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Uranium and Plutonium Solution Assays by Transmission-Corrected X-Ray Fluorescence

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URANIUM AND PLUTONIUM SOLUTION ASSAYS
by
TRANSMISSION-CORRECTED X-RAY FLUORESCENCE

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Abstract:

We have refined and tested a previously developed x-ray fluorescence analysis technique for uranium and plutonium solutions that compensates for variations in the absorption of the exciting gamma rays and fluorescent x-rays. We use ^{57}Co to efficiently excite the K lines of the elements, and a mixed ^{57}Co plus ^{153}Gd transmission source to correct for variations in absorption. The absorption correction is a unique feature of our technique. It is possible to accurately calibrate the system with a single solution standard. There does not need to be a close match in composition (i.e., absorption) between the standard(s) and solutions to be analyzed.

Specially designed equipment incorporates a planar intrinsic germanium detector, excitation and transmission radioisotopes, and specimen holder. The apparatus can be inserted into a rubber glove of a glovebox, keeping the apparatus outside and the solutions inside the glovebox, thereby protecting the user and the equipment from possible contamination. An alternate design may be used in chemical reprocessing plants, providing continuous monitoring, by measuring the trans-actinides through stainless steel piping.

This technique has been tested at the Bochvar Research Institute of Inorganic Materials in Moscow for possible use in the Russian complex of nuclear facilities. This is part of a cooperative program between laboratories in the United States and Russia to strengthen systems of nuclear materials protection, control, and accountability (MPC&A). A part of this program is to accurately measure and track inventories of materials, thus the need for good non-destructive analytical techniques such as the one described here.

Background:

A cornerstone in the prevention of nuclear weapons proliferation is the control of the materials that make these weapons possible[1]. In order to protect these materials from diversion, the United States Department of Energy and its national laboratories are engaged in a cooperative program with the Russian Federation's nuclear laboratories to strengthen systems of nuclear materials protection, control, and accountability. As part of this multi-laboratory program, the Lawrence Livermore National Laboratory (LLNL) and the A.A. Bochvar Research Institute of Inorganic Materials (VNIINM) are collaborating in testing an improved version of an x-ray fluorescence assay technique for uranium and plutonium in solutions and laying the foundation for its implementation at chemical reprocessing plants in Russia.

This work was performed under the auspices of the United States Department of Energy under contract number W-7405-Eng-48.

X-Ray analysis of uranium and plutonium solutions was investigated and developed at LLNL for a number of years[2, 3,4] in conjunction with the reprocessing of spent nuclear fuel. Since the United States no longer has any active plans to reprocess nuclear fuel, the technique has not been implemented and has been held in a standby state for several years. Recently, we have examined the application of this technique at Russian reprocessing facilities. Through the joint U.S. - Russia MPC&A Program, we have satisfactorily reconfirmed the technique with uranium and done limited testing with plutonium at LLNL[5], improved the software, and done further testing on uranium at VNIINM.

Equipment and Experimental Considerations:

A schematic diagram of the equipment is shown in Figure 1. Two ^{57}Co sources (10 mCi each) are used to excite fluorescence. A mixed ^{57}Co and ^{153}Gd transmission source (2 mCi each isotope) is finely collimated to pass radiation through the solution cell. A tungsten shutter can be closed, blocking radiation from the exciter from reaching the specimen, and allowing only passive radiation from the specimen and transmitted radiation from the transmission source to reach the detector. All radiation sources are shielded so that no stray radiation reaches the detector. If concentrated plutonium is to be analyzed, a rhodium foil may be inserted between the specimen and detector to attenuate the intense 59.6 keV radiation from ^{241}Am present in aged plutonium. The specimen cell may be any precision bore cylindrical tube, such as glass or stainless steel, with an inside diameter larger than the detector's collimator.

