

## Department of Energy

Washington, DC 20585

November 1, 2002

The Honorable John T. Conway  
Chairman  
Defense Nuclear Facilities Safety Board  
625 Indiana Avenue, NW  
Washington, D.C. 20004

Dear Mr. Chairman:

This is in response to your July 12, 2002, letter regarding the use of Thermogravimetric Analysis (TGA) to measure residual moisture in stabilized plutonium oxides. The enclosure addresses each of the five specific points raised in your staff report.

The approval of TGA was based on technical studies summarized in a Los Alamos National Laboratory report, "Certification of TGA with Moisture Detection Systems for Water Determinations on 3013 Materials," LA-UR-02-2233 with pure plutonium oxide and surrogate materials. These studies showed that TGA, coupled with either a Mass Spectrometer (MS) or a Fourier Transform InfraRed detector (FTIR), was an adequate analytical method for moisture measurement. Subsequently, the technical basis to use TGA for impure oxide material types is documented in "Thermal Gravimetric Analysis with Moisture Detection Systems for Water Determinations: A Study on Selected 3013 Materials," LA-UR-02-3728-Rev 1. This report was updated and re-issued on October 18, 2002, and includes more recent results and offers detailed technical guidance for TGA-MS and TGA-FTIR measurements. As more material is analyzed and the technical base expands, this report will be updated and reissued.

The technical basis to "Stablization, Packaging, and Storage of Plutonium-Bearing Materials," the Department of Energy (DOE) Standard (STD) 3013-2000, states that the predominant volatile constituent of interest to long-term storage performance of stabilized oxides in 3013 containers is water. Recent work conducted by the Material Identification and Surveillance Studies (MIS) group show that TGA-MS and TGA-FTIR techniques are capable of detecting other species that could be present and potentially cause pressurization of 3013 containers. The MIS studies further concluded that no mechanism other than those involving water could pressurize or corrode the 3013 containers above design limits during long-term storage.

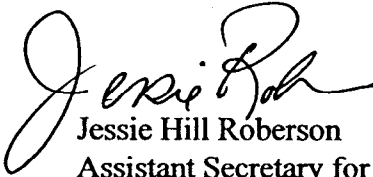


Based on these results, DOE is not requiring measurement or analysis of constituents beyond those required in DOE-STD-3013-2000. However, we will continue our Research and Development shelf life studies at LANL to ensure that this conclusion remains valid. If there is any evidence that other species could cause pressurization or corrosion of packages beyond the limits specified in DOE-STD-3013-2000, we will task the MIS group to investigate the issue, and keep the Board informed.

Additionally, I have directed the Rocky Flats Field Office to send their final TGA-MS and TGA-FTIR techniques procedure to other sites to assure continued compliance with DOE-STD-3013-2000.

If you have any further questions, please contact me at (202)586-7709 or Mr. Paul Golan, Chief Operating Officer, at (202) 586-0738.

Sincerely,

  
Jessie Hill Roberson  
Assistant Secretary for  
Environmental Management

Enclosure

## Background

On May 14, 2002, the Department of Energy (DOE) Assistant Secretary for Environmental Management (EM) issued a memorandum approving the use of Thermogravimetric Analysis (TGA), coupled with either a Mass Spectrometer (MS) or a Fourier Transform InfraRed Detector (FTIR), to meet the moisture measurement requirements of DOE-STD-3013-2000. The accompanying 3013 Technical Review Board recommendation on which that approval was based specifies, in part, "sites must provide documentation that there is adequate technical basis for the material types to be analyzed and ensure that the materials are represented in the MIS [Material Identification and Surveillance] inventory. The MIS WG [Working Group] should develop a list of materials with an existing technical basis for applying this method of moisture measurement." Work to establish that technical basis and the list of materials is currently being conducted at Los Alamos National Laboratory (LANL).

