TEST PLAN APPROVAL FORM

TEST PLAN FOR HEADSPACE GAS SAMPLING OF REMOTE- HANDLED TRANSURANIC WASTE CONTAINERS AT LOS ALAMOS NATIONAL LABORATORY

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**TEST PLAN FOR HEADSPACE GAS
SAMPLING OF REMOTE-HANDLED
TRANSURANIC WASTE CONTAINERS
AT LOS ALAMOS NATIONAL LABORATORY**

February 24, 1998

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ACRONYMS AND ABBREVIATIONS

%R	percent recovery
%RSD	percent relative standard deviation
CH	contact-handled
CMR	Chemistry and Metallurgy Research Facility
COC	chain-of-custody
DQO	data quality objective
eV	electron volt
GC	gas chromatograph
HCF	hydrogen content factor
LANL	Los Alamos National Laboratory
LCS	laboratory control standard
MDL	method detection limit
MS	mass spectrometer
N/A	not applicable
NIST	National Institute of Standards and Technology
QAO	quality assurance objective
QAPP	<i>Transuranic Waste Characterization Quality Assurance Program Plan (DOE 1996)</i>
RH	remote-handled
RPD	relative percent difference
SARP	<i>Safety Analysis Report for the RH-TRU 72B Waste Shipping Package (VECTRA 1995)</i>
SCF	solidified cans factor
TA	Technical Area
TRU	transuranic
VOC	volatile organic compound
WIPP	Waste Isolation Pilot Plant

1.0 SUMMARY

Seventeen remote-handled (RH) transuranic (TRU) waste canisters (hereinafter referred to as waste canisters) currently are stored in vertical, underground shafts at Technical Area (TA)-54, Area G, at Los Alamos National Laboratory (LANL). These 17 RH TRU waste canisters are destined to be shipped to the Waste Isolation Pilot Plant (WIPP) for permanent disposal in the geologic repository. Currently, these canisters represent the only RH TRU waste packaged in canisters. As the RH TRU canister is likely to be the final payload container prior to placement into the 72-B cask and shipment to the WIPP, these waste canisters provide a unique opportunity to ascertain representative flammable gas concentrations in packaged RH-TRU waste.

Hydrogen, which is produced by the radiolytic decomposition of hydrogenous constituents in the waste matrix, is the primary flammable gas of concern with RH TRU waste. Title 10 *Code of Federal Regulations* Part 71, "Packaging and Transportation of Radioactive Material," and the *Safety Analysis Report for the RH-TRU 72-B Waste Shipping Package* (VECTRA 1995) (SARP) limit the hydrogen concentration in any layer of confinement in a shipping package or payload, during a 60-day shipping period, to less than or equal to five percent by volume. The SARP allows waste generators two options for demonstrating compliance with the hydrogen concentration limits: 1) show compliance with the maximum allowable gas generation rate; and 2) show compliance with the maximum allowable wattage (i.e., decay heat) limits.

The primary objectives of the experiment that is described by this test plan are to sample and analyze the waste canister headspace gases to determine the concentration of hydrogen in the headspace gas and to calculate the hydrogen gas generation rate for comparison to the applicable maximum allowable hydrogen generation rate (mole/sec) limits specified in the SARP. The key data to be produced in this experiment are the hydrogen concentration in the canister, hydrogen gas generation rate, and effective hydrogen G-value. The effective G-value provides a measure of the number of molecules of hydrogen formed per 100 electron volts (eV) of ionizing radiation absorbed by the waste matrix. It is a goal of this experiment to determine the headspace gas concentrations of other gases (e.g., oxygen, nitrogen, carbon dioxide, carbon monoxide, and volatile organic compounds [VOCs] with molecular weights less than 60 g/mole) that are produced by radiolysis or present when the waste was packaged. Additionally, the temperature, pressure, and flow rate of the headspace gas will be measured.

A maximum of 10 waste canisters will be sampled due to budget limitations. A detailed analysis of the waste canister characterization data was performed to identify the canisters with the highest potential to generate hydrogen gas through radiolysis. Appendix A (LANL 1997) describes the multicriteria decision-making technique that was used to select the 10 waste canisters for sampling. The headspace gas of the 10 selected waste canisters will be sampled once per month at TA-54, Area G during February through September 1998. The samples will be analyzed in the field using a portable gas chromatograph (GC) and in the analytical laboratory at the Chemistry and Metallurgy Research Facility (CMR) using either a GC or a mass spectrometer (MS). The effective hydrogen generation rate of the waste canisters will be calculated from the analytical results and compared to the SARP limits to evaluate compliance with transportation requirements.

2.0 BACKGROUND

2.1 Statement of Mixed Waste Treatment Need

A review of the waste characterization data indicates that 16 of the 17 waste canisters are classified as content code LA 325A, and the remaining canister is classified as content code LA 325C. The maximum allowable hydrogen gas generation rates for content codes LA 325A and LA 325C are 1.934×10^{-7} mole/sec and 4.150×10^{-7} mole/sec, respectively (SARP). The corresponding decay heat limits for content codes LA 325A and LA 325C are 0.6903 W/canister and 1.2268 W/canister, respectively. Based on the calculated decay heats for the canisters listed in Table I of Appendix A (LANL 1997), nine of the canisters (LA07 through LA15) exceed the allowable wattage limits by at least a factor of five. Thus, based on decay heat comparisons with SARP limits, these canisters can not be certified for shipment. The only other option for certifying the canisters is to determine the actual hydrogen gas generation rates through testing and compare the rates to the SARP limits. These nine canisters are among the 10 that will be tested/sampled. The experiment will also establish effective G-values that may be used to support revised lower G-values, as discussed in Section 2.3 of this test plan.

