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Author(s):	Lav Tandon, Kevin Kuhn, Lawrence Drake, Diana Decker, Laurie Walker, Lisa Colletti, Khalil Spencer, Dominic Peterson, Jaclyn Herrera, Amy Wong
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DESTRUCTIVE ANALYSIS CAPABILITIES FOR PLUTONIUM AND URANIUM CHARACTERIZATION AT LOS ALAMOS NATIONAL LABORATORY

Lav Tandon, Kevin Kuhn, Lawrence Drake, Diana Decker, Laurie Walker, Lisa Colletti, Khalil Spencer, Dominic Peterson, Jaclyn Herrera, Amy S. Wong

ABSTRACT

Los Alamos National Laboratory's (LANL) Actinide Analytical Chemistry (AAC) group has been in existence since the Manhattan Project. It maintains a complete set of analytical capabilities for performing complete characterization (elemental assay, isotopic, metallic and non metallic trace impurities) of uranium and plutonium samples in different forms. For a majority of the customers there are strong quality assurance (QA) and quality control (QC) objectives including highest accuracy and precision with well defined uncertainties associated with the analytical results. Los Alamos participates in various international and national programs such as the Plutonium Metal Exchange Program, New Brunswick Laboratory's (NBL's) Safeguards Measurement Evaluation Program (SME) and several other inter-laboratory round robin exercises to monitor and evaluate the data quality generated by AAC. These programs also provide independent verification of analytical measurement capabilities, and allow any technical problems with analytical measurements to be identified and corrected. This presentation will focus on key analytical capabilities for destructive analysis in AAC and also comparative data between LANL and peer groups for Pu assay and isotopic analysis.

INTRODUCTION

The AAC group in the Chemistry Division at LANL provides expertise in chemical and radiochemical analysis of materials where actinide or fissile materials make up a significant portion of the sample. These analyses range from assay of the major components down to trace analysis of impurities – spanning over seven orders of magnitude of chemical analysis capability and consist of both non-destructive and destructive analyses. Only the destructive analyses will be discussed in this paper. A listing of these analytical techniques is shown in Table 1. The selection of the best method depends upon the concentration of the element being measured, the degree of accuracy required for the analysis, and the material form, estimated purity, and quantity of the sample. In support of these capabilities, the group has the necessary facilities, glove boxes, hoods, analytical instrumentation, and technical expertise for handling and analyzing milligram to kilogram quantities of special nuclear material safely.

Table 1. Analytical Capabilities at Los Alamos National Laboratory

Analytical Technique	Information
High Resolution Gamma-ray Spectrometry (Radiochemistry)	Applied both nondestructively and destructively for isotopic composition of Np, Am, U, Th, and Pu, daughter and fission products
Alpha/Beta Spectrometry (Radiochemistry)	Isotopic composition of Np, Am, U, Th, and Pu, daughter and fission products
Titration	High accuracy and precision determination of U and Pu content
Coulometry	High accuracy and precision determination Pu and Np content
Spectrophotometric	High accuracy and mid precision determinations for Pu composition as well as individual trace elements such as Fe and Si

Analytical Technique	Information
Inductively Coupled Plasma (ICP) Methods (ICP-atomic emission spectroscopy (AES), ICP-mass spectrometry (MS)	Quantitative impurity content, trace elements, elemental distribution, and mass balance
Mass Spectrometry (TIMS, IDMS)	High accuracy and precision isotopic composition of U and Pu, impurities, U and Pu content
X-ray Fluorescence Methods (XRF)	Elemental distribution and total elemental content of particles and surface
Cold-Vapor Atomic Fluorescence	Mercury
Gas Mass Spectrometry	Burn up and reprocessing indicators
Interstitial Gas Analysis	Impurities (C, H, N, O, S, and halogens) which are critical parameters for nuclear fuels and mass balance

ELEMENTAL ASSAY

The plutonium (Pu) Assay team uses a suite of chemistry techniques to assay plutonium (Pu), uranium (U), and neptunium (Np). These assay methods fill an important role for many programs of both national and international importance. For instance, assay is used in certifying the material quality of the metals, oxides and other forms needed by United States (US) Department of Energy (DOE) programs in defense, nonproliferation and nuclear accountancy/safeguards, counter-proliferation, nuclear materials technologies, basic science and is a primary tool for nuclear accountancy and material control and accountability (MC&A). Many non-destructive assay instruments used throughout the (DOE) complex are calibrated with matrix matched standards that were standardized against destructive assay techniques such as coulometry and titrimetry. The requirements (e.g. sample quantity, reproducibility, repeatability, uncertainty, and use) for Pu assay methods are shown in Table 2.

