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An Independent Technique for Fissile Inventory Verification of Holding Tanks in the Nuclear Fuel Cycle Status Report

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A02 Microfiche A01

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ORNL/TM-10814

Analytical Chemistry Division

AN INDEPENDENT TECHNIQUE FOR FISSILE INVENTORY VERIFICATION OF HOLDING TANKS IN THE NUCLEAR FUEL CYCLE STATUS REPORT

J. A. Carter, D. H. Smith, R. L. Walker, and M. P. May

Date Published: May 1988

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AN INDEPENDENT TECHNIQUE FOR FISSILE INVENTORY VERIFICATION OF HOLDING TANKS IN THE NUCLEAR FUEL CYCLE

J. A. Carter, D. H. Smith, R. L. Walker, and M. P. May

ABSTRACT

A technique for determination of the liquid volumes of solutions in holding tanks and for their fissile material content has been developed and tested. It is independent of the size of the tank, the fraction of full capacity occupied, and void volumes caused, for example, by build up of solid deposits or gas bubbles. Because the amount of spike added to the tank is accurately known, the inventory is also independent of solution volume and density. It involves use of isotope dilution mass spectrometry through application of a double spiking technique using lutetium. A known amount of natural lutetium is added to the subject tank. After thorough mixing, an aliquot of solution is withdrawn from the tank. A known amount of lutetium enriched in the 176 isotope is added to the aliquot. Mass spectrometric analysis and the technique of isotope dilution allow determination of the volume of liquid in the tank. The same aliquot used for volume determination can be used for assay of uranium and plutonium for both isotopic composition and concentration. This allows determination of total fissile weight contained in a given tank.

INTRODUCTION

One of the most challenging tasks faced by any safeguards program is to determine the amount of uranium and plutonium contained in the various holding tanks used in the nuclear fuel cycle. These tanks contain solutions of spent fuel that include substantial quantities of fission products and trans-plutonium elements in addition to the elements of interest. This constitutes an exceptionally hostile environment for the analyst since the solutions are highly radioactive; specialized equipment and methodologies are thus required. The problem is compounded by the fact that the solutions can fill the tanks to any fraction of full capacity. The tanks are usually irregular in shape, making a simple approach (such as determining the depth of solution) unsatisfactory: too many uncertainties creep in that lead to unacceptably high errors in the determination of the volume of liquid. Many tanks contain void volumes in the form of insoluble material that builds up on the bottom or gas bubbles generated by decay of radionuclides. Temperature gradients within the tank can also cause problems for conventional techniques. The complex plumbing necessary for a reprocessing plant also contributes a poorly defined volume to the total. It is normally necessary to determine the volume as accurately as possible to allow calculation of the amounts of uranium and plutonium present in solution. Isotope ratio mass spectrometry in conjunction with isotope dilution techniques allow the analyst to determine the isotopic composition of uranium and plutonium and their concentrations; knowledge of the total weight of solution then allows calculation of the amounts of these two elements.

In the course of the calculation of uranium and plutonium content, solution volume cancels out. This makes knowledge of solution density unnecessary, a measurement that is often relatively imprecise. Thus, by this technique, determination of total fissile content can be made in an entirely independent manner, requiring only accurate knowledge of the amount of initial spike added to the tank and its concentration after its addition in grams Lu per gram of solution. Algebraically, using uranium as an example:

$$c_{Lu} = g_{Lu}/V$$
$$c_U = g_U/V$$
$$V = g_{Lu}/c_{Lu}$$
$$g_U = c_U\ V = c_U\ g_{Lu}/c_{Lu}$$

where c represents concentrations, g represents weights, and V is the volume of the solution. Note that concentrations here are in units of grams of element per gram of solution, which makes it unnecessary to know the density.