^{57}Co is an ideal exciter for this application, because its 122.1 keV gamma ray lies just above the absorption edges of uranium and plutonium (115.6 keV and 121.7 keV, respectively). ^{153}Gd is likewise ideal: its 97.4 and 103.2 keV gamma rays are close in energy to the Kα lines of U (94.6 and 98.4 keV) and Pu (99.5 and 103.7 keV) and therefore can be used to correct for absorption of the fluorescent lines by the solution. ^{57}Co in the transmission source corrects for the exciter attenuation by the solution, as well as providing lines for energy calibration for each spectrum measured. Nature is again kind to us, as the half-lives for ^{57}Co and ^{153}Gd are similar (270 days and 242 days, respectively).

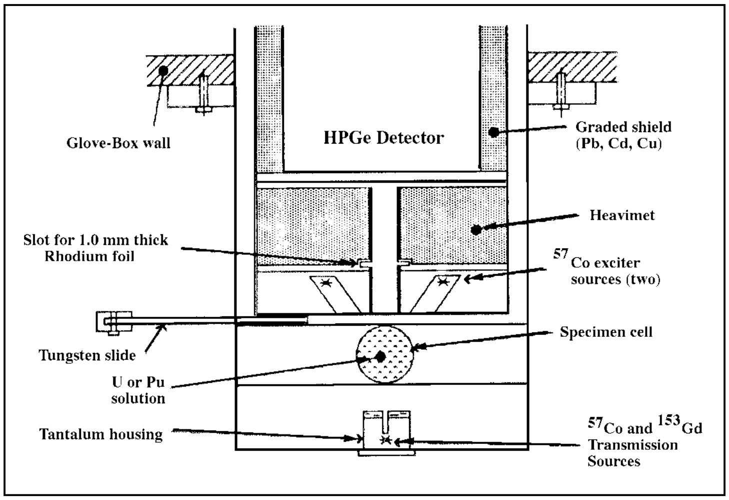

Figure 1. Schematic drawing of one adaptation of the equipment mounted to a wall. Here, we use a system which fits into a rubber glove in a glovebox. It also omits the Rh foil.

Software:

Passive and active spectra from a uranium solution are shown in Figure 2. The key to precise and accurate measurements is the extraction of net peak intensities from what may be quite complex spectra. Overlapping peaks are deconvolved using a sophisticated peak shape fitting code that includes a Gaussian function, a Lorentzian profile for x-rays, short-term low-energy tailing, and background continuum. We measure both Ka_2 and Ka_1 lines of uranium and plutonium. The deconvolution algorithm is able to extract peak intensities quite nicely in cases where there are overlapping peaks, as seen in Figure 3 for a plutonium solution.

The net intensities for the measured fluorescent x-rays are a non-linear function of concentration due to self-absorption. Because an equation for absorption cannot be written for the near-field geometry used here, as can be done for far-field geometry, we calculate an absorption correction factor for the ^{153}Gd and ^{57}Co lines by numerically integrating over the cylindrical volume which is in the field of view of the detector. This calculated correction factor (CF) effectively corrects for solution self-absorption, as seen in Figure 4. The concentration is then calculated simply as

$$\mathrm{Conc_{meas}} = \mathrm{K} \bullet \mathrm{CF_{meas}} \bullet \mathrm{Intensity_{meas}}$$

$$\mathrm{K} = \mathrm{Conc_{std}} \div (\mathrm{CF_{std}} \bullet \mathrm{Intensity_{std}})$$

where K is the calibration constant and $\mathrm{CF_{meas}}$ and $\mathrm{CF_{std}}$ are the calculated absorption correction factors for the unknown and standard, respectively. The linearity of the corrected response is manifested in the same calibration constant being measured, regardless of concentration (Table 1).