2.2 Technology Concept and Function

Straightforward techniques and off-the-shelf, commercially available equipment will be used to sample the headspace gas of the waste canisters. The canisters will be sampled in place and all analyses will be conducted at LANL using standard laboratory equipment calibrated with known gas standards.

2.3 Current Status or State of Development

This experiment will provide valuable information concerning radiolytic gas generation and matrix depletion issues that must be resolved to effectively manage RH TRU wastes. A large fraction of the RH TRU waste currently in storage is in jeopardy of failing the wattage limits and, therefore, the hydrogen gas generation limits established by the SARP. The SARP wattage limits are based on the assumption that the G-values remain constant from the time the waste is packaged until the waste is disposed at the WIPP. Thus, the current SARP wattage calculations are overly conservative and overestimate the gas generation rate due to radiolysis. This experiment will determine the effective G-value for each of the 10 RH TRU waste canisters. Bounding effective G-values will be established for wastes that have undergone matrix depletion effects through the matrix depletion program (Connelly et al. 1997) and from controlled laboratory gas generation testing of newly generated RH TRU wastes. This experiment will support revised effective G-values by demonstrating that the selected values are indeed bounding. Specifically, the effective G-values obtained in this experiment will be shown to be statistically less than the bounding effective G-values obtained from controlled experiments after matrix depletion has taken place.

The phenomena of matrix depletion have been demonstrated by experiments with contact-handled (CH) TRU wastes. Matrix depletion occurs over time as alpha particles interact with and transform the target material (by evaporation, reaction, or decomposition) into a material of lower gas generation potential. As time passes, the ionizing radiation produced by the radionuclides continues to deplete the number of available targets in the material and, therefore, the material experiences a time-dependent decrease in G-value. The G-value of material will also decrease with time as the activity of radionuclides with short half-lives decreases. However, radioactive decay has a minor effect upon the time-dependent decrease in the G-value of CH and RH-TRU waste because the activity of these wastes is dominated by radionuclides with long half-lives.

The fraction of the alpha energy that is absorbed by the target material is dependent upon how the radionuclides (i.e., source material) are dispersed in the waste. Alpha particles deposit their energy over very short distances characterized by their range. When the source material is dispersed in or on the target material as clumps of particles, only that target material in a small shell-shaped area around each source particle will absorb the alpha energy. Also, if the diameter of the source material clumps is greater than the range of the alpha particles, a fraction of the alpha energy will be self-absorbed and will not be available to interact with the target material. When the alpha-emitting radionuclides are finely and widely dispersed

throughout the target material, a larger fraction of the alpha energy from the source material target material will be available to interact with the target material. Additionally, some energy will be lost in the surrounding nonhydrogenous material (e.g., air) that is not available for the liberation of hydrogen. The net effect of these reactions is represented by the "effective G-value," which only considers the fraction of energy that is expended toward gas generation. The information gained from this experiment will be of interest to all sites that manage RH TRU waste and will be used to support a future revision of the SARP wattage limits.

2.4 Needed Technology Improvements

No technology improvements are needed to perform this experiment.

3.0 REQUIRED DATA AND ACQUISITION APPROACH

During this experiment, the headspace gas of the selected waste canisters will be sampled and analyzed to determine the concentrations of hydrogen and other gases (e.g., oxygen, nitrogen, carbon dioxide, carbon monoxide, and VOCs) that are produced by radiolysis or present when the waste was packaged. Sampling lines that communicate with the headspace of the waste canisters will be installed. Samples of the headspace gas will be withdrawn periodically (e.g., monthly) and analyzed using a GC and possibly an MS. The temperature of the waste canister and the headspace gas will be monitored using a digital thermometer or a temperature thermocouple installed at the top of the waste canister. The pressure of the headspace gas will be measured using a pressure transducer. Attempts will be made to use a wet test meter to measure total flow through the sample tube. The analytical results will be used to calculate the hydrogen gas generation rate and effective G-value. This information will be used to determine whether the waste canisters meet the applicable transportation requirements and to establish revised G-values for wastes that have undergone matrix depletion effects.

A summary of the experimental design, equipment, and sampling methodology is provided in this test plan. The *Sampling Procedure for Remote-Handled Transuranic Waste Containers at the Los Alamos National Laboratory* (LANL 1998a) provides detailed descriptions of the operational aspects of the sampling. This test plan also outlines the methodology for analyzing the data to arrive at effective G-values and hydrogen gas generation rates. Details of the data reduction, validation, reduction, analysis, interpretation, and

reporting are provided in the *Data Reduction, Validation, and Reporting Procedure for the Sampling of Remote-Handled Transuranic Waste Containers at the Los Alamos National Laboratory* (LANL 1998b).

4.0 TEST OBJECTIVES

4.1 Design Data Objectives

No design data objectives are applicable to this experiment.

4.2 Operating Data Objectives

No operating data objectives are applicable to this experiment.

4.3 Regulatory Strategy Data Objectives

The primary data objective is to quantitatively determine the hydrogen gas concentrations in the headspace of the waste canisters stored in shafts at LANL TA-54, Area G. The experimentally determined hydrogen gas concentrations will be used to calculate the hydrogen gas generation rates and effective G-values of the waste canisters. The calculated hydrogen gas generation rates will be compared to the maximum allowable gas generation rate limits specified by the SARP to determine whether the waste canisters meet the transportation requirements for shipment to the WIPP.