Los Alamos has historically been involved with providing assistance in either fabrication of materials or providing independent analysis for certification purposes on several Pu assay and isotopic reference materials (RMs). The techniques, coulometry and titration, are generally used to measure and certify the purity of Pu or other nuclear standards produced by internationally recognized certificating agencies such as National Institute of Standards and Technology (NIST), New Brunswick Laboratory (NBL) etc. and provide bias free, highest accuracy and lowest uncertainty measurements.

Controlled Potential Coulometric (CPC) is the primary assay technique in AAC at LANL for determining the purity of Pu and Np materials and can provide measurement uncertainties of 0.1% or better which meet the Safeguards International Target Values (ITV)[1], American Society for Testing and Materials ASTM[2] and American National Standards Institute (ANSI) requirements. This method is based on coulombs and grams (primary measurement units) and thus is considered a "first principles" method. Certified reference material (CRM) 126a, Pu metal matrix is used to calibrate the method and a well characterized, homogeneous, plant plutonium oxide (PuO_2) material that has been analyzed for 20 years as a quality control sample.

Ceric Titration is also utilized to perform Pu assay and is well suited to glove box applications. This method provides highest accuracy and lowest uncertainties for any Pu assay method at LANL. This method is also used by certification laboratories and uses CRM 126a as the

calibration standard. This method is only used on materials with certain levels of purity due to its narrow range of calibration.

Spectrophotometric Determination of Plutonium is based on the Pu (III) spectra in a chloride media. In house plutonium metal material is calibrated by coulometry against CRM 126a and used as a secondary standard to calibrate the instrumentation. This method is primarily used for Pu Assay of ^{238}Pu heat source materials. High specific activity causes reproducibility problems leading to higher uncertainty (0.3%) for ^{238}Pu materials. For materials made primarily from ^{239}Pu material, this method does meet the ASTM requirements. This is the preferred method for plutonium containing materials that may have large amounts of unknown impurities.

Table 2. Plutonium and Uranium Assay Methods

	Coulometry	Ceric Tritration	Spectrophotometric	Davies and Gray Titration
Materials	Pu metals, Oxides, Nitrides, Carbides, Mixed Oxides	Pu metals	Impure Pu metal, Oxides, ^{238}Pu heat sources, Miscellaneous Materials	U metals, Oxides, Carbides, Nitrides, Mixed Oxides
Sample Size	0.25 to 1.0 g	0.25 g	0.25 to 1.0 g	0.25 to 1.2g
Standard Required	0.005 g	0.25 g	0.10 g	0.025g
Concentration Range	60-100%	98-100	75-88%	40-100%
Uncertainty	0.10%	0.05%	0.30% (^{238}Pu) 0.14% (^{239}Pu)	0.10%
Required Corrections	Fe	Fe, U, Np	none	none
Safeguards Accountancy Verification Measurements – Qualified?	Yes	Yes	Yes	Yes
Performing Testing Programs	Yes	in process	No	Yes
Meet ASTM and ITV requirements?	Yes	Yes	Yes (^{239}Pu only)	Yes

Davies and Gray titration is the primary assay technique for determining the purity of uranium materials and has a precision of 0.1% or better which meets the safeguards ITV and ASTM requirements. This is the standard method of U assay and is also a method of choice by RM certification laboratories. Standard RM 960 (reissued as CRM 112a), U metal, is used to calibrate the method and a well characterized uranium metal is used as a sample control material. This control material has also been completely characterized by another independent laboratory.