We have recently made several improvements to the software. Broad Compton scatter peaks and other slowly changing background components are first stripped from the spectrum[7]. This results in better background subtraction, peak center location, and peak fitting. Next, a precision energy calibration relating observed peak positions to their energies is performed. We first find the 122 and 136 keV peaks of ^{57}Co that are always present from the transmission source. With this preliminary calibration, other peaks are located and identified. A linear least squares energy calibration is then performed. During spectrum fitting, the peaks' full width at half maximum is optimized using the minimum chi-square criterion for goodness of fit. In an operator-selectable high-precision mode, further refinement of peak center location is also performed, again optimizing chi-square. The analytical results of these changes are a zero intercept when

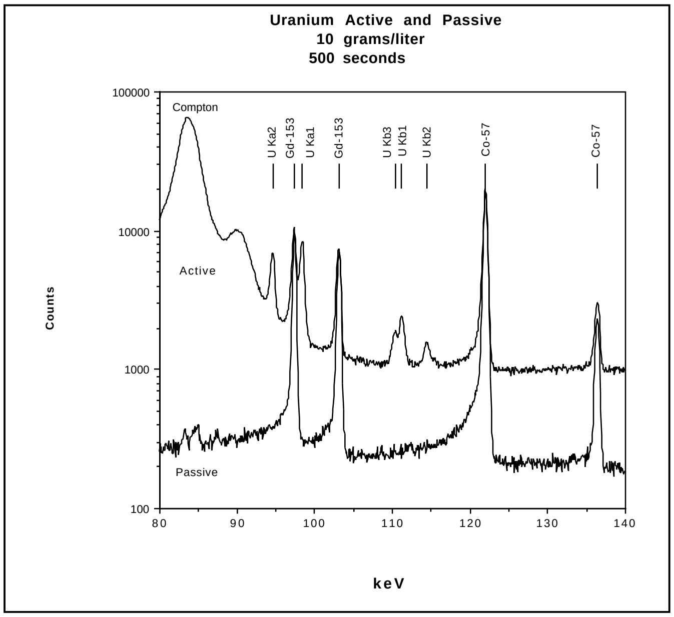

Figure 2. Active and passive spectra from a 10 gram/liter solution of uranium; 500 seconds.

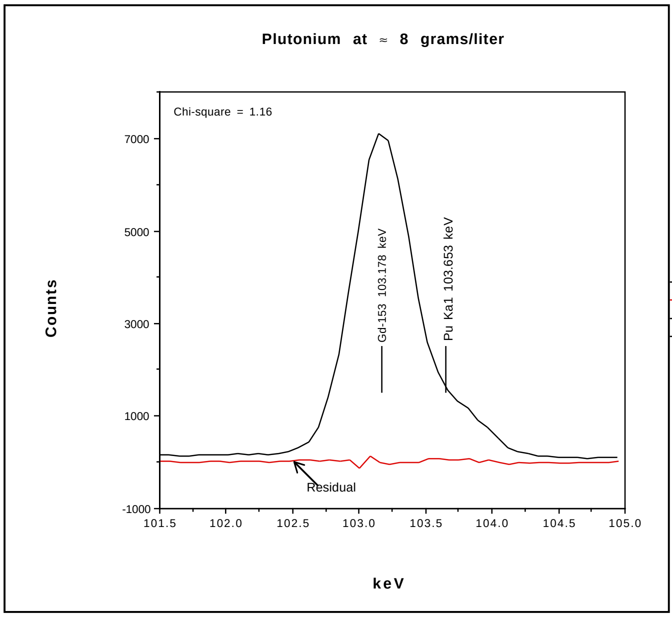

Figure 3. Residual after deconvolution of Gd-153 and Pu Kα1 peaks (103.178 and 103.653 keV, respectively). Reduced chi-square is 1.16. Gd = 99.6 c/s; Pu Kα1 = 18.2 c/s.

plotting peak intensities with respect to known concentrations for standard solutions, close agreement in the analyzed concentrations when using the Kα1 and Kα2 lines, and reduced scatter of calculated concentrations. With the user in mind, new features have been added to allow easy editing of calibration data and averaging with statistical analysis of replicate analyses.