5.0 DATA QUALITY OBJECTIVES

5.1 Level I Data Quality Objectives

The primary objectives of this experiment are to determine the concentration of hydrogen in the headspace gas and to calculate the hydrogen generation rate for comparison to the SARP limits. The headspace gas of the waste canisters will be sampled at a minimum of once per month during the experiment. The headspace gas samples will be analyzed using either a GC or an MS. Level I data quality objectives (DQOs) will be established for the analysis of hydrogen because these data are mandatory for the success of this experiment. The quality assurance objectives (QAOs) established by the *Transuranic Waste Characterization Quality Assurance Program Plan* (U.S. Department of Energy 1996) (QAPP) will be instituted as Level I DQOs for the hydrogen analysis.

Pure gases will be used for laboratory control standards (LCSs) in the calibration the GC and MS instruments and to determine their accuracy. Standards that contain mixtures of gases will be obtained from reputable vendors. The GC and MS instruments will be calibrated to ensure that the observed hydrogen concentrations fall within their calibration range. At least one LCS will be included with each batch of samples where 20 or less samples comprise one batch. Each batch will also include at least one duplicate LCS or sample to determine the precision of the experiment. Additionally, each batch will include at least one field blank to determine the background levels of the analytes and one equipment blank to verify that the analysis system is not contaminated. Table 5-1 summarizes the Level I DQOs and includes DQOs for temperature and volume measurements because this information is required for gas generation calculations.

Table 5-1. Quality Assurance Objectives for Calibration Standards

Data Point	Precision	Accuracy	MDL	Field Blank
Hydrogen	≤25 %RSD or RPD	70-130 %R	0.05 vol% (500 ppm)	<3 x MDL
Temperature	±5.0°F	±2.0°F	N/A	N/A
Gas Volume	±5 cm ³	±1 cm ³	N/A	N/A

%R	=	percent recovery
%RSD	=	percent relative standard deviation
MDL	=	method detection limit
N/A	=	not applicable
ppm	=	part(s) per million
RPD	=	relative percent difference

5.2 Level II Data Quality Objectives

Secondary objectives of this experiment are to determine the headspace gas concentration of other gases (e.g., oxygen, nitrogen, carbon dioxide, carbon monoxide, and VOCs with a molecular weight less than 60 g/mole) that are produced by radiolysis or present when the waste was packaged. The purpose of collecting oxygen, nitrogen, carbon dioxide, and carbon monoxide concentrations is to provide some insights into the radiolytic chemistry that is occurring. The concentrations can be used to estimate the generation or consumption rates of these gases in the same manner as for hydrogen (i.e., by taking the product of the gas concentration and the gas specific diffusion characteristic of the drum filter). An attempt

will be made to measure total gas flow through the sample tube. If successful, this would provide yet another measure of the generation/consumption rates of these gases as well as for hydrogen. If, after repeated samplings, the concentrations of VOCs are below detection limits, the most appropriate action to take will be based on a complete analysis of the data collected and in consultation with the program coordinator. Level II DQOs will be established for these constituents because: 1) although these data are desirable, they are not mandatory to this experiment; 2) the SARP does not require the headspace of RH TRU waste containers to be analyzed for these constituents; and 3) physical factors (e.g., freezing weather) and analytical difficulties (e.g., concentrations below the method detection limit) may limit the quality of these data. Level II DQOs are target DQOs. Best efforts and the best available technology will be implemented to maximize the quality of these data so that they can be utilized by others investigating gas generation and matrix depletion issues; however, Level II DQOs may be revised during the experiment. Table 5-2 summarizes the Level II target QAOs. A GC/MS analysis will be performed on those canisters that indicate substantial quantities of VOCs. Level II DQOs are also established for barometric pressure measurements because these measurements are not critical since the waste canisters will remain open to the environment throughout the duration of the experiment.

Table 5-2. Level II Target Quality Assurance Objectives

Data Point	Precision	Accuracy	MDL	Field Blank
VOCs(<60MW)	≤25% RSD or RPD	70-130 %R	0.01 vol% (100 ppm)	<3 x MDL
CO, CO ₂	N/A	N/A	N/A	N/A
O ₂ , N ₂	N/A	N/A	N/A	N/A
Pressure	5 mm Hg	1 mm Hg	N/A	N/A
Gas flow	±1.0%	±0.5%	N/A	N/A

%R	=	percent recovery
%RSD	=	percent relative standard deviation
MDL	=	method detection limit
N/A	=	not applicable
ppm	=	part(s) per million
RPD	=	relative percent difference

6.0 DATA ACQUISITION DESIGN

6.1 Identification of Point Data Sets

Point data sets are those measurements that characterize a single process parameter. The following point data sets will be obtained during the experiment:

- Concentration of hydrogen in the headspace of the sampled waste canisters
- Temperature of each waste canister at the time of sampling
- Atmospheric pressure at the time each waste canister is sampled

Attempts will be made to obtain the following point data sets during the experiment:

- Identify and determine concentration of VOC gases, with molecular weights less than 60 g/mole, in the headspace of the sampled waste canisters
- Concentration of oxygen in the headspace of the sampled waste canisters
- Concentration of nitrogen in the headspace of the sampled waste canisters
- Concentration of carbon dioxide in the headspace of the sampled waste canisters
- Concentration of carbon monoxide in the headspace of the sampled waste canisters
- Changes in the observed headspace gas concentrations over the course of the experiment (i.e., are the observed concentrations at steady-state, increasing, or decreasing?)

6.2 Specifications for Obtaining Data for Each Point Data Set

Standard methods will be used to obtain each point data set. The following methods will be used to obtain point data sets:

- Concentrations of hydrogen, VOCs, oxygen, nitrogen, carbon dioxide, carbon monoxide, and VOCs in the headspace gas will be determined using GC and MS analytical methods.
- Digital thermometers or thermocouples will be used to measure temperature.
- Pressure transducers will be used to measure ambient pressure.

