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Author(s): Laura Worl, NMT-11
Catherine French-Sidoti, JCNNM
Lawrence Kreyer, PS-1

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METROLOGY AND QUALITY ASSURANCE FOR SURVEILLANCE OF GAS COMPOSITIONS OVER PuO_2

Catherine French-Sidoti, Lawrence Kreyer, Laura Worl
Los Alamos National Laboratory
Los Alamos, NM 87544

INTRODUCTION

Until the late 1980s, a primary mission of the Department of Energy (DOE) has been the production of nuclear materials for nuclear weapons. Termination of the Cold War in 1989 and the subsequent nuclear weapons treaties dramatically decreased the inventory needs for nuclear weapons. These activities resulted in the consolidation of nuclear material inventories and activities, generating substantial amounts of surplus nuclear materials ranging from plutonium metal and pure oxides to impure plutonium residues. Packaging and storage of these materials in physically and environmentally safe configurations for significant time periods were required.

In 1993 the Defense Nuclear Facility Safety Board (DNFSB) and the DOE Office of Nuclear Safety examined the storage of metal and oxides at the Rocky Flats Plant that ultimately resulted in recommendation 94-1, calling for a standard to define the processing and storage of plutonium bearing materials. This recommendation generated a standard for storage of plutonium metals and oxides, DOE-STD-3013-2000, which is now in its fourth revision. The current DOE 3013 Standard is limited to metal and oxides, which contain greater than 30 weight percent plutonium and uranium. The 3013 Standard requires that the oxide be calcined to 950^{0}C for two hours in an oxidizing environment. Before packaging, the oxide is required to have less than 0.5 weight percent moisture. Up to five kilograms of the stabilized oxide material is subsequently sealed in a set of two-nested welded stainless steel container, which must have a power less than 19 Watts.

The processing, handling, and storage of plutonium metal has been understood for many years based on results from plutonium manufacturing and storage of components. However, the long-term storage of pure and impure plutonium oxides in hermetically sealed containers is not well understood and presents some unique challenges in storage. Of current concern is the pressurization of the sealed containers loaded with actinide oxides, where several causes of pressurization have been identified. Chemical and radiolytic reactions can generate gases in the containers from material decomposition and the reactions and rates of reactions are areas of ongoing research. Plutonium oxides strongly adsorb gaseous species such as water and the subsequent decomposition of the adsorbed species can lead to pressurization of a sealed container. Contact of plutonium oxides with organic materials will also result in gas generation. Chloride salts are frequently present in oxide residues, which can also adsorb water. In addition there is a potential for the production of Cl_2 or HCl from these salts resulting in subsequent container corrosion.

Vaporization of adsorbed species due to a temperature increase inside the container may lead to a nominal pressurization. Water vaporization, for example, could contribute up to ~300 psi to container pressurization, and is limited by the equilibrium between the water liquid and vapor phases. Additionally, a container with a combustible atmosphere could experience a deflagration or a detonation, depending upon the conditions in the container. From past experience, these pressure pulses are not considered a concern for containers packaged to the 3013 Standard

criteria because it is believed that the atmosphere will not reach combustible limits. The current 3013 Standard includes a conservative equation for derivation of a bounding pressure increase based on complete decomposition of water to generate hydrogen. From this equation, pressurization up to 700 psi can be derived. The equation is conservative and considers only factors that contribute to pressurization and not those factors that may limit it.

To ensure failures do not occur while the sealed containers are being maintained, a DOE complex-wide integrated surveillance program is established to define the behavior of these materials. At Los Alamos National Laboratory (LANL), the Shelf Life Surveillance Project monitors gases over oxide materials in a limited number of large-scale 3013 inner containers and in many small-scale containers with samples taken from site-wide representative materials actually being stored. This information provides invaluable, defensible results for assuring safe long-term storage of these materials in sealed containers.

