LA-UR- 99-3019

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Title:

A Comparative Study of Methods for the Determination of Residual Water in Impure Plutonium Oxides and Recommendation of Method for Site Implementation

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Submitted to:

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LA-UR-99-3019

A Comparative Study of Methods for the Determination of Residual Water in Impure Plutonium Oxides:

Recommendation of Method for Site Implementation

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Executive Summary

A series of comparative studies is underway to determine the applicability of various analytical methods to replace Loss On Ignition (LOI) as a method for moisture determination in impure plutonium oxides. The results of this study lead to a recommendation by LANL that neutron moderation, along with a second, complimentary method be implemented at those sites stabilizing and packaging plutonium oxides as soon as possible. Immediate deployment of neutron moderation is believed necessary in order to accelerate collection of the data required for development of the computer modeling. The recommended complimentary method, supplying the empirical data for neutron moderation, is supercritical fluid extraction.

The Moisture Measurement Review Board, composed of DOE HQ (EM-66), site representatives, and DNFSB, met at LANL on May 13, 1999 and endorsed the recommendations of neutron moderation and supercritical fluid extraction as analytical methods and immediate deployment of these methods at DOE sites.

This report gives details on the engineering/facility/cost information on the analytical methods under evaluation, experimental results of the comparative study obtained to date, LANL recommendations, and the text of the recommendations made by the Moisture Measurement Review Board.

I. Background

A comparative study was recently undertaken to evaluate the relative accuracy and precision of Loss On Ignition (LOI), supercritical fluid extraction (SFE), interstitial gas analysis (IGA), thermogravimetry (TGA) and neutron moderation, using materials of known chemistry and processing history. The first sample used for this study (CCLANL025) was chosen by LANL because (a) a complete chemical analysis was previously performed (Table 4 in Appendix B), (b) the net weight of this sample was sufficiently large for neutron moderation measurements, (c) the sample was a free-flowing powder so that sub-sampling errors would be minimized, (d) the LOI results, even after calcining at 950°C for two hours, showed a *very large weight loss* (> 6.7 wt.%), (e) the results of SFE and IGA after calcining showed essentially *no residual water content.*

Recommendations made by the MIS Working Group resulted in the selection of four additional materials, each containing a specific impurity (high Pu, high U, high Mg and high chloride) and are meant to represent material derived from site-specific processes. Table 3 in Appendix B gives the make up of the five materials used in these comparative studies and their major impurities.

Currently, measurements have been completed on three of the materials: the High Chloride (CCLANL025), High Pu and High U. Tables 5, 6 and 7 in Appendix B give a summary of experimental results for these three sets of comparative measurements.

II. Observations and Conclusions

The experimental results obtained thus far, summarized in Tables 5, 6 and 7, lead to the following observations:

1. After thermal stabilization, as specified by DOE-STD-3013-96, storage of pure and impure materials in the LANL vault for periods of several months results in a minimal amount of moisture re-uptake (see Figures 10 and 18).
2. The thermal stabilization treatment specified by DOE-STD-3013-96 is sufficient to remove the moisture intentionally added during the comparative studies (see Figures 13 and 17).
3. The LOI measurements grossly overestimate the amount of moisture and cannot be expected to provide reliable data on residual moisture of impure samples. This observation is even more apparent from the results of the 33 impure materials sent from RFETS and Hanford to LANL for characterization as part of the MIS program.
4. The IGA measurements for *total water* (pyrolysis at 300°C) are the most accurate of the methods tested, while the measurements for *total hydrogen* (pyrolysis at 900-950°C) results usually show a slight positive bias. The standard deviations for both total water and total hydrogen are small. However, the small sample size required by this technique, < 0.5 g, will make the routine use of this method, in its current configuration, difficult for the highly inhomogeneous, impure oxides to be packaged. It is, in principle, possible to scale the experimental apparatus to handle larger samples, but such a system would have to be constructed on-site from separate components.
5. The SFE results are most accurate for low water contents, but for highly impure materials that eventually cause plugging of the restrictor, the method shows a positive bias. This positive bias increases as the flow rate through the restrictor decreases. The plugging problem can be addressed in two ways: (a) the restrictor can be replaced on a routine basis,

prior to its occurrence (this operation requires approximately 30 minutes) or (b) an engineering fix can be incorporated, consisting of an automated backpressure regulator. The equipment necessary for this engineering fix has been procured and is currently being tested. When analyzing highly impure samples, the standard deviation for the SFE results is usually larger than for IGA and neutron moderation. The restrictor-plugging problem did not occur for either the High Pu or the High U materials and in these cases the standard deviation is less than all of the other methods.

6. The neutron moderation results obtained thus far indicate that the method is affected by several experimental variables, including biases related to the presence of interfering elements, inhomogeneities of the oxide matrix, and fill height of the container. At present, these variables dictate separate calibrations be made for individual material types (High Pu, High U, *etc.*). However, the results obtained for a given material type appear promising, with results that are improving in relative accuracy and which have a relatively small standard deviation.

Based on the results of this study, the following conclusions are drawn:

1. For extremely pure oxides, LOI can be used for routine moisture analysis. It must always be borne in mind that the presence of only 0.5 mass percent of total impurities, if they are volatile, is enough to produce a failing LOI. SFE, IGA and neutron moderation can also be used for these materials.
2. Since most of the material to be packaged will contain considerable levels of impurities, LOI cannot be expected to provide reliable data for routine packaging operations. Either IGA or SFE can provide results that should greatly reduce the number of false positive results. Both methods show slight positive biases, so that *false negative results should not be a problem*. SFE can probably be more quickly implemented based on the commercial availability of the turn-key system, ease of operation and maintenance (relative to IGA), relatively modest cost (relative to TGA-MS), and the fact that an approved, documented hazards analysis in a Category I facility exists.
3. Neutron moderation appears, ultimately, to be the method of choice since it can perform non-contact measurements on “as-packaged” lots. This capability could also be used for future surveillance of packaged material. However, the observed experimental biases make it necessary to obtain further experimental data, so that the experimental configuration can be optimized, computer modeling can be refined, and software developed and incorporated into the quantitation protocol prior to routine use.

III. Recommendations

Based on the engineering, facilities and cost information contained in Appendix A, the experimental results given in Appendix B, and the observations and conclusions made during the course of this experimental evaluation, LANL makes the following recommendations:

1. Neutron moderation

The validation of the neutron moderation technique, using experimental data from other analytical methods, is promising but is still in the developmental stage. The three remaining comparative studies (see Appendix B) will provide valuable additional data on the effects of specific impurities (chloride and magnesium). However, it is strongly recommended that data collection be accelerated by implementing the method at DOE sites as soon as possible. This is especially important since it is anticipated that the first materials to be packaged will be of relatively high purity, and least problematic for neutron moderation analyses. Such data will be invaluable in developing the method by allowing baseline effects to be incorporated into the computer model and operating software. Once these relatively pure materials are packaged, it will probably not be possible to re-acquire the supporting, independent moisture data using the other, intrusive methods. Also, this data will extend the use of the method to more impure materials.

2. SFE

Since the computer modeling and software development for the neutron moderation method requires experimental moisture data, it is recommended that a second method be concurrently deployed. This second method will, at the same time, act as a back up to LOI measurements, allowing packaging operations to proceed. In terms of analytical capability, SFE and IGA are comparable. However, since all of the components for SFE can be purchased commercially as an essentially turnkey system while analyzing larger samples, and since documentation, including hazard analysis, analytical procedure, and training requirements can be provided immediately, this method would be preferred. The primary drawback to the SFE method is the requirement for sub-sampling, but this also applies to LOI and IGA.

3. Deployment

It is recommended that the neutron moderation and supercritical fluid extraction equipment be procured by the sites, but that initial training and hardware setup be done at LANL. In this way, operators can familiarize themselves with equipment set up at a non-radiological facility, while gaining operating experience analyzing actual materials using an identical system operating in a LANL radiological facility. Subsequently, the trained personnel, along with the equipment set up and tested in the non-radiological area, can return to their respective sites for implementation. During the time that site operators are training at LANL, the appropriate facilities arrangements, safety reviews, work authorizations, etc. can be initiated at the sites. It is recommended that RFETS deployment proceed first, with lessons learned to be incorporated into deployment at PFP and SRS.

4. Implementation

An Implementation Team has been formed to expedite transfer of the technologies and ensure continuing technical, facilities, QA and ES&H support. This team, addressing recommendations made by the Moisture Measurement Review Board (see Appendix C) consists of the following personnel:

A. Project Leader. *Function*: To oversee project control and execution.

LANL	
Jim Rubin CST-12 MS E537 505 667 3294 : phone 505 667 6561 : fax E-mail : jbr@lanl.gov	

B. Technical Leads for neutron moderation and supercritical fluid extraction. *Function*: Method development and technical interaction with individual site representatives.

LANL	
William K. Hollis (SFE) CST-12 MS G740 Los Alamos, New Mexico 87545 505 665 5656 : phone 505 665 4737 : fax E-mail : hollis@lanl.gov	Lynn Foster (neutron moderation) NMT-4 MS E513 Los Alamos, New Mexico 87545 505 665 8261 : phone 505 665 6160 : fax E-mail : laf@lanl.gov

C. Statistical support. *Function*: To develop statistical sampling methods and data analysis concurrently with method implementation. Also, definition of method biases leading to defensible confidence limits for each method.

LANL	
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D. Quality assurance. *Function*: To develop a QA regime, including documentation control, procurement requirements, *etc*. concurrently with method implementation.

LANL	
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RFETS	
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PFP	
Don Groth, PFP-QA BWHC, MISN T4-15 PO Box 1200 Richland, WA 99352-1200 509 373 5029 : phone 509 373 1349 : fax E-mail : Donald_R_Don_Groth@apimc01.rl.gov	

SRS	
TBD	

LLNL	
TBD	

E. Site representatives (RFETS, PFP, LLNL and SRS). *Function*: To define facility requirements, engineering design criteria and installation. It is recommended that at least two representatives from each site should be fully involved in method implementation. Knowledge of and authority for site-specific facility operations and technical operations is essential.

RFETS	
Mark Brugh Rocky Flats Environmental Technology Site Safe Sites of Colorado Building 559 P.O. Box 464 Golden, CO 80402-0464 303 966 7709 : phone 303 966 5715 : fax E-mail : mark.brugh@rfets.gov	Duane Hunter Rocky Flats Environmental Technology Site Safe Sites of Colorado Building 559 P.O. Box 464 Golden, CO 80402-0464 303 966 7597 : phone 303 966 5715 : fax E-mail : dhunter@rfets.gov
Stephen Wing Rocky Flats Environmental Technology Site Safe Sites of Colorado Building 559 P.O. Box 464 Golden, CO 80402-0464 303 966 7709 : phone 303 966 5715 : fax E-mail : stephen.wing@rfets.gov	

PFP	
Susan Jones MSIN T5-12 P.O. Box 1200 B & W Hanford Company Richland, WA 99352-1200 509 373 3347 : phone 509 373 4889 : fax E-mail : Susan_A_Jones@rl.gov	Thurman Cooper MSIN T5-12 P.O. Box 1200 B & W Hanford Company Richland, WA 99352-1200 509 373 2543 : phone 509 373 4889 : fax E-mail : Thurman_D_Cooper@rl.gov
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SRS	
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LLNL	
Patrick M. 'Pat' Epperson LLNL B235 R1055 MS L-352 925-423-9704 : phone 925-422-0049 : fax E-mail : epperson1@llnl.gov	

F. Site operating technicians (TBD by LANL, RFETS, PFP, LLNL, and SRS). *Function*: To ensure appropriate training at the operator level. It is recommended that at least one method operator be fully cognizant of the technical aspects of the implementation process, statistical protocols and QA procedure. This individual(s) is included in the Implementation Team at the discretion of the sites

G. DOE representation, (DOE-Albuquerque and sites). *Function*: To ensure adequate DOE involvement for successful implementation. It is recommended that at least one representative from each of the respective DOE field offices be involved in the implementation process.

DOE-AL	
Gary D. Roberson Nuclear Materials Stewardship Project Ofice 806-477-3012 : phone E-mail : jroberson@DOEAL.GOV	

DOE-SR	
TBD	

DOE-RF	
TBD	
DOE-RL	
Harry E. Bell U.S. Department of Energy Richland Operations Office Transition Programs Division Mail Stop : R3-79 Bldg. 2704HV, Room F217 P.O. Box 550 Richland, WA 99352-1200 509-376-2347 : phone 509-376-0695 : fax E-mail : Harry_E_Bell@rl.gov	

5. Continued Method Development

It is strongly recommended that LANL, in concert with the off-site members of the deployment team, engage in a continuing campaign of method development, including experimental design and engineering. Also, monitoring of new and emerging technologies for moisture measurement should be a part of the wider, ongoing material characterization process.

6. Statistical Support

It is recommended that a statistical analysis be undertaken to search for correlations between measured physical and chemical data obtained for individual packaged materials (experimentally determined moisture content versus elemental composition, material process history, IDC code, *etc*.). Such data already exists for many impure oxide materials (through MIS characterization) and correlations, if found, could lead to a value-added predictive capability. This analysis would be conducted at LANL on existing data, data derived from continuing MIS characterization, and characterization data collected at the individual sites on packaged material.

7. Analytical Standards

It is recommended that inter-site moisture standards be developed. Such standards would be used for periodic calibration of the various analytical methods.