DOE-STD-3013-2000 defines stabilized material as that which "will not cause the design basis of the container ... to be exceeded through pressure generation, corrosion, or excessive stress over a design life of 50 years, and is not reactive in air upon reopening of the container." [DOE-STD-3013-2000, Section 5.2] This standard specifies a stabilization acceptance criterion for oxides as: "The moisture content of Oxide to be packaged in any type of sealed container shall be less than 0.5 wt% at the time of packaging." [DOE-STD-3013-2000, Section 6.1.2.3] This criterion is designed to assure that hydrogen (H<sub>2</sub>) generation from decomposition of water cannot produce problematic pressure levels in the container. The standard states that other mechanisms for pressure generation from impurities have been considered, but that "research supporting this Standard has also shown that the stabilization process removes or destroys all materials that pose a threat to the integrity of the container except for re-adsorbed moisture on the oxide material. This Standard allows moisture-specific measurements to be used as an alternate to the LOI [Loss On Ignition] test to verify stability." [DOE-STD-3013-2000, Section A.2].

The May 14, 2002, memorandum approves the use of TGA/MS and TGA/FTIR as alternatives to LOI for verifying that pure and impure plutonium oxides meet the DOE-STD-3013-2000 specification for maximum water content prior to packaging. The principal advantage of both TGA/MS and TGA/FTIR is that they can measure water content in the presence of other volatile impurities that would contribute to LOI but that do not contribute significantly to long-term pressurization.

The Defense Nuclear Facilities Safety Board (Board) has requested, in a letter dated 12 July 2002, that the DOE address several concerns shown in a Board staff report attached to the Board letter. Each concern is quoted below and then discussed.

## Response to Staff Issues

- 1) DOE's approval memorandum gives general approval for the use of TGA-FTIR/MS methods with the caveat that each site must provide documentation of an adequate technical basis for the material types to be analyzed. However, the findings in "Certification of Thermal Gravimetric Analysis with Moisture Detection Systems for Water Determinations on 3013 Materials," LA-UR-02-2233, refer to work performed exclusively on surrogate or pure oxide materials. Studies using more representative matrices have not yet been completed. The referenced technical basis clearly states, "The application of TGA-FTIR/MS techniques to impure materials is underway as stated in the experimental section. An evaluation of those data is needed before an unqualified endorsement of this method is made."

The May 14, 2002, DOE approval of the use of TGA/MS and TGA/FTIR methods on a material type is contingent on the (1) existence of an adequate, documented technical basis for their use on that material type, and (2) representation of that material type in the MIS inventory. Development of the technical bases for all material types to be packaged is the subject of ongoing laboratory work and documentation. Identification of materials approved for analysis by TGA-FTIR/MS methods and the corresponding technical bases are documented in "TGA (Inert as LOI, TGA-MS and TGA-FTIR) Techniques as Analytical Tools to Measure Water on Pure and Impure Plutonium and Uranium Oxides," LA-UR-02-4634.

LA-UR-02-2233, reports on moisture measurement on surrogates and pure plutonium oxide by TGA/MS and TGA/FTIR. The results detailed in LA-UR-02-2233 demonstrate that TGA/MS and TGA/FTIR have adequate precision and accuracy for measuring moisture in relatively pure plutonium oxide. LA-UR-02-2233 was not intended to provide the only technical basis for applying these techniques to impure materials.

Since the DOE approval memorandum of May 14, 2002, another report, "Thermal Gravimetric Analysis with Moisture Detection Systems for Water Determinations: A Study on Selected 3013 Materials," LA-UR-02-3728, has been issued reporting results of applying TGA/MS and TGA/FTIR to some impure oxides. Materials included in LA-UR-02-3728 were selected because they represent impure material types that are to be packaged and they contain impurities judged to be potentially problematic such as chloride salts. Several questions have been raised about the contents of LA-UR-02-3728 by MIS working group members and by Board staff. The report has been revised and reissued as LA-UR-02-3728-Rev 1. The revision includes data on additional materials, a more detailed method of FTIR quantification of water in the presence of interferences, and an appendix collecting specific technical guidance.

It is anticipated that sites will identify additional materials beyond those included in LA-UR-02-2233 and LA-UR-02-3728-Rev 1 for which further study and reporting is required in order to meet the conditions of the DOE approval. These studies will be

conducted and documented as the needs are identified.

