Simulation of Absorption Edge Densitometry

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by

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ABSTRACT

A method for simulating absorption edge densitometry has been developed. This program enables one to simulate spectra containing any combination of special nuclear materials (SNM) in solution. The method has been validated with an analysis method using a single special nuclear material in solution or a combination of two types of SNM separated by a Z of 2. This computer simulation has been used to explore the bias caused by the presence of, for example, plutonium in a determination of uranium concentration. We have also used this program to explore better methods of analyzing densitometry data.

I. INTRODUCTION

Absorption-edge densitometry has become an important analytical tool for safeguarding reprocessing plants. It has been used successfully to measure the product uranium and plutonium solutions generated from the plutonium recovery plants.¹ It has also been used, in conjunction with the x-ray fluorescence (XRF) technique, to determine simultaneously the plutonium and uranium concentrations of dissolver solutions: the input solution of plutonium recovery plants.^{2,3}

This report describes a method for computer-simulated absorption edge densitometry. The applications of such a technique are several-fold. First, the simulation can be used as a training tool; an operator can input the concentrations of special nuclear materials (SNM) and the attenuated spectrum can be displayed for that solution. Second, simulation can be used as a research tool. Although most of the work should be done by actually preparing the solutions and measuring the solutions with the densitometer, such a process is time consuming, and the preparation of samples is expensive. Because of the time and expense, a limited number of studies have been done, with the majority of the work performed on the dissolver solutions of reprocessing plants. The presence of minor isotopes such as neptunium and americium leads to interference, which may potentially cause bias in the assay results. Simulations can be performed to study the effect of minor isotopes upon densitometry determination. Third, the densitometry technique has the potential of being quite precise for the simultaneous assay of solutions containing a mixture of plutonium and uranium; this has not been explored thoroughly. Simulation can be used to study the different ways of analyzing data. Finally, simulation may also help in deciding the ideal sample thickness for various concentration ranges.

This is the first portion of a two-part report. Our goal is to simulate spectra from the hybrid densitometer system, namely both the XRF and densitometry processes. Because densitometry is more straightforward than XRF, we decided to simulate the densitometry process first.

The densitometry process is physically simple. A continuous-energy x-ray beam with a specific end point is directed through a solution containing SNM. Some of the beam is absorbed by the atoms in the solution, generating the characteristic x-rays of the element. Some of the incident x-rays will undergo Compton scattering. The beam is, therefore, attenuated as it goes through the solution. Finally, some of the beam will emerge from the solution without losing energy; this transmitted beam is measured by the densitometer detector. A narrow collimator, typically 0.75 mm in diameter, is placed between the detector and the solution, thereby minimizing detection of multiple scattering processes.

II. SIMULATION METHOD

There are at least two different ways to simulate the densitometry process. For example, a Monte Carlo particle-transport method could be used to generate a simulated spectrum. However, because we strive for at least 0.01% or better calculational precision, the required computing time would be prohibitively long.

The other alternative is to start with the reference spectrum. This is the spectrum obtained from the densitometer by using a sample vial that contains only the nominal matrix solution. A sample reference spectrum is shown in Fig. 1. Because this spectrum was taken with the actual densitometer system, all the multiple scattering events are taken into account and measured by the detector. The difference between the sample solution and the reference solution is, therefore, the presence of SNM. To generate the simulated spectrum for the SNM solution, we need to attenuate the net reference spectrum, channel by channel, according to the following equation:

$$I(E) = I_0(E) \cdot \prod_{i=1}^j \exp(-\mu_i(E) \cdot \rho_i \cdot x) \quad (1)$$

where E is the energy corresponding to a channel, i is the SNM element index, j is the number of SNM elements in the solution, μ_i is the mass absorption coefficient of element i at energy E , ρ_i is the known density of element i in the solution, and x is the thickness of the solution.

Figure 2 shows the simulated spectrum, using this method, for a solution that contains 200 g/l of uranium. The lower curve in Fig. 2 shows the spectrum measured with an actual 208 g/l solution. It is observed that the two curves are quite similar. The only exception is that near the absorption edge, where the simulated spectrum shows a sharp discontinuity, the actual spectrum is more "rounded." This difference is a result of the finite resolution of the detector, which tends to distribute some counts near the edge into neighboring channels. This difference does not affect the analysis because the data near the edge are not used in data analysis.