8. Memorandum of Understanding

It is recommended that a Memorandum of Understanding be prepared between the individual sites and appropriate DOE field offices, to clearly define scopes of work and responsibilities for the deployment process.

9. Standardization of Equipment

It is recommended that all equipment at all sites be sufficiently similar that data can be directly compared.

10. Schedule for Deployment

Appendix D gives the deployment schedule (Gantt chart).

11. Projected LANL effort for FY99 :

Table 1 gives the LANL personnel and equipment effort required, for the remainder of FY99 (7/1/99 to 9/30/99), to meet the schedule and deliverables outlined in these recommendations. Table 2 is an estimate of the personnel and equipment effort required by REFETS.

Table 1. Projected LANL effort for site implementation (FY99).

Team Member	**Level of Effort**	**Cost projected through FY99**
Project Leader	1 FTE	90 K
Technical Leads		
SFE	0.25 FTE	20 K
Neutron Moderation		
a) hardware development		
b) software development	1.0 FTE	90 K
	0.5 FTE	45 K
Statistical support	0.25 FTE	23 K
Quality assurance	0.5 FTE	45 K
Neutron moderation equipment (for RFETS)	1 complete system	90 K
Travel	8 trips total (LANL-to-PFP, LANL-to-RFETS) @ 2K/ea	16 K
		Σ = 419 K

Table 2. Projected RFETS effort for site implementation (FY99).

Team Member	**Level of Effort**	**Cost projected through FY99**
Site Technical Representatives	2 FTE	72 K
QA	0.5 FTE	45 K
Facilities/engineering	2 FTE	126 K
Supercritical fluid extraction equipment (two for RFETS)	2 complete systems	140 K
		Σ = 383 K

Appendix A – Facilities and Engineering Requirements for Installation of Methods into DOE Facilities

The discrepancy between LOI results and operating experience with packaged and stored oxides is well known. The fundamental problem with the LOI method is that the weight loss is measured with no discrimination as to the nature of the volatilized species. In many cases, it is suspected that the majority of the measured weight loss represents volatilized, inorganic salts, which do not contain either hydrogen or water. Since false positive LOI measurements result in unnecessary material re-processing, an alternative measurement technique has been sought.

The purpose of this report is to make a recommendation on the deployment of alternative analytical methods to meet moisture determination requirements of the storage standard (DOE-STD-3013-96). Supporting information given in this Appendix includes (a) a brief description of each analytical method, and (b) information on engineering/facility requirements, personnel and training requirements, initial cost and annual operating cost of each method if used as a routine analytical method.

1. Loss On Ignition (LOI)

LOI is the method currently specified by DOE-STD-3013-96.[1] It involves heating of the oxide at 1000°C for at least two hours, followed by gravimetric weight loss determination.

A. Initial Capital Cost

The Loss On Ignition (LOI) method requires only a muffle furnace, desiccator, and an analytical balance, Figure 1. The muffle furnace can be purchased for less than $ 3.5K and an appropriate balance can be purchased for less than $ 4K. Platinum crucibles are required and each crucible costs less than $ 3K. Typically, samples are run in duplicate so that at least two crucibles are required. The total initial cost is therefore approximately $ 14K.

B. Estimated Annual Operating Cost

The only utility required by this equipment is electricity and the annual cost should be less than $1 K. Additional platinum crucibles might be required.

C. Personnel & Training Requirements

A single technician can perform routine analysis.

D. Facilities Requirements

The muffle furnace requires a 27” deep, 14” wide, by 19” high space in a glovebox. The furnace should operate in an air box. If, however, the furnace must be located in an inert atmosphere glovebox, then air must be brought to the furnace. The analytical balance requires a smaller space, with the actual footprint depending on the type of balance used.

Installation of the furnace in an existing glovebox that contains/has contained radioactive materials will probably require that the furnace be put through a glovebox window. Preparation

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[1] “Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage”, DOE-STD-3013-96 (US Department of Energy, 1996).

and performing this task could require perhaps two persons for one week. The balance can probably be brought into the glovebox through the regular portals. Installation of the furnace and balance require standard electrical outlets and the furnace temperature controls must be certified.

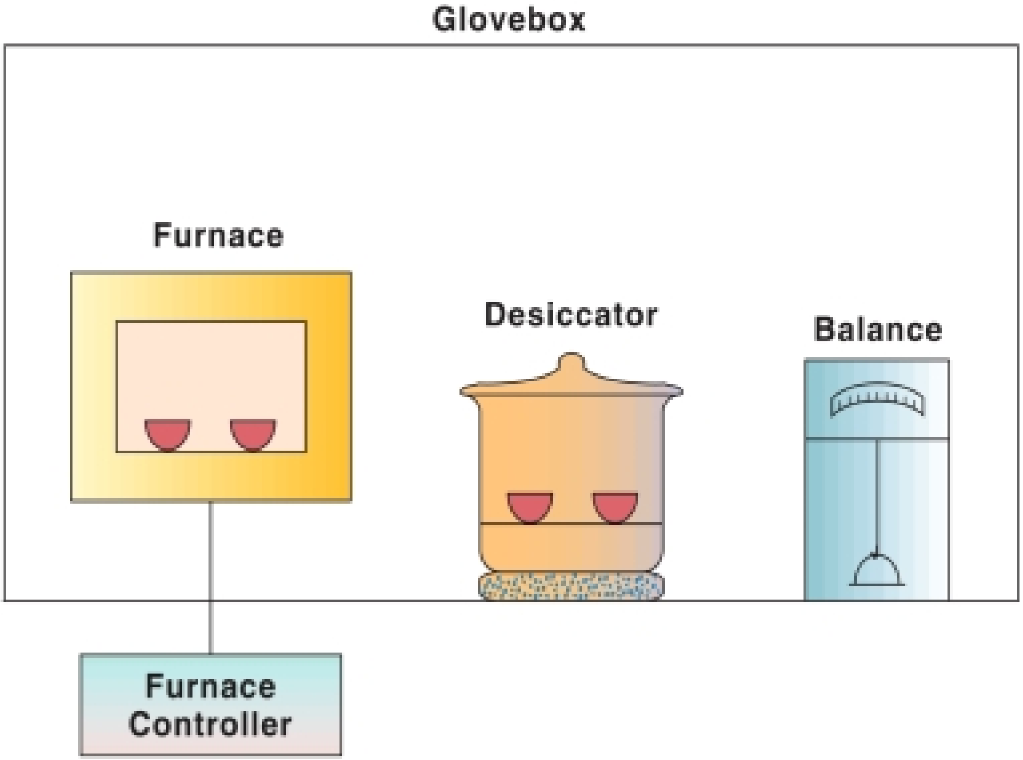

Figure 1. Schematic illustration of an LOI apparatus.

E. Advantages/Disadvantages of the Method for Routine Analysis

- Advantages
  - — This technique is very simple.
  - — Typical samples are 5 g, but can be larger (10 grams or more). Compared to IGA and TGA, these larger sample sizes may alleviate sub-sampling concerns.
  - — This technique will measure all species that will volatize at or below the test temperature.
  - — This technique is recognized as suitable for moisture measurements for very pure oxides.

- Disadvantages
  - — This method gives erroneously high results for oxide samples containing volatile, non-hydrogenous components.
  - — If the sample is relatively free of volatile, non-hydrogenous components yet contains non-volatile, oxidizible compounds, an erroneously low value may result.
  - — This technique is time intensive, requiring a minimum of 8-10 hours per analysis. However, more than one sample can be analyzed simultaneously.

2. Interstitial Gas Analysis (IGA)

This is a combustion technique that measures either total water or total hydrogen content. A schematic drawing of the measurement system is given as Figure 2. The furnace temperature is maintained at 300_C for a total water determination, and 900-950_C for a total hydrogen measurement. The sample is initially suspended above the furnace until the furnace stabilizes at the desired temperature. Dropping into the furnace then pyrolyzes the sample. The gases evolved during pyrolysis are swept out of the furnace by an inert carrier gas (dry argon) to a detector. The detection system, a non-dispersive infrared detector in the LANL system, requires that the analyte (H_2O or H_2) be in the form of water vapor. For a total hydrogen measurement, the evolved hydrogen gas is swept through a bed of CuO held at 500–900°C. The CuO bed converts the hydrogen to water vapor through the reaction

$$CuO + H_2 \xrightarrow{500-900^0 C} Cu + H_2O$$

(For a total water measurement, the CuO bed is by-passed.) Afterward, the Ar stream, with the dissolved water vapor, is passed through the detector, and the resulting voltage-time response integrated electronically to obtain an integrated area. This area is compared to the response obtained for injections of known amounts of hydrogen gas.

As far as individual samples are concerned, the IGA apparatus is a once-through system, meaning that once a sample is dropped into the pyrolyzing furnace, it remains there. As a result, the furnace (≈ 50 ml internal volume) accumulates metals and oxide materials, requiring the removal of these materials at regular intervals. At furnace temperatures in excess of 300°C, metal oxides residing in the furnace can oxidize any hydrogen liberated during the pyrolysis of a freshly introduced sample

$$MO_2 + 2\ H_2 \xrightarrow{>300^0 C} M + 2\ H_2O\ \ .$$

The furnace would therefore act in the same capacity as the CuO bed. If this reaction were allowed to occur, by maintaining the furnace temperature above 300°C, a total water measurement would contain a contribution from hydrogen. To eliminate this problem, total water measurements are made with the furnace temperature at no higher than 300°C.

IGA has been used for moisture determination in nuclear reactor fuel pellets in the United States [2,3] and Europe [4,5,6] since the 1970’s. This method is specified by IAEA [7] and

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2. M.E. Smith, D.E. Vance and G.R. Waterbury, “Determination of water evolved from FFTF reactor fuel pellets”, Los Alamos Scientific Laboratory Unclassified Report LA-4681 (1971).
3. M.E. Smith, D.E. Vance and G.R. Waterbury, “Determination of total amount of volatiles in mixed-oxide reactor fuel pellets”, Los Alamos Scientific Laboratory Unclassified Report LA-5108 (1973).
4. W.J. Bartscher, “Coulometric Determination of the Water Content in Uranium-Plutonium Oxide and in Uranium Oxide”, Mound Laboratory Report MLM-2396(TR) (1977).
5. J.M. Bonnerot and D. Warin, “Automatic Technique for Simultaneous H_2 and H_2O Titration in MOX fuels”, J. Nucl. Mater. 178 (1991) pp. 254-257.
6. V.I. Ivanov and G.A. Timofeev, “Determination of Microgram Quantities of Moisture in Crystalline Plutonim(IV) Oxide”, Radiokhimiya 25 (1983) pp. 794-800.

ASTM [8,9,10] for the measurement of moisture content in reactor fuel pellets and reactor-grade UO_2, PuO_2 and mixed oxide powders. Commercial units are available.

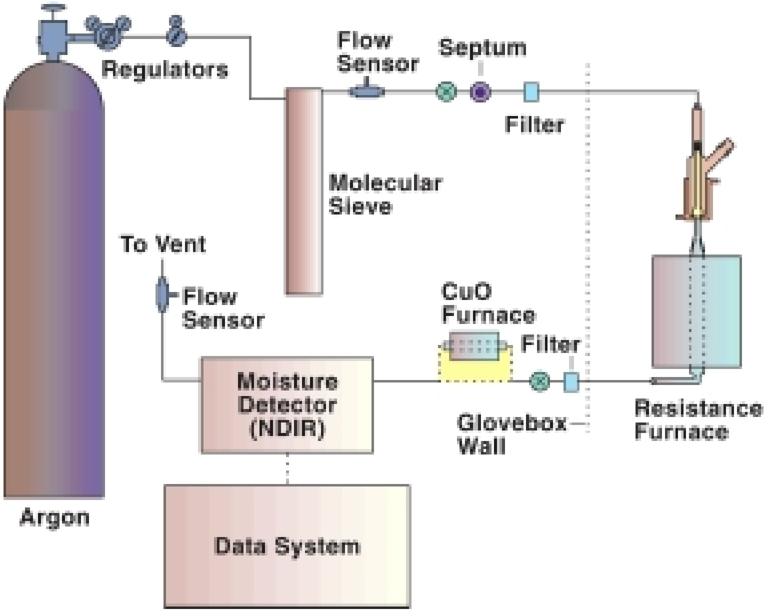

Figure 2. Schematic drawing of an IGA apparatus.

A. *Initial Capital Cost*

The NDIR Analyzer is approximately $ 10K, while a furnace equivalent to that currently used should cost less than $ 1K. There would also be fabrication costs and costs for miscellaneous hardware (valves, tubing, heat tape, Variacs, Swagelok™ fittings, *etc*). The amount of CuO required is approximately 100 ml/year. The data system hardware can be purchased for about $ 4K. The flowmeters cost about $ 1K per pair. A gas purification tube is available from Fisher or VWR for < $ 0.1K. The argon cylinder and regulators would be another $ 0.1K. The total price is therefore expected to be less than $ 20K.

B. *Estimated Annual Operating Cost*

The annual operating costs are expected to be less than $ 1K, including electricity.

C. *Personnel & Training Requirements*

A single technician can perform routine analysis.

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7. Guidebook on Quality Control of Water Reactor Fuel, IAEA-Tech. Rep. Ser. No.221 (IAEA, Vienna, 1983) pp. 170.
8. “Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets”, ASTM C-696-93 (ASTM, West Conshohocken, PA, 1998).
9. “Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets”, ASTM C-697-98 (ASTM, West Conshohocken, PA, 1998).
10. “Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ($(U,Pu)O_2$)”, ASTM C-698-98 (ASTM, West Conshohocken, PA, 1998).

