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The Joint PNC-ORNL Tank Calibration Experiment of 1991

D. H. Smith
D. A. Bostick
E. H. McBay
J. A. Carter
M. H. Ehinger

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D. H. Smith, D. A. Bostick, E. H. McBay, and J. A. Carter
Analytical Chemistry Division

and

M. H. Ehinger
Robotics and Process Systems Division

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D. H. Smith, D. A. Bostick, E. H. McBay, and J. A. Carter
Analytical Chemistry Division

and

M. H. Ehinger
Robotics and Process Systems Division

ABSTRACT

A tank calibration experiment was carried out using the lutetium double spike technique as part of the joint PNC-DOE effort to establish nuclear safeguards at reprocessing plants. The experiment used a 3000 liter tank containing about 100g/L depleted uranium. Results were less than ideal, but the reasons for this are understood. The discussions between the two organizations were highly beneficial. The experiment served to identify two problems in the procedure that must be solved before anything else is tried:

1. Quantitative mixing of tracer and tank contents has not been achieved at PNC. This must be corrected.

2. A chemical procedure to isolate lutetium in a form compatible with good mass spectrometric analysis must be developed. It must be amenable to use in a hot cell.

INTRODUCTION

One of the most difficult stages of the nuclear fuel cycle for which to establish a material balance is the holding tanks that contain solutions of spent fuel. Such tanks comprise an extremely hostile environment and can contain substantial quantities of fissile material. For the purposes of nuclear safeguards it is essential to gain the information necessary for accountability of this material. The information required is the concentrations and isotopic compositions of uranium and plutonium in the tank and the amount of solution in it. Methods of measuring uranium and plutonium, while not at all simple, are well known; isotope dilution mass spectrometry is usually the analytical method of choice. It is the knowledge of the amount of solution in the tank that is the challenge and is the subject of this report.

We first reported a lutetium double spiking method ideal for this application some years ago.[1] Its viability was confirmed in an experiment carried out in Great Britain.[2] The method involves introducing a known amount of natural lutetium to the tank in question (the tracer), mixing it thoroughly with the solution in the tank, and withdrawing an aliquot. A known amount of a spike of enriched ^{176}Lu is added to the aliquot, and a mass spectrometric isotope dilution analysis is performed that yields the concentration of natural lutetium in the aliquot. Knowledge of the amount of natural tracer originally added provides the information necessary to calculate the total amount of solution in the tank.

The element used for this purpose need not be lutetium, of course. There are several other candidates, and some of them would almost certainly work as well as lutetium. To be considered for this purpose, the element must have at least two naturally occurring isotopes, and at least one of them must be available in high enrichment to serve as the isotope dilution spike. It is highly desirable that the element be present at low concentrations (if at all) in the dissolver solutions to reduce blank corrections as far as possible. The tracer must not interfere with subsequent processing of the solution at the plant. And, finally, it must be amenable to mass spectrometric analysis. Lutetium meets all these criteria; so do a number of other elements. Erbium has recently received attention on the basis of it being less costly than lutetium,[3] but the savings in cost per gram would probably be offset by the need to use more of the element as a tracer. Erbium has six stable isotopes as opposed the lutetium's two. To obtain a comparably strong ion beam in the mass spectrometer would thus require three times as much erbium as lutetium.

Rare earth elements are desirable to use in this application because they ionize readily via thermal ionization and are unlikely contaminants; magnesium, another element that has received some attention, would be extremely difficult in its implementation because it is so common that it would be virtually impossible to avoid contaminating the sample. The lower rare earths, such as neodymium and samarium, are fission products, and using them would introduce numerous problems. It is our opinion that lutetium, ytterbium, and erbium are the best candidates for this assignment.

The work described in this report was funded by the Office of Safeguards and Security of DOE and is part of a cooperative program between them and the Power

Reactor and Nuclear Fuel Development Corporation (PNC), operators of the nuclear fuel reprocessing plant in Tokai, Japan. This project (SMA-3) has been under way for several years and has resulted in good, if not spectacular, progress. There are problems facing the chemist at PNC that are unique to that establishment, and some of them present tremendous challenges. An example is that PNC uses gadolinium as a neutron poison; it is in their dissolver solutions at concentrations about 5,000 times greater than that anticipated for a natural lutetium tracer. Gadolinium has an isotope at mass 160, and its oxide ion falls at mass 176. This is one of the lutetium isotopes, and, even though rare earths do not form oxide ions with great abundance during thermal ionization, the great excess of gadolinium with respect to lutetium means that GdO^+ will be significant. To address this problem, we have developed a procedure that separates lutetium from gadolinium and, indeed, from all the other rare earths.[4]

Because of the difficulties of communication by letter, it was decided to have PNC staff members visit ORNL and observe first-hand the execution of a tank calibration experiment. At the same time, ORNL staff, through consultation with the PNC people, would be able to learn more of the situation at PNC and be better able to plan the future direction of the project.