The techniques presently used to determine volumes of solution in holding tanks are the precision-limiting steps in the process of determining fissile content. Several other techniques based on double-spiking and mass spectrometry have been proposed and evaluated. Among these are systems based on lithium[1] and magnesium[2]. Both of these systems suffer from difficulties encountered in mass spectrometric analysis. Because of the relatively light masses of the isotopes involved, both elements suffer from a high degree of fractionation during the evaporation-ionization process. It is desirable to use an element more readily amenable to thermal ionization mass spectrometry. The criteria that any candidate for a double spike must meet are summarized in Table 1.

Table 1. Criteria for a Double Spike

1. Ideally, the element must not be present in the original solution. If it is, its concentration must be accurately measured.

2. It must have at least two naturally occurring isotopes.

3. An isotopically enriched spike must be available.

4. It must be amenable to mass spectrometric analysis, preferably via thermal ionization.

5. It must not interfere with subsequent chemical operations on the original solution.

6. Minimum chemical preparation for isotopic analysis is highly desirable because of the radioactivity of the solution.

The double spiking technique requires introduction to the solution in the tank a known amount of some element; this is the first spiking, and the element must meet the criteria outlined in Table 1. The contents of the tank are thoroughly mixed to ensure uniform distribution of the spike throughout the solution. Aliquots are withdrawn, and a spike (the second spike) added to each. This spike is enriched in one isotope with respect to the first; mass spectrometric measurement of the ratio of isotopes in the aliquot, when compared to the same ratio in the first spike, allows calculation of the concentration of the first spike in the tank in units of grams of lutetium per gram of solution. To convert this to a volume, it is necessary to know the density of the aliquot in addition to the weights of the two spikes. This calculation is not necessary to calculate the amount of fissile isotopes in the solution; these crucial results can be based on the accurately known amount of the initial lutetium spike.

In the system we have developed,[3] we use natural lutetium as the initial spike and lutetium enriched in the 176 isotope as the second. Lutetium meets all the criteria listed in Table 1. Like all the rare earth elements, it ionizes readily under thermal conditions and has fractionation characteristics that are well within acceptable limits. It is not produced during reactor operation and does not interfere with fuel reprocessing. With mass spectrometers of high sensitivity, a nanogram is sufficient sample for a reliable isotopic analysis. It has the additional advantage of being relatively inexpensive in its natural form so that, even though rather large quantities of the initial spike are required, the total cost remains reasonable. Table 2 lists the isotopic compositions of natural lutetium and the two enriched spikes we have used.

Table 2. Isotopic Composition of Lutetium

	%175	%176
Natural	97.40	2.60
Spike 1	28.58	71.42
Spike 2	1.48	98.52

The second spike was made to increase the sensitivity when used in isotope dilution.

EVALUATION OF THE TECHNIQUE BY ORNL

Our early experiments were aimed at evaluating lutetium for this application in a rigorously controlled environment. A 200-liter (55-gallon) tank was obtained and a plastic liner inserted to protect the metal drum from attack by the acidic sample solutions. Approximately 40 liters of distilled water were acidified with 400 mL of concentrated nitric acid to simulate the solutions used to hold spent fuels. 58.542 g of natural lutetium were added as the initial spike. The solution was thoroughly mixed and then weighed. A 20-gram aliquot was withdrawn. Subsequent additions of 40-L increments were made until the drum was full. Aliquots were taken after each addition, but no more natural lutetium was added. Approximately 0.5 g of enriched spike (Spike 1 in Table 2) were added to enough sample (0.5-1.5 g) to produce a 175/176 ratio of about 1.0. This amount of sample reduced weighing errors to insignificance and provided the most favorable ratio for mass spectrometric analysis. Each aliquot was spiked independently four times to improve the statistical reliability of the study. Each such spiking from each aliquot was analyzed in duplicate, resulting in 40 analyses. The results of this experiment are summarized in Table 3.