The Shelf Life Surveillance Project is a key element of bounding safety scenarios and long-term surveillance activities for the 3013 containers. Critical to the success of this Surveillance project are the controls of the Inspection, Measurement, and Test Equipment (IM&TE) and of the data produced and analyzed from the IM&TE. The Project reviewed all the MD&TE in used for their affects on quality and data. Only those instruments that contributed directly to the required data or safety measurements required calibration and were placed on a calibration schedule. Also since a major "product" of this project is data, quality assurance measures were developed to specify basic protective measures on the instrumentation and on the quality objectives of the data.

ENGINEERING DESIGN

The LANL shelf-life surveillance project has two parallel studies. Small ten gram samples are monitored for relatively short time periods, and a limited number of large samples equivalent in size to the 3013 storage container capacity are monitored for long periods of time. The small samples will allow a database of many material types prepared according to various site-specific packaging methods to be compiled. Large-scale studies will give the behavior of a limited number of samples in the precise geometry and environment in which material will be stored. Comparison between the two sample geometries will determine the degree of confidence in small sample experiments and fundamental measurements in predicting the long-term behavior of real materials.

We have designed instrumented storage containers that mimic the inner storage can specified in the 3013 standard at both large- and small-scale capacities (2.3 liter and 0.0045 liter, respectively). The containers are designed to maintain the volume to material mass ratio while allowing the gas composition and pressure to be monitored over time. The large-scale cans are instrumented with a Raman fiber-optic probe, a gas chromatography (GC) / mass spectrometer (MS) sampling port, an acoustic resonance chamber, two corrosion monitors, and pressure and temperature sensors. Data collection for the large-scale containers is automated in order to reduce worker exposure. The small-scale containers are designed with a microliter gas-sampling

capability (GC and MS) and pressure and temperature sensors. The small-scale containers will be stored in a heated array in order to reproduce the increased temperatures observed in the large-scale experiments arising from radioactive self-heating. Figure 1 shows the large- and small-scale containers.

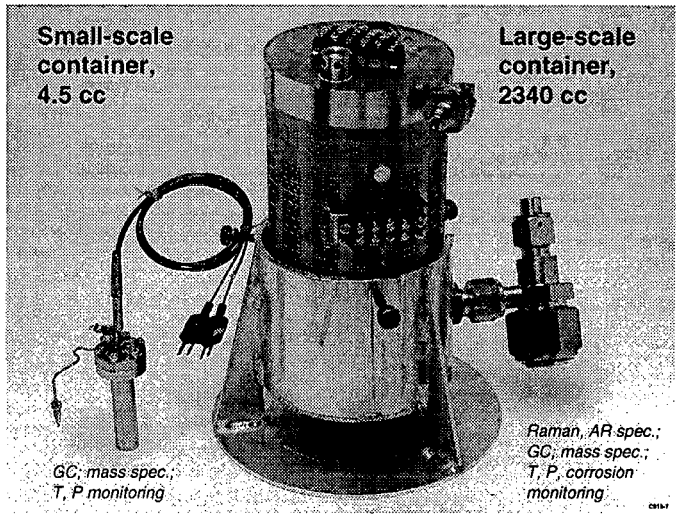

Figure 1. Instrumented shelf life surveillance containers.

For the large-scale study, multiple cans containing up to 5 kg of material will be prepared for study. Materials will be sealed in BNFL inner containers that were designed to the DOE 3013 Standard. In order to minimize the effect of invasive gas sampling on the experiment, an effort is made to limit the gas sampling for gas chromatography / mass spectrometry to 10% of the initial gas loading over the course of the experiment. Raman spectroscopy will be used for frequent interrogation of gas composition. GC will be used less frequently because it consumes sample. The GC data will be used as a cross-check of the Raman data as the GC technique has widespread acceptance as a gas analytical technique and good sensitivity to a wide range of gaseous species. The design limits organic exposure to the oxide by minimizing the organic content of the assembly components. The modified lid is welded to the container inside the glove box after the plutonium oxide has been transferred to the container. The modified lid is designed with a burst disk for pressure release in the event of a highly unlikely H_2-O_2 deflagration within the container. A rack system that holds the containers is located in a plutonium glove box. It has a heated gas-manifold to minimize the effect of gas condensation enabling quantitative GC analysis. All data acquisition is controlled remotely so that little or no manipulation in the glove box gloves will be required once the cans are in place.