The week of August 26-30, 1991, saw two staff members of PNC visit ORNL to observe the lutetium calibration procedure as applied to a uranium holding tank. This was a visit of great value for all concerned. Benefits were reaped on at least two levels: the purely technical one of problems encountered in the separation of Lu from the tank solution, and the more general one of discussing problems specific to PNC and how best to address them. It is now clear that some of these problems should be solved before doing anything else.

The two most pressing of these are:

1. Developing a procedure that reproducibly delivers a clean lutetium sample to the mass spectrometer filament and that is amenable to use in a hot cell.

2. Developing a method for quantitative delivery of the tracer lutetium to the tank and then mixing it with the tank contents to make a homogeneous solution.

Both of these are discussed below.

EXPERIMENTAL

A schedule for the week is given in Figure 1 and a more detailed description of the procedure in Figure 2. The proceedings started with a short meeting to outline the experiment and to familiarize everyone with the operation. Through the courtesy of Mike Ehinger and his staff of the Robotics and Process Systems Division, which operates the Integrated Equipment Test Facility (IETF), a 3,000-liter tank was at our disposal for this work. The IETF was built to demonstrate advanced processing equipment and procedures for fuel recovery facilities. It is an integrated processing facility, operated on depleted

Schedule for Lu Tank Calibration Experiment
Joint PNC-ORNL Exercise
August 26-30, 1991

Monday, August 26:	Introductory Meeting	8:45-9:30
	Introduce tracer to tank Sparge Take Samples	9:30-10:30
	Take aliquots Add enriched spike	10:30-12:00
	Transport samples to 4500S	12:00-12:15
	Lunch	12:15-1:15
Tuesday, August 27:	Dissolve in HCl Remove corrosion products and uranium	9:00-11:00
	Dry samples	11:00
Wednesday, August 28:	HDEPH extraction Dry samples	All day
Thursday, August 29:	Load mass spectrometer filaments	9:00-11:00
	Analyze samples	1:00
Friday, August 30:	Evaluate results Discuss future interaction Wrap-up	

Figure 1

REMOVAL OF REMAINING STAINLESS STEEL CORROSION METALS FROM AQUEOUS LUTETIUM SAMPLES WITH DI-(2-ETHYL-HEXYLPHOSPHORIC ACID) (HDEHP)

1. Add 100 µL 8 M HNO_3 to evaporated sample to redissolve metal salts. Add 4 mL H_2O so that the sample is < 0.3 M HNO_3.

2. Add 1 mL 0.75 M HDEHP to 4 mL Lu sample.

3. Vortex 5 minutes, centrifuge and discard lower aqueous phase.

4. Scrub organic phase with 4 mL H_2O. Discard aqueous phase. Repeat this step if the corrosion metal concentration is high.

5. Strip Lu from organic phase using 2 mL 8 M HNO_3. Vortex 5 min, centrifuge 3 min. Strip organic phase three more times to obtain 75% Lu recovery.

6. Combine aqueous strip solutions. Evaporate combined samples.

7. Add 50 µL 30% H_2O_2 to decomposed organic residue. Add 50 µL conc. HNO_3 to destroy remaining organic residue and H_2O_2. Repeat this step several times.

8. Dry down sample. Add 25 µL 1 N HNO_3 to redissolve Lu.

9. Analyze 1 µL sample for Lu-175:Lu-176 ratio.

Figure 2

uranium as surrogate for recovery plant feed materials. The facility contains equipment and processes for dissolution and accountancy measurement, solvent extraction recovery, product concentration and accountancy measurement, waste processing, and chemical recovery. The facility has a throughput capacity of 0.5 metric tons uranium per day, with most of the equipment as prototypic of a fuel reprocessing plant.

Tank Description

The tank used for this experiment serves the function of feed adjustment during operation of the facility. The tank is of cylindrical design, with a diameter of 122 cm (48 in). The tank has a nominal height of 3.7 m, constructed with standard dished heads on top and bottom. The tank is equipped with internal coils for heating and cooling. An internal air-lift is provided for tank mixing.