III. VALIDATION

The critical test of this method is that, when analysis is performed upon a simulated spectrum, the calculated SNM content should be identical to the "known" content. For example, if we simulate a spectrum for a solution that contains 200 g/l of uranium (200 gU/l), and this spectrum

Fig. 1. Reference spectrum of the densitometer taken with the matrix solution, in this case 3 molar HNO_3 .

Fig. 2. Simulated uranium spectrum and actual uranium spectrum taken with x-ray generator based densitometer.

is submitted for densitometry analysis, the assay result should indicate 200 gU/l. In fact, the assay results should be identical to the known contents for arbitrary concentrations of uranium and plutonium.

Table I shows several comparisons of known and calculated uranium concentrations. The calculated concentrations were obtained by performing densitometry analysis upon simulated spectra. As shown in equation (1), the mass absorption coefficient must be determined, for each SNM element present, at the energy of every channel in the simulated region. Because different values of μ are reported in various cross-section tabulations, it is important that we identify the source of our μ data. We obtained mass absorption (total minus coherent scattering) cross sections from Storm and Israel.⁴ Values of μ between energies listed in Storm and Israel were obtained via linear interpolation in $\log(\mu)$ versus $\log(E)$ space. A solution thickness of 2 cm was assumed in all calculations.

In Table I, the first column shows the known uranium concentration used for simulating the assay spectrum. The second column shows the calculated uranium concentration that results from densitometry analysis upon the simulated spectrum. The analysis is based on straight line fitting in $\log\log(1/\text{Transmission})$ versus $\log(\text{Energy})$ space, where "log" indicates the natural logarithm function. The fitting ranges are those which include approximately 6 keV above and 6 keV below the K-edge as shown in Fig. 3. The fourth column lists the precision from the assay, calculated using the error analysis outlined in Ottmar's report.³ Because our reference spectrum was collected for 10 000 s, the counting time for each simulated spectrum is also 10 000 s. Therefore, each analysis performed on a simulated spectrum must have a precision which corresponds to a 10 000 s counting time. The final column lists the precision after being adjusted to a 1000-s assay time, multiplying by the square root of 10. Figure 4 shows a graph of both the ratio and the precision for 1000-s assays.

TABLE I. Known Uranium Concentrations and Assayed Values from Simulated Spectra.

Known U (g/l)	Assayed U (g/l)	Ratio (Assayed/Known)	Precision (%) 10 000-s assay	Precision(%) 1000-s assay
1	1	1.000	8.160	25.805
5	5	1.000	1.649	5.213
10	10	1.000	0.835	2.640
30	30	1.000	0.293	0.927
50	50	1.000	0.183	0.587
75	75	1.000	0.133	0.420
100	100	1.000	0.107	0.339
150	150	1.000	0.083	0.264
200	200	1.000	0.074	0.234
250	250	1.000	0.070	0.223
300	300	1.000	0.071	0.223
350	350	1.000	0.073	0.232
400	400	1.000	0.078	0.247
450	450	1.000	0.085	0.269
500	500	1.000	0.094	0.297

Fig. 3. Regions of data analyzed for a single element densitometer. The fitting region is 6 keV wide above and below the absorption edge.

Uranium Simulation

Fig. 4. Analysis of simulated uranium spectrum from 1 g/l to 500 g/l. The ratio is that of the analyzed to known concentration. The precision values correspond to an assay time of 1000 s.

Table I and Fig. 4 show the comparison between the known and the assayed values for uranium; Table II and Fig. 5 show the results of similar trials using plutonium. These tables and figures show that the method does pass the critical test of simulation: namely, the known and assayed SNM concentrations are in perfect agreement. The calculated precision is also quite reasonable, 0.59% at 50 g/l and 0.23% at 200 g/l for uranium determination. These values are in good agreement with our actual measurements and also with values reported by Ottmar³ and our measurements.

We have also simulated solutions that contain a mixture of plutonium and uranium. We used the analysis method of Ottmar for solving two simultaneous equations to obtain the plutonium and uranium concentrations. We used a solution with a known U/Pu ratio of 2. The fitting region for the analysis of mixed solution is shown in Fig. 6. Table III summarizes the results. We observed that the ratio of calculated concentration to known concentration was unity for each SNM element. The precision for each concentration is plotted in Fig. 7. These precisions are, again, in good agreement with measurement. In general, the precision in analysis of mixed SNM solutions is worse than that of single-element solutions because, in the mixed case, the interval between the two K-edges is approximately 2 keV in width, whereas in the single element case, the fitting interval is 6 keV in width. As a result, the linear fit includes data from one-third as many channels. The narrow fitting range increases the uncertainty of the end point determination (the log-log(1/T) intercept), which boosts the amount of relative error in the concentration value. For the minor isotope, the precision also degrades as the ratio of U/Pu increases; the limit of ratio is around 10. Beyond 10, the precision of plutonium approaches 20% or more.