MASS SPECTROMETRY

The isotopic distributions of actinide elements vary depending on the burn up and enrichment levels of a sample. Measuring these distributions is the key to acquiring a complete understanding of the material. While elemental assay measures show how much total Pu (or U or Np, or Am or Th) is present, the isotopic analysis yields the distribution of the isotopes (e.g., ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, etc.). Program customers must know what mix of isotopes is in the material being utilized to ensure the material is consistent with their purposes. Isotopic content is also vital to MC&A of special nuclear material. A summary of the measurement requirements and uses for Mass Spectrometry at LANL is shown in Table 3. All the methods in Table 3 are matrix independent and therefore, can be applied for any sample and form submitted to the group.

Table 3. Mass Spectrometry measurement requirements

Measurement	U Isotopic Analysis	Pu Isotopic Analysis	Trace U isotopic Analysis	Trace Pu isotopic Analysis
Sample size for MS analysis	200 ng	20 ng	1-5 ng	1-2 ng
Uncertainty for Isotopics	≥0.02%, for major isotopes. Higher for minor & trace	≥0.02% for major isotopes. Higher for minor & trace	≥0.5% for major isotopes. Higher for minor & trace	≥0.5% for major isotopes. Higher for minor & trace
Isotope Dilution Mass Spectrometry (IDMS) Uncertainty for Elemental Assay	0.1 % of total	0.1 % of total	1-2 %; Conc. and blank dependent	1-2 %; Conc. and blank dependent
Corrections	Isobaric, thru chemistry	Isobaric, thru chemistry	Fractionation, isobaric	Fractionation, isobaric
Safeguards Accountancy Verification Measurements – Qualified?	Yes	Yes	Yes	Yes
Performing Testing	Yes	Yes	Yes	Yes
Meets ASTM and ITV requirements?	Yes	Yes	Not Applicable (NA)	NA

Thermal Ionization Mass Spectrometry (TIMS) is used for both the determination of isotopic composition and for the measurement of elemental assay using an isotope dilution analysis

technique. Chemical preparation provides isolated portions of the Pu, U, Am, or other elements to be determined. A drop of the isolated material is then placed on a sample filament and dried. The mass spectrometer separates the ions in a magnetic field based on their mass-to-charge ratio. Certified reference material (CRMs) 136, 137, 138, (Pu sulfates) and 126 A (Pu metal) are used for quality control RM. Certified RM 126a and CRM 112a are used for spike calibration of Pu and U respectively by IDMS. Certified RM series CRM U005 through CRM U930 (uranium oxides, nitrates solutions etc.) and NRM 199 (uranyl nitrate solution) are used as quality control (QC) reference materials for uranium analyses.

Since the isotopes are determined by their mass-to-charge ratio, the analysis is not influenced by the radiochemical specific activity of the isotope – each isotope has an equal sensitivity. The measurement of ^{240}Pu is just as sensitive as ^{238}Pu. This distinction is important in comparing isotopic measurement by TIMS to isotopic measurement by gamma spectroscopy or radiochemical techniques. The TIMS instruments are high precision, high sensitivity, and high resolution, and provide the reference measurement to which performance of all other isotopic measurements are compared.

Isotope Dilution can be coupled with TIMS to provide a high precision measurement of elements that exist in more than one isotopic form, particularly the actinides. In this method, a "spike" of known concentration is added to the sample during the chemical dissolution and separation steps of isotopic analysis. The spike is selected to have as isotopically distinct a composition as possible from the sample being analyzed. From the isotopic measurement, the concentration of the sample is back-calculated by equations comparing the size of the spike signal to the size of the sample signal. Thermal ionization mass spectrometry provides high accuracy with low uncertainty isotopic measurements, therefore, the precision of the isotope dilution method is limited by the quality of the spike calibration, sample weighing, and the quality of the chemical processing, including spike equilibration with the sample.

The isotope dilution technique is currently used for measurement of trace U, Am, Ga and other elements in the presence of Pu, down to sub-parts per billion levels. IDMS can also be used to measure trace Pu in U or other materials or to do percent level measurements of any of these elements. To achieve the accuracy and uncertainty required by various customers, all the measurements listed in this section and elemental assays are carried out by gravimetric means.

