LA-UR-96-4002

Approved for public release; distribution is unlimited.

CONF-970335--20

Title: Los Alamos National Laboratory Transuranic Waste Sampling Projects

RECEIVED
FEB 14 1997
OSTI

Author(s): David R. Yeamans, CST-7
Pamela S. Z. Rogers, CST-7
Eugene J. Mroz, CST-7

MASTER

Submitted to: Waste Management '97 Conference
Tucson, Arizona
March 2-7, 1997

Los Alamos
NATIONAL LABORATORY

Full Paper

"Los Alamos National Laboratory TRU Waste Sampling Projects"

David Yeamans, Pamela Rogers, and Eugene Mroz
Chemical Sciences and Technology Division, Los Alamos National Laboratory,
Los Alamos, New Mexico, 87545

Abstract

The Los Alamos National Laboratory (LANL) has begun characterizing transuranic (TRU) waste in order to comply with New Mexico regulations, and to prepare the waste for shipment and disposal at the Waste Isolation Pilot Plant (WIPP), near Carlsbad, New Mexico. Sampling consists of removing some head space gas from each drum, removing a core from a few drums of each homogeneous waste stream, and visually characterizing a few drums from each heterogeneous waste stream. The gases are analyzed by GC/MS, and the cores are analyzed for VOC's and SVOC's by GC/MS and for metals by AA or AE spectroscopy. The sampling and examination projects are conducted in accordance with the "DOE TRU Waste Quality Assurance Program Plan" (QAPP) and the "LANL TRU Waste Quality Assurance Project Plan," (QAPjP), guaranteeing that the data meet the needs of both the Carlsbad Area Office (CAO) of DOE and the "WIPP Waste Acceptance Criteria, Rev. 5," (WAC).

INTRODUCTION

DRIVERS FOR SAMPLING AND DATA QUALITY

Two documents require LANL to sample its TRU waste. First, the New Mexico Environment Department (NMED), being the enforcing agency for the United States Environmental Protection Agency (EPA) regarding the Resource Conservation and Recovery Act (RCRA), issued the unilateral Federal Facilities Compliance Order (FFCO) that, among other directives, orders LANL to place its mixed TRU waste into a compliant storage configuration. Compliance requires a sampling and analysis program to determine the hazardous constituents of the waste. Second, the Department of Energy (DOE) Order 5820.2b requires sites to evaluate their waste for disposal at suitable sites including the Waste Isolation Pilot Plant (WIPP), near Carlsbad, New Mexico. The evaluation requires sampling and analysis to determine compliance with WIPP WAC rev.5. The program quality is guided by the DOE Carlsbad Area Office (CAO) "Quality Assurance Program Description"[1] (QAPD) that calls for adherence to ASME NQA-1 standards, and by the DOE "TRU Waste Characterization Quality Assurance Program Plan" [2] (QAPP), and by guidelines approved by NMED. Activities are carried out by the "LANL TRU Waste Characterization Quality Assurance Project Plan" [3] (QAPjP). The program also meets Department of Transportation (DOT) and Nuclear Regulatory Commission requirements for characterizing the waste prior to transporting it to WIPP.

TYPES OF SAMPLING

LANL performs three types of sampling or intrusive characterization: 1) head space gas sampling, 2) coring cemented or solid waste forms, and 3) visual examination that verifies existing documentation of the matrix and contents. LANL samples every drum of waste for head space gas, but samples only a statistically significant portion of the drums for non-gaseous RCRA constituents and for visual verification purposes. Analysts test the waste samples for flammable and RCRA hazardous constituents.

RANDOM SELECTION FOR SAMPLING

Waste generators and waste managers classify LANL TRU wastes that are produced from the same location, process, and materials into waste streams. The TRU Waste Characterization Program Site Project Officer (SPO) randomly selects a statistically significant subset of drums to represent a waste stream, and specifies the samples to be taken or the drums to be inspected.

DATA QUALITY

To insure that data quality meets the requirements of the "WIPP Waste Acceptance Criteria, Rev. 5," [4] (WAC), each analysis system that LANL uses qualifies in the CAO Performance Demonstration Program.

