOE should be provided for review.

Response

A copy of DOE Method OG015 will be forwarded to NMED for review.

51. **Section 3.4, Interferences, page 440.2-4**: The method states that "the laboratory where volatile analysis is performed should be free of solvents that could potentially contaminate the samples." Include a list the solvents which may cause contamination.

Response

The Methods Manual has been revised as, "The list of solvents that may cause contamination are those included in the analyte list."

Method 620.1

52. **Section 9.0 Calculations, page 620.1-3**: Provide the exact equation to be used for the dilution calculation that is referenced in this section of the method.

Response

The specific equation to be used is as follows:

Concentration (wet weight) (mg/kg) = C x V/W

where: C = digest concentration (mg/L)
V = final volume in liters after sample preparation
W = weight in kg of wet sample

If dry weight is needed, divide by S, where

S = weight in kg of wet sample

This equation has been included in the Methods Manual.

Method 630.1

53. **Section 1.1, Scope and Application, page 630.1-1**: Table 1 of the method includes vanadium; however SW-846 Method 6020 does not include this compound on its target analyte list. Justify inclusion of this analyte and ensure that the methods are able to detect this analyte.

Response

Vanadium has been deleted from Table 1 of this procedure.

Method 650.2

54. **Section 1.0, Scope and Application, page 650.2-1**: Table 1 is referenced for the various Graphite Furnace Atomic Absorption (GFAA) Spectroscopy analytical methods for several analytes. However, many of the methods listed are not GFAA, but rather direct aspiration (flame AA) methods. For example, the following methods are incorrectly listed on Table 1:

- Barium: Table 1 lists method 7080A; however, the correct method is 7081;
- Beryllium: Table 1 lists method 7090; however, the correct method is 7091;
- Cadmium: Table 1 lists method 7130; however, the correct method is 7131;
- Chromium: Table 1 lists method 7190; however, the correct method is 7191;
- Lead: Table 1 lists method 7420; however, the correct method is 7421;
- Nickel: There are no established GFAA methods for nickel; therefore, the inclusion of the compound in the target list is unclear;
- Silver: Table 1 lists method 7760A; however, the correct method is 7761;
- Thallium: Table 1 lists method 7840; however, the correct method is 7841;

Discuss these discrepancies and revise the table to include the correct methods. Also, revise Method 650.2 to ensure that the methods referenced to the associated SW-846 Methods is accurate.

Response

This error is addressed in Table C12-11 of the WAP. These corrections have been made in the Methods Manual.