- 2) *In general, the DOE guidance addresses exclusively the detection of moisture. While moisture is the primary concern in a fully stabilized material, other potentially problematic impurities indicative of incomplete stabilization (e.g., organics, carbonates, and sulfates) could be missed unless mass loss from sources other than moisture is carefully considered. The guidance attached to the DOE approval memorandum specifies that mass numbers 17 and 18 (corresponding to water and the hydroxyl ion) are of interest for TGA-MS. The document provides no guidance for TGA-FTIR, except that the sites are allowed to choose their own regions of interest on the infrared spectrum, provided they document possible interferences. Both analytical techniques have the capability to detect and differentiate among various volatile species and could be used to identify inadequately stabilized materials if properly applied. More definitive guidance from DOE is warranted.*

TGA/MS and TGA/FTIR offer enhanced capabilities to detect volatilized water in the presence of other mass changes upon heating. The Board staff letter suggests that additional information beyond water content could be acquired during the measurements, and that the additional information would be useful in verifying stabilization. This raises two questions regarding the verification of stabilization.

The first question is whether the analytical measurement at the verification stage should be part of the Quality Assurance (QA) process to assure that stabilization to the specified criteria had been performed. At present, the verification measurement prior to packaging is intended to assure that moisture content meets specifications because of the possibility of moisture re-adsorption between stabilization and packaging. The verification measurement is not intended to assure that the stabilization process was performed as specified. Assurance that a batch of material to be packaged has been stabilized according to the requirements of DOE-STD-3013-2000 is the responsibility of each packaging site, and the methods by which this assurance is achieved are defined in their QA programs.

The second question is whether DOE-STD-3013-2000 stabilization requirements are adequate with respect to issues other than moisture re-adsorption. They would not be adequate if material stabilized to DOE-STD-3013-2000 requirements could pressurize or corrode the container during long-term storage by a mechanism other than one involving water. While additional material species have been identified by recent MIS studies, water remains the primary driver for pressurization and corrosion. The requirement that all types of material to be packaged must be represented in the MIS Program is intended to identify any mechanisms of concern.

DOE-STD-3013-2000 specifies a procedure to produce stabilized material and establishes a criterion for sufficient stabilization based on measurement of residual moisture content. The possibility that other impurities could result in pressurization is addressed in Appendix A, Section A.6.1.2.5 of DOE-STD-3013-2000. Scenarios not involving water have proven unlikely for material that has undergone the prescribed stabilization process.

The Board staff letter specifically mentions organics, carbonates and sulfates. Studies (e.g., "*Gas Pressurization from Calcined Plutonium Oxides*," LA-UR-99-3804) have shown that organics are destroyed during calcination at significantly lower temperatures and times than those specified in DOE-STD-3013-2000. Inorganic oxyanions such as carbonates and sulfates may survive calcination depending on the chemical environment, but there is no indication from the scientific literature or from ongoing laboratory studies that they contribute to pressurization or corrosion potential under storage conditions.

The selection of analytical methods to verify stabilization has focused on techniques measuring mass loss because adsorbed water can be removed by heating and is then much easier to measure than when bound within the solid matrix. The fact that water can be measured by volatilization does not, however, imply that any component that is volatile under heating presents gas generation potential.

Though it is considered unlikely, ongoing shelf-life studies are designed to identify impurities other than water in stabilized material that could have significant pressurization potential. Unless and until such additional problematic impurities (and their threshold concentrations of concern) are identified, measurement criteria for target constituents other than water for TGA/MS or TGA/FTIR to detect and quantify cannot be defined.

FTIR or MS data could be analyzed for qualitative identification of volatilized species other than water. Available information will be collected and archived to enable such potential future analyses to occur.

The sites are responsible to report and resolve anomalies observed during stabilization and packaging. Such reports could include anomalous TGA/FTIR or TGA/MS verification measurements, such as mass loss at low temperatures that is not ascribable to water or significant mass loss at temperatures below salt volatilization. The MIS working group will support the resolution of anomalies as requested. Many anomalies are likely to be resolved by re-stabilization.

