ENVIRONMENTAL EVALUATION GROUP

AN EQUAL OPPORTUNITY / AFFIRMATIVE ACTION EMPLOYER

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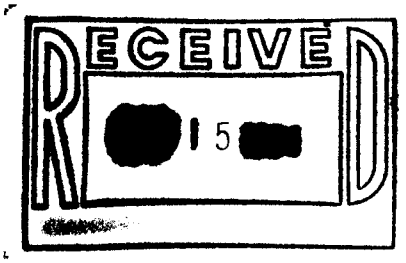

November 10, 1994

Mr. Steve Zappe
Radiation Protection Bureau
New Mexico Environment Department
Harold Runnels Building
1190 St. Francis Drive
Santa Fe, NM 87503

Dear Mr. Zappe: Steve

As agreed yesterday, a copy is enclosed of our August 29, 1994 review of the Waste Characterization QAPP.

Sincerely,

Robert H. Neill
Director

RHN:js

cc: Benito Garcia, NMED

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August 29, 1994

Mr. George Dials
Manager
U.S. Department of Energy
Carlsbad Area Office
P.O. Box 3090
Carlsbad, NM 88221-3090

Dear Mr. Dials:

In accordance with your July 8, 1994 request to review the Draft TRU Waste Characterization Quality Assurance Program Plan (QAPP), CAO-94-1010, Revision B, July 8, 1994, the following comments are provided by EEG. Those sections of the QAPP that are not commented on appear to be satisfactory. In order to ensure full understanding of these comments, a meeting might be productive.

If you have any questions, please contact Dr. Ruth Weiner.

Sincerely,

Robert H. Neill
Director

RHN:RW:js:ss
Enclosure

cc: Mark Matthews, DOE/CAO
Reid Rosnick, USEPA/OSW
Larry Weinstock, USEPA/ORIA

DRAFT COMMENTS ON TRU WASTE CHARACTERIZATION QAPP

Organization

The QAPP does not specify a position for a quality assurance (QA) manager or auditor. Such a position should be created, and that individual should report directly to the Manager of the Carlsbad Area Office (CAO). The QA manager should sign off on all QAPPs and QAPjPs prior to approval by the CAO manager. This position should be indicated on the organization chart, (Figure 1-1, Section 1.0). The Chief, CAO Compliance Branch is properly situated in the organization chart, however, if that person is also the QA manager, QA will occupy most of the individual's time. QA should be the full-time responsibility of one individual, in order to retain the requisite degree of independence from the rest of the operation. The QA manager should also be responsible for archiving all documents.

Section 1.0, page 8 gives the National TRU Program Office (NTPO) Waste Characterization and Technology Program Manager responsibility for implementation of DOE/HQ policy, program guidance, and technical direction, including issuing this QAPP. The NTPO Manager's responsibilities ought not to include both issuing and reviewing the QAPP. The essence of QA is independent review.

The Site Project QA Officers should report directly to the Site Project Managers, and this reporting line should be explicit in the description in Section 1.1.4.2., page 10.

The document review procedure is adequate, but should state explicitly that documents and data entry be reviewed by someone qualified to do the original work who did not do it. Since there is no statement to this effect in the document, add one. This provision is particularly important in reviewing technical adequacy and data entry. Members of DOE or M&O staff, other than those indicated, may be needed for QA reviews from time to time.

Program Description (Sections 1.1 through 1.4)

Sections 1.3 and 1.4, pages 15 through 31, provide a brief summary description of the WIPP program and the waste intended for disposal. In other documents and contexts, EEG has commented extensively on the all facets of the program described in these two subsections, and will therefore not comment on them here.

In Section 1.1.3.4, page 8, the only responsibility identified in the area of QA for the Chief, CAO Experimental Programs Branch is to review this QAPP. The document is not clear as to whether this constitutes the sole QA responsibility for this individual.

Table 1-2, Section 1.0, page 6, lists the Site Project Manager the only one responsible for implementing QAPJPs. Is this an accurate portrayal of the Site Project Manager's QA responsibilities?

The responsibility of the NRC for certifying the shipping container for RH-TRU waste should be added to Section 1.3, page 17, line 23. Moreover, the wording of Section 1.3, page 20, line 9, should be clarified to show that the NRC Certificate of Compliance is only for the shipment of certain CH-TRU wastes, does not cover Pu-238 heat source wastes or RH-TRU.

Documentation and Records (Sections 1.7, 1.8, 2.2, 3.4, 4.6, 6.0)

Documentation and verification of calculations and computer programs should be included in lifetime records rather than as non-permanent records.