Volume/mass measurements are made in the tank using a standard pneumatic dip tube bubbler system. As typical for a reprocessing plant design, the differential pressure measurement devices are located in a transmitter room located above and outside the process area. Purge air rate in the dip tube system is typically 0.2-0.5 standard cubic feet per hour. Normal process control transmitters (manufactured by Bristol Instrument Company) are used for routine measurements of differential pressure to determine density and liquid level. For this experiment, a fluid manometer was installed in parallel to the process control differential pressure transmitters. Temperature is measured by thermocouple.

Each tank in the IEFT has been calibrated by procedures that are typical of an operating reprocessing plant. Calibration equations relating liquid level to volume are available. The tracer method under study here is designed to certify volume measurements and the calibration equations by an independent method.

While several tanks in the IETF are equipped with vacuum assisted, air-lift recirculating samplers typical of remote sampling operations, the particular tank used here is equipped with a local sampler system, referred to as a vacuum assisted gravity drain, push/pull sampler. The operator uses a vacuum supply to draw sample solution into a sample chamber. The procedure requires the operator to fill and empty the chamber before filling the chamber for the sampling operation. This flushes the sample lines to ensure the sampled solution is representative of the tank contents. When the sample chamber is filled, the operator isolates the chamber and applies pressure to the chamber to run about 25 mL of solution into a waste bottle installed on the sampler needle block. This operation flushes the sampler. He then installs the sample bottle on the needles to draw the sample. The sample chamber is emptied (returned to the tank) after samples are withdrawn.

For this experiment, the tank contained about 1700 liters (see results) of solution at about 1.5 N HNO_3, with about 100 g/L of uranium. As discussed below, the solutions also contained relatively high concentrations of other contaminants (principally iron, chromium, and nickel).

Prior to the addition of the lutetium tracer material, the tank was mixed thoroughly (for about 30 min.) using the internal air-lift mixing system. Several samples were withdrawn to serve as blanks in the experiment.

The tank is equipped with an inspection port covered by a flange. A funnel is attached to the flange to allow direct addition of solutions to the tank. While this type of direct access is not available in remote facilities, this method was used to ensure complete addition of the tracer to the tank contents. This allows the focus of the experiment to be on the procedures for analysis of the samples. Later experiments could be conducted using equipment in the IETF that is more representative of a reprocessing plant to investigate tracer addition techniques.

The natural lutetium tracer (0.464 g) was added to the tank through the funnel flange. Mixing of the tank was initiated. The tank was mixed for a total of 30 minutes. A set of samples was drawn five minutes after the start of mixing, and at intervals of five minutes over the total mixing time. Part of the experiment was to compare results between sample sets to establish that complete mixing of the tracer with tank contents had been achieved.

The experiment went smoothly, and no problems were encountered. Note that the aliquots removed from the tank were divided in two. One set (called the A series) was analyzed while the PNC staff members were at ORNL, the other (the B Series) during the following week.

Chemical Preparation

An outline of the chemical procedures is given in Figure 3. There are several distinct steps required to separate lutetium from the various elements that interfere with a good mass spectrometric analysis. The processing sequence includes: (1) organic extraction of uranium using tributylphosphate (TBP), followed by (2) removal of iron and a portion of the chromium using anion exchange chromatography, and, finally, (3) separation of lutetium from alkali metals and any remaining stainless steel corrosion products using di-(2-ethylhexyl)phosphoric acid (HDEHP) as an extraction agent. Isotope dilution analysis requires equilibration of the spike with the entire amount of analyte element in the aliquot. Once this has been achieved, quantitative recovery is unnecessary. Because approximately 50% of the lutetium in a sample is lost as a result of these clean-up procedures, accurate assay of lutetium demands introduction of a known quantity of lutetium-176 spike to each tank sample prior to chemical processing. The lutetium spike used in this experiment contained 98.511 and 1.489 atom percent of the 176 and 175 lutetium isotopes, respectively. Each 5-mL tank sample was spiked with approximately 880 ng of the lutetium spike so that the ratio of $^{175}Lu/^{176}Lu$ was near unity. After spike addition, each sample was mixed on a wrist arm shaker for ten minutes to equilibrate the normal and spike lutetium. In future experiments, more accurate lutetium analysis may require complete sample dry-down to ensure isotopic equilibration.