GAS SAMPLING AND ANALYSIS

Analysts sample head space gas by inserting a needle through the filtered vent of a drum and pumping the head space gas into a gas chromatograph sample loop. They store up to 24 samples, control standards, and field duplicates in a gang of sample vessels, and set the instrument to analyze them automatically and sequentially during the night shifts. After sampling each drum, the samplers replace the filtered vent with a new one. Chemists analyze the gas for 30 volatile organic compounds (VOC's) by gas chromatograph /mass spectrometer (GC/MS) (alcohols and ketones by gas chromatograph /flame ionization detector (GC/FID)) and for hydrogen and methane by GC.

CORE DRILLING AND SAMPLING

After gas sampling, sampling personnel take cores from a number of the drums in each waste stream of homogeneous waste. The waste form is cemented or solidified process residues or is soil and gravel. Personnel use the Drum Coring Glove (DCG) box to extract the samples by rotational coring methods and then separate a sample of the core in an isolated section of the DCG. The sample is sent to either the mobile Analytical Glove box or to a fixed laboratory facility for analysis.

The DCG is a glove box and drill machine designed and assembled at LANL (see Figure 1). It is about 10 feet long, 10 feet high at its maximum, and 36 inches wide. Its compact size allows it to fit into a mobile container so it can be shipped and operated at any of several sites. Drillers attach drums to the glove box by either the conventional bag-on method or by the bagless posting method that reduces secondary waste to near zero and eliminates the use of an overpack container for the cored waste drum. The drill head is composed of industrial machine components typically found in milling machines. The 5 kW head traverses on a slide rail system and feeds up and down on a dovetail slide, allowing full depth coring on 55-gallon drums from any location across the radius of the drum. Random location sampling is accomplished by rotating the drum to a randomly chosen angle beneath the spindle.

