Development of Total Uranium Analytical Method by L X-Ray Fluorescence

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DEVELOPMENT OF TOTAL URANIUM ANALYTICAL METHOD
BY L X-RAY FLUORESCENCE

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ABSTRACT

This paper describes development of an L x-ray fluorescence technique to perform total uranium analysis using an internal excitation source which is added directly to the sample. The method has been demonstrated with synthetic U samples in the limited concentration range of 1g/l to 15g/l, and provides the advantages of simplicity, involving no mechanical parts which would normally be found in an external excitation source. Total uranium is determined by counting L x-rays fluoresced by a microCurie level spike of Cd-109 added directly to the sample and without shielding the excitation source from the detector. A method for correction of sample self-absorption is included in the analysis.

INTRODUCTION

This paper describes the development and testing of an L x-ray fluorescence method of analysis to determine total uranium in samples with U content in the range of 1 g/l to 15 g/l and Pu content less than 10 mg/l. The technique described uses a spike of about 2 μ Ci of Cd-109 internal to the sample to fluoresce the U L x-rays and therefore does not require an external x-ray fluorescence device or external Cd-109 source. The technique of x-ray fluorescence is well known, and diverse analytical instruments exist which provide analysis of multiple elements at a time, including uranium¹. These instruments use external excitation devices and generally are designed to measure each element by fluorescence of the K x-ray doublet. At the Savannah River Site we have developed and demonstrated an on-line type instrument which uses a Co-57 source to excite the K x-rays to measure total uranium in the presence of Pu and several fission products². In each case for these instruments it has been necessary to expose the sample to the excitation source and then to remove the source behind a shield so that the instrument's detector is not exposed to it.

The use of Cd-109 as an excitation source for the U L x-rays is especially advantageous. Its decay produces the five x-ray and γ -ray transitions listed in Table 1. The Cd-109 transitions near 22 keV are just above the L electron absorption edge for uranium (21.8 keV), and so they are particularly suited to ionize the L electrons and to fluoresce the uranium L x-rays. Yet they are *not* energetic enough to fluoresce the L x-rays of *any* of the $Z > 92$ elements, and we can expect to obtain active L fluorescence spectra which are very clean of anything but the uranium transitions.

In the technique we describe here, the Cd-109 spiked activity is introduced directly into the liquid sample, and the sample and excitation source are counted simultaneously. The cross section for ionization of the U L x-rays is large enough that we are able to count the fluoresced L x-rays without shielding the detector from the Cd-109 spiked activity. The advantages of this technique over others sensitive in this range are simplicity, speed, and that this technique empirically subtracts interferences. If the Pu content is low, no chemical preparation of the sample is necessary. No interaction with the counting instrument is necessary after the analysis is initiated.

Note we require that the Pu content of the sample is very low. Pu α -decays to U and produces large quantities of the U L x-rays, which are the same photons we wish to count in this fluorescence analysis. Since all Pu isotopes decay with half-lives much shorter than either of U-235 or U-238, atom contents of Pu up to $1/100^{\text{th}}$ of the U atom content would result in significant interference in this analysis. One mitigating factor in this interference is that the L x-rays from Pu decay are passive transitions and do not contribute to the active fluorescence spectrum. Thus the passive U L x-rays are part of the blank sample spectrum and can be easily background subtracted from the active spectrum.

In the event that the Pu content of the sample is too large, no bias is introduced in the analysis. Rather the imprecision in the measurement begins to dominate the results. That is the subtraction of the passive background spectrum from the active spectrum represents the difference of two large numbers to yield a net small number. Thus a large uncertainty in the data obtained signals that the sample must be further treated to remove Pu.

PRINCIPAL OF MEASUREMENT

The mode of fluorescence used in this technique of analysis is depicted in Figure 1. Cd-109 decays with a 463-day half-life to excited states of Ag-109, emitting K x-rays with energies of 21.990-, 22.163-, and 25.603-keV and a γ -ray of energy 88.034-keV. The two lowest energy K x-rays are particularly suited in energy to fluoresce U L x-rays. The x-ray absorption cross section for this fluorescence can be estimated from available data³ to be $43 \text{ cm}^2/\text{g}$. Thus a 1 g/l U solution with a 1 cm absorption path length will absorb these K x-rays at the rate

$$I = I_0 \exp [(-1)(43)(0.001)] = 0.958I_0, \quad (1)$$

where I_0 is the initial intensity of Cd-109 K x-rays. The fluorescent yield for these L x-ray holes is approximately $0.51^{(4)}$, so the rate of production of L x-rays from a $1\mu\text{Ci}$ spike of Cd-109 is

$$0.51(1 - 0.958)(3.7 \times 10^4) = 790 \text{ (U L x-rays)/sec.} \quad (2)$$

Thus the ratio of U x-rays to transmitted Ag x-rays is in the range of 0.02, and we can count the fluoresced L x-rays in the presence of the excitation source without shielding the detector from the source. The energies and relative intensities of the U L x-rays obtained are shown in Table 2.