Uranium was removed from the spiked samples using 30% tributylphosphate (TBP) in a n-dodecane diluent. Prior to its use, the organic extractant was acidified with 4 M HNO_3. Each 5-mL tank sample was extracted four times with 4-mL TBP additions. The

SAMPLE PREPARATION SEQUENCE
FOR LU ISOLATION

5 mL Lu-175 Spiked Tank Liquor

160 mg U/mL
175 ng Lu-175/mL
3-5 M HNO_3
Tank Corrosion Products
(Fe, Cr, Ni)

A) Weigh 5 mL Sample

B) Add 870 ng Lu-176 to sample and mix

C) Filter sample

D) TBP Solvent Extraction of U

1) Add 4 mL 30% TBP (0.25 M HNO_3), mix 5 min.; centrifuge 3 min.; discard organic phase

2) Repeat TBP extraction three more times (until the aqueous phase is colorless)

3) Transfer majority of aqueous phase to a glass vial and evaporate to almost dryness (50 μL)

E) Remove Iron From Sample Using Dowex-1 Ion Exchange Resin

F) HDEHP Extraction of Lu

G) Determine The Lu-175/Lu-176 Ratio in Sample

Figure 3

samples were shaken with the organic extractant for five minutes on a wrist arm shaker; phase separation was accomplished by centrifuging the samples for three minutes. The organic phase from each extraction step was discarded. No visible yellow tint could be observed in the final aqueous sample phase, indicating that nearly all of the uranium had been removed from the tank samples. The final aqueous samples were transferred to clean glass vials and evaporated to near dryness.

The solutions at IETF have been held in 304L stainless steel tanks for several years. During this time, enough of the constituents of stainless steel (Fe, Ni, Cr) have dissolved so that special treatment of the tank samples was required for their removal. The extent of sample contamination was very evident in the dried, extracted samples, a large volume of rust being present. Table 1 summarizes the concentrations of the major metal contaminants present in the extracted tank samples prior to aqueous phase evaporation. Because approximately 4.5 mL of the aqueous phase was dried down for each tank sample, the actual quantities of metal present in each sample are at least four times greater than those values presented in the table. In addition to stainless steel corrosion products, the quantity of alkali and alkali earth metals would prevent efficient ionization of lutetium if the extracted samples were analyzed mass spectrometrically at this point.

TABLE 1. CONCENTRATION OF METAL CONTAMINANTS IN URANIUM-FREE SAMPLE

METAL	CONCENTRATION (PPM)
Al	13
Ca	53
Cr	120
Cu	4
Fe	410
Mg	130
Mo	2
Na	240
Ni	62
Pb	12
Si	4
Ti	2
Zn	39

A common technique to remove iron from solutions is to convert the sample matrix to concentrated hydrochloric acid. Iron will then be present as a complexed ferric chloride anion that can be removed by either organic extraction or by anion exchange chromatography. An attempt was made to extract the ferric chloride with 30% TBP. Four

mL of the organic extractant was shaken with a 3-mL solution containing sample residue dissolved in 6 M HCl. The extraction distribution ratio for ferric ion under these experimental conditions is greater than 1000.[5] The majority of the iron was removed from the sample with three or four extractions. The difficulty in using this procedure is that phase separation in HCl is very poor. In addition, the density of the TBP loaded with large amounts of iron is so great that portions of the organic phase actually appear at the bottom of the aqueous phase.

Anion exchange chromatography proved to be a more reliable technique for the removal of iron. The uranium-free sample residues were dissolved in 1 mL of warm 6 M HCl. Ion exchange columns were prepared by washing Dowex 1X4, 50-100 mesh, anion exchange resin batch-wise with 6 M HCl until no further leaching of an orange organic material was apparent in the acid. Approximately 4 mL of the wet resin was then transferred to a 1 cm (O.D.) plastic column. A dissolved sample was placed at the head of the column. After the sample had passed through the column, 6 mL of 6 M HCl, added in 1 mL increments, was used to rinse the sample from the column. Elution of the sample from the column could be followed visually as the green nickel ion in the sample passed through the column. No yellow color from the ferric chloride was observed in the eluted sample. The eluted sample was then evaporated to near dryness, resulting in a deep green residue. A fresh resin column was used for each tank sample.

Isotope dilution analysis of the iron-free residue from the column was attempted at this point. No significant lutetium ion signal was observed, however. Presumably the presence of large amounts of nickel, chromium, and alkali metals suppressed ionization of lutetium.

A second organic solvent, HDEHP, was used to isolate lutetium from the remainder of the sample contaminants (Figure 4). Lutetium can be extracted from dilute aqueous acid solutions with 0.75 M HDEHP diluted in n-dodecane. Lutetium can be extracted from either HNO_3 or HCl media; the only prerequisite is that the sample should be free from iron. If extraction is made from HNO_3, ferric ion will form an insoluble polyphosphate complex that will precipitate and contaminate both the organic and aqueous phases. Although cumbersome, it may be possible to remove iron particulates from the organic phase using a 0.45 μm filter. When lutetium is extracted from HCl solutions, ferric chloride will be coextracted, resulting in iron contamination in the final sample.