D. Facilities Requirements

Installation would require a single glovebox large enough for the analytical furnace. Depending on site requirements, a radiological hood might be required to house the remaining equipment other than the data system. The analytical furnace footprint is about 1 ft^2, the NDIR footprint is about 3 ft^2, and the data system footprint is about 4 ft^2. The connecting tubing, gas cylinder, CuO "furnace", *etc*. require another 3 ft^2.

Weighing of samples requires an analytical balance capable of weighing semi-micro quantities (0.01 mg) and clean laboratory conditions are required for the smallest samples. Isolation from the production equipment might be necessary.

E. Advantages/Disadvantages of the Method for Routine Analysis

- Advantages
  - Shorter analytical time than SFE, LOI, and TGA.

- Disadvantages
  - Possible interference from CO_2, which absorbs energy at some of the same wavelengths as water in the IR detector. However, 10 mol% CO_2 in the carrier gas will result in an interference equivalent to only 50 ppm H_2O in the carrier gas. This would be detectable, but not significant relative to the 0.5 wt. % water limit.
  - Highly impure samples, apparently those containing high concentrations of chloride, can plug the 2 µm filter at the exit from the glovebox. Analyses made at the higher temperature require monitoring of the carrier gas flow rate and periodic, manual increases in the carrier gas pressure to compensate for this plugging. The plugging problem can sometimes be avoided by back-flushing the filter between analyses.
  - Highly inhomogeneous samples may present a concern, as the maximum sample size is currently 100 mg. The actual sample size for a particular analysis depends on the expected amount of water/hydrogen, and is adjusted to keep the amount of evolved hydrogen within the limits of the detector, 0.1 to 70 µg H_2. For example, a sample aliquot of 1 mg would be used if 25% water were expected. Eleven injections of 0.6 µg of hydrogen were measured with a percent relative standard deviation of ±3%.

3. *Supercritical Fluid Extraction (SFE)*

This technique, shown schematically in Figure 3, involves permeating the sample with a constant flow-rate of dry, supercritical carbon dioxide (CO_2). The CO_2 acts as a sweep gas, carrying the solubilized water to a detector. The amount of water dissolved in the CO_2 stream is quantitated using a high-pressure Fourier Transform Infrared (FTIR) cell. The response of the FTIR cell is compared to that obtained from an injection of a known amount of water.

SFE has been in routine, commercial use for approximately 30 years.[11] It has traditionally been applied to the extraction of organic material from organic matrices, but the methodology is well established and systems are commercially available.

A. *Initial Capital Cost*

The major components are commercially available and would total approximately $ 60K. These components include (a) extractor/pump/pump controller, (b) FTIR detector system/high pressure cell, and (c) computer/software

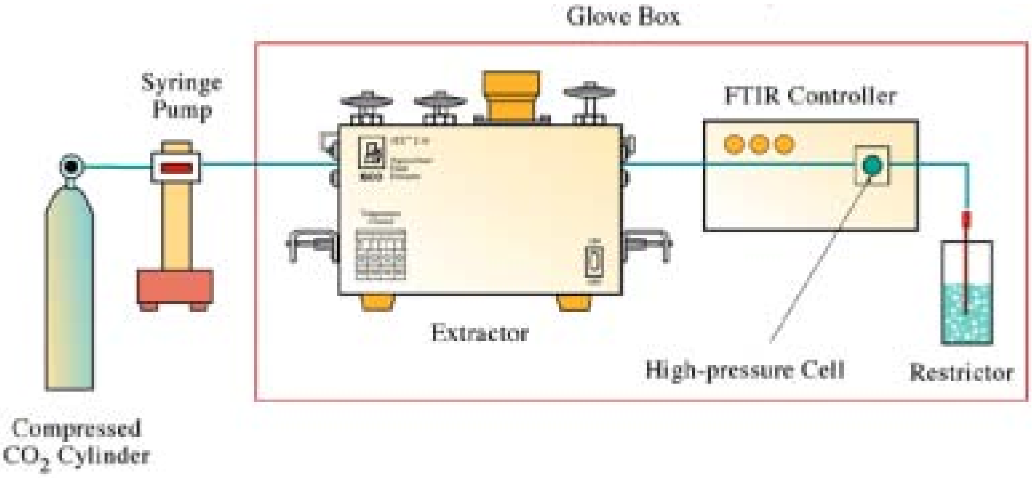

Figure 3. Schematic drawing of a supercritical fluid extraction system.

B. *Estimated Annual Operating Cost*

Annual cost for operation would depend largely on the number of highly impure (high salt) samples that would be run. If the process samples are similar to those run at LANL over the past year, then the estimated disposable cost would be approximately $ 10K, which would include (a) replacement restrictors, (b) replacement transfer lines, and (c) extraction cartridges.

C. *Personnel & Training Requirements*

The operating group (CST-12) requires that 2 trained personnel be present during operation. This is a safety requirement that is part of the DOE approved method in the CMR building. The procedure and training for this method are formalized and would take 1-2 weeks to implement at a

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[11] M. A. McHugh and V.J. Krukonis, Supercritical Fluid Extraction : Principles and Practice, 2nd edition (Butterworth Publishers, Stoneham, MA, 1994).

new site. It would be preferable to have a Technical Staff Member, with an analytical chemistry background, to oversee the process and for data analysis/reporting.

D. Facilities Requirements

This operation requires a double glovebox setup. This glovebox needs to have feed-through ports for (a) CO_2 gas feed and (b) a RS 232 data transfer cable linking the FTIR to the computer. Also required is either a feed-through port or open front box to transfer materials and samples into the glovebox.

E. Advantages/Disadvantages of the Method for Routine Analysis

- Advantages:
  - The sample size (nominally 5 g, with a maximum of approximately 20 g) is large enough to cope with most heterogeneous materials.
  - Shorter run times than for LOI, with an average on the order of 30 - 60 minutes with real-time data acquisition. This analysis time could be shortened if only a qualitative (< 0.5 wt. % or > 0.5 wt. %) result is acceptable.
  - Minimal waste generation (< 1L of liquid per year).
  - The method and operation has been approved by DOE LAAO for use in a CAT-1 nuclear facility.
  - Quantitation is software automated.

- Disadvantages:
  - Highly impure (high salt) samples may plug the restrictor and require replacement and re-calibration (1 day downtime + associated cost).
  - The high-pressure FTIR cell window is susceptible to degradation in highly acidic environments (2 – 4 days downtime + associated cost).
  - Hydrated water will cause false positive determinations due to the increased time to completely remove the water. This applies to hydrated compounds whose decomposition temperature greatly exceeds the normal operating temperature of 140°C.

4. Thermo-Gravimetric Analysis-Mass Spectrometer (TGA-MS)

This method is similar to LOI in that the sample is pyrolized in a furnace and the weight loss determined. In the TGA method, however, the weight loss measurement is made in real time while the sample is heated at a known, constant rate. With the Mass Spectrometer (MS) attachment, the identity of the volatilized species giving rise to the weight loss can be determined, also in real time.

TGA is a well-established analytical method for determining the concentration of volatile components. TGA systems with coupled mass spectrometers, residual gas analyzers (RGA) and differential scanning calorimeters (DSC) are commercially available.

A. Initial Capital Cost

A TGA-MS unit, shown in cutaway view as Figure 4, would cost $ 100K to $ 350K, depending on (a) the level of automation, (b) sample size (commercial instruments have a maximum sample size of approximately 1 g), (c) mass spectrometer resolution and scanning range, and (d) data logging speed (i.e., how fast mass spectrum can be collected vs. ramp rate of the TGA, *etc*.)

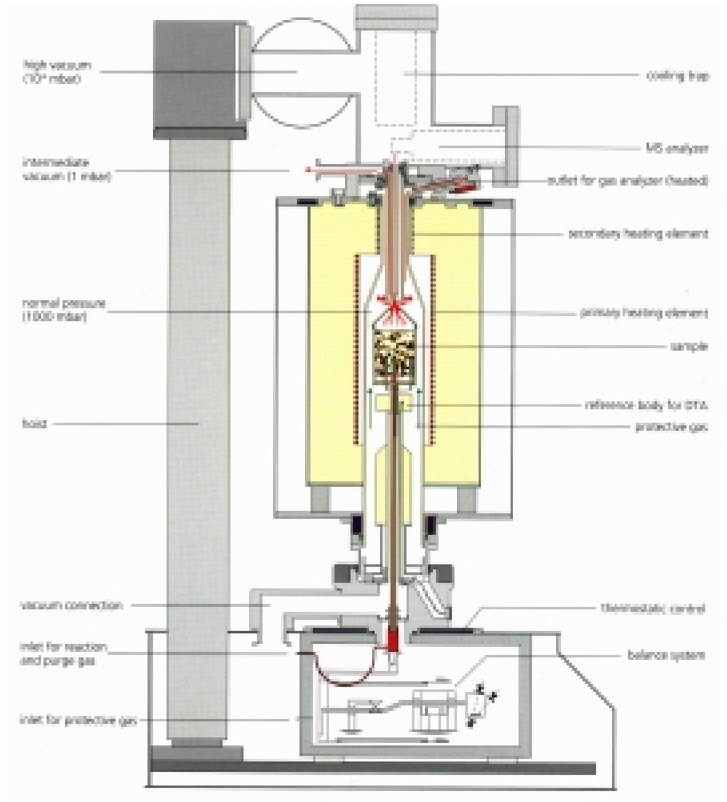

Figure 4. Cutaway view of a TGA-MS instrument.

B. Estimated Annual Operating Cost

For routine analyses of impure PuO_2 samples, the major upkeep on the mass spectrometer will involve the ion source and the multiplier. Spares of each should be kept on hand. For the TGA part of the apparatus, it is expected that the sample holder and heat shields would have to be replaced annually. The actual lifetimes of these components would depend on the number of samples. Total down time is estimated to be approximately three weeks per year for replacement of the above-mentioned components, routine maintenance on the vacuum system, and re-calibration of the instrument.

Annual consumables cost is estimated to be approximately 12.5K, and would include (a) flow gases: ≈ 0.5K, (b) estimated upkeep: ≈ 1K, (c) crucibles: ≈ 1K, (d) ion source: ≈ 5K, and (e) multiplier: ≈ 5K.

C. Personnel & Training Requirements

One full time technician can run the analyses after approximately one month of training.

D. Facilities Requirements

Basic facility requirements are cooling water, power (110 V and 208 V single phase), and a glovebox with an attached slotbox. The installation should allow for high voltage (up to 5 kV, but minimal amperage) feedthroughs to operate the mass spectrometer portion of the system. Some 110 V or 208 V feedthroughs for the TGA furnace and the mass spectrometer pumping system. Also, associated low-power feedthroughs for control and data acquisition. If a cold glovebox is used, then an estimate of at least a full time technician with some staff supervision for a period of two months will be required for installation and cold testing. These requirements will vary depending on the instrument and custom glovebox design, if needed. LANL currently operates a TGA instrument in a glovebox space of 3’ x 2’ x 3’.

E. Advantages/Disadvantages of the Method for Routine Analysis

- Advantages:
  - The TGA-MS technique directly measures mass change as function of time, with the *simultaneous identification* of the volatilized species (water, hydrocarbons, CO, CO_2, H_2, other inorganic compounds)
  - The DTA-MS method directly follows heat flow as function of time, providing quantitative information on chemical reactions, solid-state phase changes, etc.
  - Because mass loss is recorded in real time, the mass spectrometer does not require full calibration to interpret the mass spectral data. The mass spectrometer scale needs to be calibrated routinely but this involves a scan on a standard gas mixture.
  - The real advantage of this combined technique is that the conversion of the mass spectrometer data from intensity to pressure to amount of material is not necessary and hence a complicated calibration is not needed. This is because mass loss is measured directly, while the mass spectrometer is only used to identify the vapor species responsible for the mass losses.

- Disadvantages:
  - High cost, relative to the other techniques
  - Operation of an instrument and analysis of the data requires technical expertise on the part of the analyst.

- Servicing and maintenance in a glovebox will be more difficult than for LOI, IGA, and SFE.
- The typical sample size is only 5 to 500 mg, although some instruments may be able to analyze up to 1 g. If a new generation instrument is purchased, it may be possible to specify a larger sample size, perhaps up to 10 g. With larger (impure) sample sizes, however, comes the possibility that the instrument may require more frequent maintenance.

5. Neutron Moderation

This method measures the shift in neutron energy spectrum produced by the thermalization of neutrons by *hydrogen* atoms (protons) in the sample. The neutrons are generated using a ^{252}Cf source, placed on one side of the PuO_2 container, Figure 5. Detectors sensitive to thermal neutrons (containing, for example, ^{3}He or ^{10}B) are placed at various locations around the container. The entire container/detector assembly is surrounded by a 3”-4” thick wall of iron to moderate the source neutrons and reflect them back into the sample.

When water is present in the PuO_2 matrix, the neutrons are partially thermalized, or reduced in kinetic energy, by collisions with protons and the neutron detectors measure an increase in the count rate associated with the slightly larger number of these lower-energy neutrons. The increase in the neutron detector count rate is therefore proportional to the number of protons present, and therefore to the amount of water, in the sample. Empirical calibrations are used to obtain quantitative measures of the moisture concentration of the radioactive material.