The containers are monitored for pressure and temperature multiple times an hour, and recorded with data acquisition hardware and software at fifteen minute intervals. In the large-scale containers, gas analysis is done by Raman spectroscopy and gas chromatography. For GC, a gas sample is withdrawn from the container, decreasing the container pressure by 0.04 Torr per gas sample. For the large containers, the primary method of sampling is with Raman spectroscopy with fiber optic coupling, where a sensitivity limit on the order of 0.5 Torr has been demonstrated for most gases. GC sampling is done periodically to confirm Raman spectroscopy results and offer a quantitative cross-check on the gas constituents for the large containers. GC

will also be able to detect most monatomic gases (He, Ne, but not Argon) that Raman spectroscopy is unable to detect. GC measurements have been taken for various calibration mixtures that include gas components that may be observed during the course of the experiments. It is expected that the current configuration allows a GC gas determination of 1.2 Torr partial pressure in the container.

The design of the Raman collection chamber is such that gases are detected within an enclosure without sample removal or pre-concentration. The chamber contains an unfiltered, non-imaging fiber-optic probe and a black, colored glass filter tilted to direct reflections away from the probe tip. The fiber-optic probe head consists of a fiber-optic bundle with one center excitation optical fiber and six surrounding collection optical fibers. The container is isolated from the oxide material by a two micron filter.

Raman spectra of gas mixtures exhibit distinct vibrational peaks characteristic of each gas present in the sample (excluding monatomic gases such as He and Ar). Peak areas are proportional to gas concentration, with the proportionality factor being dependent on the gas and on the instrumentation, which is calibrated using gas mixtures of known composition. In order to compensate for variation of the proportionality factors due to variations in individual fiber-optic probes, peak areas can be compared to an internal standard within the sample being measured. The ratios of the proportionality factor of the gas to be measured and the internal standard can be determined by measuring a known gas mixture. These ratios can then be used to determine unknown gas concentrations of mixtures containing the internal standard at a known concentration.

QUALITY PROGRAM STRUCTURE FOR THE PROJECT

All work done at the LANL Plutonium Facility is under the quality assurance mandates of the 10 CFR 830, Nuclear Safety Management, Subpart A, Quality Assurance Requirements, Section 830.122, Quality Assurance Criteria. These requirements apply to all DOE contractors operating nuclear facilities. There are ten major Criteria within three major topical areas in this CFR, which are a condensing of other major QA systems (ISO 9000, ASME NQA-1, etc.). The Criteria are as follows:

Management

1. Program – The structure, organization, and management of the quality program must be described
2. Personnel Training and Qualification – Must have a system to both qualify the personnel and train them in needed methods and procedures
3. Quality Improvement – Both active containment of problems and proactive methods are required
4. Documents and Records – Must have a system to control the creation of documents and records and to store and handle them

Performance

5. Work Processes – Must have the controls and procedures for work. This also includes the requirements for calibration and maintenance of measuring equipment.
6. Design – Must have controls for the creation, use and disposition of designs and their documents (validation, verification, interfaces, etc.)
7. Procurement – Have controls on the purchase of items, materials and services, and on the associated documents (requirements, vendor qualification & monitoring, etc.)
8. Inspection and Acceptance Testing – Need to inspect/test items, services, and processes per defined requirements, using maintained and calibrated measuring equipment

Assessment

9. Management Assessment – All managers review operations/activities to find and implement improvements
10. Independent Assessment – Plan and conduct assessments by outside independent entities, ensure technical competence of assessors

The Quality Management Plan, NMT-PLAN-001, and its sub-tier Administrative Procedures (AP) direct the overall quality program and quality-affecting activities in LANL's Nuclear Materials and Technology (NMT) Division. There are other requirements and drivers for compliance, which include the safety documents for this Project. The Hazard Control Plan, NMT11-HCP-008, Surveillance of 3013 Containers, and Work Instructions define the operating parameters and practices for safety. In addition, there are facility requirements that mandate the preparation of plans and documents for the project. These include the readiness reviews, piping and instrument diagrams, and structural analysis. Additionally reviews for criticality, nuclear material accountability and ALARA (as low as reasonably achievable) were completed prior to obtaining the authorization to operate.