6.3 Formulation of Data Quality Requirements for Each Point Data Set

Each of the 10 selected waste canisters will be sampled at least once each month throughout the experiment, which is scheduled to run from February through September 1998. The GC and MS instruments will be calibrated as directed and at the frequencies specified by approved procedures using National Institute of Standards and Technology (NIST)-traceable sources. The GC and MS instruments will also be calibrated if they fail quality assurance tests and before being placed in service after being repaired. The GC and MS instruments must meet the DQOs for precision and accuracy specified in Section 5.0 of this test plan. All data will be recorded and documented following standard LANL laboratory policy.

6.4 Preparation of Data Requirements Package for Each Test Technical Objective

Seven or eight monthly samples will be obtained from each selected waste canister. Temperature and pressure measurements will be recorded each sampling period. All sampling and analysis will be conducted as directed by approved procedures. Samples will be analyzed in the field using a GC system. Samples will be analyzed in the analytical laboratory (located in Room 3128 in the CMR at TA-3) using either a GC or an MS. Completed chain-of-custody (COC) forms will be used to transfer samples to the analytical laboratory.

7.0 DESIGN OF EXPERIMENTS

7.1 Experimental Design

The headspace gas of the waste canisters will be sampled periodically (e.g., monthly) over the course of the experiment. All headspace gas samples will be obtained following standard laboratory techniques and as specified by approved procedures. The temperature of the waste canister and ambient pressure readings will be obtained each time a waste canister is sampled. The date, time, and waste canister identification number will be recorded on approved data forms. All samples will be analyzed using GC and MS techniques. All GS and/or MS analyses will be performed as specified by LANL-approved procedures, and instruments will be calibrated using NIST-traceable standards. Sample analysis results will be used to calculate the hydrogen generation rates and effective hydrogen G-values of the waste canisters. The calculated hydrogen generation rates will be compared to the maximum allowable hydrogen generation rates specified by the SARP to determine whether the waste canisters meet the gas generation requirements specified in the SARP.

7.2 Equipment Design

Attempts will be made to select durable equipment that can tolerate the ambient temperature variations that will occur during the experiment and potentially affect equipment left outside. A MTI 200 GC will be used in the field to analyze the samples for hydrogen, VOCs, and other gases. Either a Tremetrics 540 or 541 GC or an MTI GC will be used in the analytical laboratory at the CMR. Confirmatory analysis may be performed by MS in the CMR. Volume calibrated No-Con syringes will be used to obtain and transfer headspace gas samples for laboratory analysis. Digital thermometers or thermocouples will be used to measure the headspace gas temperature at the time of sampling. A pressure monitor will be used to measure the pressure of the headspace gas at the time of sampling. A wet test meter may be used to measure total gas flow through the sample tube. Leaktight sampling lines that communicate with the headspace of the waste canisters will be used to sample headspace gas. Between sampling events, these sampling lines will be left open to the atmosphere so as not to disturb the established gas equilibrium in the canisters.

7.3 Instrumentation, Process Monitoring, and Control Design

Figure 7-1 provides a process flow diagram of the experimental design.

8.0 RUN PLAN SUMMARY

8.1 Operations Plan

Currently, no experimental hydrogen generation data exist for RH TRU waste. This experiment is necessary to obtain and analyze RH TRU waste gas generation data that can be used to derive more realistic SARP limits concerning gas generation. This experiment will sample the headspace gas of the waste canisters and analyze the samples for hydrogen. Attempts will also be made to determine the sample concentrations of other gases (e.g., oxygen, nitrogen, carbon dioxide, carbon monoxide, and VOCs) that are produced by radiolysis or that are present during waste packaging. Samples will be analyzed in the field using an MTI GC and in the analytical laboratory using either a GC or an MS. All analyses will be carried out as directed by approved procedures.

The waste canisters stored in vertical underground shafts at TA-54, Area G will be sampled once per month during the course of the experiment. The top of the shaft is covered by a cement plug, which provides a barrier of protection against precipitation. However, the waste canisters are relatively

Figure 7-1. Process Flow Diagram of Experimental Design

unprotected from ambient temperature variations. The changing ambient weather conditions may provide an opportunity to study the effects of temperature on gas generation. Freezing winter weather and hot summer days will challenge the durability of the equipment used to sample and monitor the waste canisters. Equipment failures may lead to down time and subsequent data loss until suitable replacements can be put on-line. Ambient temperature variations are not anticipated to affect data quality.

The waste canisters are equipped with filters for venting to the atmosphere and are considered to be open systems at steady-state conditions. Because the sampling process is nonintrusive, the sampling should have no impact on filter performance or integrity. This experiment proposes to measure gas concentrations using this open system model. If the data from this experiment are uninterpretable and cannot be used to support waste characterization issues, the experimental design will be evaluated and modifications will be made to create a closed system. Attempts will then be made to measure hydrogen concentrations and gas generation rates of the closed system.

