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Wayne D. Ruhter
David C. Camp

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TRANSMISSION-CORRECTED X-RAY FLUORESCENCE ANALYSIS OF URANIUM AND PLUTONIUM SOLUTIONS USING A DUAL TRANSMISSION SOURCE

Wayne D. Ruhter and David C. Camp
Lawrence Livermore National Laboratory
P. O. Box 808
Livermore, CA 94550
(415) 422-5762/422-6680

ABSTRACT

The energy-dispersive x-ray fluorescence analysis (XRFA) technique has been implemented at several spent nuclear fuel reprocessing facilities for nondestructive measurements of uranium and/or plutonium concentrations in process streams and product storage tanks. An important factor in these quantitative measurements is the absorption of the fluoresced x-rays by the solution matrix, which must be taken into account to accurately quantify the U or Pu concentrations. We describe a new, accurate method using a dual transmission source of Gd-153 and Co-57 to correct for matrix effects. Results of measurements on uranium and plutonium solution standards show the methodology to be better than 0.5%, which includes statistical precision, over the concentration range from 1 to 250 g/l.

INTRODUCTION

Some of the many requirements in nuclear fuel reprocessing facilities are process control and nuclear materials accountancy information. Process streams must be monitored to regulate stream concentrations and to satisfy criticality safety conditions. These requirements involve the determination of uranium (U) or plutonium (Pu) elemental concentrations throughout the facility. Precise and accurate accountability measurements of the U or Pu concentrations in product storage tank solutions are also needed. These measurements can be done practically and economically using nondestructive analysis (NDA) techniques. Energy dispersive x-ray fluorescence analysis (XRFA) is one NDA technique that can fulfill concentration measurement requirements for criticality monitoring, inventory control and accountability purposes.[1,2]

In this application of XRFA, the atoms of U and Pu within a solution sample are fluoresced, and their concentrations are determined from the measured intensities of the characteristic x rays. We use radioactive Co-57 (halflife = 270d) which emits a 122.05-keV gamma ray to optimally fluoresce U (Kab = 115.59 keV) and Pu (Kab = 121.72 keV) K x rays. The stimulated uranium or plutonium K x rays are detected by a collimated high-purity germanium (HPGe) detector. From the measured x-ray intensities we can determine the concentrations of U or Pu in the solution sample.

The observed x-ray intensities are not only dependent on the abundance of the U or Pu in the sample, but also depend on the strength of the exciting radiation, the attenuation of the exciting and fluoresced radiations by the sample itself (sample self-attenuation), and the x-ray detection efficiency. The strength of the exciting radiation and the detection efficiency are factors that can be determined by calibration of the instrument.

Attenuations of the exciting and fluoresced radiations are dependent on the concentration of the U or Pu in the solution and the solution matrix, thus the fluoresced x-ray intensities are not directly proportional to the concentration of the U or Pu atoms, especially at higher actinide concentrations. A calibration procedure to determine this nonlinear relationship requires at least six solution standards with uranium or plutonium concentrations that span the concentration range of interest, and that are chemically similar (acid molarity, etc.) to the solutions to be measured. The resulting calibration curve would most correctly determine uranium or plutonium concentrations for solution matrices similar to the standards, but may not necessarily determine accurately the U or Pu concentrations in other solution matrices.

The presence of any elements in the solutions to be measured that are different from those in the calibration solutions may compromise the validity of the calibration curve. Because the reprocessing chemistry cannot be controlled exactly, the unknown effects of attenuation by the solution matrix must be evaluated for each individual measurement. To determine the attenuation of the solution matrix we have developed a method to measure transmissions

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through the solution at two different energies, which allows us to accurately correct the x-ray intensities for sample self-attenuation. This new method offers two dramatic improvements. First, it eliminates the need to prepare calibration standards that are chemically similar to the process stream and product storage tank samples. Second, it reduces the number of standards required to fully calibrate an XRFA system over the entire range of concentrations to be measured.

In the following we describe the formulation and methodology of this new method, and report and discuss results obtained on uranium and plutonium solution standards with concentrations ranging from 1 to 250 g/l.