Using the anion exchange column prior to HDEHP extraction prevents these problems from arising. When 250 μL of 1 M HNO_3 is used to acidify the green column residue and 4 mL of water is added to reduce the sample acidity, no white precipitate is observed on the addition of 1 mL of the HDEHP extractant. After the extractant is shaken with the dissolved sample for 5 minutes, the phases are separated by centrifugation. The organic phase is transferred to a clean vial and washed twice with 3 mL Milli-Q water. Lutetium is stripped from the washed HDEHP phase with 2 mL of 8 M HNO3. The acidified sample is shaken with the HDEHP for 5 minutes before the sample is centrifuged. A clean pipet is used to transfer the aqueous phase to a glass dry-down vial. The organic phase is similarly stripped with 3 consecutive additions of 2 mL of 8 M HNO_3; all aqueous phases are combined for sample evaporation.

TANK VOLUME CALIBRATION EXPERIMENT

TANK DESCRIPTION: 3000 LITER TANK
50-75 % FULL
160 G/L U
3-5 M HNO_3

EXPERIMENTAL PROCEDURE:

A) Mix Tank Contents for 30 Min.

B) Withdraw 2-1O mL Samples for Blank Lu-175/Lu-176 Analysis

C) Discontinue Tank Sparging

D) Add 0.4 g Lu-175 Contained in 500 mL 1 N HNO_3 to Top of Tank

E) Rinse Lu-175 Container With 3-50 mL Rinses and Add to Tank

F) Begin Tank Mixing

G) Remove 10 mL Sample Every 5 Minutes Over a Half-Hour Period

H) Spike Tank Samples With Lu-176

I) Chemically Isolate Lu From Tank Samples

J) Analyze Lu Samples by IDMS

K) Calculate Tank Volume

Figure 4

One of the disadvantages in using the HDEHP extractant is that it is partially soluble in the aqueous sample. The entrained HDEHP must be destroyed prior to IDMS analysis of the sample. Organic destruction was attempted by adding 50 μL of concentrated high purity HNO_3 to the sample residue. After acid evaporation, 50 μL of high purity 30% H_2O_2 was added to the residue further to decompose the organic material. The alternate addition of concentrated acid and H_2O_2 to the sample was continued until the original brown residue had been decolorized. The final residue was then redissolved in 25 μL of 1 M HNO_3 and submitted for mass spectrometric analysis.

Even after efforts to destroy chemically the organic residue in the sample, HDEHP almost certainly contributed contamination to the mass spectrum. The PNC staff uses the same organic reagent and has encountered similar contamination in the mass spectrum.

Mass Spectrometry

The mass spectrum obtained from these samples featured a peak at every mass; Figure 5 was taken just prior to the analysis of the A Series blank and Figure 6 just prior to analysis of Sample 5 of the A Series. Lutetium has isotopes at 175 and 176; all the other peaks in the spectra are from contamination. Even though the relative intensities of the contaminant peaks would have declined with respect to the lutetium isotope peaks during data taking, it is clear that high-quality results cannot be expected when contamination is this high. Background contamination with this pattern of peaks (even mass intensities somewhat higher than odd) is almost always caused by excessive organic material on the mass spectrometer filament. HDEHP was a new extractant for us, and we were thus unaware of some of the problems in its use. Because HDEHP is partially soluble in dilute acid solutions, it is not easy to remove all of it before loading the sample on the mass spectrometer filament. Such contamination will show in the results as excessive uncertainty in the values of isotopic ratios; the signal due to the contaminant varies during an analysis (it tends to burn off with time, but never fully disappears), and the amount of organic material varies widely from filament to filament, making replicate analyses agree much less well than they otherwise would. The variability of the contaminant contribution makes it impossible to make a satisfactory correction for it.