Table 3. Results of Laboratory Study

Nominal Vol, L	Expected Conc, μg/g	Expected Weight, kg	Measured Conc, μg/g	Measured Weight, kg	Ratio Ex/Me, c	Ratio Ex/Me
40	1.4636	40.00	1.4641	39.985	1.00034	0.99963
80	0.73196	79.98	0.73191	79.985	0.99993	1.00006
120	0.48818	119.92	0.48838	119.870	1.00041	0.99958
160	0.36605	159.93	0.36631	159.816	1.00071	0.99929
200	0.29283	199.92	0.29277	199.963	0.99980	1.00022

Each experimental value reported in Table 3 represents the average of eight analyses: duplicate measurements were taken on each of four individual spikings. Each experimental value in Table 3 is within 0.1% of the expected value.

Encouraged by these results, arrangements were made with personnel of the ORNL Integrated Engineering Test Facility (IETF) to test the lutetium double spike on a 2500-liter feed adjustment tank. A drawing of this tank is given in Figure 1. The tank was filled with approximately 2400 L of 3.5 N nitric acid containing 160 g/L of depleted uranium; this is the approximate concentration of uranium expected in holding tanks at fuel reprocessing plants. The natural lutetium spikes were added via two routes: a flanged access port on the top of the tank and through an airlift sampling port normally used for access to the contents of the tank. This port is convenient to use and remote from the tank. The objective here was to determine if the mixing, which is driven by air, was satisfactory. Operation of this mixer is shown schematically in Figure 2. Samples were drawn from two ports at different levels on the side of the tank and from the airlift port to allow evaluation of the mixing process. These ports are shown in Figure 1.

The results we obtained in this experiment are summarized in Table 4. Standard deviations are quoted at the one sigma confidence level.