TRANSMISSION-CORRECTION FORMULATIONS

To understand the effects of sample self-attenuation in XRFA, consider the following for a planar sample of thickness x and a far-field geometry (i.e., the dimensions of the detector and sample thickness are small compared to the distance between them, so $1/Y^2$ effects may be ignored) as shown in Fig. 1. As the exciting gamma rays penetrate the solution their strength is attenuated by the solution due to scattering of the gamma rays and the photoelectric effect which generally produces the x rays of interest. Consequently, the flux of exciting gamma rays is not as great at the rear of the sample cell as it is at the front. In fact, for very concentrated solutions, atoms of uranium or plutonium at the rear of the cell "see" very little of the exciting gamma rays. The x rays produced by the exciting gamma rays are also attenuated by the solution, i.e. the x rays produced at the rear of the cell do not escape as easily towards the detector as those produced at the front of the cell. The result is that the observed uranium or plutonium x-ray intensity is not linearly related to the uranium or plutonium concentration; and furthermore will depend on the solution matrix constituents.

The intensity of the detected U or Pu x rays, I, is related to the U or Pu concentration, C, by[3]

$$I = A \cdot CF(T) \cdot C \qquad (1)$$

where A is dependent on the strength of the exciting radiation, the sample volume fluoresced, the detection efficiency of the U or Pu x rays; and A is determined by calibration. The correction factor, CF(T), for sample self-attenuation is given by

$$CF(T) = -(1-T)/\ln T. \qquad (2)$$

T is dependent on the absorptions of the exciting and fluoresced radiations and may be expressed as

$$T = \exp -(\mu_e + \mu_d)x, \qquad (3)$$

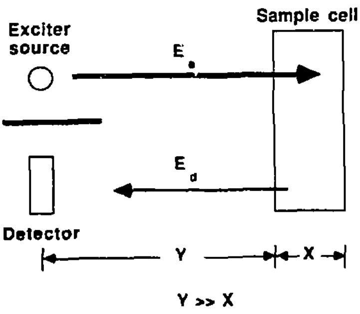

Fig. 1 Schematic view of an XRFA measurement with a far-field, planar geometry in which $1/Y^2$ effects may be ignored.

where μ_e and μ_d are the linear attenuation coefficients of the sample at the exciting (122.05-keV) and detected (98.4- or 103.7-keV) photon energies, E_e and E_d, respectively. Because $T_e = \exp -\mu_e x$ and $T_d = \exp -\mu_d x$ are the transmissions through the solution at these energies, $T = T_e T_d$ may be determined by measuring the transmissions T_e and T_d. Consequently, CF(T) can be determined for each solution by measuring T_e and T_d for that solution. If the x-ray intensity I, CF(T), and A are known, we can determine the uranium or plutonium concentration from Eq. 1. The parameter A is determined by calibration of the instrument with a solution of <u>known</u> concentration. In principle, the calibration could be done with a single standard solution (more are preferable for verification), and it is <u>independent</u> of changes in the solution matrix.

The transmission T_e is determined by using a Co-57 transmission source. Our answer to measuring the value of T_d at the energy of either the uranium or plutonium $K\alpha 1$ x rays is to use Gd-153 as an additional transmission source. It has gamma rays at 97.4- and 103.2-keV that are nearly ideally suited for determining the transmission T_d through the solution near the $K\alpha 1$ energies of uranium and plutonium (see Fig. 2). It is also nearly ideal because the half life of Gd-153 (240 days) is sufficiently close to that of Co-57 (270 days) so that the two isotopes may be placed on the same source mounting and replenished at the same time.

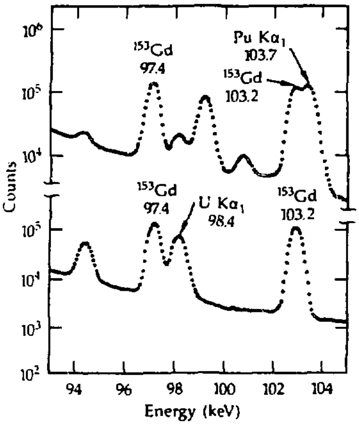

Fig. 2 Partial uranium and plutonium x-ray fluorescence spectra showing the positions of the Gd-153 gamma rays relative to the U and Pu Kα1 x rays.