QUALITY CONTROL

The various analytical techniques must meet increasingly stringent quality assurance (QA) and QC guidelines as part of nuclear material safeguards accountancy and customer specifications. As a result, measurements require a high degree of confidence in both the initial characterization of material and in the analytical tools used to periodically confirm these measurements. To this end AAC participates in various national and international exchange programs such as the Plutonium Metal Exchange Program, New Brunswick Laboratory's (NBL's) Safeguards Measurement Evaluation Program and international programs such Joint Working Group (JOWOG) with Atomic Weapons Establishment (AWE). Actinide analytical chemistry at Los Alamos also maintains a rigorous internal QA/QC program. Representative examples of these QC efforts will be illustrated for two critical destructive analysis techniques, elemental assay and Mass Spectrometry.

Coulometry QC: Daily use of a CRM ensures the traceability to the NIST standards. In absence of availability of matrix matched RM with appropriate concentration ranges and to meet nuclear safeguards accountancy requirements, chemist at LANL decided stated using a QC sample since 1986. This control sample is only used during routine assay of plutonium samples.

Criteria for a QC sample are that it be representative of the sample materials analyzed (Pu), stable, relatively pure, homogeneous, well characterized, and internally traceable. At LANL, this PuO_2 material easy to store and access, and small analytical samples from a parent source are simple to prepare for follow on chemistry; thus, Pu material was chosen as a universal matrix matched control sample for all Pu matrices. When plotted, the control sample offers a continuous measure of the method precision and gives the ability to observe bias and trends in the analysis over time. Control data charted from 2002 to the present are shown in Figure 1. Because the material is radioactive, the accuracy of the assay over time depends on performing accurate decay corrections so that a meaningful control chart can be constructed.