Results and discussion:

When precision-bore cells are used, high precision and accuracy can be achieved. This is illustrated in Table 1[8]. Since there is only one calibration constant, the results from many standards can easily be averaged. In this particular case, the relative standard deviation for the calibration constant is less than 0.5% over a wide concentration range. Thus, a single calibration solution is all that is required. Without the correction procedure used here, five or more standards are required to adequately fit the uncorrected calibration curve shown in Figure 4 over the full concentration range.

U conc., g/l	U Kα1 Calib. Constant (K)	Pu conc., g/l	Pu Kα1 Calib. Constant (K)
240.9	10.662	238.95	14.008
178.8	10.659	178.29	14.074
105.0	10.613	119.54	14.032
52.67	10.584	41.95	13.950
21.23	10.549	19.80	13.988
10.56	10.650	5.158	13.964
5.333	10.645	1.774	14.089
2.143	10.699	0.995	13.992
1.099	10.619		
weighted mean:	10.623 ± 0.42%		14.015 ± 0.40%

Table 1. Calibration Constants. There is only one calibration constant which is measured at every concentration. Precision can be quite good when precision-bore tubing is used and counting statistics are commensurate with the desired precision.

Standard solutions were prepared by dissolving uranium dioxide in nitric acid, followed by dilution to yield the desired concentrations. The 99.7 ± 0.7 gram/liter solution was intended for calibration and was therefore subjected to coulometric assay and found to have a concentration of 99.3 ± 0.7 g/l, agreeing with the intended value within the limits of error. This solution was analyzed 21 times, yielding a calibration constant of 16.3 ± 0.1 (2 sigma). The rest of the solutions were then analyzed four times each, for 300-1000 seconds depending upon the concentration. The results are tabulated in Table 2. We see from this tabulation that the determined concentrations are within the expected errors, and further that the calibration is

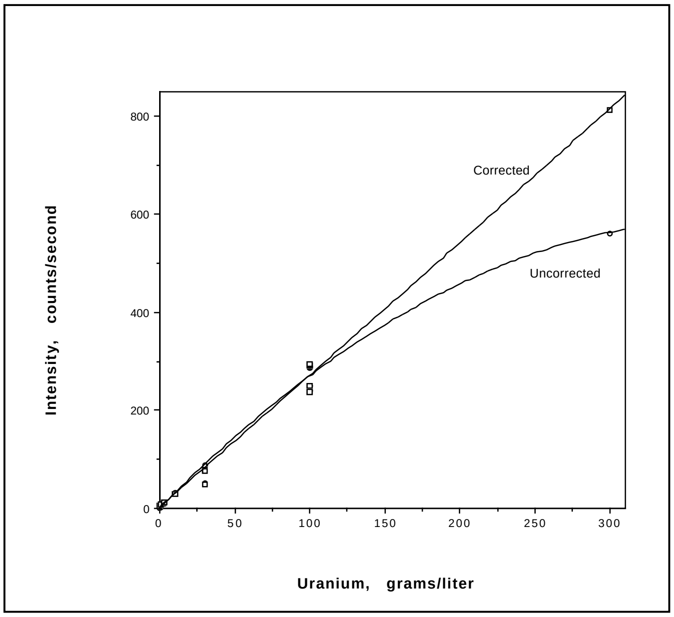

Figure 4. Corrected and uncorrected U Ka1 intensities.