Thus, the absorption effects on the exciting and fluoresced radiations may be determined by measuring the transmissions T_c and T_d. To determine transmissions T_c and T_d through the solution being assayed, it is necessary to measure the intensities of the 122.0-, 97.4- and 103.2-keV gamma rays through the cell when it is empty; and then, measure their transmitted intensities through the solution being fluoresced. The empty cell transmission measurement does not have to be performed for each individual assay, but can be done periodically; and then decay correct the measured empty-cell intensities to the time of the current assay for determination of the transmissions T_c and T_d

EXPERIMENTAL EQUIPMENT AND PROCEDURES

We tested this formulation by making measurements on both uranium and plutonium solutions using the hardware diagrammed in Fig. 3. Two 15-mCi (when new) Co-57 sources are collimated to irradiate the solution in a 2.5-cm-diameter by 3.0-cm-high stainless steel cell. Because Co-57 emits 570- and 692-keV gamma rays with branching intensities of about 0.16%, as well as others, their intensities are shielded from the detector by 37 mm of heavimet (tungsten alloy). Cadmium or rhodium and copper liners on the surfaces of the heavimet shielding attenuate lead or tungsten x rays excited by the source gamma rays.

The HPGe detector (200 mm^2) had a 13 mm active depth to maximize the 100 keV efficiency. The detector resolution was 500 eV at 122 keV. The diameter of the collimator used to reduce gamma-ray interactions at the edges of the detector (16mm diameter) is 10 mm. The length of the collimator is 4.5 cm and the center of the sample cell is 9.1 cm from the front of the detector.

Two shutters are controlled by computer using pressurized-air actuators. A 2.5-mm-thick tungsten shutter nearest the sample cell is used to eclipse the exciter sources so that the transmission intensities and the natural radioactivity gamma emissions from plutonium solutions can be measured. The shutter nearest the detector is 1.0-mm-thick rhodium and is inserted into the collimator to attenuate the intense 59.53-keV radiation from Am-241, if it is present in an excessive amount.

A third source consisting of two millicuries (when new) each of Co-57 and Gd-153 is housed in a hollow tantalum collimator. A 0.8-mm exit hole in a lead-rhodium-stainless steel face plate located 12.5 mm from the source activities allows the 97.4-, 103.2- and 122.05-keV gamma rays of interest to pass through the solution into the detector. It is important that the transmission gamma rays are well collimated and that they pass through the center of the sample cell. This is necessary to give a well-defined path length for the gamma rays through the solution in order to accurately determine the linear attenuation coefficients for the solution at the appropriate energies.

To calculate CF(T) from the measured values of T_c and T_d for the system diagrammed in Fig. 3, the inverse square dependence must be included in the integral expressions that physically describe the situation. The resulting expressions cannot be integrated in terms of elementary functions as they were for the physical geometry that led to Eq. 2; and instead, numerical integration methods must be used. A 3-dimensional numerical integration code was obtained from the author of reference 4 and modified for our particular situation. The original code was developed to calculate self-attenuation effects on gamma- or x-rays emitted from a sample. We modified it to also include the attenuation of the exciting gamma rays as they penetrate the solution.

The calculations are basically a problem in geometry that requires determination of distances and path lengths for the exciting gamma rays and the fluoresced x rays. These must be calculated for many

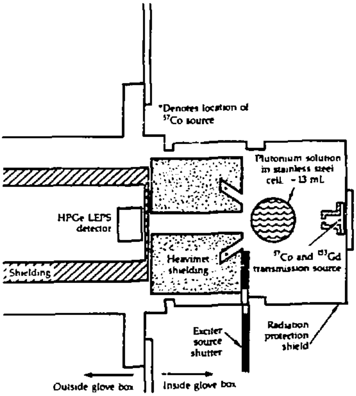

Fig. 3 Schematic top view of the XRFA cell used to evaluate transmission-corrected x-ray fluorescence measurements on uranium and plutonium solutions.

different points in the solution volume. In our calculations, we divided the sample cell into 10^5 volume elements. For each volume element the code calculates the probability of an exciting gamma ray reaching the element from the exciter source and the probability of an x-ray reaching the detector from that particular element. The sum of the product of these probabilities determines CF(T) or the correction to the observed x-ray intensity. The probabilities are calculated using the linear attenuation coefficients determined from the measured values for T_e and T_d and the calculated path lengths in the solution for the corresponding gamma or x rays. The linear attenuation coefficients are determined by using the expressions $\mu_e = \ln(T_e)/x$ and $\mu_d = \ln(T_d)/x$ where x is the path length through the sample cell for the transmission gamma rays.