8.2 Data Acquisition and Sampling Plan

The following discussion is an overview of the proposed data acquisition and sampling plan. Specific details will be provided after finalization of this test plan. All work involving the preparation of the waste canisters for sampling will be conducted under an approved radiological work permit to ensure that radiological exposures are maintained as low as reasonably achievable. Temporary sample tubes, which communicate with the waste canister headspace, will be attached to each waste canister selected for sampling. A forklift or crane will be used to remove the cement plug that covers the top of the vertical underground storage shafts that house the waste canisters. A lead shield designed and fabricated at LANL will be used to shield personnel from radiation while the waste canister is prepared for sampling. A forklift or crane will be used to lower the lead shield so it rests over the top of the waste canister shaft. With the lead shield in place, technicians will attach a flexible sample tube ($\approx 0.25''$ diameter $\times \approx 4'$ long) to the waste canister such that the sample tubes communicate with the waste canister headspace. The sample tubes will extend out from the underground storage shaft and allow the waste canisters to be sampled remotely, thereby minimizing the potential for radiation exposures while sampling the waste canisters. A two-way valve will be attached, in series, near each end of the sample tube (i.e., one two-way valve will be located near the top of the waste canister and one two-way valve will be located near the sampling end of the sample tube). The two-way valve at each end of the sample tube will be opened to allow the waste canisters to aspirate. A digital thermometer or thermocouple will be used to measure the temperature of the waste

canisters. A wet test meter may be attached to the sampling end of the sample tube to measure total gas flow through the sample tube.

After one waste canister is prepared for sampling, a forklift or crane will be used to remove the lead shield and reposition the concrete plug over the top of the underground storage shaft. The above process will be repeated until all selected waste canisters have been prepared for sampling. The following steps will be performed to sample the headspace gas after the waste canisters have reached steady-state conditions:

1. Close the two-way valve near the top of the waste canister.
2. Attach a vacuum line to the sampling end of the sample tube and withdraw all air in the sample tube to remove all atmospheric gases that may have diffused into the sample tube.
3. Close the two-way valve at the sampling end of the sample tube to prevent atmospheric gases from entering the sample tube.
4. Open the two-way valve located near the top of the waste canister.
5. Wait until the headspace gas diffuses into the sample tube to ensure a representative sample of the headspace gas will be obtained.
6. Attach the portable MTI GC to the sampling end of the sample tube.
7. Open the two-way valve located at the sampling end of the sample tube and allow a sample of the headspace gas to be drawn into the MTI GC for analysis.
8. Record the results of the MTI GC analysis and save the corresponding electronic data file.
9. Close the two-way valve located at the sampling end of the sample tube and allow the headspace gas to diffuse into the sample tube.
10. Optionally, attach a No-Con syringe of a known volume to the sampling end of the sample tube.
11. Close the two-way valve located near the top of the waste canister.
12. Open the two-way valve located at the sampling end of the sample tube and draw a sample of the headspace gas into the No-Con syringe.
13. Verify that the two-way valve at each end of the sampling tube are left in the open position to allow the waste canisters to aspirate.
14. Label the No-Con syringe with the date, time, and waste canister identification number and transport to the analytical laboratory for analysis with COC documentation.

15. Record the pressure indicated by the pressure transducer.
16. Record the temperature of the waste canister indicated by the digital thermometer or thermocouple.
17. Record the total flow recorded by the wet test meter (if one is utilized).
18. Complete all data records and COC forms and submit the samples to the analytical laboratory for analysis.
19. Repeat the above procedure until all selected waste canisters are sampled.
20. Resample the waste canisters at a frequency of about once per month throughout the duration of the experiment.

9.0 DATA ANALYSIS

For the purposes of this test plan, it is assumed that the waste canisters have aspirated for a sufficient period of time (i.e., the aspiration time defined in Appendix 3.6.11 of the SARP) to attain steady-state equilibrium conditions between layers of confinement. At steady-state conditions, the rate of gas generation by radiolysis equals the release rate of gas across each layer of confinement. The gas concentrations in the headspace gas will be used to calculate the hydrogen gas generation rate. It is assumed that the concentration of gases in the headspace gas samples are at steady-state equilibrium conditions and follow a normal distribution. Statistical analyses will be performed to evaluate when and if the hydrogen gas generation rates are constant (i.e., at steady-state).

The hydrogen gas generation rate of the waste canister is calculated from the observed hydrogen gas concentration using Equation 9-1.

$$C_g = X_H \times L_{CF} \quad (9-1)$$

where

C_g = hydrogen gas generation rate (mole/sec)

X_H = the concentration of hydrogen gas in the waste canister headspace (mole fraction)

L_{CF} = diffusion characteristic of the waste canister filter corrected for temperature using Equation 9-2.

The diffusivity of the filters used to vent the waste canisters varies with temperature, and the variations in the filter diffusivity impact the headspace gas release rate. It is necessary to correct the filter diffusivity for temperature because the waste canisters are stored in underground shafts in an open environment and the ambient temperature will vary significantly over the course of the experiment, which is scheduled to run from February through September. The waste canister filter diffusivity characteristic is corrected for temperature using Equation 9-2, which is derived from the Chapman-Enskog theory (Brodkey and Hershey 1988):

$$L_{CF,corrected} = L_{CF} \frac{T^{1.75}}{(293K)^{1.75}} \quad (9-2)$$

where

$L_{CF,corrected}$ = diffusion characteristic (mole/sec/mole fraction) of the waste canister filter corrected for temperature

L_{CF} = experimentally determined diffusion characteristic (mole/sec/mole fraction) of the waste canister filter at 293°K (values are listed in Appendix 1.3.5 of the SARP)

T = temperature of the waste canister filter at the time of sampling (°K)

293K = room temperature (°K).

The average hydrogen gas generation rate of the waste canisters is calculated using Equation 9-3.

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (9-3)$$

where

$\bar{x}$ = the average hydrogen gas generation rate of the waste canister

n = the number of times the hydrogen gas generation rate of the waste canister was measured

x_i = the hydrogen gas generation rate of the waste canister as calculated from the i th sample of the headspace gas.