While the NMT quality documents describe and direct the overall quality system and requirements, there is the need for project-specific documents that cover the project's details not addressed otherwise. The Project decided that a calibration plan was required for the measuring instruments used in the surveillance. Since a major result of the project is the analyzed data, a plan to cover the quality of the data was also required. In other projects using data and producing analyses, there are regulatory requirements for data quality planning and control. While this Project does not have those regulations, there still is the need to describe good practices to ensure the integrity of the data and the data quality objectives for measurable parameters.

DATA QUALITY PLAN

Since a major "product" of this Project is data obtained from measurements of the containers and oxide materials, quality assurance measures were developed to specify some basic protective measures and directions for the quality objectives of the data. The Data Quality Plan (DQP) addresses the specific practices and data objectives required for each of the Measurables in the Surveillance Project. This document starts with the introductory section to define the purpose and scope of the DQP, provide definitions, define roles and responsibilities, and list resource requirements. Next are the sections that describe how data quality is implemented through the

General Practices and then Specific Practices for Measurables. Finally, the DQP summarizes performance measures, provides references for the DQP, and contains attachments with the Gas Sampling Schedule. In the General Practices section, specific requirements are given for those parts of the surveillance that apply to any measurement practice, such as Data Objectives, M&TE handling, Data Collection, Data Protection and Storage, Data Analyses/Reduction, Data Verification and Validation, etc.

The next section is the Specific Practices for Measurables. There are eight primary Measurables for the project:

- Quantification of Solid Sample Charge
- Total Available Interior Gas Space Of The Containers
- Water Content
- Gas Chromatography Analysis (GC)
- Raman spectroscopy Analysis
- Pressure and Temperature
- Corrosion Analysis
- Other Measurables

Within each part for an individual Measurable, there is a Description of the Measurable. For some of the Measurables, there are the special Sampling Procedures afterwards. Then for all Measurables the Data Objectives are given that define technical targets, such as the measurement precisions. Next are any unique Data Reduction and Analyses practices. Finally listed are any Other Data Activities, such as unique Verification and Validation. A short description of each Measurable is given below:

1. Quantification of Solid Sample Charge
   Characterized oxide materials will be sealed in the test containers that have unique identification numbers traceable to the oxide material. The oxide material is sampled and characterized for elemental composition, specific surface area, and particle size distribution prior to receipt.
   The Data Objectives are as follows: Material for the containers will be weighed on calibrated balances to an accuracy of 0.5 gram. Net weight and plutonium content will also be verified by calorimetry, which has a separate set of precision and accuracy maintained by a different Group.

2. Total Available Interior Gas Space Of The Containers
   After the container is filled with oxide and sealed, the void volume of the container is determined. The void volume is determined by either of two methods: 1) evacuation of the gas volume of the container and subsequently expand a gas from a calibrated volume, or 2) determination of the volume of empty container from machining tolerances and the crystal density of the material. The allowable errors for method 1 are 16 ml and for method 2 are 20 ml.
   The Data Objectives are as follows: The void volumes of the large containers are determined to 20.0 ml.

3. Water Content
   Moisture is added to select containers identified in the Project's material matrices for the large and small-scale projects. Moisture is added by one of two methods:
   1) Exposure of the oxide to a humid gas (typically 60% relative humidity) for a period of time until the maximum allowed moisture is adsorbed or an equilibrium state is obtained, or
   2) Addition of water to the oxide container prior to sealing for the small scale containers.