It is believed that neutron moderation is in use at some European nuclear fuel fabrication facilities for moisture determination in reactor-grade oxide materials.

A. Initial Capital Cost

The prototype neutron moisture monitor currently in use in the LANL Plutonium Facility was assembled for approximately $ 40K. This includes instrument manufacture and procurement of the detector, electronics, and the neutron source. Neutron moderation can be operated as a stand-alone laboratory system, or can be used in-line. For the latter, the cost of installation in a glove box well will also be incurred.

The other major cost contributing to the procurement of a production system will be the software development. Estimates for one-time software development for the production system are approximately $ 60K.

B. Estimated Annual Operating Cost

Maintenance costs should be minimal. The system contains very robust components and no moving parts in its current configuration. A conservative estimate of maintenance costs is $ 10K per year.

C. Personnel & Training Requirements

One person can easily operate the system, although throughput considerations would ultimately dictate the staffing level required for routine operation. An extended campaign of five samples per day per year might require a maximum of 0.5 FTE.

The software will automate the analysis and make operation nearly transparent. A lower-level technician with less than 1 week of training can operate the instrument. There will need to be a staff-level supervisor to oversee instrument operation and calibration.

D. Facilities Requirements

The instrument has two components: the instrument body and the electronics. The body is basically an iron block (14” wide × 14” deep × 16” high) on a stand that is approximately 20 in^2 at the base. Realistically, the unit is too heavy for installation inside a glovebox, but can be placed near a glovebox for in-line measurements, as is currently done in the Plutonium Facility. The electronics consist of one rack-mountable NIM bin with assorted NIM modules.

E. Advantages/Disadvantages of the Method for Routine Analysis

- Advantages:
  - The method is nondestructive
  - No sub-sampling is required, so that an in situ assay of the entire "as packaged" material is performed. The maximum sample size would be the load limit for the 3013 can (5 kg net). The minimum sample size would be based on the required detection limits and confidence intervals. Work done to date gives an estimated detection level of approximately 1.4 g of water. This corresponds to a detection limit of 0.5 w% for a 280 g net weight container. If it is determined that the 0.5 wt. % should be at least three times the detection limit, then the minimum sample size would be approximately 850 g. A practical limit might be around 1 kg.
  - Rapid turn-around time, with results obtained in less than 30 minutes.

- Disadvantages:
  - Interferences from impurities. Current modeling suggests that potential elemental interferences are uranium, which might be handled using multiple calibration curves, excessive carbon content, and beryllium.
  - The experimental accuracy for analysis of "real world" samples is undetermined. Further validation experiments are necessary to establish this.
  - Results to date indicate that matrix inhomogeneities, such as density, fill height, and spatial distribution of the moisture can also introduce measurement errors.

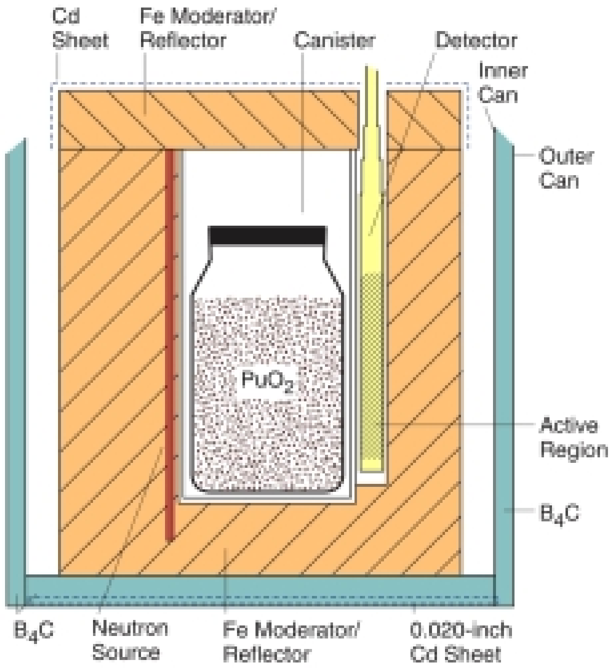

Figure 5. Schematic illustration of the current neutron moderation system.

Appendix B – Experimental Results

Supporting information in this Appendix includes (a) a brief description of the fabrication of the moisture standards, (b) a brief description of the sampling protocol, and (b) experimental results of the comparative study obtained to date.

1. Fabrication of Moisture Standards

It was decided by LANL that known water contents in the materials used for the comparative study were to be established using spikes of solid crystalline hydrates. Gypsum ($CaSO_4 \cdot 2H_2O$) was initially chosen and was used in the first study (High Chloride material, CCLANL025). It was subsequently suggested by members of the Materials Identification and Surveillance (MIS) Working Group that chloride- and/or alkaline earth-bearing salt hydrates, such as $CaCl_2 \cdot 6H_2O$, $Ca(OH)_2$, $MgCl_2 \cdot H_2O$ and $Mg(OH)_2$ be considered as these more closely resemble those hygroscopic impurities likely to be present in actual impure oxides. These hydrates, however, all have relatively low decomposition temperatures and several are deliquescent, meaning that they dissolve in their own water of hydration. Such salts therefore have variable water content and would result in systematic measurement errors. An attempt was made to examine a different, less hygroscopic hydrate: borax ($Na_2B_4O_7 \cdot 10H_2O$). A comparative study was made on the High Pu material using this hydrate as a spike. This proved not to be a good choice, probably owing to the small amount of hydrate needed (because of the large number of hydrated waters relative to that contained in the gypsum) and the resulting incomplete homogenization of the material by one hour of V-blending. It was decided to use gypsum for the subsequent comparative studies.

2. Sampling Protocol

Table 3 gives a brief description of the five materials chosen for the comparative study. Materials having high levels of chloride, uranium and magnesium, in addition to a nominally pure PuO_2 material, are to be studied. The selection of these materials was made in concert with the MIS Working Group, and was meant to simulate the types of impure oxides to be packaged at the various sites.

The experimental protocol is described in the remainder of this Appendix. All five of the comparative studies are conducted in essentially the same manner.

First, the initial moisture content of the sample must be determined. After the sample is recovered from the vault, it is sent, in total, for neutron moderation analysis, Figure 6. Afterwards, the sample is returned to the sampling glovebox and a 30 g archive sample is taken. Additional samples for LOI (a pair of 5 g samples) and SFE (a pair of 5 g samples) are taken. The SFE, IGA and TGA apparatus reside in a different Technical Area (CMR building) and these samples are transferred from the Plutonium Facility to the CMR building during regularly scheduled shipments. Once received at the CMR building, one of the SFE samples is given to IGA, which removes a sub-sample on the order of 0.5 g for multiple analysis. A separate SFE sample is given to TGA, which removes a sub-sample of approximately 0.5 g for multiple analyses. (TGA was made part of the comparative study beginning with the High Pu material.) The remainder of each SFE sample after IGA and TGA sub-sampling is returned for SFE analysis.

Table 3. Description of the five samples to be used for the comparative moisture analysis test.

Sample type	Sample ID	Net sample Weight	"Target" Impurity Concentration	Spike
High Cl	**CCLANL025**	1375.9 g	0.4 wt % Mg 2.9 wt % K 5.9 wt % Cl 1.0 wt % Na	$CaSO_4 \cdot 2H_2O$
		Σ = 1376 g		
High Pu	U1730	≈ 800 g		$Na_2B_4O_7 \cdot 10H_2O$ $CaSO_4 \cdot 2H_2O$
	E7001	≈ 1000 g		
	P1608	≈ 990 g		
	R2750	≈ 930 g		
		Σ = 3720 g		
High U	SCP711-46	4188.3 g	71.7 wt% U 6.0 wt% Pu	$CaSO_4 \cdot 2H_2O$
		Σ = 4188 g		
High Mg	0020	≈ 850 g	6 % wt% Mg	$CaSO_4 \cdot 2H_2O$
	A1589	≈ 890 g	2.3 wt% Mg	
	6032	≈ 980 g	2 wt % Mg	
	7013	≈ 1100 g	1.3 wt % Mg	
	0089	≈ 1190 g	0.5 wt % Mg	
		Σ = 5010 g		
High Cl	3038	≈ 1040 g	4.5 % Cl	$CaSO_4 \cdot 2H_2O$
	0695	≈ 950 g	5.5 % Cl	
	2282	≈ 995 g	0.7 % Cl	
		Σ = 2985 g		

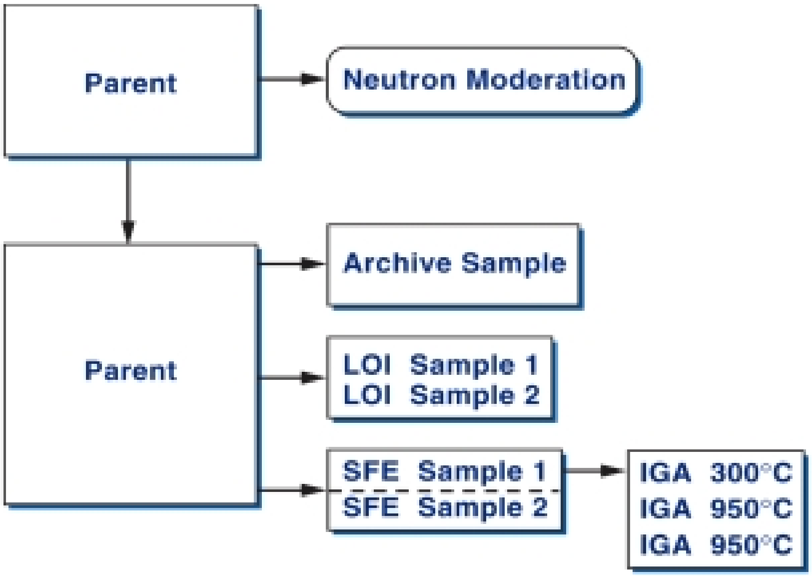

Figure 6. Determination of Initial Moisture Content.

The parent material remaining after removal of the initial moisture samples is then spiked to approximately 0.3 wt. % water using a known amount of gypsum ($CaSO_4 \cdot 2H_2O$). This spiked sample is V-blended for one hour and sent for neutron moderation analysis. The parent materials is then returned to the sampling glovebox and a second round of samples for LOI, IGA, SFE and TGA analyses is taken, Figure 7.

The parent materials remaining after removal of the 0.3 wt. %-spiked water samples is then spiked to a total of approximately 0.7 wt. % water by adding an additional 0.4 wt. % water as gypsum. This spiked sample is V-blended for one hour and sent, in total, for neutron moderation analysis. The parent material is returned from neutron moderation to the sampling glovebox and a third round of samples for LOI, IGA, SFE and TGA analyses is taken, Figure 8.

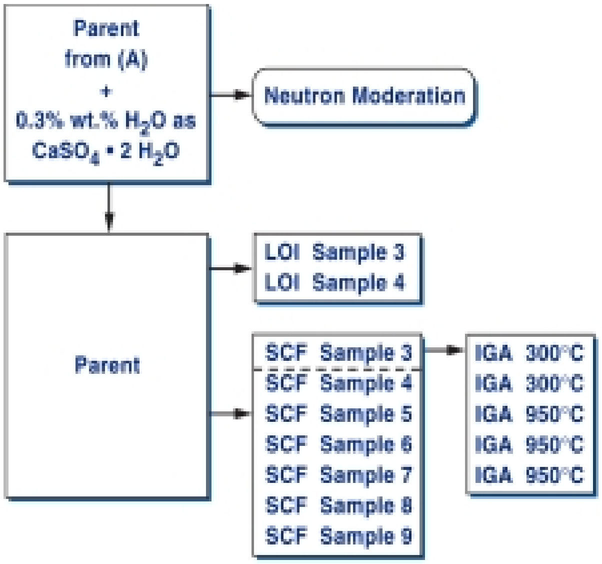

Figure 7. Fabrication and Analysis of the 0.3 wt. % spiked material.

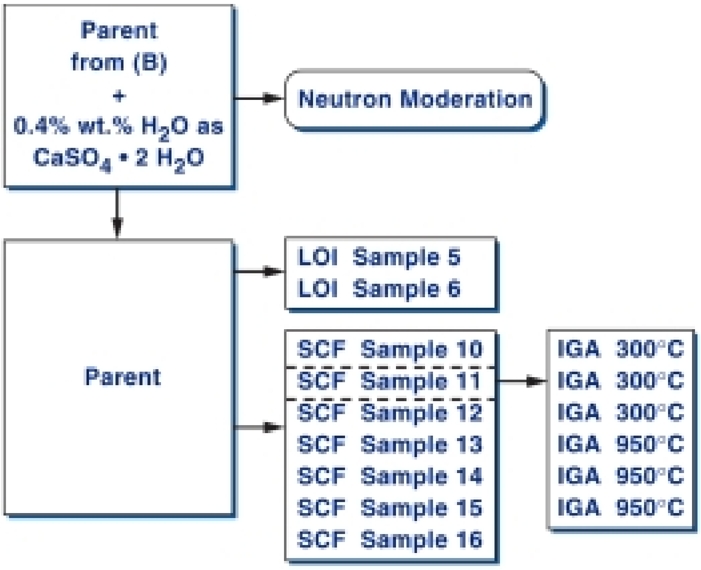

Figure 8. Fabrication and Analysis of the 0.7 wt. % spiked material.