	Day Zero			Day 10		
Prepared Conc. g/l	Measured Average Conc. g/l	Difference g/l	Combined Errors g/l	Measured Average Conc. g/l	Difference g/l	Combined Errors g/l
$c_p \pm \Delta_p$	$\bar{c}_m \pm \Delta_m$	$\lvert c_p - \bar{c}_m \rvert$	$\sqrt{\Delta_p^2 + \Delta_m^2}$	$\bar{c}_m \pm \Delta_m$	$\lvert c_p - \bar{c}_m \rvert$	$\sqrt{\Delta_p^2 + \Delta_m^2}$
2.00 ± .05	2.05 ± 0.05	0.05	0.06	1.99± .02	0.01	0.05
4.90 ± 0.1	4.80 ± 0.1	0.10	0.14	4.8 ± 0.2	0.1	0.2
9.50 ± 0.2	9.35 ± 0.17	0.15	0.26	9.3 ± 0.15	0.2	0.25
49.4 ± 0.7	48.5 ± 0.4	0.9	0.8	48.7 ± 0.4	0.7	0.8
99.7 ± 0.7	99.9 ± 0.4	0.2	0.8	98.7 ± 0.4	1.0	0.8
150.0 ± 2.0	152.4 ± 0.8	2.4	2.15	150.0 ± 2.5	0.0	3.2
200.0 ± 3.0	200.0 ± 1.0	0.0	3.1	199.0 ± 2.5	1.0	3.9
250.0 ± 4.0	252.0 ± 2.0	2.0	4.5	251.0 ± 2.5	1.0	4.7
300.0 ± 4.0	293.0 ± 13	7.0	13.6	306.0 ± 1.4	6.0	4.2

Table 2. Replicate analyses of prepared solutions of uranium nitrate of known concentration. Calibrated using 99.7 g/l solution. Error ranges for measurements are standard deviations for 4 replicate measurements. Analysis time was 300-1000 seconds, depending upon concentration. Difference between results obtained by different methods is insignificant if $\lvert c_p - c_m \rvert < \sqrt{\Delta_p^2 + \Delta_m^2}$.

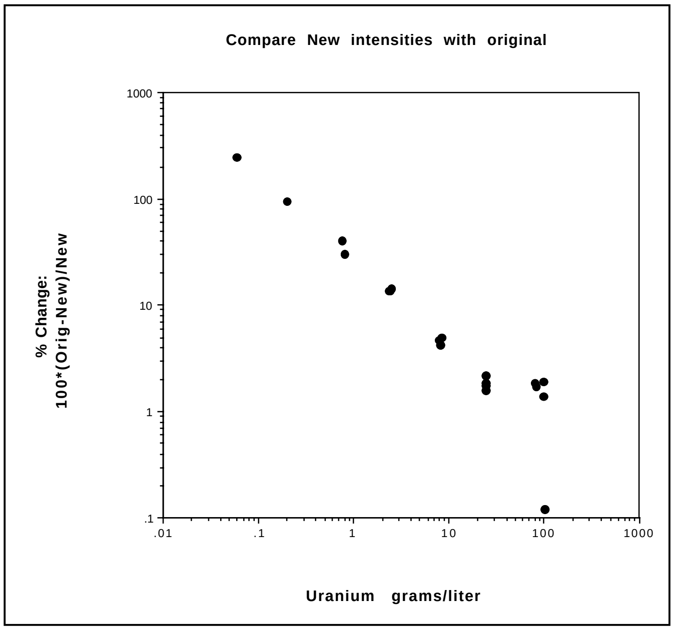

Figure 5. Percent difference between original intensities and new intensities using new, optimized version of the software.

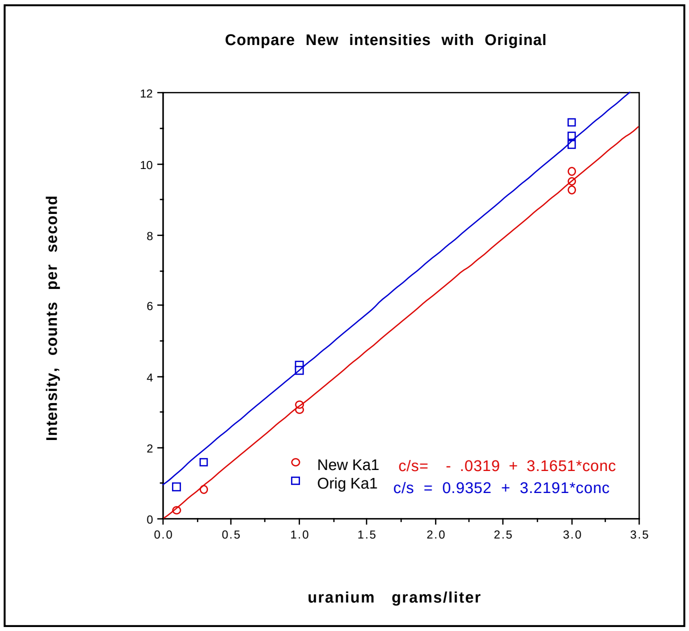

Figure 6. With the optimized version, there is now a zero intercept, among other improvements.