Audits

Written audit procedures are referred to in Section 2.0, pages 1 through 7, but their location is not specified. Provisions for audit requirements external to DOE should be included in this

section, because "independence" (as in Section 2.1.5, pages 5 and 6) is not characterized adequately. Audit or assessment of a program at a given site (e.g., INEL) by someone not involved with that program, however laudable, is not truly an independent assessment. When DOE offices, or divisions, sites, or contractors assess each other, the audit is valuable to the subject, but is not independent. Independence implies an external audit by an agency external to DOE.

Data Entry, Data Reduction and Tabulation, Data Review (Sections 1.3-1.9, 3.0, 4.0)

Section 3.1.3, pages 4 and 5, should incorporate the following: the QA manager should ensure that all compilations of data, data analyses, and identifications according to USEPA regulations, and tables of data and results should be reviewed and checked item by item, and the document signed by the QA reviewer. This includes, but is not limited to, experimentally generated data like drum headspace gas concentrations, verification of concentration limits for flammable volatile organic compounds (VOCs) and other flammable compounds, listing of hazardous materials under 40 CFR Part 261, meeting data quality objectives (DQOs), waste analysis data, data indicating compliance with Waste Acceptance Criteria (WAC) and transportation criteria. This provision should also be included explicitly in Section 1.3, page 20.

Contrary to the assertion of Section 3.2, pages 5 through 8, statistical analysis is entirely appropriate for estimating representativeness of any sample. In fact, the overview of a statistical analysis of the number of drums that needed invasive characterization under a variety of circumstances, as described in Section 5.3, pages 5 through 13, is appropriate for much of the waste. This statistical procedure should be referenced in Section 3.2, page 5, line 25. The criteria listed on page 9 of Section 3.0 cannot be determined to have been satisfied without statistical analysis.

The statistical analysis cited above may be much more appropriate for segregated waste streams like those at Rocky Flats and INEL than for unsegregated waste like that at Hanford or Savannah River Plant. Statistical analyses, as well as sampling and analytical methods, specific to unsegregated waste streams need to be included in the QAPP.

"Average concentration of VOCs" (Section 3.3.1, page 9, lines 6 and 7) is a meaningless concept. Average concentrations of particular compounds should be required. Sampling and analysis for the four most prevalent compounds: carbon tetrachloride, trichlorethylene, trichloroethane, and methylene chloride, will probably suffice. Lines 6 and 7 of Section 3.3.1, page 9, should read "average concentrations of CCl_4, CCl_2CHCl, CCl_3CH_3, and CH_2Cl_2 . . . ."

Section 4.5, pages 2 and 3, should include a requirement that the most recent date of calibration be posted at the appropriate instrument site.

The QAPP does not address the question of qualifying "old" or existing data. Methods are needed to qualify such data, and description of these methods should be included in Section 3.0 as an additional Section 3.5.

Sampling

Specification of a single standard sampling procedure is commendable, but may not be appropriate for very heterogeneous waste streams. A standard sampling procedure does require the QAPjPs to be consistent with each other, and the external reviewer is assured that all sampling is done by the same quality assured procedure.

The statistical method described in Section 5.3.1, pages 6 through 10, appears to be adequate for its purpose. We recommend deleting Equation 5-5, Section 5.3.1, page 8:

$$\mu^* = \frac{RTL}{2}$$

and using instead

$$n = \frac{4(Z_{1-\alpha} + Z_{1-\beta})^2 s^2}{RTL^2}$$

Substitution of half the MDL for a measurement below the detection limit may be "simple," but it is not suitable. Appropriate statistics such as those in the cited references should be used.

An example using the Equations 5-6, 5-7, and 5-8, Section 5.3.2, page 13, would be helpful, as this QA document may be used by people with varying degrees of familiarity with statistics and probability.

The chain of custody procedures in Section 6.3, pages 6 through 11 are adequate except for a confusing feature: it is not clear whether all of the bulleted requirements must be met, or only one of them. If the intent is to meet only one, the word "or" should be inserted after each paragraph..

The document is not clear as to how field reference standards (Section 7.3, page 17) will be used. More detail is needed.

Sampling techniques for solid process residues and soils are critical for the accurate determination of total volatile organic compounds (VOCs). Inaccuracies are much more likely to occur in sampling of heterogeneous mixtures than in well-established,

repeatable analytical procedures. This critical dependence needs to be recognized overtly and accounted for in the QAPP. The QAPP should include a section relating sampling errors to analytic inaccuracy.

Although the use of non-destructive radioassay (NDRA) is described well in Section 9, the following statement needs better justification.

> "The measurement of total alpha activity and independent determination of isotopic ratios, obtained by non-destructive and/or destructive RA or supportable process knowledge, are considered adequate for use in the Program"

In particular, the adequacy of the proposed NDRA should be addressed in more detail.