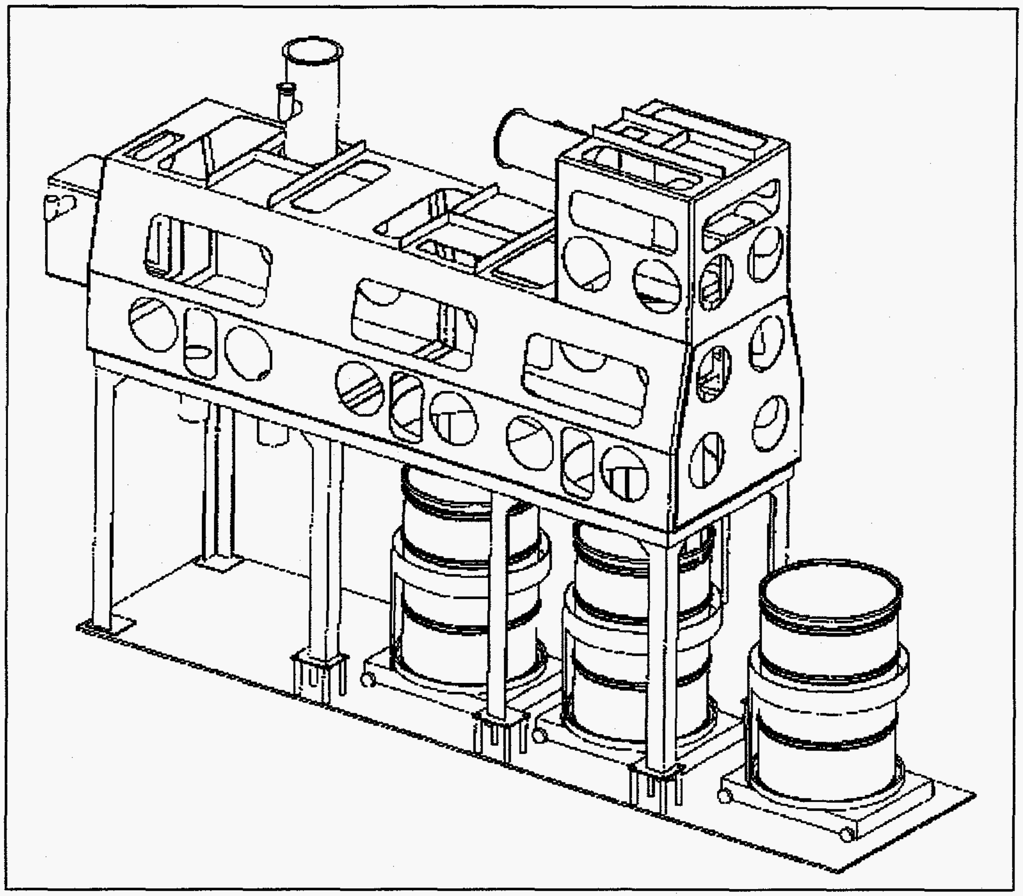

Figure 1.
Conceptual Drawing of Drum Coring Glove Box

Operators control the position, speed, and feed rate of the drill, collecting a 30-inch (76 cm) core in less than five minutes, by driving an auger that was developed jointly by DOE and hard rock drill manufacturers. [5] The auger is composed of an outer shell that cuts the matrix and elevates cuttings to the top of the hole, a concentric core barrel that does not rotate, and a Teflon® liner that closely surrounds the core. Rotation is near 300 Hz with a feed rate of 0.25 cm per second at up to 4400 newtons vertical force. After retracting the auger assembly with an intact core, the drillers remove the core barrel, with liner and core inside, from the auger and transfer it to the sampling side of the DCG. The samplers subdivide the core and package it as required for analysis by a qualified Los Alamos chemical laboratory. Sample sizes are 5 grams for VOC's, 5 grams for metals, 30 grams for semi-volatile organic compounds (SVOC's), and 30 grams for an archive sample to be held for further study. Following sampling, the drillers remove the drum from the glove box and return it to the waste stream. Throughput of the system is one to two samples per day.

RCRA ANALYSIS OF CORE SAMPLES

The QAPP lists over 30 gas volatile or total volatile organic compounds, 10 semi-volatile organic compounds, 7 PCB's, and 14 metals to be sought by analysis of the core samples. Two laboratories are available at LANL to analyze core samples for RCRA constituents, the CMR building, and the portable Analytical Glove box (AG). The AG has not been used yet for analysis of TRU waste samples, so neither it nor its accelerated solvent extraction method are described here.

The methods used for VOC's analysis were based on SW8466 for GC/MS, or on the DOE Methods Manual Procedure 440.27 5 for GC/FID for nonhalogenated VOC's. To minimize handling of the samples in the analysis glovebox, the VOC samples are packed at the coring site into two separate vials with septum tops. Water is injected into one vial, methanol into the other, and the two leachates are then analyzed for VOC's using GC/MS. For SVOC's, approximately 25 gm. of sample is pulverized and extracted for 24 hours with methylene chloride, and the leachate is analyzed by GC/MS using method SW846 6.

To date, LANL has not performed the Toxicity Characteristic Leach Procedure on waste samples to determine the leachability of metals from the waste matrix. However, the total metal content of samples has been measured by the following method. Analysts take a 5 gm split of the pulverized SVOC sample and microwave digest it in HNO3+HCl, and then analyze solution by ICP/MS and ICP/AES. Mercury analysis is performed by cold vapor atomic fluorescence spectroscopy. No LANL waste streams contain PCB's, so analysis for PCB's is not required.

VISUAL CHARACTERIZATION

The SPO selects some of the drums from each heterogeneous waste stream for visual characterization. To characterize the waste, personnel introduce a drum of waste to the portable Waste Characterization Glove box (WCG), open the drum, and record the contents of the drum on audio/video tape and in log books. They then place the waste into a new drum and return it to the waste stream. The glovebox is 4 work stations long and one wide. It has a horizontal bag-on at one end for introduction of the waste drum, and it has vertical bag-off ports underneath for repackaging the waste and for removing samples. There is an introductory airlock at one end of the box, and the box has compressed air and electrical service for scales and pneumatic tools. Video cameras mount outside the box for documenting the waste container contents.

Using approved procedures, operators open drums of waste and count and weigh the contents of all inner bags. Each item is recorded on electronic media and in the operator's logbook, and the results of the characterization are compared with radiography records and other documentation for the drum. If the two sets of documentation match, the drum was properly described in the first set, but if they do not match, the drum was miscertified and this information contributes to the miscertification rate for this waste stream. A high miscertification rate would require that more drums from the waste stream be visually characterized in future efforts.

RESULTS OF SAMPLING AND ANALYSIS

The SPO uses the analytical results from sampled drums to calculate upper and lower 90 percent confidence limits for the mean concentrations of RCRA-regulated constituents, and compares those limits to the regulatory threshold limits for the constituent. Drums are sampled in batches of 20, or the number that can be taken in two weeks if that is less than or equal to 20, and field duplicate samples are taken to ensure sampling accuracy. The data are used to determine if the waste stream is RCRA hazardous and if it meets the relevant requirements for emplacement at WIPP. The SPO also evaluates data from head space gas sampling that determine whether the drum has more than 500 ppm total flammable VOC's, a condition that would prohibit their shipment in a TRUPACT-II container.