The above paragraph describes just one of the problems encountered in sample preparation. The procedure originally developed at ORNL envisioned using a high sensitivity mass spectrometer for isotopic ratio measurements; samples would require little preparation because the amount of material was small enough that the tank solution could be loaded directly on a filament. This situation does not obtain in a production environment such as that at PNC; a pulse-counting mass spectrometer is not usually available, and the regulations controlling operations outside of contained areas (hot cells and glove boxes) are more stringent there than they are here. A larger sample (100-1000 times) is required, and extensive chemistry is required for sample preparation. We approached the situation for this experiment in what seemed like a reasonable way, but one that in the end required too much time and which would be difficult in the extreme to implement in a hot cell. Various extraction procedures were used (see Figures 3 and 4) to separate lutetium from excess uranium and then from stainless steel corrosion products. It took about two and a half days to isolate the lutetium before mass spectrometer filaments could be loaded. This is clearly too long for a production

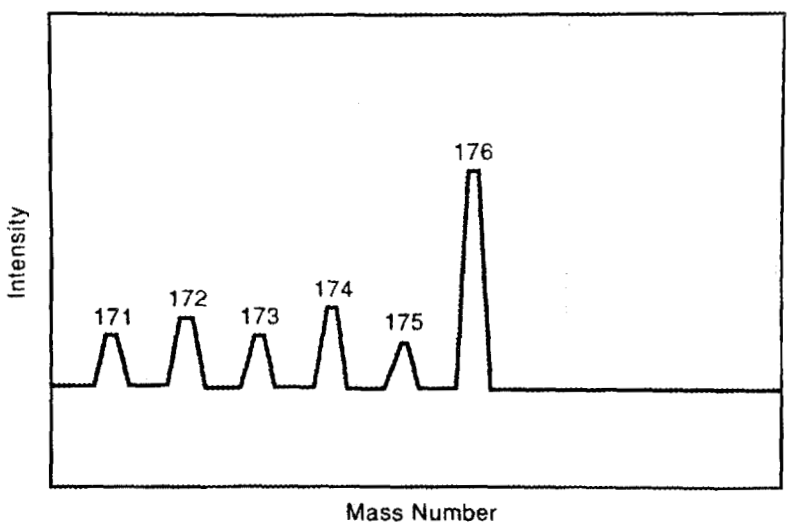

Figure 5. Mass Spectrum of a Blank
Only 176 is Lu

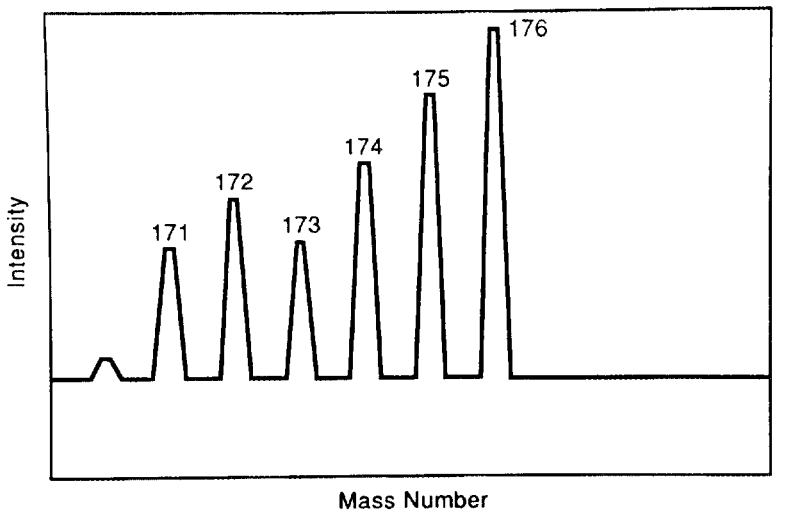

Figure 6. Spectrum of a Sample
175 and 176 are Lu

environment, especially when one considers the fact that PNC will have to separate lutetium from cerium and a large excess of gadolinium as well as from uranium, fission products, and other elements generated in reactor operation.

Another problem encountered because of the age of the solution was that there was still some lutetium left in the tank from our earlier experiment some years ago.[1] This was measured to be 44.9 ng Lu/g of solution by isotope dilution mass spectrometry and confirmed by ICP-AES. All sample concentrations had to be corrected by this amount. The blank was about 20% of the sample concentration, a significant correction to apply.

Loading mass spectrometer filaments and the subsequent analyses went smoothly. Rare earth elements in general run nicely under thermal ionization. For example, our procedure for analyzing lutetium requires 50 ng of the element, while that for uranium requires 1 μg, a 20-fold difference. This reduction in sample size is highly desirable to reduce the amount of lutetium tracer needed, both to conserve costs and to reduce the amount of material added to the subject tank.

Our VG-354 mass spectrometer uses a triple filament assembly. The center filament, made of rhenium, serves as the ionizing surface and is held at a high, constant temperature during analyses. The side filaments are made of tantalum (cheaper than rhenium); the sample solution (usually dilute nitric acid) is deposited onto them and evaporated from them. The temperature of these filaments is carefully controlled during the analysis to ensure that the same conditions of evaporation are met from sample to sample. It is only thus that bias corrections determined from some reference material are valid: data must be taken on approximately the same part of the fractionation curve for all filaments.