Finally, the parent material remaining after removal of the 0.7 wt. % water samples is re-calcined at 950°C for two hours, as per DOE-STD-3013-96. This sample is V-blended for one hour and sent, in total, for neutron moderation analysis. The material is returned from neutron moderation to the sampling glovebox and a fourth round of samples is taken, Figure 9.

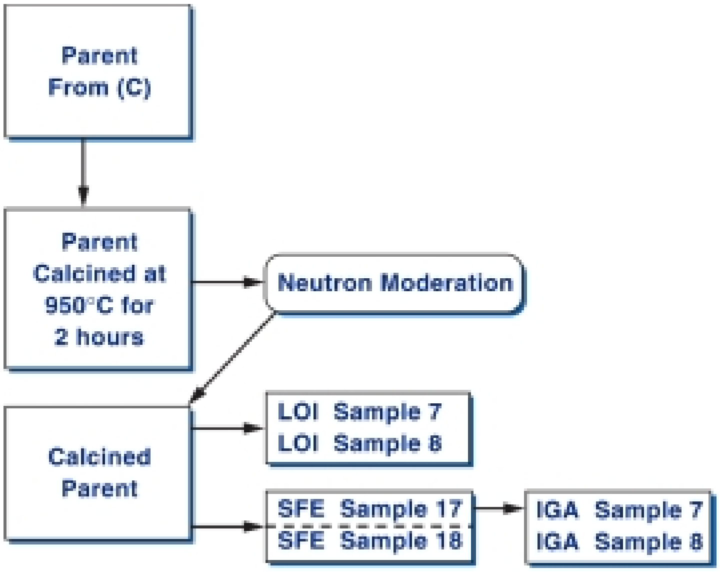

Figure 9. Fabrication and Analysis of the re-calcined material.

3. *High Chloride (CCLANL025) results*

Table 4 gives the physical and chemical information for the High Chloride material (CCLANL025). It can be seen that this material is high in chloride and alkali metals. It was chosen for the initial comparative study because (1) the chemical analysis was available, (2) the materials is a free-flowing powder, so that sampling errors would be minimized, (3) LOI measurements showed that, even after the standard 950°C calcine that the material shows a very high weight loss, and (4) after the 950°C calcine, both IGA and SFE show the material to be free of moisture.

As an example of the discrepancy between LOI and actual moisture content, an inspection of Table 4 shows that the elemental weight loss after calcining to 950°C, specifically Cl, K, Mg and Na, sum to a total of 7.4 wt. %, which compares closely with the results of the LOI measured for the calcined material (6.73 wt. %).

Table 4. MIS Physical and Chemical Property Data for sample CCLANL025.

Item	**LANL (as-received from vault storage)**	**LANL (calcined at 950°C)**
Pu by ICPMS (wt.%)	69.21	78.23
Magnesium (wt.%)	0.55	0.38
Potassium (wt.%)	5.12	2.90
Sodium (wt.%)	1.96	1.01
Chloride (wt.%)	10.00	5.90
LOI at 1000°C (wt.%)	7.87	6.73
Specific Surface Area (m^2/g)	3.95	0.49
Mean Spherical Equivalent by particle number (µm)	11.65	14.50
Mean Spherical equivalent by volume (µm)	40.70	64.95
IGA (total H_2O at 400°C) (wt.%)	0.31	<0.001
IGA (total H_2 at 950°C) (wt.%)	0.36	0.1
SFE Moisture (wt.%)	0.75	< 0.03

Figure 10 is a summary of the experimental results for the as-received CCLANL025 material. This sample was subjected to a 950°C, two-hour calcine prior to storage in the vault. These results indicate that the amount of moisture uptake while in storage was minimal. An initial moisture concentration of 0.06 wt. % was chosen as the average value reported by IGA and SFE analyses.

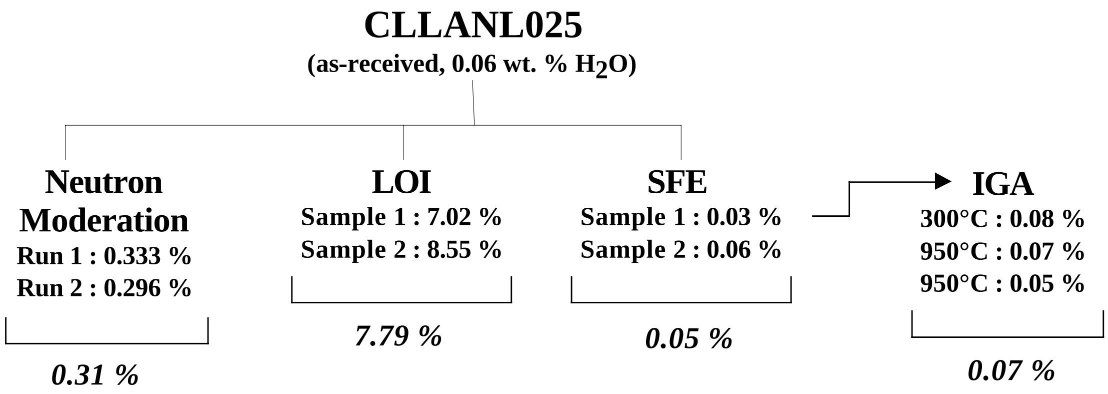

Figure 10. Experimental results for the as-received CCLANL025 material.

Figure 11 shows the results for the CCLANL025 material spiked to a nominal value of 0.30 wt. % H_2O using $CaSO_4{\cdot}2H_2O$. It was a concern that sub-sampling required for IGA and SFE may result in a large experimental variance, but proved not to be the case. The actual amount of water added, as $CaSO_4{\cdot}2H_2O$, was 0.30 wt. %, giving a total of 0.36 wt. %. Both IGA and SFE showed a slight positive bias, with the SFE bias increasing as the CO_2 flow rate decreased due to restrictor plugging (note the SFE results of samples 5 through 8).

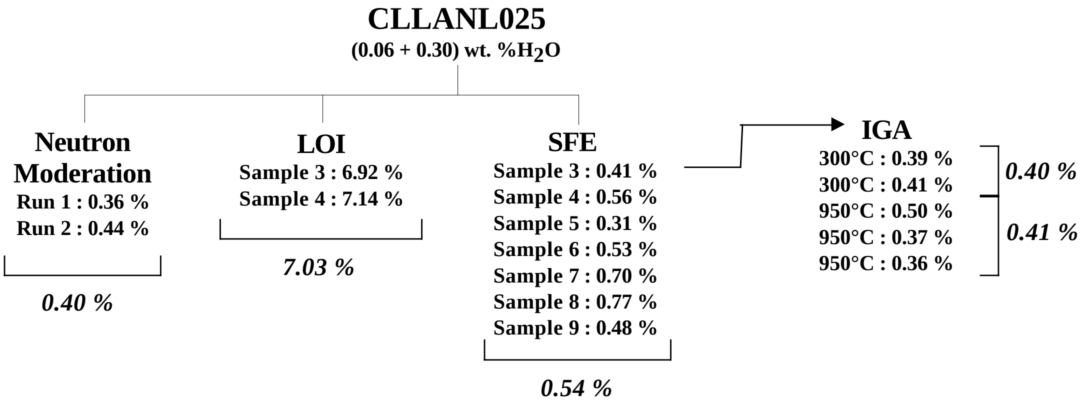

Figure 11. Experimental results for the CCLANL025 material spiked to approximately 0.30 wt. % H_2O using $CaSO_4{\cdot}2H_2O$.

Figure 12 gives the results obtained from the CCLANL material spiked to a nominal total value of 0.7 wt. % H_2O using $CaSO_4{\cdot}2H_2O$. The actual amount of water added by the second spike, as $CaSO_4{\cdot}2H_2O$, was 0.38 wt. %, giving an actual total of 0.74 wt. %.

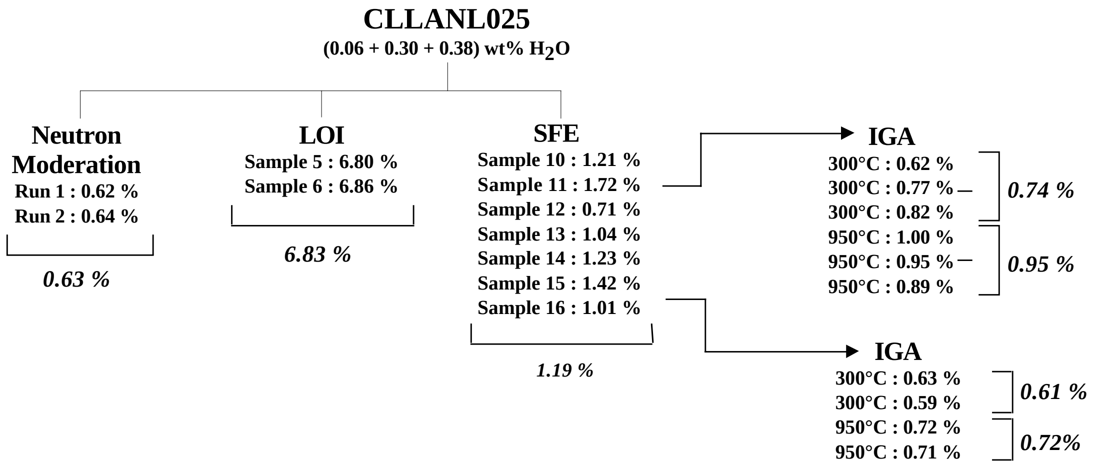

Figure 12. Experimental results for CCLANL025 material spiked to approximately 0.70 wt. % H_2O using $CaSO_4 \cdot 2H_2O$.

Finally, Figure 13 gives the experimental results for the re-calcined CCLANL025 material. The SFE and IGA results indicate that all of the moisture has been removed.

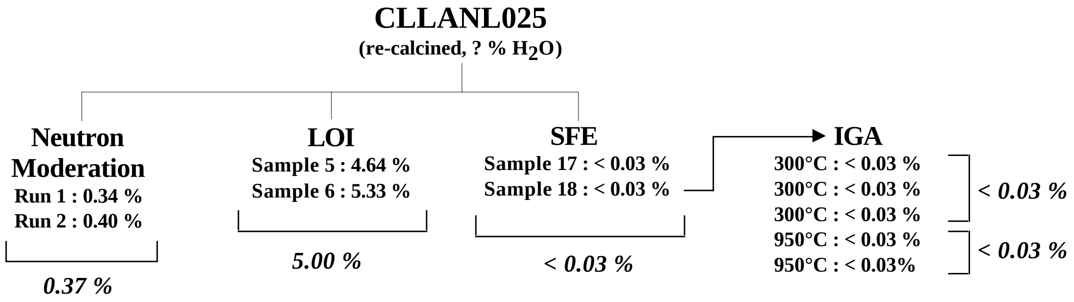

Figure 13. Experimental results for the re-calcined CCLANL025 material.

Table 5 gives a summary of the experimental results for the CCLANL025 material.

Table 5. Experimental results for the High Chloride material (CCLANL025). The neutron moderation data are not corrected for baseline bias.

As–received	**Measured moisture content, average wt. % loss**	**Standard deviation, σ,[12] of the measurements and (number of runs)**
LOI	7.79	1.08 (2)
IGA, total H_2O (300°C) and H_2 (950°C) data	0.07	0.02 (3) 0.02 (2)
SFE	0.05	— (0)
TGA	—	0.03 (2)
Neutron Moderation	0.31	
Spiked to 0.36 wt.% H_2O		
LOI	7.03	0.16 (2)
IGA, total H_2O (300°C)	0.40	0.01 (2)
IGA, total H_2 (950°C)	0.41	0.06 (3)
SFE	0.54	0.16 (7)
TGA	—	— (0)
Neutron Moderation	0.38	0.07 (2)
Spiked to 0.74 wt.% H_2O		
LOI	6.83	0.04 (2)
IGA, total H_2O (300°C)	0.74	0.10 (3)
IGA, total H_2 (950°C)	0.95	0.06 (3)
SFE	1.19	0.32 (7)
TGA	—	— (0)
Neutron Moderation	0.63	0.01 (2)
Re-calcined		
LOI	4.99	0.49 (2)
IGA, total H_2O (300°C)	< 0.03	— (3)
IGA, total H_2 (950°C)	< 0.03	— (3)
SFE	< 0.03	— (2)
TGA	—	— (0)
Neutron Moderation	0.37	0.04 (2)

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[12] Standard deviations calculated using the "nonbiased" or "n-1" method.

4. *High Pu sample results*

Figure 14 gives the experimental results for the as-received High Pu material. This sample was subjected to a two-hour 950°C calcine prior to storage in the vault. The SFE and IGA results indicate that the moisture uptake by the materials while in storage was minimal. A value of 0.03 wt. % H_2O was taken as a representative value of initial moisture content.