The standard deviation of the hydrogen gas generation rate of the waste canister is calculated using Equation 9-4:

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (9-4)$$

where

s = the standard deviation of the hydrogen gas generation rate of the waste container, and all other variables are as previously defined.

The effective hydrogen G-value is calculated using Equation 9-5.

$$\frac{G}{100} = \frac{C_g \times N_A \times 1.602 \times 10^{-19}}{Q} \quad (9-5)$$

where

G = effective G value for hydrogen gas (molecules of hydrogen generated/100 eV of emitted energy)

N_A = Avogadro's number (6.0225×10^{23} molecules/mole)

Q = decay heat of the waste canister (W)

1.602×10^{-19} = conversion factor (watt sec/eV).

The calculated, effective hydrogen generation rate of the waste canisters will be compared to the maximum allowable hydrogen gas generation rate limits. The maximum allowable hydrogen gas generation rates for content codes LA 325A and LA 325C are 1.934×10^{-7} mole/sec and 4.150×10^{-7} mole/sec, respectively (SARP). The uncertainty or error in the calculated hydrogen generation rate can be quantitated by analytically (or numerically) propagating the uncertainties of the various parameters (e.g., hydrogen gas concentration, waste canister filter diffusion characteristic, and waste canister decay heat). The specific methodology that will be implemented to correct for the uncertainties will be presented in the data reduction and analysis procedure that will be developed for this experiment.

10.0 SUPPORT REQUIREMENTS

All sampling and analysis will be conducted by the LANL Chemical Sciences and Technology Division. The principal investigator is Dr. Larry Field ([505] 665-0919, lfield@lanl.gov). The Health Physics Operations Group and the Industrial Hygiene and Safety Group will provide oversight as required by approved procedures. Support staff include trained mechanical, electronics, and chemical technicians. No special facility requirements are anticipated for this study. No radioactive waste is expected to be generated during this test. Laboratory wastes will be managed as directed by approved procedures.

11.0 REFERENCES

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APPENDIX A

Prioritization of the Remote-Handled TRU Waste Canisters for Headspace Gas Sampling and Estimation of Gas Generation Rates (LANL 1997)

PRIORITIZATION OF THE REMOTE-HANDLED TRU WASTE CANISTERS FOR HEADSPACE GAS SAMPLING AND ESTIMATION OF GAS GENERATION RATES

This report describes the methodology used to prioritize the headspace gas sampling of the 17 remote-handled (RH) transuranic (TRU) canisters (i.e., LA03-LA19) currently stored in shafts at TA-54, Area G. The headspace gas sampling program will sample the selected RH-TRU canisters to estimate the net gas and flammable gas generation rates and the corresponding G values. Multicriteria decision making was used to prioritize the canisters.

The characterization data used in this analysis was obtained from the *LANL MST-14 Waste Description Records* and the Los Alamos National Laboratory (LANL) TRU Waste Storage Records (Benchmark 1997). The quality of the available data for each canister was variable. Data for canisters LA03-LA06 and LA19 were rather incomplete in comparison to the data available for LA07-LA18. The characterization data for the canisters were reviewed and recorded in an Excel spreadsheet. The following criteria were identified as being critical to radiolytic gas generation: decay-corrected decay heat (W) due to alpha activity, decay-corrected decay heat (watts) due to beta/gamma activity, amount of hydrogenous material (defined by the hydrogen content factor [HCF]), number of 7-in. plastic alpha transfer cans, number of solidified one-gal. paint cans (defined by the solidified cans factor [SCF]), percent of the alpha cans that have a operator declared fissile mass that is within two standard deviations of the fissile mass determined by passive/active neutron assay (operator/assay agreement), and age of the waste. The alpha and beta/gamma activity were selected because radiolytic hydrogen gas generation is directly proportional to the amount of radioactivity interspersed throughout the waste. The alpha and beta/gamma activity were decay corrected to October 1, 1997. It was not possible to quantify the mass of hydrogenous material in each canister from the characterization data. However, it was possible to estimate the percent of items in the canisters that are hydrogenous. The percent of hydrogenous items was selected because it provides an estimate of the amount of hydrogenous material in each canister. The number of plastic alpha transfer cans was selected because they are constructed from polycarbonate, a hydrogenous material. The number of solidified paint cans was selected because approximately 650-850 ml of water, a hydrogenous material, was used during the solidification process. The agreement between the operator declared and assay determined fissile masses was selected because increasing agreement between these two values was associated with higher level of confidence that the reported fissile masses were correct. Finally, the age of the waste was selected because the fraction of the original hydrogenous material remaining in the waste decreases with time due to radiolytic breakdown, and therefore, higher gas generation rates are associated with younger wastes. When data for a particular criterion was not available, a value of zero was assumed.

The decision matrix with corresponding values for each canister and criterion canister values for the above mentioned criteria are presented in Table 1. Table 2 presents the values from Table 1 that have been normalized (scaled) to one as a first step in applying multicriteria decision making techniques. All criteria, except the percentage of hydrogenous items, the number of solidified cans, and the average age of the waste, were normalized using Equation 1:

$$\text{Normalized criterion value}_i = \frac{\text{criterion value}_i}{\text{criterion value}_{\max}} \quad (1)$$

where

criterion value_i = the *i*th value of a particular criterion (e.g., 29, the number of alpha transfer cans in LA04)

criterion value_{max} = the maximum value of a particular criterion (e.g., 39, the maximum number of alpha transfer cans in any canister).