TABLE II. Known Plutonium Concentrations and Assayed Values from Simulated Spectra.				
Known Pu (g/l)	Assayed Pu (g/l)	Ratio Pu (A/K)	Precision (%) 10 000-s assay	Precision(%) 1000-s assay
1	1	1.000	7.614	24.077
5	5	1.000	1.538	4.863
10	10	1.000	0.778	2.461
30	30	1.000	0.273	0.863
50	50	1.000	0.172	0.545
75	75	1.000	0.123	0.388
100	100	1.000	0.099	0.312
150	150	1.000	0.076	0.241
200	200	1.000	0.067	0.211
250	250	1.000	0.063	0.199
300	300	1.000	0.062	0.197
350	350	1.000	0.064	0.201
400	400	1.000	0.067	0.211
450	450	1.000	0.071	0.226
500	500	1.000	0.078	0.246

Plutonium Simulation

Fig. 5. Analysis of simulated plutonium spectrum from 1 g/l to 500 g/l. The ratio is that of the analyzed to known concentration. The precision values correspond to an assay time of 1000 s.

Fig. 6. Regions of data analyzed for a dual element ($\Delta Z = 2$) densitometer. The fitting regions below and above the edges are 6 keV wide; the region in between the edges is 2 keV wide.

TABLE III. Known Uranium and Plutonium Concentrations and Assayed Values from Simulated Spectra.					
Known U (g/l)	Known Pu (g/l)	Ratio U (A/K)	Ratio Pu (A/K)	Precision U(%) 10 000-s assay	Precision Pu(%) 1000-s assay
2	1	1.000	1.000	17.755	35.063
10	5	1.000	1.000	3.669	7.306
20	10	1.000	1.000	1.911	3.845
60	30	1.000	1.000	0.754	1.574
100	50	1.000	1.000	0.538	1.161
150	75	1.000	1.000	0.449	1.002
200	100	1.000	1.000	0.425	0.974
300	150	1.000	1.000	0.456	1.094
400	200	1.000	1.000	0.557	1.387
500	250	1.000	1.000	0.731	1.883
600	300	1.000	1.000	1.004	2.674
700	350	1.000	1.000	1.422	3.919
800	400	1.000	1.000	2.057	5.887

Fig. 7. Precision of a mixture of uranium and plutonium with U/Pu ratio of 2.

IV. APPLICATION OF THE SIMULATION PROGRAM

We have developed a computer program that simulates densitometry spectra, which are normally obtained using an x-ray generator. Execution of the program to simulate various concentrations of single and mixed SNM elements has demonstrated that assay results agree with known SNM content. Now the program can be used to explore different possibilities.

Assume we have a solution containing 200 gU/l ; the solution also has some plutonium. If the analyst ignores the plutonium content and analyzes the solution as a pure uranium sample, the assay will be biased; we would like to know the amount of that bias. The results are shown in Table IV and Fig. 8. It shows that there is a bias even when the plutonium is at 0.5% of the uranium; the bias increases almost proportionally to the concentration of plutonium because the 6-keV fitting region above the uranium K-edge (117.26–124.060 keV) includes the K-edge of plutonium, which has an energy of 121.8 keV.

To minimize the bias, we can reduce the fitting region to (117.26 - 119.440 keV) to avoid the plutonium K-edge. The results are shown in Table V below. We found that the bias is greatly reduced; at 10 gPu/l (5% of the uranium concentration), the bias is reduced from 2% to 0.2%. At the same time, the precision increases from 0.24% to 0.38%. The worsened precision is due to the narrower fitting region; fewer data points are now used in the linear fit.