   The Data Objectives are as follows: The water addition will be determined 0.1% of total mass (1.0 gram for the large scale studies and 0.01 grams for the small scale containers).

4. Gas Chromatography Gas Analysis (GC)
   Periodic gas samples are taken from the container headspace and analyzed through gas chromatography. Samples are captured in an evacuated sample volume and expanded to the GC for the large containers. Once the container is attached to the manifold and is verified leak tight, sampling of gas starts per a schedule for gas sampling. Two gas samples for chromatography are taken on Day 0. On the 15th day, two more gas samples are taken. Then for the next ten (10) weeks, gas samples are taken once per every two (2) weeks (biweekly). Afterwards, a gas sample is extracted once every three (3) months until the experiment is ended.
   The Data Objectives are as follows: The GCs will be calibrated with a standard calibration gas containing a majority of the analytes of interest. The accuracy of the GC measurement is defined by the analytical accuracy of the calibration gas, which is $\pm$ 5%. The precision or repeatability is $\pm$ 2 Torr and improves at higher partial pressures. Precision and sensitivity vary from one component gas to another, but is highest for hydrogen. Gas sampling for gas chromatography/mass spectroscopy shall be limited to 10% limit of the total gas volume during the experiment.

5. Raman Spectroscopy Gas Analysis
   Raman spectroscopy for gas analysis is the primary method for the large containers. Raman is not used for the small containers due to constraints of the headspace gas volume. Raman measurements start on the day that the container is connected to the manifold and verified that it is leak-free to establish a baseline. Two measurements are taken on day 0 and two are taken again on the first day. Then for the next two weeks, measurements are taken daily. This rate is then reduced to one measurement per week for the next ten (10) weeks. Afterwards, a measurement is taken once a month for the next six (6) months.
   The Data Objectives are as follows: The sensitivity limit for most gases under typical ten minute data acquisition is 5 Torr. Detection of below 1 Torr is possible with acquistion times of one hour or more. The Raman instrument will be calibrated by initial measurement of the relative response for plausible target gases and by periodic comparison with GC measurements on containers in service. Gas concentrations will be measured relative to each other with a precision of $\pm$ 10%.

6. Pressure
   The Project will continuously monitor and record the pressure of each container for the life of the experiment (approximately 15 minute intervals for the large scale 3013 cans).
   The Data Objectives are as follows: Each container (large and small scale) will have its own pressure gauge. Each gauge comes calibrated from the factory. On the large scale cans, the gauges' calibration will be maintained by comparison to an external precision pressure gauge that will be replaced yearly. Since the experimental duration of the small scale monitoring project is not planned to exceed one year, maintaining calibration is not an issue currently.
   The following are requirements for the data measurements:
   - Accuracy shall be limited to 0.05% of full scale
   - Repeatability shall be limited to $\pm$ 0.01 of full scale
   - Temperature effects shall be limited to 0.0002% of full scale per degree Centigrade

   The accuracy of the Heiss pressure gauges used on the large scale project will be 0.25% full scale (150 PSIA). The accuracy of the Ashcroft gauges used for the small containers will be 1% full scale (100 PSIG). Small drift in the zero of the Heiss gauges have been noted and may be caused by the radiation field. Periodic re-zeroing of the gauge is therefore necessary.
   In addition, pressure is corrected for variations in temperature by using the average container temperature as recorded using from 2 to 10 thermocouples and the Ideal Gas Law. Pressure is corrected for zero drift by measuring the drift in the zero readout periodically and applying the appropriate correction.

7. Temperature
   The Project will continuously monitor and record the temperature of each container continuously for the life of the experiment. Two thermocouples are placed in each of the small scale containers.
   The Data Objectives are as follows: Accuracy is 1.7 degrees C (stated accuracy for E type of thermocouples in the Omega literature). Precision (or repeatability) is mostly a function of the plant building environment, which varies about two degrees in 24 hours.
   In addition, the project will record millivolt readings of each thermocouple, which is then referenced to a cold junction sensor that is converted via the Labview software to temperature before being recorded or reported.