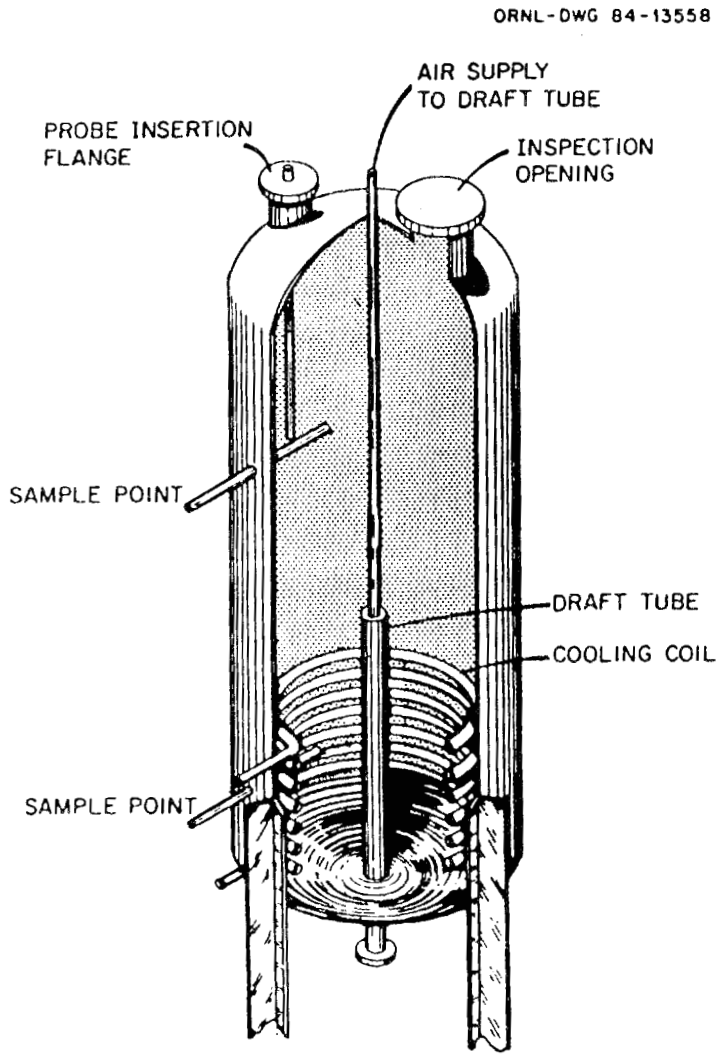

Figure 1. Feed Adjustment Tank

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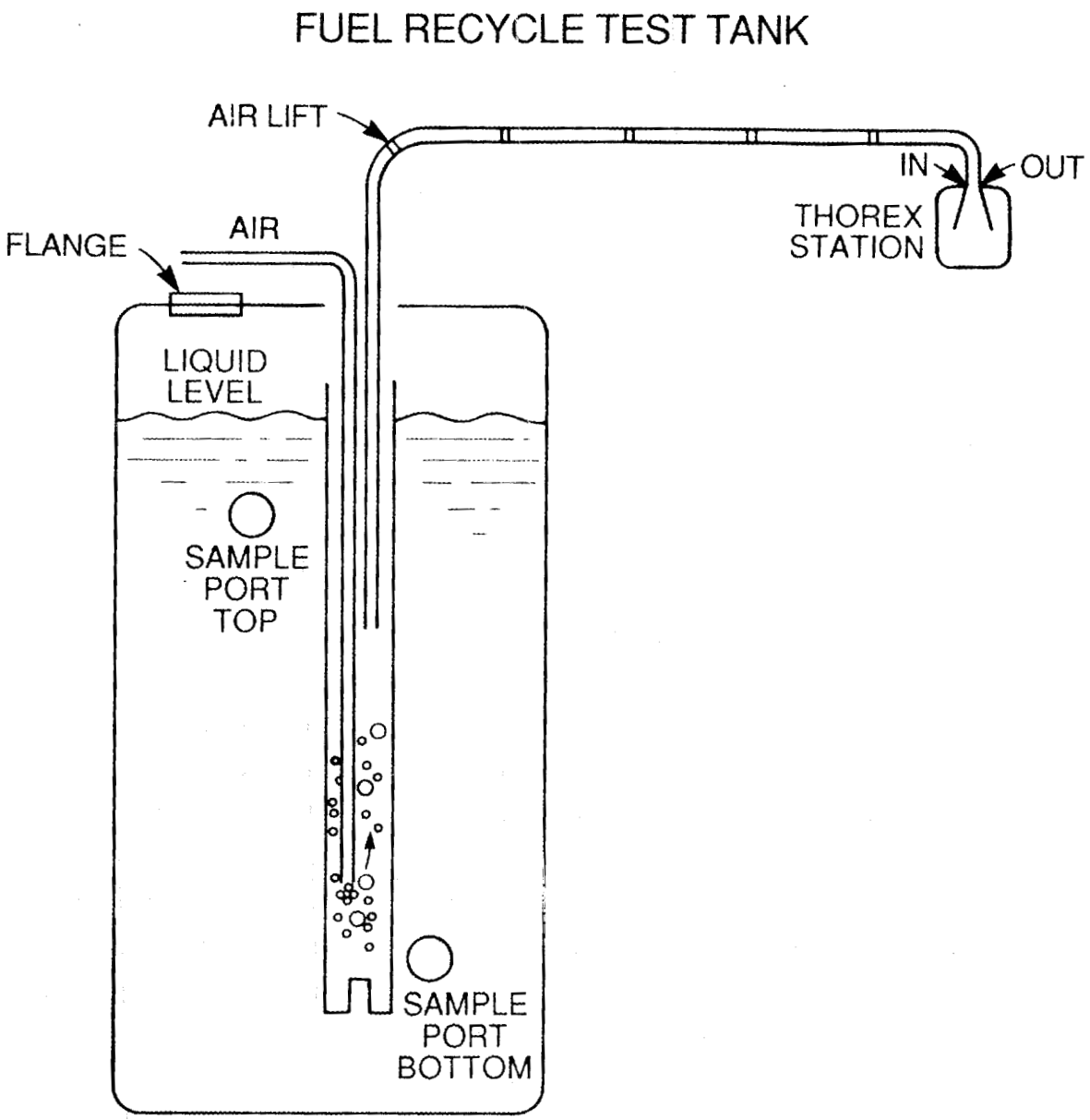