The percent hydrogenous material per canister was normalized by a two-step process. First, non-normalized HCFs were calculated using Equation 2:

$$\text{nonnormalized HCF}_i = \text{absolute value} \left[\frac{\text{percent hydrogenous material}_i - \bar{x}}{\bar{x}} \right] \quad (2)$$

where

percent hydrogenous material_i = the percentage of the total items in the *i*th canister that are hydrogenous

$\bar{x}$ = the mean percentage of hydrogenous material per canister based on values for all canisters.

Then, the normalized HCFs were calculated by substituting the nonnormalized HCFs (for each canister) from Equation 2 into Equation 1. The normalized HCFs were calculated as described above because this method assigned the higher criterion values to canisters containing either large or small amounts of hydrogenous materials and lower criterion values were assigned to those canisters with average amounts of hydrogenous material. Therefore, canisters with large or small amounts of hydrogenous material were favored over canisters with average amounts of hydrogenous material.

The number of solidified cans was also normalized by a two step process. First the non-normalized SCFs were calculated using Equation 3:

$$\text{nonnormalized SCF}_i = \text{absolute value} \left[\frac{\text{number of solidified cans}_i - \bar{x}}{\bar{x}} \right] \quad (3)$$

where

number of solidified cans_i = the number of solidified cans in the *i*th canister

$\bar{x}$ = the mean number of solidified cans per canister based on values for all canisters.

Then, the normalized SCFs were calculated by substituting the non-normalized SCFs (for each canister) from Equation 3 into Equation 1. This method was used to calculate the normalized SCFs because

canisters with a large or small number of solidified cans were favored over canisters with an average number of solidified cans.

The average age of the waste was normalized using the following Equation 4:

$$\text{Average age of waste}_i = 1 - \frac{\text{average age of waste}_i}{\text{average age of waste}_{\max}} \quad (4)$$

where

$\text{average age of waste}_i$ = the average age of the waste in the i th canister
 $\text{average age of waste}_{\max}$ = the average age of the waste in the canister having the maximum age.

This method was used to normalize the average age of the waste because it assigned higher values to younger canisters and, therefore, was consistent with the other criteria and assigned higher values to canisters having more desirable characteristics.

Three sets of weights for the criteria were derived. The first set was calculated through the weighted least squares method (Hwang and Yoon 1981) using a criteria comparison matrix (Table 3) whose elements are the values of the intensity scale of importance developed by Saaty (Hwang and Yoon 1981). The values in Table 3 were selected by Benchmark personnel based on their value judgments in comparing the criteria two at a time. A value of 1 indicates the criteria are considered to be of equal importance. A value of 3 indicates there is weak importance of one criterion over another. A value of 5 indicates an essential or strong importance of one criterion over another. A value of 7 indicates demonstrated importance of one criterion over another. The second set of weights for the criteria was calculated through the entropy method (Hwang and Yoon 1981). Two separate FORTRAN computer programs were developed to implement the two different criteria weighting methods. The third set was obtained by combining the least squares method set with the entropy method set. Table 4 presents the three sets of criteria weights.

Seven different preference orderings for the canisters were obtained by using the three sets of criteria weights with two different multicriteria decision making methods: (1) simple additive weighting, and (2) technique for order preference by similarity to ideal solution (or TOPSIS) (Hwang and Yoon 1981). A spreadsheet application was used to derive overall scores for each canister using simple additive weighting and a FORTRAN computer code was developed to provide scores using the TOPSIS method. Table 5 lists the seven different preference orderings. Following the preference ordering, three ordering techniques were applied to aggregate the seven sets of preference orderings (Hwang and Yoon 1981). The first technique (average ranking procedure) ranks the canisters according to their mean rankings. The second (Borda method) is based on majority rule binary relation. The third procedure (Copeland method) is a modification of the majority rule case taking into account "losses" as well as "wins." A FORTRAN program was developed to perform the aggregation using each of the three procedures. Table 6 summarizes the results of the aggregation. The last step in prioritizing the canisters for sampling consisted of a synthesis phase, which analyzed the results of the three ordering procedures to arrive at a single overall ranking of the canisters that is based on all available data, different perspectives, and a variety of analytical tools. Thus the developed ranking is technically defensible and is based on a structured formal methodology. Table 7 lists the final ranking of canisters in decreasing preference for headspace sampling. LA15, LA07, and LA10 are most likely to generate gases via radiolytic processes and, therefore, should be given the highest

priority for headspace gas sampling. LA09, LA08, and LA11 are least likely to generate gases via radiolytic processes because of the normalized HCF and, therefore, should also be given high priority for headspace gas sampling.

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Table 1. Characteristics of RH-TRU Canisters

Canister	Alpha Activity (W)	Beta/Gamma Activity (W)	Percentage of Hydrogenous Items	Number of Alpha Cans	Number of Solidified Cans	Operator/ Assay Agreement	Age of Waste (yr)
LA03	2.20E-2	1.54E-1	11.90	0	0	0	7.46
LA04	7.26E-4	5.11E-3	6.25	29	0	0	7.09
LA05	1.98E-3	1.39E-2	21.62	39	0	0	6.98
LA06	7.08E-3	4.98E-2	9.52	17	0	0	6.66
LA07	7.97E-1	5.60	2.73	36	0	19.44	0
LA08	7.92E-1	5.56	16.00	36	0	13.89	7.71
LA09	7.83E-1	5.50	31.68	36	2	29.41	7.66
LA10	6.84E-1	4.81	40.23	36	4	31.25	7.76
LA11	7.26E-1	5.09	16.78	36	3	30.30	7.73
LA12	6.97E-1	4.89	40.27	36	3	6.06	7.87
LA13	6.97E-1	4.89	33.82	36	5	16.67	7.64
LA14	6.27E-1	4.40	32.71	36	8	0	7.50
LA15	4.67E-1	3.27	57.18	36	18	0	7.40
LA16	6.55E-2	4.59E-1	9.30	12	0	8.33	7.56
LA17	8.53E-2	5.99E-1	37.93	12	2	0	7.48
LA18	3.44E-2	2.42E-1	17.19	16	1	6.67	7.33
LA19	4.71E-2	0	0	0	0	0	0