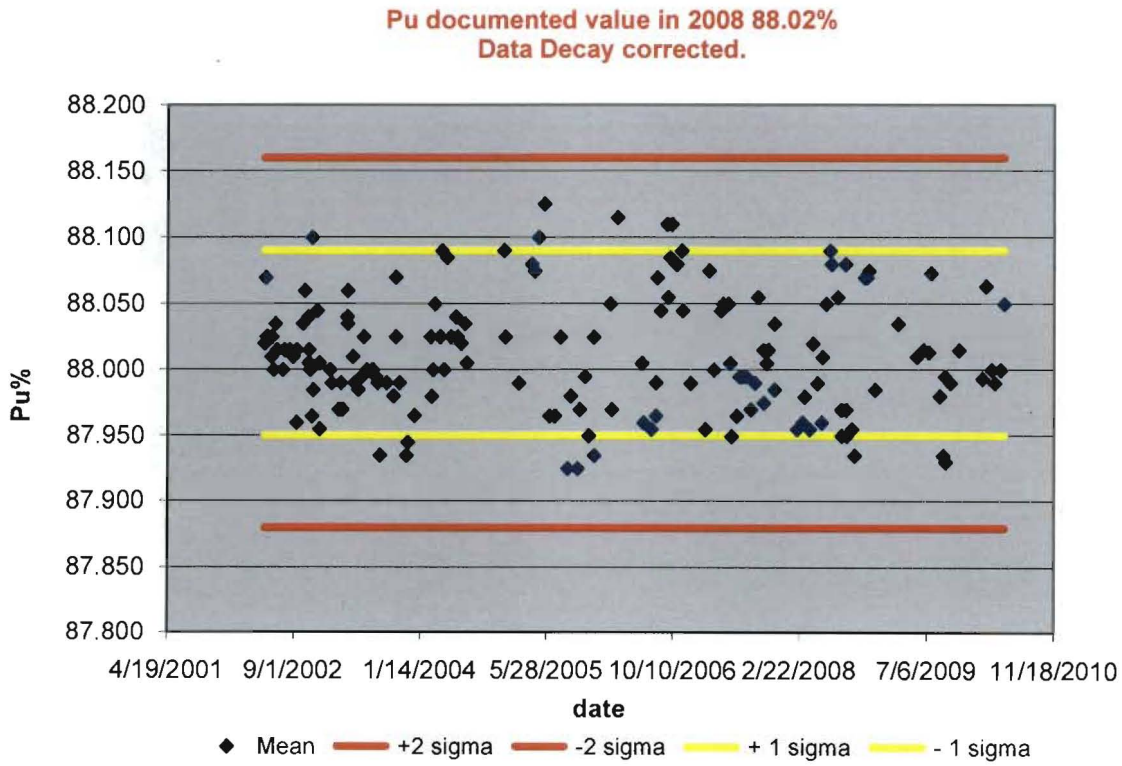

FIGURE 1. Control chart of CPC assay for a Pu oxide control sample.

Plutonium isotopic QC. Recently a majority of Pu analyses are performed on nominally weapons grade materials, so both the absolute and relative uncertainties are based on that isotopic composition with its low abundances of minor isotopes ^{238}Pu, ^{241}Pu, and ^{242}Pu. Example QC charts for Pu isotopic ratios for CRM126a are shown in Figure 2. These results span over a period of four years. Use of a CRM not only ensures traceability but also accuracy since the results compared to the certified values, with appropriate coverage factors.

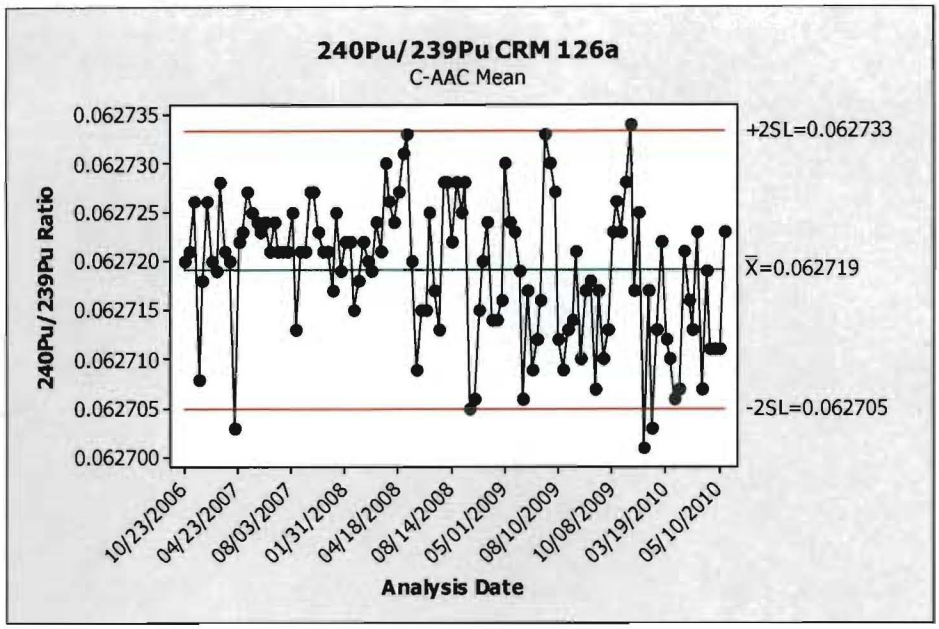

Figure 2. Quality control charts for Pu isotopic ratios for CRM 126a.

INTERLABORATORY COMPARISONS

Plutonium Standards Exchange

Reproducible destructive measurements on plutonium metals are extremely challenging due to matrix effects. Although measurement precision can be established by following a plan for repeated measurements, establishing measurement accuracy requires comparison with standard plutonium metals. Unfortunately, traceable plutonium reference materials have not been developed for impurities in pure and alloyed plutonium metals. The lack of Pu RMs makes the Exchange Program the only available means to estimate the accuracy of measurements on plutonium metal matrices.

The Alamos Exchange Program has been in continuous existence since 2001. In the past up to seven laboratories participated each year in the program. Four different metals used to be submitted in duplicate each year to participating analytical laboratories for analyses. The analyses are further broken down to two metals analyzed per round. Plutonium metal samples in the program are submitted to all participants as "single blinds".