Headspace gas analysis has been conducted on unstabilized materials in storage for many years at ambient external temperature [see "*Gas Generation over Plutonium Oxides in the 94-1 Shelf Life Surveillance Program*," LA-UR-02-0583 and "*Analysis of Gas Constituents From Sealed Containers of Plutonium Oxide Materials*," LA-UR-02-0584]. To date, no evidence of pressurization has been found. The headspace air shows significant depletion of oxygen and moderate depletion of nitrogen. Partial pressures of other gases have also been measured. Helium partial pressures have been noted to increase to 0.04 atmosphere, and carbon dioxide partial pressures increase to 0.15 atmosphere. Hydrogen has been detected in a few cases at partial pressures up to 0.5 atmospheres, while carbon monoxide and nitrogen oxides (NO<sub>x</sub>) have been detected in several cases at levels below 0.01 atmosphere. Each of these gases would be observable by TGA/MS if they evolve from the material during heating. Small organic molecules (i.e., those with mass-to-charge ratio less than 75) and sulfur oxides (SO<sub>x</sub>) can be

observed down to trace levels.

- 3) *The DOE guidance allows heat-up rates of up to 20\_C/minute. However, the data presented in the technical justification for TGA-FTIR/MS does not appear to justify the use of rates of temperature increase up to 20\_C/min. In addition, no guidance is given for gas flow rate. The supporting data show significant differences in the integrated peaks when heat-up or flow rates are varied. It is unclear whether these differences could have a significant impact on the accuracy of the measurements.*

Data reported in LA-UR-02-2233 show the effects of various heating and flow rates. Those data indicated that acceptable results were achieved using heating rates of 10 to 20\_C/min and flow rates used in that study were typically 40 to 60 ml/min. The sites have the flexibility to choose specific operation parameters within those ranges. Of course, production measurements and routine instrument calibrations must be performed using the same set of conditions for heating and flow rates. Further technical guidance on acceptable parameter ranges will be provided to the sites if the results of ongoing studies indicate that further restrictions should be placed on operating parameters for some materials.

- 4) *The current equipment setup may prohibit the detection of some inorganic vapor species due to condensation in sample lines. The gas transfer lines between the TGA and FTIR units are heated only to 200\_C. As highlighted in LA-UR-02-2233, many salts condense well above that temperature.*

The advantages of TGA/FTIR or TGA/MS over TGA is that they allow accurate measurement of water removed by heating even in the presence of potential interferences from other volatile impurities or other sources of mass changes. Volatilized species originating from water will not condense in the sample lines at 200\_C and will be detected by the FTIR or MS. Heating the sample lines and sample cells higher than 200\_C would have adverse impacts on equipment operation, maintenance schedules, and safety, without clear benefit.

- 5) *At this time, the [RFETS] procedure is vague with regard to exactly what constituents would be considered unacceptable. It may be appropriate for DOE to develop a list of constituents that are considered contaminants of concern for pressurization during long-term storage. Future guidance for the implementation of TGA-FTIR/MS techniques should address the detection of these constituents of concern.*

Contaminants of concern for pressurization were considered in the technical basis of DOE-STD-3013-2000, as detailed in its Appendix A. The list of constituents of concern contains only water at this time. Verification of stabilization therefore targets quantification of water. In the unlikely event that ongoing shelf-life studies identify other constituents of concern for pressurization, the quantification needs and methods for

detection will be addressed in future direction to sites.

Both TGA/MS and TGA/FTIR are capable of measuring more than the water content of a sample of stabilized material prior to packaging. This additional information can not be used at present to verify adequate stabilization prior to packaging because problematic levels of constituents other than water have not been identified. However, any large discrepancy between a mass loss indicated by the TGA and the water mass indicated by the FTIR or MS would be considered an anomaly, and would have to be explained using the technical basis for that material type prior to packaging. Alternatively, the material could be re-stabilized and re-verified.