stable over a period of time. (It is interesting to note that the first time the 300 g/l solution was measured, the concentration was found to be only about 200 g/l. The room temperature at the time was 12˚C; when the solution temperature was raised to 40˚C, the concentration was measured to be 293 g/l. There is limited solubility of the uranium salt at the lower temperature.)

If 3 times the standard deviation for the background in 1000 seconds is used as the definition of minimum detectable level (MDL_{1000}), the U Kα1 line yields 70 mg/l and the U Kα2 line yields 170 mg/l. This is typical for uranium K-lines excited by radioisotopes; Jedlovec[9] reported a detection limit of 100 mg/l using ^{57}Co excited fluorescence detected with a planar high-purity germanium detector, a system comparable to that described here. Detection limits below 1 mg/l are reported in the Russian literature[10-13] when using uranium L-lines excited by x-ray tubes and detected by either wavelength-dispersive or energy-dispersive x-ray spectrometers. The higher detection limits using K-lines are due to higher background from Compton scatter in the solution and in the detector. K-lines can be measured through glass, rubber gloves, and steel tubing which cannot be done with the softer L-lines. L-lines also could not be used to measure as high concentrations as can be done with K-lines due to loss of sensitivity from the stronger absorption (50x higher). Clearly, each type of measurement has its niche applications: L-lines for dilute solutions and trace analyses, K-lines for more concentrated solutions, where contamination prevention is desirable, and for in-plant monitoring through pipes and vessel walls.

The effect of the improved software is marked at low concentrations. Comparisons between the new version and the original[5] are illustrated in Figures 5 and 6. The relative error of the older version could be quite large for dilute solutions due to the non-zero intercept as concentration approaches zero. The primary emphasis of the work here is nuclear fuel reprocessing where the concentrations encountered are anything but dilute, but it is pleasing to extend the range of accuracy of the technique. Furthermore, the technique has been suggested for continuous monitoring of waste streams in order to achieve more complete materials balance.

Conclusion:

We have improved and tested a x-ray fluorescence technique for the determination of uranium and plutonium concentrations in solutions, applicable over a wide range of concentrations (less than 1.0 g/l to greater than 300 g/l). Measurements can be made through barriers, such as rubber gloves in a glovebox or even stainless steel tubing in a reprocessing plant; contamination and waste generation are thereby avoided. The method is relatively fast, 10's of seconds to minutes. The equipment is relatively simple and relatively inexpensive. Only one solution standard is required, and its matrix need not be identical to the solutions being measured. Precision of 0.5% relative has been demonstrated. In practice, we carry along the counting statistics, correcting for the various numerical operations involved in background subtraction, deconvolution, and calibration. Typically, these random errors are about 1-2% relative at 10 g/l with a 500 second counting time.

An enhancement we plan to implement is to complement the fluorescence technique with an absorption edge (densitometer) technique[14]. All the data needed are already being measured, namely two transmission peaks below the absorption edges of uranium and plutonium, and two transmission peaks above. All that is needed computationally is to extrapolate to the edges and relate the jump to concentration. Having two independent measurement techniques adds assurance to the analytical results. This should be particularly useful for concentrated solutions where errors in the transmission technique are small.

The next step toward implementation of the technique in nuclear reprocessing plants is demonstration with plutonium and mixed solutions and further quantitation of precision and accuracy using the newest version of the software.

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