Analytical methods for plutonium assay applied to plutonium metal exchange samples are shown in Table 4. The methods are Controlled Potential Coulometry (CPC), Corpel Titration (CPC) a version of the ceric titration, ICPMS and IDMS/TIMS. All plutonium assay data reported by participating laboratories from each of these methods was compiled and decay corrected. Decay corrections were completed using Pu assay, Pu isotopic, U analysis, U isotopic, and Am analysis results and correcting each Pu assay result to a common date.

Summary statistics for all laboratory and measurement method combinations applied to metal "A" are also presented in Table 4. An initial Pu assay result on this metal was provided by Rocky Flats analytical as 99.11 wt%. Nearly all participating laboratory method results (means) fall within this 95% confidence interval. The exception is the IDMS mean result for lab C which was adversely impacted by method development efforts that led to wider variation and lower values. Comparisons of method mean results (column 3) suggest that the TIMS/IDMS method is systematically low with respect to the consensus value. The difference is observed for all laboratories reporting plutonium assay results by IDMS. The TIMS method also tends to have poorer measurement precision compared to coulometry and titrimetric methods as indicated by larger measurement standard deviations. The Los Alamos IDMS method is producing accurate plutonium assay data albeit with poorer precision than the CPC method.

Table 4. Summary statistics for all laboratory participant methods applied to a metal A

Lab	Method	Mean (wt%)	SD (wt%)	n
A	CORPEL	99.15	0.05	9
LANL	CPC	99.11	0.05	30
B	CPC	99.03	0.11	9
C	CPC	99.05	0.10	42
D	ICP-MS	99.11	0.03	2
E	IDMS	98.99	0.28	11
F	IDMS	99.01	0.27	11
LANL	IDMS	99.05	0.25	16
B	IDMS	98.90	0.04	4
C	IDMS	98.32	0.49	8
CONSENSUS	ALL	99.06	1.00	131

Los Alamos CPC measurement statistics for each relevant exchange date are presented in Figure 2 for delta metal "A". A plot such as this provides an indication of overall trends in the measurement method. Mean measurement results do not show any trends. Five of six means are located above the overall consensus mean. Although this appears to indicate a slight measurement bias, it is impossible to assign bias when the measurement difference is less than the uncertainty in the consensus standard deviation (NIST Publication 829). All Los Alamos CPC mean results and associated uncertainties fall within the 95% confidence interval around the consensus mean indicating that the measurement process is in control. The precision of Los Alamos CPC measurement as indicated by the uncertainty bars is consistent across the entire time interval (2002-2007).