Figure 2. Operation of the Mixer

Table 4. Tank Volume Determination

Port	Lu, μg/g	Volume, L
A	16.48	2484.7
	16.46	2488.2
	16.53	2477.5
B	16.54	2476.0
	16.52	2478.7
	16.54	2476.5
Airlift	16.48	2484.2
	16.53	2478.0
	16.53	2477.5
Mean	16.51	2480.1
SD	0.03	4.4
RSD, %	0.18	0.18

Mixing times of about 30 minutes were used. The results of Table 4 showed that complete mixing had been attained and that no bias was introduced when samples were taken through the airlift port. This is an important finding: it seems probable that mixing apparatus already installed in holding tanks will provide good enough mixing for safeguards' purposes, obviating the need for procurement and installation of additional, costly hardware. Airlift sampling devices usually provide remote access to the tanks, minimizing exposure of staff members to hostile environments.

The volumes listed in Table 4 give a relative standard deviation of about 0.2% at the one sigma confidence level. This is better than demanded by safeguards, so that less-than-optimum analyses would yield satisfactory results.

Uranium concentrations were determined mass spectrometrically by using isotope dilution. The average concentration was found to be 154.5 ± 0.3 g/L. For comparison, independent measurement of the uranium concentration was made using a potentiometric technique that yielded an estimated precision of ± 1%.[4] It yielded 155.9 ± 1.6 g/L, in good agreement with mass spectrometric results. Using the volume determined by the lutetium double spike method, this uranium concentration was converted to the total amount of the element present. This gave a figure of 382.3 kg. Similar analyses and calculations can be performed for plutonium when it is present, thus providing safeguards with the quantity of each fissionable isotope in any given tank.

A diversion was simulated by having IETF personnel remove a quantity of solution from the tank that was unknown to our measurement team. We measured this to be 4.83 ± 0.08%; the actual amount removed was 4.77%. This is excellent agreement and indicates that much smaller diversions could be detected. The relatively high uncertainty emphasizes the need for measurements of the highest possible precision and accuracy.

INDEPENDENT EVALUATION

The lutetium double spike method has been evaluated by Reed, et al. at the Sellafield plant in the United Kingdom.[5] They used it both to determine tank volumes and the concentration of plutonium in the plant's product solution. Because the technique was being tested for possible use as an assay of product material, with no further purification steps anticipated, it was necessary to minimize the amount of lutetium added to the solution. They added 200 ng/g (200 ppb) to the plutonium nitrate product solution. The high level of plutonium necessitated separation of lutetium from the solution prior to mass spectrometric analysis. Their results confirmed ours with respect to precision and accuracy. They obtained better than ±0.1% (often as low as 0.04%) for their suite of results for three separate experiments. They concluded that the lutetium double spike method was a viable

candidate for determination of volumes of tank contents and warranted further evaluation under a variety of conditions.

CURRENT EXPERIMENT

A joint experiment is under way between ORNL and the personnel of the Savannah River Plant to assess the lutetium double spike technique at a tank with a capacity of approximately 20,000 L on the Savannah River reservation. The tank was spiked and a pneumatic port was used to sample its contents. Mixing was accomplished using a double paddle wheel arrangement. Samples were taken as the tank was filled incrementally; the samples are now in the process of being isotopically analyzed. Initial measurements are promising when compared to Savannah River Plant's pressure measurements.

CONCLUSIONS

The experiments described in this document demonstrate the potential of the lutetium double spiking technique to provide determination of tank volumes and their content to a high degree of precision and accuracy. Fissile content calculations can be made so that it is unnecessary to know the volume of solution in the tank. Demonstration of the technique at a large scale facility is in progress. This has been undertaken in collaboration with the Savannah River Plant; results are anticipated within the next few months. After these results are fully assessed, the next step is to evaluate the lutetium double spike technique in an international environment, where procedures unique to the test facility will have to be developed. This will allow comparison of the technique to other methods with regard to ease of use, precision, and timeliness.

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