The derivation of Equation 9-1, Section 9.1, page 5, should be included in the QA document, if only as an appendix. Qualitative discussion of the assumptions behind the equation and qualitative mention of an alternate equation do not suffice. A derivation with a clear rationale would be better than a qualitative discussion of assumptions and alternatives. Moreover, all sites should define the method detection limit (MDC) consistently.

The document states (Section 9.1, page 6) that the ability to achieve the quality assurance objective (QAO) for total uncertainty "will be determined from an evaluation by an expert panel . . . ." Use of expert panels is fraught with pitfalls (e.g., panel bias, questionable expertise, questions about completeness of the information presented to the panel) and should be undertaken only very carefully and as a last resort. Because total uncertainty in NDRA is propagated throughout the sampling system, the use of an expert panel is critical. The QAPP should detail how the panel is selected, how it operates, what information will

be presented to panel members and in what format, and how the results of the expert panel elicitation will be aggregated. Without this detail, the QAPP is not complete. Alternatively, total uncertainty can be defined as the propagation of all quantifiable uncertainties, and the result either meets the QAO or it doesn't.

Analyses

Section 11.1, page 1, of the QAPP requires that methane and hydrogen headspace gas concentrations be reported in volume % (the same as ppmv). We recommend that these concentrations be reported in a more fundamental unit like mole %, partial pressure, mole/liter, or grams (micrograms)/liter. Moreover, the two required analytical methods, gas chromatography and mass spectroscopy, have a considerably better potential precision than +/- 25% of the relative standard deviation or difference, and should have considerably better recovery than +/- 30%. If the imprecision and inaccuracy are inherent in the sampling rather than in the analysis the QAPP should so state. Specifying a degree of imprecision and inaccuracy such that every outlying value and excursion is included defeats the purpose of quality control and quality assurance. Some explanation of these values is needed if they are to remain in place.

The same comment applies to analysis of both gaseous and total VOCs. Table 12-1, Section 12.1, page 2, seems to be either incorrect, incomplete, or both. The table lists precision, accuracy, MDL, PRQL, and completeness for only two compounds: benzene and acetone. Does the table imply that these values obtain for the other compounds listed, or are there no such criteria for the other compounds? If the latter, why not? Instrumentation and sampling and analytical procedures observed on site visits to INEL and LANL indicate that at these laboratories, precision and accuracy are at least an order of magnitude better than that given in Table 12-1. In fact, the table is

inconsistent with the description of the methods described in the remainder of Section 12.0. If the precision and accuracy given in Table 12-1 (Section 12, page 2) and Table 13-1 (Section 13.1, page 2) are those to be used, a great deal more explanation is needed for this relatively poor performance.

The equilibrium vapor pressure of volatile organic compounds (VOCs) provides a quick and easy check on the measured concentrations: i.e., the measured headspace concentration of the gas phase of any particular VOC should be about the same as that given by the Raoult's Law calculation from the measured concentration of the total VOC in question. This check could be incorporated into the data validation system.

DOE should include the use of an acceptable organic solvent blank as well as a water blank, (Section 13.3, page 7) since not all analyses will be done in or from water solution. Moreover, laboratory control samples should be prepared using the appropriate organic solvent.

The precision given for total metals analysis in Table 15-1, Section 15.1, page 2, does not seem to be what the methods and instrumentation are capable of producing. An explanation for this relatively poor precision is needed.

High concentration samples should be diluted to bring them within the maximum instrument detection limits (IDL). Dilution is certainly the time-honored method for making concentrations to be measured congruent with instrument capability. Measurements that exceed the maximum IDL are usually meaningless; most instrumentation is reliable only well below the maximum IDL.

Even though different waste streams at different sites require different sample preparation methods, the methods should be standardized, or one of a standard suite of methods should be used. Otherwise, measurements made at one laboratory may not be

comparable with those made at another laboratory. The QAPP suggests this scheme, but does not require it.

Definitions

All terms of art used in the program and in this document should be defined in the "Definitions" section. Ordinary technical definitions and definitions found in regulations, where applicable, should be included along with the definitions specific to this program. The document should probably also be reviewed for the express purpose of suggesting additions to the "Definitions" section. The suggestions listed below are doubtless far from complete.

- Inadequate definitions:

  characterization
  chain of custody
  gases (give the physical chemical definition!)
  VOCs

- Definitions that need to be added:

  gas chromatography
  mass spectroscopy
  minimum detectable concentration
  nonconformance
  PCBs
  process residue
  semi-VOCs
  Toxicity Characteristic Leaching Procedure (at least give a reference