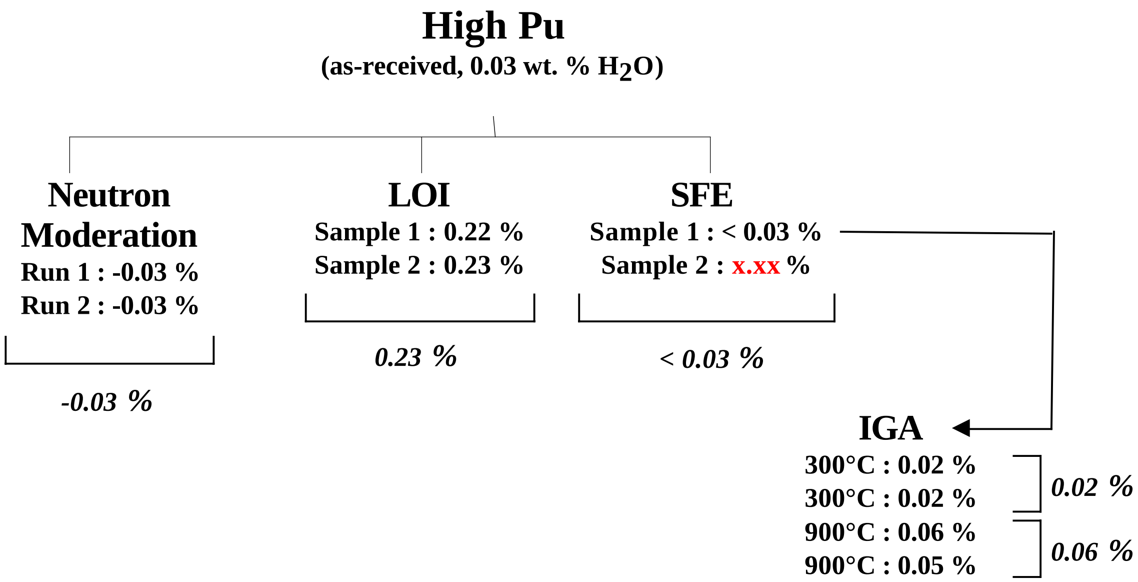

Figure 14. Experimental results for the as-received, High Pu material. "orphan samples" refers to TGA and IGA samples taken directly from the parent, and not from a sample used for parallel SFE analysis.

Figure 15 shows the results for the High Pu material spiked to a nominal value of 0.30 wt.% H_2O using $CaSO_4 \cdot 2H_2O$). The actual amount of water added, as gypsum, was 0.30 wt. %. IGA, giving a total of 0.33 wt. %. SFE and IGA (total hydrogen) results are in excellent agreement with this value, indicating that sub-sampling is not a problem.

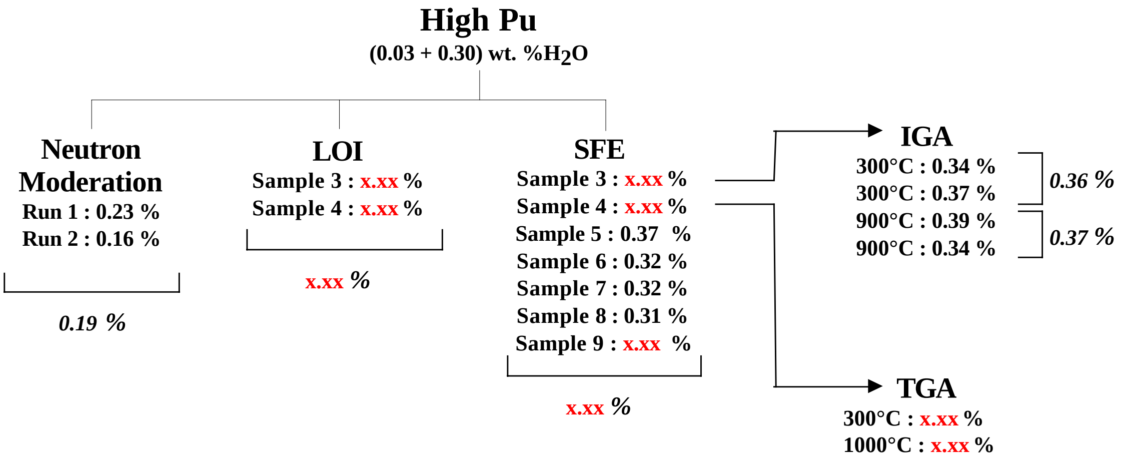

Figure 15. Experimental results for the High Pu material spiked to approximately 0.30 wt. % H_2O using $CaSO_4{\cdot}2H_2O$.

Figure 16 gives the results obtained for the High Pu material spiked to a nominal, total value of 0.7 wt. % H_2O using $CaSO_4{\cdot}2H_2O$. The actual amount of water added at the second spike, as gypsum, was 0.41 wt. %, giving a total of 0.74 wt. %. SFE and IGA both give values that are slightly below this value, but still in substantial agreement.

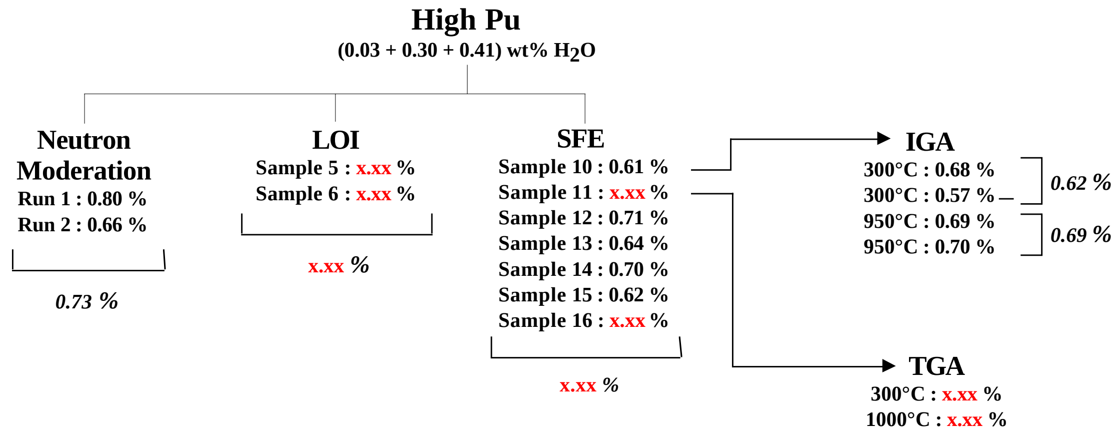

Figure 16. Experimental results for the High Pu material spiked to approximately 0.70 wt. % H_2O using $CaSO_4{\cdot}2H_2O$.

Finally, Figure 17 gives the experimental results for the re-calcined, High Pu material. SFE shows no residual moisture.

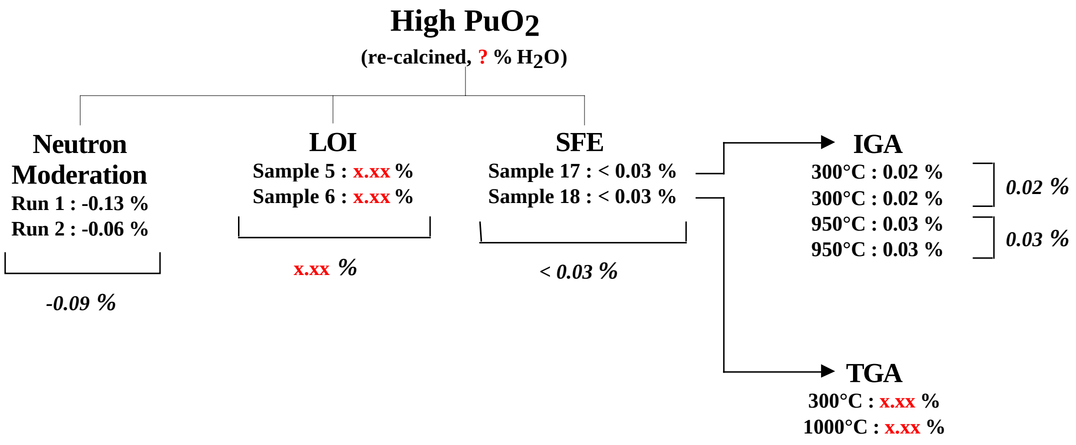

Figure 17. Experimental results for the re-calcined, High Pu material.

Table 6 gives a summary of the experimental results for the High Pu material.

Table 6. Experimental results for the High Pu material. The neutron moderation data are not corrected for baseline bias.

	Average moisture Content (wt. %)	**Standard deviation, σ,[13] of (n) moisture content measurements**
As–received		
LOI	x.xx	x.xx (2)
IGA @ 300°C	0.02	0.00 (2)
IGA @ 900°C	0.06	0.01 (2)
SFE	x.xx	x.xx (2)
TGA @ 300°C	x.xx	x.xx (x)
TGA @ 1000°C	x.xx	x.xx (x)
Neutron Moderation	-0.03	0.00 (2)
Spiked to 0.3 wt.% H_2O		
LOI	x.xx	x.xx (2)
IGA @ 300°C	0.36	0.02 (2)
IGA @ 900°C	0.37	0.04 (2)
SFE	x.xx	x.xx (7)
TGA @ 300°C	x.xx	x.xx (x)
TGA @ 1000°C	x.xx	x.xx (x)
Neutron Moderation	0.20	0.05 (2)
Spiked to 0.7 wt.% H_2O		
LOI	x.xx	x.xx (2)
IGA @ 300°C	0.63	0.08 (2)
IGA @ 900°C	0.70	0.01 (2)
SFE	x.xx	x.xx (7)
TGA @ 300°C	x.xx	x.xx (x)
TGA @ 1000°C	x.xx	x.xx (x)
Neutron Moderation	0.73	0.10 (2)
Re-calcined		
LOI	x.xx	x.xx (2)
IGA @ 300°C	0.02	0.00 (2)
IGA @ 900°C	0.03	0.00 (2)
SFE	< 0.03	— (2)
TGA @ 300°C	x.xx	x.xx (x)
TGA @ 1000°C	x.xx	x.xx (x)
Neutron Moderation	-0.10	0.05 (2)

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[13] Standard deviations calculated using the "nonbiased" or "n-1" method.

5. *High U sample results*

Figure 18 gives the experimental results for the as-received High U material. This material, originally derived from uranium carbide, was calcined at a temperature of between 400°C and 600°C for an unknown length of time to produce UO_2 prior to storage in the vault. The SFE results show that the moisture uptake while in storage was minimal. The LOI and TGA results showed large weight gains, indicating that the calcining treatment prior to storage was insufficient to fully oxidize the material. It was therefore decided to re-calcine the as-received material (950°C for two hours) to fully convert to UO_2, thereby establishing stable initial weights for subsequent moisture determinations. Figure 19 shows the results for the High U material after this calcination. SFE, IGA, LOI, and TGA ($T \leq 775$) all show an initial moisture content of < 0.03 wt. %. An initial value of 0.02 wt. % was chosen as representative.

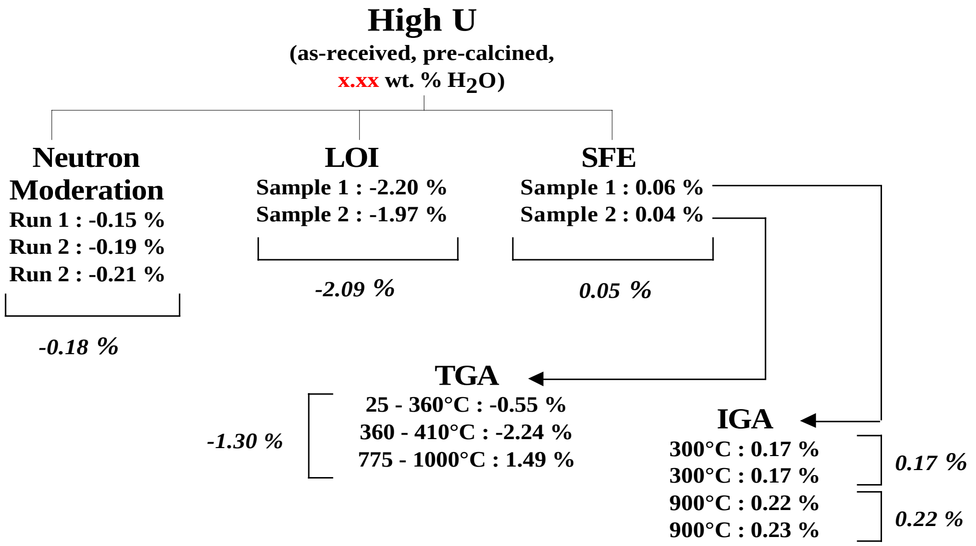

Figure 18. Experimental results for the as-received, pre-calcined, High U material.

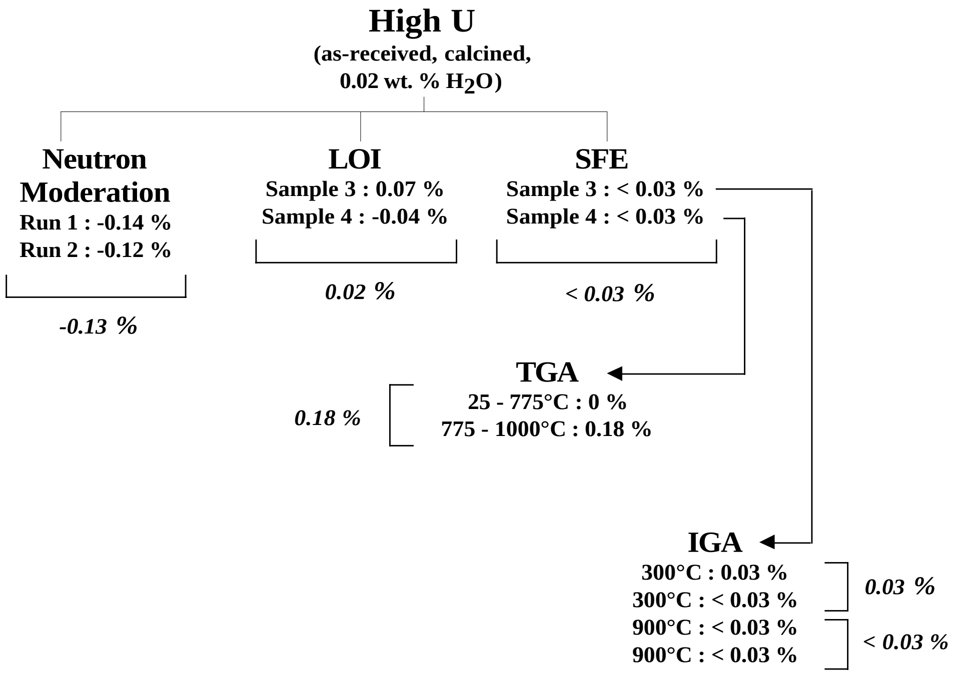

Figure 19. Experimental results for the as received calcined, High U material.