The detector is modeled as an infinitely thin, disc detector centered 6mm behind the rear of the collimator. This permits the calculations to take into account the fact that some x rays are fluoresced in places within the sample cell where only a portion of the detector is seen through the collimator. The efficiency of the "detector" is assumed to be independent of where or at what angle the x rays strike it. These calculations must be done for each analysis and take approximately 1 minute on a DEC MicroVAX II for 10^5 volume elements.

EXPERIMENTAL RESULTS

Measurements were made on both pure uranium and plutonium nitrate (6M) solutions ranging in concentration from 1 g/l to 250 g/l. At 10 and 50 gU/l, solutions of 1,3,7 and 9 acid molarity were also made. Solutions with concentrations of 20 g/l of plutonium were made at several molarities as well as two solutions that included trace amounts (<1M) of Al and KF ions.

For all solutions both an active fluorescence spectrum and a passive (exciter-source shutter closed) spectrum were taken. The gamma-ray transmission intensities were determined from the passive measurements. For the plutonium measurements the passive spectra were also subtracted from the active spectra to remove the interferences that occur from the natural plutonium gamma radiations. The transmission intensities were decay corrected to the time of the last empty cell measurement for determination of T_e and T_d. All x- and gamma-ray peaks of interest in the spectra were fit using a peak-fitting code that includes a Gaussian function, a Lorentzian profile for x rays, short-term tailing, and a background algorithm.[5] Peak-shape parameters are determined for the detector from strong singlet gamma-ray peaks. Once defined, they remain constant and only the Gaussian FWHM, peak positions and heights are variables in the fitting process.

Results from these measurements are summarized in Tables 1 and 2. Listed are the concentrations of the uranium or plutonium solutions (col. 1), the values of A determined at each concentration (col. 2), and the percent relative standard deviation (one sigma) on each value of A (col. 3). From Eq. 1 we would expect A to have the same value at each concentration, if the correction factor, CF(T), is determined properly at each concentration. The results in Tables 1 and 2 show A to be constant to better than 0.5% for each element. The value of A differs between the two sets of data, because different sets of exciter sources were used for the two separate experiments.

The errors on the calibration constant, A, given in col. 3 of Tables 1 and 2 represent the statistical uncertainties in the Kα_1 intensities and the errors in CF(T) which are due to the statistical uncertainties in the transmission intensities. An error of 0.2% on T_e=0.1824 and an error of 0.3% on T_d=0.3948 result in an error of 0.14% on CF(T)=2.345. These values are representative of a 120 g Pu/l solution. The measurement precisions on the Kα_1 and transmission intensities have a reciprocal relationship as a function of concentration for a fixed counting time. We see that as the concentration increases the Kα_1 statistical uncertainty will improve, but the transmission intensity statistical precisions will get worse. Consequently, total counting times (active + passive) will need to be nearly the same for all solution concentrations for a desired precision.

Table 1. Measured calibration constant, A, at various uranium concentrations determined from the uranium Kα1 intensity and transmission values at 122-kev and 97.4-keV.

Conc. of U g/l (error)	Calibration constant, A	Error A % (1)
240.95(23)	10.662	0.17
178.78(16)	10.659	0.18
104.96(16)	10.613	0.16
52.67(1)	10.584	0.16
21.230(4)	10.549	0.18
10.560(4)	10.650	0.20
5.333(2)	10.645	0.25
2.143(1)	10.699	0.30
1.099(3)	10.619	0.50
Weighted mean=	10.623 ± 0.42%	

Table 2. Measured calibration constant, A, at various plutonium concentrations determined from the plutonium Kα1 intensity and transmission values at 122-kev and 103.7-keV.