The remaining bias can be corrected by the bias correction:³

$$\text{Bias (g/cm}^3\text{)} = 1/\Delta\mu_A * \sum_i \Delta\mu_i * \rho_i \quad (2)$$

For plutonium and uranium, the $\Delta\mu_{\text{Pu}}/\Delta\mu_{\text{U}} = 0.0331$. Therefore at 10 gPu/l, the assayed value of uranium is 199.67 g/l. The bias correction is 0.0331×10 or 0.331 g/l. Therefore the final assayed value of uranium is 200.001 g/l, which shows very little bias. The bias correction is valid for plutonium concentrations as high as 100 g/l. The only penalty is that the precision is worse, from 0.23% (wide fitting range) to 0.37% (narrow fitting range) or more. This means that the counting time needs to be doubled to achieve the same precision.

We see that it is possible to correct for the presence of plutonium by narrowing the fitting region and also applying the bias correction; the penalty is worsened precision. The other related

TABLE IV. Known Uranium and Plutonium Concentrations Assayed as Single Element Uranium.				
Known U (g/l)	Known Pu (g/l)	Assayed U (g/l)	Ratio (Assayed/Known)	Precision(%) 1000-s assay
200	1	199.59	0.998	0.234
200	2	199.18	0.996	0.235
200	5	197.95	0.990	0.236
200	10	195.95	0.980	0.239
200	20	192.06	0.960	0.245
200	30	188.33	0.942	0.250
200	40	184.73	0.924	0.256
200	50	181.26	0.906	0.263
200	75	173.10	0.865	0.279
200	100	165.56	0.828	0.297

Fig. 8. Bias in the 200 g/l uranium concentration determination due to the presence of plutonium in the solution. The spectrum is analyzed as a single element with a wide fitting range.

Known U (g/l)	Known Pu (g/l)	Assayed U (g/l)	Ratio (Assayed/Known)	Precision(%) 1000-s assay
200	1	199.97	1.000	0.375
200	2	199.93	1.000	0.376
200	5	199.83	0.999	0.377
200	10	199.67	0.998	0.380
200	20	199.34	0.997	0.385
200	30	199.01	0.995	0.390
200	40	198.68	0.993	0.396
200	50	198.34	0.992	0.401
200	75	197.52	0.988	0.415
200	100	196.69	0.983	0.430

problem is that when the fitting region is changed, the calibration factor, in this case the $\Delta\mu$ value, also changes and needs to be reevaluated.

There is another method for analyzing the data. Assume we know the ratio of Pu/U from another means (say, the XRF measurement). Instead of fitting a narrow data range, we will correct the spectrum for the presence of the minor isotope, in this case plutonium. From the known concentration of plutonium (which is also required for the bias correction), we can remove the attenuation due to plutonium for every channel in the fitting range. The results of this approach are shown in Table VI. The results show that the bias has been removed by this technique. In

TABLE VI. Known Uranium and Plutonium Concentrations Assayed as Single Element Uranium. (The data in the fitting region have been corrected for the attenuation of the plutonium. The fitting region is the same as for the single element uranium.)

Known U (g/l)	Known Pu (g/l)	Assayed U (g/l)	Ratio (Assayed/Known)	Precision(%) 1000-s assay
200	1	200.00	1.000	0.234
200	2	200.00	1.000	0.234
200	5	200.00	1.000	0.234
200	10	200.00	1.000	0.234
200	20	200.00	1.000	0.234
200	30	200.00	1.000	0.234
200	40	200.00	1.000	0.234
200	50	200.00	1.000	0.234
200	75	200.00	1.000	0.234
200	100	200.00	1.000	0.234

addition, the precision of the uranium determination is improved from 0.37% to 0.23% because the fitting regions above and below the edge are 6 keV wide. In this example, because the uranium fitting regions were used to determine the uranium concentration, uranium was the "key" element. Because the plutonium concentration was determined from the uranium concentration (using the known Pu/U ratio), plutonium was a "secondary" element.

This method of analyzing data has a further advantage: it can also be applied to the cases in which the proton number Z of the secondary element differs by one from that of the key element ($\Delta Z = 1$). Two examples of this case are the elements neptunium and americium, with plutonium as the key element. In each case the difference of the two K-absorption edges is only about 3 keV, leaving no region for fitting between the elements' edges. This method has the added advantage in that the same calibration constants ($\Delta\mu$) for single elements can also be used for mixed solutions.

V. CONCLUSION

This report summarizes our approach to generating simulated K-absorption edge densitometer spectra. The simulation program has provided densitometry spectra from known concentrations of SNM, which closely resemble actual spectra obtained in the laboratory. The program also serves as a cost-effective tool for the investigation of different analysis techniques, providing simulated spectra for user-defined SNM solutions without the need to prepare actual samples.

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