Figure 20 shows the results for the High U sample which was spiked to a nominal value of 0.30 wt.% H_2O using $CaSO_4 \cdot 2H_2O$. The actual amount of water added, as $CaSO_4 \cdot 2H_2O$, was 0.30 wt. %, giving a total value of 0.32 wt. %. Sub-sampling errors are not apparent, as evidenced by the consistency of the IGA and SFE results.

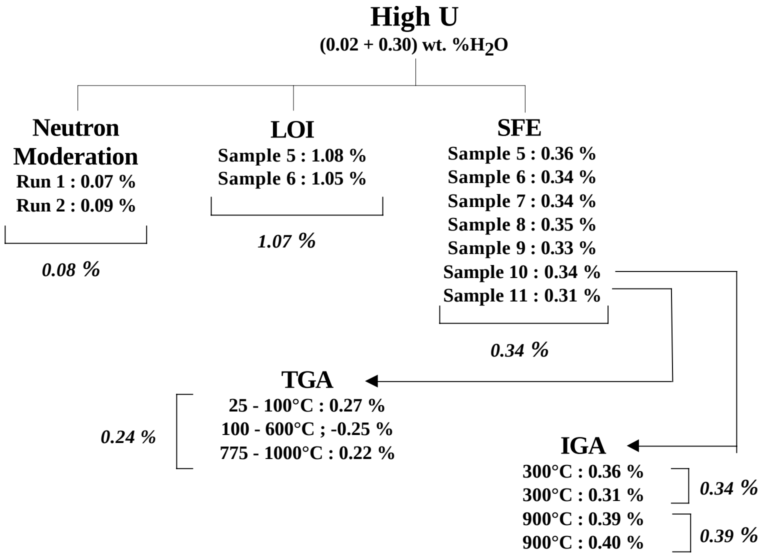

Figure 20. Experimental results for the High U material spiked to approximately 0.3 wt. % H_2O with $CaSO_4 \cdot 2H_2O$.

Figure 21 gives the experimental results for the High U material spiked to a nominal value of 0.7 wt. % H_2O using $CaSO_4 \cdot 2H_2O$. The actual amount of water added, as $CaSO_4 \cdot 2H_2O$, was 0.40 wt. %, giving a total of 0.72 wt. %. SFE gives an average value of 0.73 %t, while IGA gives a slightly lower value. The reason for the high LOI measurements is not known.

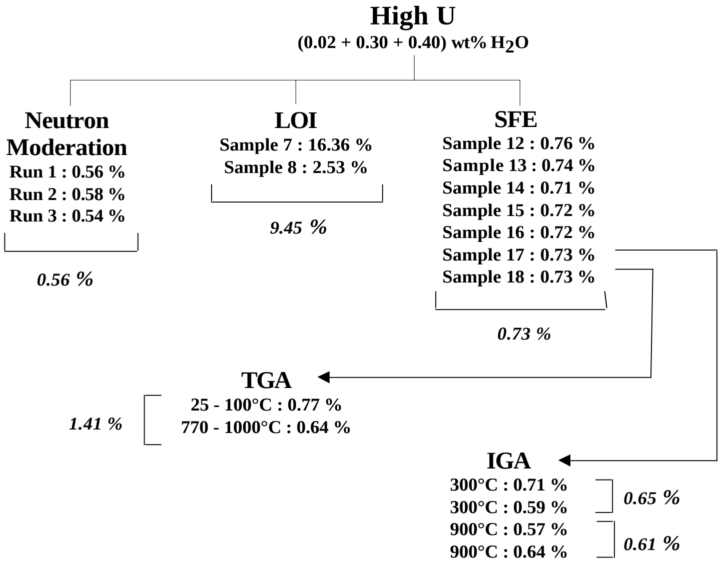

Figure 21. Experimental results for the High U material, spiked to approximately 0.7 wt. % H_2O with $CaSO_4 \cdot 2H_2O$.

Finally, Figure 22 gives the experimental results for the High U material after calcining at 950°C for two hours. Initial SFE results show no residual moisture, while IGA reports a residual moisture content of 0.1 wt. %.

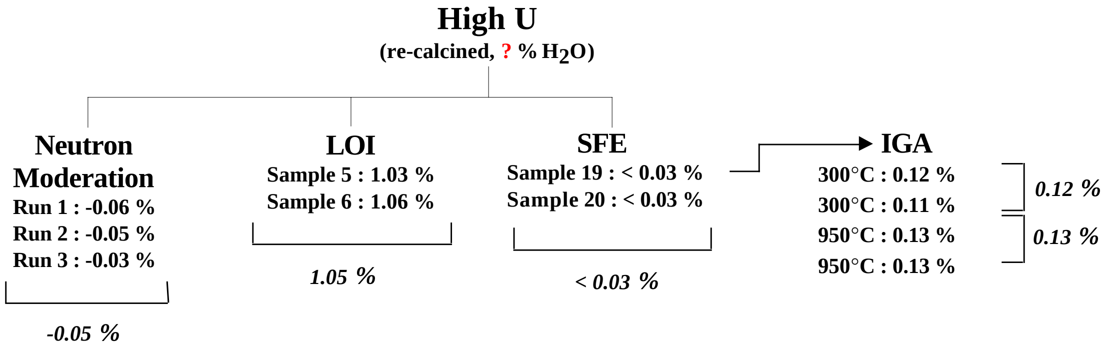

Figure 22. Experimental results for the re-calcined, High U material.

Table 7 gives a summary of the experimental results for the High U sample.

Table 7. Experimental results for the High U material. The neutron moderation data are not corrected for baseline bias**.**

	Measured moisture content, Average wt. % loss	**Standard deviation, σ,[14] of the measurements and (number of runs)**
As–received, pre-calcined		
LOI	-2.09	0.16 (2)
IGA, total H_2O (300°C)	0.17	0.00 (2)
IGA, total H_2 (900°C)	0.22	0.01 (2)
SFE	0.05	0.01 (2)
TGA @ 1000°C	-1.30	— (1)
Neutron Moderation	-0.18	0.03 (3)
As–received, calcined		
LOI	0.02	0.08 (2)
IGA, total H_2O (300°C)	< 0.03	— (2)
IGA, total H_2 (900°C)	< 0.03	— (2)
SFE	< 0.03	— (2)
TGA @ 1000°C	0.18	— (1)
Neutron Moderation	-0.13	0.01 (2)
Spiked to 0.3 wt.% H_2O		
LOI	1.07	0.02 (2)
IGA, total H_2O (300°C)	0.34	0.04 (2)
IGA, total H_2 (900°C)	0.39	0.01 (2)
SFE	0.34	0.02 (7)
TGA @ 1000°C	0.24	— (1)
Neutron Moderation	0.08	0.01 (2)
Spiked to 0.7 wt.% H_2O		
LOI	9.45	9.78 (2)
IGA, total H_2O (300°C)	0.65	0.08 (2)
IGA, total H_2 (900°C)	0.61	0.05 (2)
SFE	0.73	0.02 (7)
TGA @ 1000°C	1.41	— (1)
Neutron Moderation	0.56	0.02 (3)
Re-calcined		
LOI	1.05	0.02 (2)
IGA, total H_2O (300°C)	0.12	0.01 (2)
IGA, total H_2 (900°C)	0.13	0.00 (2)
SFE	< 0.03	— (2)
TGA @ 1000°C	x.xx	x.xx (x)
Neutron Moderation	-0.05	0.02 (3)

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[14] Standard deviations calculated using the "nonbiased" or "n-1" method.

6. Continuation of Validation/Verification of Moisture Measurement Techniques

The neutron moderation method relies on empirical results to develop a baseline calibration, which must incorporate data from material containing suspected interfering elements (U, Be, *etc*.). In addition, during the course of the three comparative analyses completed to date, it has become apparent that other factors related to the matrix also affect the results. These factors include the fill height of the oxide in the container and homogeneity of the oxide (density variations, *etc*.). Modifications will be made to the source/detector geometry to alleviate these factors. As it is recommended that neutron moderation, along with supercritical fluid extraction, be implemented at the DOE sites, part of the implementation strategy should be to conduct initial design changes at LANL, with timely transfer of these modifications to the corresponding systems at the sites.

Appendix C. Report of the Moisture Methods Review Board

On May 13, 1999, the Moisture Methods Review Board met at LANL to review the status of the experimental program on moisture determination methods and to make a site-wide recommendation as to implementation of one or more of these analytical methods.

1. Selection Criteria and Ranking of the Moisture Determination Methods

The Moisture Methods Review Board used the following nine criteria to rank the five analytical techniques:

1. "High specificity to water in the presence of most or all anticipated matrix components, in oxides of 30 – 88 % PuO_2"
2. "Sufficient sensitivity to detect 0 – 0.5 wt. % water with high reliability without regard to how highly the water is physically or chemically bound in the solid matrix"
3. "Short analytical turnaround/Sampling time/Sample size"
4. "Operational capability/Safety/Simplicity/Ease to setup for routine analysis on Pu"
5. "Complete cost, including capital, annual operation, personnel qualification (training), facilities, waste"
6. "Reliability towards all expected impure materials in the absence of detailed compositional information"
7. "Technical maturity"
8. "Applicability to Stabilization Process Control"
9. "Applicability to Conditioning/Storage surveillance"

Based on these nine criteria, and the results of the comparative study (as of May 18, 1999), the Board selected three analytical methods: Supercritical Fluid Extraction (SFE), Interstitial Gas Analysis (IGA) and Neutron Moderation (NM), as being the most promising. The Board then assigned a numerical ranking for each of the nine criteria for each of these three analytical methods, Table 8. The results of this ranking are:

1. Supercritical fluid extraction
2. Neutron moderation
3. Interstitial gas analysis

2. Recommendations of the Moisture Methods Review Board

The Moisture Methods Review Board made the following recommendations:

1. "The Board endorses the implementation of SFE in the short term and in the medium term NM, which appears very promising, but which requires additional R&D to become qualified for all of the (packaged) materials."
2. "Use multivariate analysis and statistical techniques to develop valuable information on existing and future data to accelerate NM modeling"
3. "Use statistical sampling techniques to develop confidence levels"

4. “All of the moisture techniques need design and value engineering to meet operational requirements (to involve personnel from RFETS, PFP and SRS engineers and operators)”
5. “Continue to develop and optimize moisture standards”
6. “Complete a hazards assessment for all of the techniques”
7. “Develop a QA regime for moisture methods leading to 0.5 % ± error”
8. “Optimize NM geometry based on theoretical neutron/proton theory”
9. “Accelerate NM data collection to develop working model over the 30 – 88 % PuO_2 (see Footnotes 1 & 3)”
10. “Develop an integrated plan to accomplish items 1 through 9 by June 4 giving schedule. Budget and impacts.”

3. Footnotes to recommendations

1. “The Board’s choice for selecting NM instead of IGA is justified by the fact that this technique (NM) has the determining advantage to be a non-intrusive measurement that should be applied to the conditioning and storage of each elementary container.”

2. “This recommendation will provide better decision making on the existing data and also will allow the extraction of the data for modeling purposes.”

   “Multivariate data handling techniques need to be allied to existing data in order to develop correlations between the observed moisture measurements and other analytical data gathered on the samples, such as elemental and isotopic. Effective mining of this data via Chemometric techniques may allow for pattern recognition, which can explain “false positive and negative” results and may subsequently allow adjustment of the “true” moisture measurement numbers. As more data is gathered, the models can be further developed and validated.”

   “Chemometric approaches are available within LANL from folks like John Qualagno and Pat Brug (NMT), or via project interaction with the Center for Process Analytical Chemistry (CPAC) at the University of Washington (M. Koch).”

3. “This recommendation will help engineers in charge to conduct the operation more effectively. Engineering handbooks are available that address the concept of statistical sampling procedures for a variety of matrices. John *[Psaras]* will send a reference book, and the recent additions to Perry’s Handbook would be another reference point. The mining and environmental fields have been faced with similar sampling problems.”

4. “To involve, ASAP, the engineers of the different sites to develop a research approach which will be acceptable. It is necessary to build a small group of the three site representatives who will be in charge to define criteria for designing a standard device.”

   “Operational requirements (such as ruggedness, reliability, safety, ease of maintenance, etc.) need to addressed soon. Joint agreement needs to be achieved across the sites involved and such agreement must include production and instrument engineering representation. Design engineering for effective positioning of detectors and sources is a key reason to pool resources and discuss resource problems, engineering requirements, and operational restrictions.”