Conc. of Pu g/l (error)	Calibration constant, A	Error A % (1)
238.952(356)	14.008	0.21
178.295(196)	14.074	0.23
119.540(121)	14.032	0.21
41.947(87)	13.950	0.25
19.804(41)	13.988	0.31
10.947(38)	14.023	0.35
5.158(11)	13.964	0.42
1.774(4)	14.089	0.51
0.995(2)	13.922	1.00
Weighted mean=	14.015 ± 0.40%	

The corrections to the Kα1 x-ray intensities for sample self-attenuation as given by CF(T) ranged from 40% at 1 g/l to 246% at 240 g/l. On the left ordinate axis of Fig. 4 are plotted the values of the calibration constant, A, determined from the plutonium solution standards. Figure 4 shows how 1/CF(T) plotted on the right ordinate axis varies as a function of plutonium concentration.

In Table 3 we show the concentration results obtained on uranium and plutonium solutions with varying acid concentrations. The uranium solutions had concentrations of 10 and 50 g/l and nitric acid molarities of 1, 3, 7 and 9 M. While the Kα1 x-ray intensity varied by almost 5% for the 10 g/l solutions, the measured uranium concentration varied by only 0.4%. Plutonium solutions with concentrations of 20 g/l and varying acid molarities and trace impurities behaved similarly.

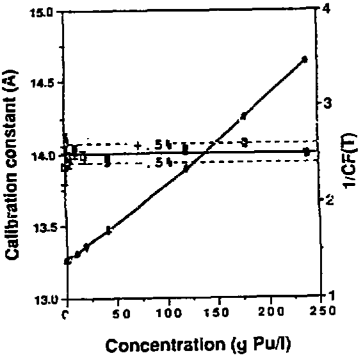

Fig. 4 A plot of the calibration constant, A, (left axis) and values for 1/CF(T) (right axis) versus plutonium solution concentrations.

Table 3. Measured concentrations for uranium and plutonium solutions of with varying acid concentrations and trace impurities.

Uranium conc. g/l	Acid/Trace Molarity	Measured conc. ± (1)
10.04(03)	1 M	10.02 ± 0.05
10.04(03)	3 M	10.03 ± 0.05
10.04(03)	7 M	10.05 ± 0.05
10.04(03)	9 M	10.06 ± 0.05
50.18(15)	1 M	50.00 ± 0.23
50.18(15)	3 M	50.19 ± 0.22
50.18(15)	7 M	50.28 ± 0.22
50.18(15)	9 M	50.25 ± 0.24
Plutonium conc. g/l		
19.993(26)	1 M	20.036 ±0.101
20.040(25)	3 M	20.027 ±0.095
20.001(25)	9 M	19.995 ±0.089
20.011(25)	.04M KF	19.978 ±0.097
20.009(25)	.33M $Al(NO_3)_3$	19.944 ±0.094

SUMMARY

We have demonstrated a method to correct the observed fluoresced x-ray intensities from uranium and plutonium solutions for sample self-attenuation by measuring transmissions through the solution at the exciting energy and at energies near those of the fluoresced radiations. In a reprocessing facility, where the processing chemistry cannot be controlled exactly, this method offers assurance that the concentration results from nondestructive x-ray fluorescence analyses will be independent of changes in the solution matrix. The method is nondestructive and requires no modification to previously developed x-ray fluorescence analysis measurement hardware, but requires an additional transmission source and some modifications to the analysis software. The combination of Co-57 and Gd-153 for transmission measurements is nearly ideal for several reasons. The 97.4- and 103.2-keV gamma rays from Gd-153 are sufficiently close in energy to the Kα1 x rays of uranium and plutonium so that there is very little error in determining the attenuation affects on these x rays with the transmission measurements of the Gd-153 gamma rays. In addition, the 240-day halflife of Gd-153 is sufficiently close to the 270-day halflife of Co-57, so that both isotopes may be placed on the same source mounting and replenished at the same time.

Finally, because the transmission-correction method requires, in principle, only one solution standard for calibrating an x-ray fluorescence analysis system, considerable savings in time and money are realized by reducing the number of standards that need to be prepared and measured. This modification to the x-ray fluorescence analysis technique should prove to be very cost effective and useful in nuclear fuel cycle facilities that utilize XRFA for process control and accountability requirements.

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