Since the technique is based on the sample absorption of 22 keV x-rays, it is obvious that the fluoresced L x-rays of approximately 17 keV x-rays will themselves be strongly self-absorbed by the sample. We require a method to measure the sample self-absorption and to correct for it. We describe our sample self-absorption correction below based on the approach used in reference 5.

EXPERIMENT AND RESULTS

To demonstrate the fluorescence technique we made five U solutions in 2M HNO₃ with U contents of 1-, 4-, 6-, 8-, and 15-g/l. Then 5ml aliquots of each were pipetted into plastic vials of 25 ml capacity. The vials are screw cap items with a 4-cm circular base and a wall thickness of 2 mm. They are designed to sit on an up-looking photon detector to provide maximum surface exposure of the liquid sample to the detector active area and to minimize absorption of photons by the vial.

Each of the samples was placed on the up-looking surface of a Si(Li) low energy photon detector with an active surface area of 80 mm² and an operating voltage of -1000 V. The detector had a 2 μ Ci Fe-55 source implanted in it to produce a doublet of K x-rays at 5.9 keV and 6.5 keV to assist in energy calibration. A 300 sec passive x-ray spectrum of the energy range 5 keV to 30 keV was taken for each sample and stored in the 2048 channel memory of a Canberra Series 90 Multichannel Analyzer (MCA).

Each sample was then spiked with 50 λ from a 40 μ Ci/ml Cd-109 source and counted in the same configuration [shown in Figure 2(a)] for 1000 sec. A blank sample was also spiked and counted. The spectrum obtained for the 8 g/l sample is shown in Figure 3. Note in the figure that an MCA deadtime of only 3.4% was obtained. The previously stored background spectrum was then normalized to 1000 seconds and subtracted channel by channel from the active spectrum. For each of the resulting spectra, the area under the 13.6-, 16.6-, and 17.2-keV L x-ray peaks was summed. Also the area under the Cd-109 22.2-keV K x-ray peak was obtained. The ratio between these two quantities is tabulated as x_s in Table 3.

The data of x_s are shown plotted in Figure 4 in the lower curve. As expected, the curve is significantly concave downward due to the sample self-absorption of the uranium L x-rays. It is clear that sample absorption of L x-rays causes a negative bias in the detected fluorescence rate as the U content increases.

To correct for the sample self-absorption effect, we constructed a vial as shown in Figure 2(b). This vial has a 2 gram sample of natural uranium glued by epoxy to the under surface of the screw cap. The uranium foil was suspended 1 cm above the surface of the sample, and the active L x-ray spectrum was again collected for 1000 sec for each sample and for the blank with the foil in place. This U L x-ray to Ag K x-ray ratio is tabulated in Table 3 as x_t .

In the configuration of Figure 2(b), Ag K x-rays escape the sample and fluoresce the U L x-rays in the U foil in the same mechanism that occurs in the sample. These foil-fluoresced L x-rays must then traverse the sample to reach the detector, and in this way the active spectrum is a sum of sample fluorescence and foil fluorescence. Since sample x-rays and foil L x-rays both suffer from sample absorption, this technique of analysis provides a very good method of empirically subtracting the effect of sample self-absorption.

Using the method of reference 5 for photon transmission, we calculate transmission correction factors and corrected detection rates for each sample as shown in the following. We determine the sample self-absorption factor $\alpha(i)$ for each sample from

$$\alpha(i) = \frac{x_t(i) - x_s(i)}{x_o}, \quad (3)$$

where x_o is the x_t value obtained for the blank.

For example, since x_t for sample 1 is 0.02360, and x_s is 0.01246, and x_o is 0.01397, then

$$\alpha(i) = \frac{0.02360 - 0.01246}{0.01397} = 0.7974.$$

We then determine a correction factor $CF(i)$ for each sample by

$$CF(i) = \frac{-\ln \alpha(i)}{1 - \alpha(i)}. \quad (4)$$

So the correction factor for sample 1 is 1.117. The corrected fluorescent yield for each sample is

$$CC(i) = CF(i) \times x_s(i), \quad (5)$$

where $CC(i)$ is the corrected count (L to K ratio) of sample i , and $CF(i)$ is the calculated correction factor. Equations (3) through (5) are derived in reference 5 pages I-1 through I-12.