Table 1 is a summary of data from a typical sampling batch of 20 drums. Results from the VOC and SVOC analyses indicate that methanol is the only RCRA hazardous substance in the core samples. Trichloroethylene, known to be used in the plutonium processing stream, is not present in the core samples. Waste water treatment sludge that is F001-listed5 did not contain detectable quantities of the target compounds. Metals analyses reveal that the wastes contain regulated amounts of cadmium, chromium, nickel, and zinc, all of which are expected as the result of plutonium processing operations.

Head space gas analysis indicates that toluene is present in the head space of nearly all of the waste containers except for those in the pyrochemical salts waste stream, but that it is below the project required quantitation limit (PRQL) of the QAPjP. Trichloroethylene and other F-listed constituents were not observed in any of the head space samples. Over 10 tentatively identified compounds have been noted in the cemented waste streams but only one from the pyrochemical salts. There is no requirement at this time to identify or quantify them. Hydrogen is present in two of the waste streams at about 0.2 volume percent.

CONCLUSIONS

Through a combination of visual verification, 100% waste sampling, and statistical sampling, LANL is characterizing its waste by waste stream so the waste can be shipped to WIPP. The

[5] Containing the following spent solvents used as degreasers—tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride or chlorinated fluorocarbons.

data meet quality assurance objectives and are valid for certifying waste to requirements of the "WIPP Waste Acceptance Criteria, Rev. 5," (WAC).

THIS PAGE RESERVED FOR TABLE 1

[1] *Quality Assurance Program Description.* CAO-94-1012, Current Revision, Carlsbad, New Mexico, Carlsbad Area Office, U.S. Department of Energy (1994).

[2] *Transuranic Waste Characterization Quality Assurance Program Plan,* Revision 0. CA0-94-1010, Carlsbad, New Mexico, Carlsbad Area Office, U.S. Department of Energy (1995).

[3] *Los Alamos National Laboratory Transuranic Waste Characterization Quality Assurance Project Plan.* Revision 0. CSTDO-PLAN-002,R.0, Los Alamos, New Mexico, Los Alamos National Laboratory (1995).

[4] *Waste Acceptance Criteria For The Waste Isolation Pilot Plant.* Revision 5. DOE/WIPP-069 Carlsbad, New Mexico, U.S. DOE Carlsbad Area Office (1996)

[5]. Connolly, Michael J., *Idaho National Engineering Laboratory Simulated Solidified Transuranic Waste Sampling Program*, EGG-WM-1122, Bechtel National, Inc., San Francisco, (1994).

[6]. *Transuranic Waste Characterization Sampling and Analysis Methods Manual*, Revision 0, DOE/WIPP-91-043, Carlsbad, New Mexico, U.S. DOE Carlsbad Area Office (1995).

[7]. *Test Methods for Evaluating Solid Waste, Volume 1A: Laboratory Manual Physical/Chemical Methods*, Current Revision, Washington, DC, U.S. Environmental Protection Agency (1986).

TABLE 1

AVERAGE CONCENTRATION OF RCRA HAZARDOUS CONSTITUENTS BY WASTE STREAM OF SELECTED TRU WASTE AT LOS ALAMOS NATIONAL LABORATORY