5. “A special attention should be paid to select calibration (gypsum & others) appropriate to the moisture method. Alternate moisture standards need to be developed and optimized. It is desirable to use reference materials that contain a known moisture content in the range of that to be detected. M. Koch will contact industry this week in order to receive suggestions on what materials could be considered. Molecular sieve-type compounds or NIST related standards will be evaluated.”

6. “To gain a better understanding of the hazards associated with any of the methods, review and document the safety, industrial hygiene, and environmental compliance issues for each of the procedures involved with the moisture measurement techniques under consideration. This should include sampling, sample conditioning, and sample storage.”

7. “The criteria of moisture content lower than 0.5 mass percent is incontestable. (Do we mean higher than 0.5 mass percent?) The associated error should be considered as a cumulative one including sampling and analytical device errors. This QA concern should be brought up at the site level running the method.”

   “In order to address the need for a Quality Assurance Program, a Standard Operating Procedure for Method Development is presented here. To ensure method uniformity, the following topics must be addressed fully in each method.”

Proposed Standard Operating Procedure for Method Development

Scope

The method should state explicitly what compounds may be determined using the procedure and to what sample matrices the procedure is applicable. It should also detail sample interferences that affect the accuracy of the procedure.

Equipment

This is a section that will vary widely depending on the analytical technology that is utilized. It may range from a simple detector device and the associated sources to more sophisticated equipment such as SFE/FTIR. In the case of a sophisticated instrument, the specific requirements for an instrument should be specified rather than requiring a specific brand of instrument. This will accommodate differences existing among various laboratories. If a restrictor tube or specific valve is required, these should be specified along with the name and address of the supplier. If a custom valve or IR cell must be fabricated, instructions for fabricating these should be given in sufficient detail so that a person skilled in the art could duplicate it.

Reagents

This section contains a list of the reagents necessary to carry out the procedure, the purity required for each, and a supplier for acquiring the material. In addition, when solutions are required, a procedure for making those solutions should be specified.

Standardization

The procedure should detail the preparation of the appropriate standards. It should encompass the entire spectrum for preparation of the concentrated stock solution to the preparation of serial dilutions. Typically a procedure is detailed for using these standards to generate a calibration graph. From this graph (or computerized calibration table) the response obtained from the sample can be related to concentration.

Sample Preparation

This section will vary widely depending on the extent to which the sample matrix must be modified for the specific analysis. It could vary from the simplest extreme of dilution prior to injection to a very complex series of extractions and/or other types of isolation procedures for the specific components of interest. The key is to provide sufficient detail that a person skilled in the art of laboratory analysis can perform the required steps of the procedure.

Analysis

This section contains the actual steps necessary for analyzing the sample after preparation for analysis (steps following those detailed in the sample preparation section). The contents of this section can vary widely depending on the complexity and sophistication of the technique. Regardless of the technology involved, enough detail should be presented to allow the analyst to perform the test in the same manner in which it would be performed in other laboratories.

Calculations

Most quantitative procedures require calculations to relate the response of calibration standards to the response(s) obtained for the sample. The calculations should provide sufficient information so that an individual familiar with laboratory procedures could successfully relate the test response to the actual concentration of compound of interest in the test specimen.

Precision

This section provides information concerning the precision and standard deviation for the data obtained using the procedure.

Safety

This section will provide safety warnings for hazardous materials that may be used for a particular analysis and will call attention to any safety concerns in dealing with laboratory equipment used for the analysis. This section is NOT designed to replace MSDS (materials safety data sheets) for the materials involved in the analysis, but rather to call attention to any operations which might pose a hazard to the analyst and, in general, to raise the level of safety awareness.

References

These are literature sources that could supplement the analysts understanding of the technology employed in the method. They could include literature articles, review articles, book chapters, etc.

In addition, to the above topics that should be thoroughly discussed in the body of the method itself, the data generated in support of the method during the development process should include the following:

Spiking and Recovery studies

A sufficient quantity of typical sample matrices must be fortified with the component(s) of interest over the entire applicable range of the method to ensure that quantitation can be achieved over this range and that the recovery of the procedure is reasonable.

Stability of the Compounds of Interest in the Sample Matrix

It is critical that the compound(s) of interest be stable over the time period in which the sample is taken and the sample is analyzed in the laboratory. This situation may exist naturally with the nature of the sample matrix or stabilization procedures may have to be instituted at the time the sample is taken. Data must be obtained to support that the sampling procedure outlined in the method maintains sample integrity throughout the period from the time that the sample is taken until the final analysis.

Identification of Components found in a Typical Sample

Many sample matrices are complex in nature and contain multitudes of trace organic compounds. It is necessary to ascertain, and have appropriate support data, to verify that the components being quantitated and reported is indeed the right compound and not an artifact in the procedure.

Precision and Accuracy Data for the Procedure

To ensure a high level of credibility in the quantitation of the compounds of interest, it is necessary to establish the reproducibility of the procedure over a number of days. Calculations included in this section will document precision and standard deviation.

8. Different loading and detection limits might be used for the neutron moderation technique. Consider multiple detector and/or alternate detector positioning, in order to allow for testing containers with varied fill volumes and content make-up.

9. To achieve this challenging task a joint collaboration needs to be put in place between the R&D people and the field people. As the initial calibration data for the neutron moderation technique is dependent on results from other analytical techniques run on the same samples, the additional data will help develop a calibration model. This will improve on the confidence of the neutron moderation methodology. This, together with advanced mathematical handling of the data (Chemometrics) will enhance the utility of this technology.

10. The Board's expectation on this recommendation is to review a sound integrated plan realistic in timing and identifying the involvement of some key representatives of the three sites.

There needs to be a sustained effort to assess the present attributes of the present technologies (SFE/IR and neutron moderation) versus emerging technologies in the area of moisture measurement. Some of these potential methods for moisture determination include:

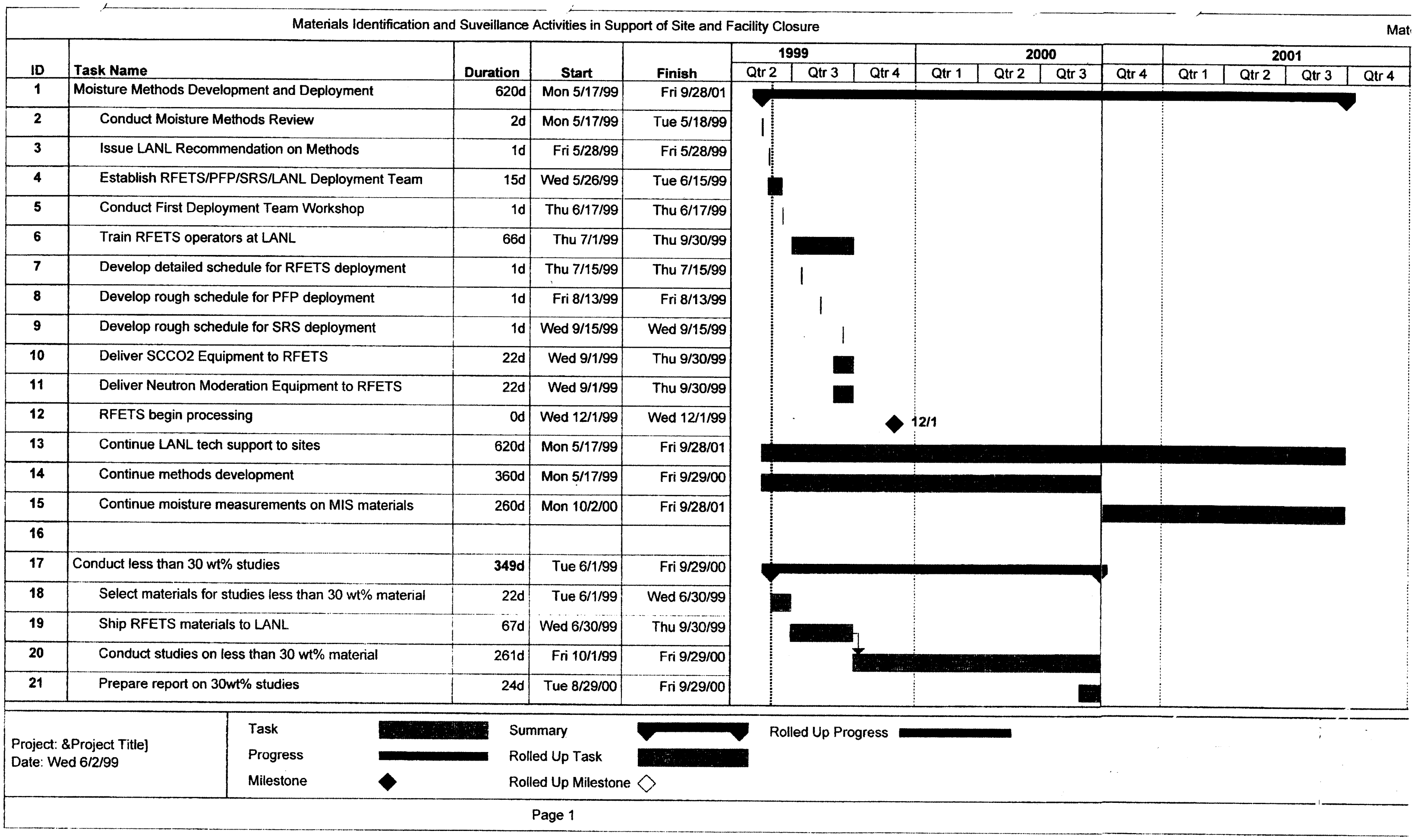
A. Pulsed NMR (the Bruker Instruments web page should be checked for capabilities of this field)
B. Moisture probes (NIR, Vapochromic sensors, etc.)
C. Imaging technologies (MRI, acoustics, etc.)

4. *Ranking the LANL developed Pu moisture Determination methods*

Table 8. Ranking of the LANL-developed plutonium oxide moisture determination methods.

	SFE	**neutron moderation**	**IGA**
“High specificity to water in the presence of most or all anticipated matrix components in oxides of 30 – 88 % PuO_2”	7.4	4.4	7.6
“Sufficient sensitivity to detect 0 – 0.5 wt. % water with high reliability without regard to how highly the water is physically or chemically bound in the solid matrix.”	9.0	6.0	9.0
“Short analytical turnaround/Sampling time/Sample size”	4.6	8.2	3.2
“Operational capability/Safety/Simplicity/Ease to setup for routine analysis on Pu”	5.8	7.0	5.2
“Complete cost, including capital, annual operation, personnel qualification (training), facilities, waste”	6.2	7.2	5.6
“Reliability towards all expected impure materials in the absence of detailed compositional information”	7.6	3.4	7.6
“Technical maturity”	6.2	4.2	7.2
“Applicability to Stabilization Process Control”	8.0	7.43	7.0
Subtotal	54.8	47.8	52.4
“Applicability to Conditioning/Storage surveillance”	0.0	9.2	0.0
Grand total	54.8	57.0	52.4

Appendix D. Schedule for RFETS deployment



Materials Identification and Suveillance Activities in Support of Site and Facility Closure

Mat

ID	Task Name	Duration	Start	Finish
1	Moisture Methods Development and Deployment	620d	Mon 5/17/99	Fri 9/28/01
2	Conduct Moisture Methods Review	2d	Mon 5/17/99	Tue 5/18/99
3	Issue LANL Recommendation on Methods	1d	Fri 5/28/99	Fri 5/28/99
4	Establish RFETS/PFP/SRS/LANL Deployment Team	15d	Wed 5/26/99	Tue 6/15/99
5	Conduct First Deployment Team Workshop	1d	Thu 6/17/99	Thu 6/17/99
6	Train RFETS operators at LANL	66d	Thu 7/1/99	Thu 9/30/99
7	Develop detailed schedule for RFETS deployment	1d	Thu 7/15/99	Thu 7/15/99
8	Develop rough schedule for PFP deployment	1d	Fri 8/13/99	Fri 8/13/99
9	Develop rough schedule for SRS deployment	1d	Wed 9/15/99	Wed 9/15/99
10	Deliver SCCO2 Equipment to RFETS	22d	Wed 9/1/99	Thu 9/30/99
11	Deliver Neutron Moderation Equipment to RFETS	22d	Wed 9/1/99	Thu 9/30/99
12	RFETS begin processing	0d	Wed 12/1/99	Wed 12/1/99
13	Continue LANL tech support to sites	620d	Mon 5/17/99	Fri 9/28/01
14	Continue methods development	360d	Mon 5/17/99	Fri 9/29/00
15	Continue moisture measurements on MIS materials	260d	Mon 10/2/00	Fri 9/28/01
16				
17	Conduct less than 30 wt% studies	**349d**	Tue 6/1/99	Fri 9/29/00
18	Select materials for studies less than 30 wt% material	22d	Tue 6/1/99	Wed 6/30/99
19	Ship RFETS materials to LANL	67d	Wed 6/30/99	Thu 9/30/99
20	Conduct studies on less than 30 wt% material	261d	Fri 10/1/99	Fri 9/29/00
21	Prepare report on 30wt% studies	24d	Tue 8/29/00	Fri 9/29/00

Project: &Project Title]
Date: Wed 6/2/99

Task	▬	Summary	▬	Rolled Up Progress	▬
Progress	▬	Rolled Up Task	▬		
Milestone	◆	Rolled Up Milestone	◇		

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