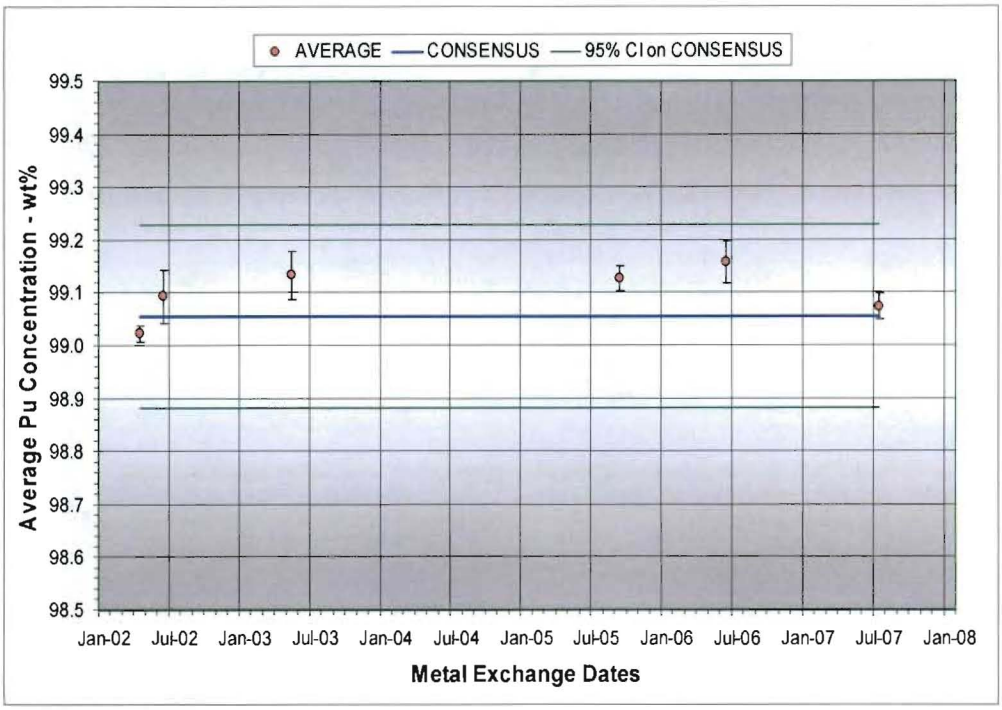

Figure 3. Trend plot for plutonium assay measurement on a metal A by Los Alamos CPC

Uranium Material Exchanges

Los Alamos also participates in several U exchanges that cover a variety of materials including metals and solutions and various isotopic compositions. These exchanges are run by independent laboratories and in some cases, the DOE orders require the laboratory's participation for not only U but Pu too. Los has been participating in these programs for decades. Below, in Figure 4, there graph from one of last year's exchanges in which three laboratories participated. Assay of the U metal material was analyzed by the Davies & Gray method by two laboratories and by IDMS by two laboratories. As can be seen from this data the agreement between all laboratories and methods are good. Davies and Gray titration the primary method of choice of LANL provides tightest precision and compare well with LANL's IDMS results.

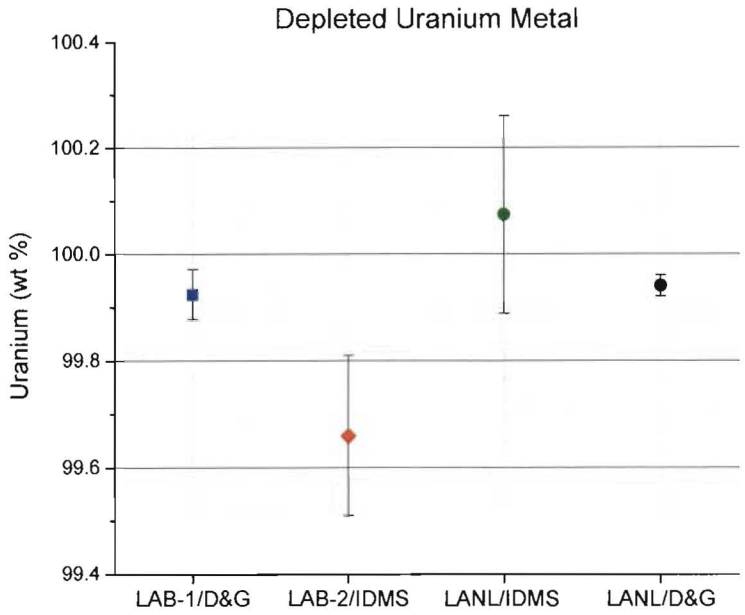

Figure 4. Plot for uranium assay measurements on a uranium metal by both Davies and Gray and IDMS

SUMMARY

Analytical data for use in any decision process must be technically sound and defensible. The basic requirements for producing reliable data include the selection of an appropriate methodology applied using good laboratory and measurement practices. The quality of the data must be assessed and validated by use of RMs or performance evaluation studies to evaluate bias, precision and uncertainties. This requires development of a statistical plan for sampling, measurement, and selection of methodology which has been demonstrated to be reliable, maintenance of statistical control of the measurement process, and assessment of the quality of data by concurrent measurement of suitable materials. So for any analytical method to be validated or considered "qualified", it has to meet these requirements. At Los Alamos analytical methods are constantly assessed and validated through review of QC data, control charts and various exchange programs. The data from these programs show that the laboratory is meeting or exceeding ITVs and ASTM requirements.

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