8. Corrosion Analysis
   The Project will later determine the data quality objectives and practices for this Measurable.

9. Other Measurables
   The Project will determine the data quality objectives for all other measurables with the assistance of subject matter experts. Some other measurables may include post-experimental analysis through metallography, acoustic resonance spectroscopy, or mass spectroscopy data.

CALIBRATION REQUIREMENTS FOR SURVEILLANCE PROJECT

Most of the Measurables previously listed in the DQP have critical measuring equipment needed to achieve the activities and the Data Objectives. All of the Inspection, Measurement, and Test

Equipment (IM&TE) were defined in the Process and Instrument Diagrams (P&ID). A Calibration Requirements Analysis was then performed to determine which of these IM&TE require periodic calibration. The procedure used to determine which instruments require periodic calibration is NMT-AP-579, R1 "Control of Measuring and Test Equipment". Calibration is required if the instrument quantitatively monitors or controls safe conditions to prevent hazards to personnel or the environment, or if it or monitors or controls process parameters. Calibration is not required if the instrument is not used for any of these reasons.

From the large scale experiment P&IDs, 108 sensors were identified that collect data for the 10 large scale containers. The signals were categorized as quantitative or qualitative measurements. The quantitative measurements are those where accuracy is important to the validity of results. The qualitative measurements are those where accuracy does not significantly affect the validity of results. This graded approach allowed selection of equipment that required calibration. These are listed below in Table 1. Significantly, the analysis reduced the calibration requirements to 16 measurements.

Table 1. IM&TE Requiring Periodic Calibrations for the Large Scale Containers

Signal	Description
PT-401	PRESSURE TRANSDUCER, STORAGE CAN # 1
PT-402	PRESSURE TRANSDUCER, STORAGE CAN # 2
PT-403	PRESSURE TRANSDUCER, STORAGE CAN # 3
PT-404	PRESSURE TRANSDUCER, STORAGE CAN # 4
PT-405	PRESSURE TRANSDUCER, STORAGE CAN # 5
PT-406	PRESSURE TRANSDUCER, STORAGE CAN # 6
PT-407	PRESSURE TRANSDUCER, STORAGE CAN # 7
PT-408	PRESSURE TRANSDUCER, STORAGE CAN # 8
PT-409	PRESSURE TRANSDUCER, STORAGE CAN # 9
PT-410	PRESSURE TRANSDUCER, STORAGE CAN # 10
GC-101	GAS CHROMATOGRAPH
PT-411	PRESSURE GAUGE, 1000 Torr
PT-412	PRESSURE GAUGE, 100 Torr
PT-1	PRESSURE GAUGE on Staging Box
CGC	CALIBRATION GASES
SC1	BALANCE

CONCLUSIONS

The Surveillance Project at LANL is a key element in the 94-1 Program to assure the safe storage of plutonium oxide materials for up to 50 years. To support this Project, several parameters were chosen for measurement surveillance. The Measurables were defined to meet the goals of the Surveillance Program and then the appropriate instrumentation and data

acquisition equipment defined and selected to meet the measurement goals. The Surveillance has complexity due to the different Measurables and instrumentation. The Data Quality Plan supports this effort by supplementing the existing quality assurance requirements of the NMT Division. The experimental activities for this Project are not only different from facility activities, but also unique in the products obtained from the activities. Data collection and analysis required a higher level of QA, with emphasis on the precision and accuracy of the IM&TE used for collecting the data. Also needed were some basic measures of data protection. The IM&TE and the calibration requirements are also a critical part of the success of the Project. This equipment required specific reviews of their affects on quality and data and then a determination of the calibration needs for each individual IM&TE (qualitative versus quantitative). The Project has achieved these goals to assure that only those instruments that contribute directly to the data quality are in the calibration program.

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