Table 2. Normalized Characteristics of RH-TRU Canisters

Canister	Alpha Activity (W)	Beta/ Gamma Activity (W)	Hydrogen Content Factor	Number of Alpha Cans	Number of Solidified Cans	Operator Assay Agreement	Average Age of Waste (yr)
LA03	0.028	0.027	0.311	0.000	0.000	0.000	0.051
LA04	0.001	0.001	0.475	0.744	0.000	0.000	0.099
LA05	0.002	0.002	0.030	1.000	0.000	0.000	0.112
LA06	0.009	0.009	0.380	0.436	0.000	0.000	0.153
LA07	1.000	1.000	0.577	0.923	0.000	0.622	0.000
LA08	0.994	0.994	0.193	0.923	0.303	0.444	0.020
LA09	0.982	0.982	0.261	0.923	0.158	0.941	0.027
LA10	0.858	0.859	0.509	0.923	0.013	1.000	0.014
LA11	0.911	0.910	0.170	0.923	0.086	0.970	0.017
LA12	0.875	0.874	0.510	0.923	0.086	0.194	0.000
LA13	0.875	0.874	0.323	0.923	0.059	0.533	0.029
LA14	0.787	0.786	0.291	0.923	0.276	0.000	0.047
LA15	0.586	0.585	1.000	0.923	1.000	0.000	0.060
LA16	0.082	0.082	0.387	0.308	0.303	0.267	0.039
LA17	0.107	0.107	0.442	0.308	0.158	0.000	0.049
LA18	0.043	0.043	0.158	0.410	0.230	0.213	0.069
LA19	0.059	0.000	0.000	0.000	0.000	0.000	0.000

Table 3. Criteria Comparison Matrix

	α Activity	β/γ Activity	Hydrogen Content Factor	Number of Cans	Solidified Cans Factor	Operator/ Assay Agreement	Average Age of Waste
α Activity	1	1	1	1	5	7	7
β/γ Activity	1	1	1	1	5	7	7
Hydrogen Content Factor	1	1	1	1	5	5	3
Number of Cans	1	1	1	1	5	5	5
Solidified Cans Factor	0.2	0.2	0.2	0.2	1	5	5
Operator/Assay Agreement	0.143	0.143	0.2	0.2	0.2	1	1
Average Age of Waste	0.143	0.143	0.333	0.2	0.2	1	1

Table 4. Sets of Criteria Weights

Criterion	Weight Least Squares Method-Saaty (λ_i)	Entropy Method (w_i)	Combined Weighted Least Squares and Entropy (w_i^0)
Alpha Activity	0.2296	0.1429	0.2850
Beta/Gamma Activity	0.2296	0.1505	0.2997
Hydrogen Content Factor	0.2103	0.0638	0.1164
Number of Cans	0.2173	0.0534	0.1008
Solidified Cans Factor	0.0472	0.2462	0.1008
Operator/Assay Agreement	0.0326	0.2251	0.0634
Average Age	0.0334	0.1181	0.0339

Table 5. Canister Ranking by Multicriteria Decision Making Methods

Canister	Weighted Least Squares Method			TOPSIS Method			
	Standard Method	Entropy Method Weights	Combined Weights Method	Weighted Least Squares	Entropy Weights	Combined Weights	No Weights
LA03	16	16	16	15	16	16	16
LA04	10	13	12	10	14	12	11
LA05	11	14	14	12	13	14	12
LA06	14	15	15	13	12	13	10
LA07	1	6	1	2	6	4	6
LA08	5	5	3	7	4	2	4
LA09	2	1	2	5	2	3	2
LA10	3	3	4	4	5	6	3
LA11	8	2	5	9	3	7	5
LA12	6	8	6	3	10	5	9
LA13	7	7	7	6	8	8	7
LA14	9	9	9	8	7	9	8
LA15	4	4	8	1	1	1	1
LA16	13	10	10	14	9	10	13
LA17	12	12	11	11	15	11	15
LA18	15	11	13	16	11	15	14
LA19	17	17	17	17	17	17	17

Table 6. Results of Aggregation

Rank	Average Ranking Procedure	Borda Method	Copeland Method
1st	LA09	LA15	LA15
2nd	LA15	LA09	LA09
3rd	LA07	LA07, LA08, LA10	LA07, LA08, LA10
4th	LA10	LA11	LA11
5th	LA08	LA12	LA12
6th	LA11	LA13	LA13
7th	LA12	LA14	LA14
8th	LA13	LA16	LA16
9th	LA14	LA04	LA04
10th	LA16	LA17	LA17
11th	LA04	LA05	LA05
12th	LA17	LA06	LA06
13th	LA05	LA18	LA18
14th	LA06	LA03	LA03
15th	LA18	LA19	LA19
16th	LA03		
17th	LA19		

Table 7. Final Ranking of RH TRU Canisters for Headspace Gas Sampling

Rank	Canister
1	LA15
2	LA09
3	LA07
4	LA10
5	LA08
6	LA11
7	LA12
8	LA13
9	LA14
10	LA16
11	LA04
12	LA17
13	LA05
14	LA06
15	LA18
16	LA03
17	LA19