The resulting corrected count data are plotted in Figure 4 in the upper curve. These data show that the correction has straightened the fluorescence curve. The difference between the two curves demonstrates the magnitude of the self-absorption effect, which in the case of the 15 g/l sample is greater than a factor of two correction.

CONCLUSION

This experiment has demonstrated the utility of the L x-ray fluorescence analysis of uranium using an internal excitation source spike in the sample. The samples in the range of 1 g/l to 15 g/l can be determined with an overall counting time of less than one hour. The fluorescence absorption cross section for uranium using 22.1-keV x-rays as the excitation source is so large ($43 \text{ cm}^2/\text{g}$) that the detector can be exposed to the excitation source without causing an unacceptable dead time.

This technique requires no chemical treatment of the sample when it contains less than $\sim 0.1 \text{ g Pu/l}$. The only operator interaction with the analysis instrument is initiation of each count. With preparation the multichannel analyzer of the instrument can be set up to automatically store the data in the appropriate memory segment, acquire the active spectra, perform background subtraction, and provide the required ratios x_s , x_t , and x_0 for each sample run, with one task command. It can also be set up to calculate and display the precision obtained for each measurement.

The advantages that this technique of U determination provide over matrix dependent techniques and over external excitation source fluorescence techniques are elaborated below.

The system is simple to operate, as no excitation source instrument exists to complicate operation. Initiation of each spectrum collection with a single task command can be the only operator interaction required. The system automatically collects the spectrum, subtracts background, and displays the peak ratio data and errors needed for subsequent calculations using equations (3) through (5) above.

The technique empirically subtracts interferences from U self-absorption and any other matrix absorption effect. Large interferences from too much Pu in the sample are signalled by large imprecisions in the values x_s and x_t . For samples with large U L x-ray contributions from Pu decay, the values x_s and x_t will be large and very near each other in value. Then the uncertainty in these values will become larger than the difference between them, and the self-absorption factor $\alpha(i)$ calculated in (3) can go negative from random variation.

Using the ratio of U fluorescent yield to transmitted Ag x-rays automatically normalizes the data to remove deadtime corrections and decay of excitation source strength. Thus exact knowledge of the spiked activity is not required. The Cd-109 source has a long (463 day) half-life, thus assuring several years of free excitation.

The data from this experiment have demonstrated the utility of this technique over the limited range of 1 g/l to 15 g/l.

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Table 1

Energies and relative intensities of photons emitted by Ag-109 following decay of Cd-109. Energies are in units of keV.

<u>Photon Energy</u>	<u>Relative Intensity</u>
21.990	28.9
22.163	54.5
24.934	13.7
25.603	2.72
88.034	3.6

Table 2

Energies and relative intensities of Uranium L x-rays observed by L-shell vacancies produced by fluorescence from Cd-109 decay. Energies are in units of keV.

<u>Photon Energy</u>	<u>Relative Intensity</u>
13.619	3.4700
15.400	0.0268
15.727	0.0154
16.410	0.1805
16.577	0.0276
17.069	0.0046
17.222	1.0000
17.454	0.0105
20.169	0.2429

Table 3

Fluorescent yield data and corrected yield results for liquid U samples in the range 1 g/l to 15 g/l. The uncorrected data are tabulated as x_s , and the corrected data are tabulated as CC. The sample plus U foil data are tabulated as x_t . The correction factors are listed in the fourth column as CF. Corrected and uncorrected yields are explained in the text.

<u>U</u> <u>(g/l)</u>	<u>x_s</u> <u>(no units)</u>	<u>x_t</u> <u>(no units)</u>	<u>CF</u> <u>(no units)</u>	<u>CC</u> <u>(no units)</u>
0	-----	0.01397	1.000	0.01397
0.992	0.01246	0.02360	1.117	0.01392
3.970	0.03976	0.04730	1.340	0.05327
6.000	0.05600	0.06319	1.369	0.07664
7.937	0.07300	0.07627	1.896	0.1384
15.00	0.11187	0.11400	2.219	0.24826

Total Uranium Determination

FIGURE 1. Schematic Representation of U L X-Ray Fluorescence
by ^{109}Cd Decay

FIGURE 2. Counting Configurations for Obtaining Uncorrected Data (a) and Self-Absorption Corrected Data (b)

FIGURE 3. U L X-Ray Spectrum Obtained using the Counting Configuration of Figure 2(a) with an 8 g/l U Solution and a $2\mu\text{Ci } ^{109}\text{Cd}$ Spike in the Sample as Described in the Text

FIGURE 4. Linear Plots of the Corrected and Uncorrected U L X-ray Fluorescence Yield