Analyte	HEADSPACE GAS — Waste Stream (N) / Average concentration (ppm)	VOC's — Waste Stream (N) / Average concentration (mg/kg)
Benzene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Bromoform	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Carbon Disulfide	N/A	1/ u , 2/ u , 4/ u
Carbon Tetrachloride	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Chlorobenzene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Chloroform	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
1,4-Dichlorobenzene	N/A	1/ u , 2/ u , 4/ u
ortho-Dichlorobenzene	N/A	1/ u , 2/ u , 4/ u
Cyclohexane	*1/ u , 2/ u , 3/ u , 4/ u*	N/A
1,1-Dichloroethane	1/ u , 2/ u , 3/ u , 4/ u	N/A
1,2-Dichloroethane	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
1,1-Dichloroethylene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
cis- 1,2 -Dichloroethylene	1/ u , 2/ u , 3/ u , 4/ u	N/A
Ethyl Benzene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Ethyl Ether	1/ u , 2/ u , 3/ u , 4/ u	N/A
Methylene Chloride	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
1,1,2,2-Tetrachloroethane	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Tetrachloroethylene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Toluene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ 62.5
1,1,1-Trichloroethane	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
1,1,2-Trichloroethane	N/A	1/ u , 2/ u , 4/ u
Trichloroethylene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Trichlorofluoromethane	N/A	1/ u , 2/ u , 4/ u
1,1,2-Trichloro-1,2,2-trifluoroethane	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
1,2,4 -Trimethylbenzene	1/ u , 2/ u , 3/ u , 4/ u	N/A
1,3,5-Trimethylbenzene	1/ u , 2/ u , 3/ u , 4/ u	N/A
Vinyl Chloride	N/A	1/ u , 2/ u , 4/ u
p/m-Xylene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
o-Xylene	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Acetone	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Butanol	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Ethyl Ether	N/A	1/ u , 2/ u , 4/ u
Formaldehyde	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Isobutanol	N/A	1/ u , 2/ u , 4/ u
Methanol	1/ u , 2/ 160 , 3/ u , 4/ 125	1/ 243 , 2/ >1000 , 4/ 158
Methyl ethyl ketone	1/ u , 2/ u , 3/ u , 4/ u	1/ u , 2/ u , 4/ u
Methyl isobutyl ketone	1/ u , 2/ u , 3/ u , 4/ u	N/A
Pyridine	N/A	1/ u , 2/ u , 4/ u
Hydrogen (Volume %)	1/ 0.15, 2/ 0.13, 3/ u, 4/ u	N/A
Methane (Volume %)	1/ u , 2/ u , 3/ u , 4/ u	N/A

SVOC's Analyte	Waste Stream (N) / Average concentration (mg/kg)
Creasols	1/ u , 2/ u , 4/ u
1,4-Dichlorobenzene	1/ u , 2/ u , 4/ u
ortho-Dichlorobenzene	1/ u , 2/ u , 4/ u
2,4-Dinitrophenol	1/ u , 2/ u , 4/ u
2,4-Dinitrotoluene	1/ u , 2/ u , 4/ u
Hexachlorobenzene	1/ u , 2/ u , 4/ u
Hexachloroethane	1/ u , 2/ u , 4/ u
Nitrobenzene	1/ u , 2/ u , 4/ u
PCB's (not required)	N/A
Pentachlorophenol	1/ u , 2/ u , 4/ u
Pyridine	1/ u , 2/ u , 4/ u

METALS (Total) * Analyte	Waste Stream (N) / Average concentration (mg/kg)
Antimony	1/ u , 2/ u , 3/ u , 4/ u
Arsenic	1/ u , 2/ u , 3/ u , 4/ u
Barium	1/ u , 2/ u , 3/ u , 4/ u
Beryllium	1/ u , 2/ u , 3/ u , 4/ u
Cadmium	1/ 32 , 2/ u , 3/ u , 4/ u
Chromium	*1/ 225 , 2/ 299 , 3/ 169 , 4/ 502*
Lead	1/ u , 2/ u , 3/ u , 4/ u
Mercury	1/ u , 2/ u , 3/ u , 4/ u
Nickel	1/ 328 , 2/ 253 , 3/ 311 , 4/ 340
Selenium	1/ u , 2/ u , 3/ u , 4/ u
Silver	1/ u , 2/ u , 3/ u , 4/ u
Thallium	1/ u , 2/ u , 3/ u , 4/ u
Vanadium	1/ u , 2/ u , 3/ u , 4/ u
Zinc	1/ 146 , 2/ u , 3/ u , 4/ 131

	Headspace Gas	VOC's	SVOC's
Tentativily Identified Compounds (Number)	1/ 12 , 2/ 11.5 , 3/ 0.2 , 4/ 13	1/ 1.6 , 2/ 1.0 , 4/ 1.2	1/ 6.0 , 2/ 6.6 , 4/ 11.2

NOTES

u = Below the Project Required Quantitation Limit (PRQL)

VOC's and SVOC's are not present in Pyrochemical salts (waste stream 3)

	Waste Stream
1	Waste Water Treatment LA111A
2	Plutonium Processing LA114A (RCRA F-listed)
3	Plutonium Processing LA1124A (Pyrochem salts)
4	Plutonium Processing LA114A (Not F-listed)