In our case, one side filament was loaded with about 1 μL of 1 M nitric acid solution containing about 50 ng of lutetium. The sample was dried by running 0.5 A of current through the filament; it was then oxidized by heating at 2 A for 5 seconds. No outgassing of the filaments was done.

For analysis, the center filament is first set to 4.9 A and the side filaments to 1.75 A. The 187 mass position is monitored while the temperature of the center filament is raised until a Re^+ signal of 1×10^{-12} A is attained; the temperature is held here for the duration of the analysis. Once the center filament is at the appropriate temperature, the temperature of the side filaments is raised stepwise. This is to allow the filament-sample system time to stabilize; it has historically been the case that to raise a sample filament too quickly in temperature very often ruins the chances of a good analysis. When a Lu^+ current of 1×10^{-12} A is reached, preliminary data are taken before raising the temperature to obtain a current of 5×10^{-12} A. Preliminary data are again taken before bringing the Lu^+ current up to 1×10^{-11} A. Final data are taken here; an analysis consists of five runs of ten measurements each, so that a single analysis is comprised of 50 individual determinations of the ratio.

The VG-354 is equipped with a multicollector system that allows simultaneous collection of both lutetium isotopes. This is an extremely valuable feature, improving precision and reducing the amount of sample necessary. Background was monitored at mass position 176.5. Integration time for all mass positions was three seconds.

RESULTS AND DISCUSSION

Our results are given in Table 2 and are corrected for blank contribution. Concentrations in ng/mL, together with the densities of the solutions, are also included, as are the calculated tank contents in kilograms. Reference samples run at the same time as the samples gave precisions of < 0.1%. The upper table contains the results obtained while the PNC staff were at ORNL (Series A). The lower table contains results obtained from the second half of the aliquots of the same samples (Series B). Considerably more effort was expended to destroy the organic material for Series B; the samples ran better, but substantial organic contamination was still observed. We are convinced that the relatively poor agreement between tank samples is due to the organic contamination problem described above; this only serves to emphasize the importance of addressing chemical preparation as the next phase of our work.

The volume of the tank measured with a manometer by IETF personnel was 1690 L. Using a density for the solution of 1.17, the value we obtained was 1736 L. Considering the difficulties encountered, we consider this good agreement.

The results tabulated in Table 2 give relative standard deviations of about 2%. This is well above the value desired (about 0.2% for an internal experiment like this one). We have had no trouble in achieving this precision in previous experiments, including the one we did before using the same tank and one on a much larger tank at Savannah River. Precisions at this level do not come automatically; meticulous attention to detail is necessary in all phases of the operation. The chemical clean-up required to reach these levels is extensive; in addition to the question of obvious contamination that we observed here, it is also necessary to load on the mass spectrometer filament a sample solution that does not contain excessive amounts of elements that degrade ionization efficiency. The alkalis and alkaline earth elements are well-known offenders in this regard; the most common problem comes from sodium because of its prevalence in nature. Sodium contamination does not lead to background peaks in the mass spectrum, but, because it ionizes more readily than the analyte element, causes reduction in ionization efficiency and instability in the ion beam that degrade precision. A good rule of thumb for preparation of microgram-sized samples for mass spectrometry is that nothing is negligible, that one has to take great pains in all aspects of sample preparation to be sure of delivering a satisfactory sample.

We had no way of estimating the size of the organic contaminant peaks during an analysis. Our VG-354 mass spectrometer does not have what one would call "user-friendly" software. Even had we been able to monitor a contaminant peak, it would have been of no practical use. Making a background correction to a mass spectrum requires knowledge of the mass spectrum of the contaminant. Organic materials do not yield mass spectra consistent enough to allow for a viable correction. The relative intensities of peaks at different mass positions vary with filament temperature, the amount of organic

TABLE 2

MASS SPECTROMETRIC RESULTS

SERIES A

Sample	Density	Sample Wgt, g	Spike Wgt, ng	175/176	Conc, ng/g	Conc, ng/mL	Tank Contents, Kg
Blank	1.1703	5.8130	885.3	0.30999	45.6	39.0	
1	1.1720	5.8165	872.4	1.71311	223.7	190.8	2076
2	1.1693	5.7910	886.1	1.73729	233.1	199.4	1993
3	1.1703	5.8050	882.7	1.74387	232.5	198.7	1998
4	1.1682	5.8083	886.1	1.73651	232.2	198.8	2000
5	1.1680	5.7887	873.3	1.77275	235.2	201.4	1975
6	1.1665	5.7973	870.7	1.73253	227.2	194.8	2044
Avg					230.7	197.3	2014
SD					4.2	3.8	38

SERIES B

Sample	Density	Sample Wgt, g	Spike Wgt, ng	175/176	Conc, ng/g	Conc, ng/mL	Tank Contents, Kg
Blank	1.1703	5.8082	887.0	0.30017	44.2	37.8	
1	1.1720	5.8188	884.4	1.68433	222.4	189.8	2089
2	1.1693	5.8170	884.4	1.75208	233.9	200.0	1986
3	1.1703	5.8132	872.4	1.69568	220.9	188.8	2103
4	1.1682	5.7900	883.6	1.73271	231.6	198.3	2006
5	1.1680	5.8073	883.6	1.69776	224.9	192.6	2065
6	1.1665	5.7830	880.1	1.71364	227.7	194.1	2040
Avg					226.9	194.1	2048
SD					5.1	4.5	46

All concentrations have been corrected for 44.9 ng/g blank.

material on the filament in question, and probably, if one but knew, the phase of the moon. Making a quantitative correction is not possible, and making one to the levels of precision at issue here is doubly impossible.

CONCLUSIONS

As discussed above, there are two problems that need to be resolved before proceeding with anything else. Solutions to both problems are vital to the project and are essential to success. These problems are developing a suitable sample preparation procedure and developing a procedure that reliably delivers the tracer to the tank.

Our next efforts should be devoted to developing a procedure that will both eliminate the organic mass spectral background and be suitable for use at PNC. The present experiment was extremely valuable in identifying problem areas that we had not before encountered. There are promising new separations techniques, developed at Argonne National Laboratory by E. P. Horwitz and his colleagues,[6] that may well be applicable here. In addition to the purely chemical question of separating lutetium cleanly from tank solutions, the working conditions at PNC need to be explicitly addressed. Nearly all sample preparation will have to be carried out in a hot cell, and operations easy in the open laboratory are often extremely difficult, if not impossible, in a hot cell. It is for this reason that column separations are preferred to solvent extraction. It is our goal to devise a procedure that employs only a single column, but it will take considerable time in the laboratory to come up with one. We will obtain from PNC the composition of a typical dissolver solution and develop a procedure that addresses all the troublesome species in it. We plan to test any procedure we develop in a hot cell before communicating it to PNC.

The second issue that demands attention is the fact that PNC has been unable to make quantitative delivery of the tracer to the tank. PNC has demonstrated its ability to analyze lutetium mass spectrometrically to the desired levels of accuracy and precision. They also observed wide variation in results from samples taken from their test tank, indicating failure to deliver the entire amount of tracer to the tank. Clearly the whole idea of using a double spike in this application fails if quantitative delivery is not achieved, and it is crucial to the success of the project to correct the problem. The experiment described in this report used direct addition of the tracer and a "local" type sampler. There are several tanks at IETF that have recirculating samplers very similar to the ones at PNC. Using these samplers would permit simulation of conditions very close to those at PNC and allow us to characterize the delivery problems PNC faces. Our goal would be to develop a procedure that would be entirely acceptable to PNC and that would quantitatively deliver the tracer to the solution. This activity would require additional funding ($30-40K) for use of the IETF and its tanks.

Our plan would be to work in parallel on the development of a new chemical procedure and on the introduction-mixing problem. When both phases were ready, they would be synthesized in a "proof of principle" experiment and the results communicated to PNC. The final stages of this experiment would include use of hot cells or glove boxes.

In consultation with the PNC representatives we have formulated a plan that addresses their major concerns. The major of these have been discussed above. There are other, lesser, matters that also merit attention. Some of these are:

1. There is no certified isotopic standard available for lutetium. It is important that the two laboratories agree on a common reference material and calibrate their instruments using it. We suggest that one of the laboratories obtain enough natural Lu_2O_3 for both and send the other enough to meet their needs. The isotopic composition of lutetium should be defined as the IUPAC values.

2. The available stock of enriched ^{176}Lu is of some concern. ORNL's Isotope Sales has on hand 700 mg of 44.23% enriched material ($77.10/mg) and 300 mg of 70.82% enriched ($197.54/mg). They have none of the 98.51% enriched material left.

3. PNC uses large amounts of gadolinium as a neutron poison; it should be checked for possible lutetium contamination. It may be necessary to make a blank correction when the tank is assayed. This work is best done at PNC.

   Successful solution of the two problems discussed here should lead to a procedure applicable at PNC. A report describing this work will be written.

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