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**K-EDGE X-RAY FLUORESCENCE ANALYSIS FOR
ACTINIDE AND HEAVY ELEMENTS SOLUTION
CONCENTRATION MEASUREMENTS**

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K-EDGE X-RAY FLUORESCENCE ANALYSIS FOR ACTINIDE AND HEAVY ELEMENTS SOLUTION CONCENTRATION MEASUREMENTS*

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INTRODUCTION

There are currently no plans for the commercial reprocessing of nuclear fuel in the U.S. This is not the case in Japan, England, France, Germany, or the USSR. The U.S. does, however, include the reprocessing of spent nuclear fuel as a part of its defense programs. The Office of Safeguards and Security of DOE's Defense Programs has funded the development and optimization of numerous nondestructive analysis techniques including K-edge x-ray fluorescence analysis. This paper reviews some of the implementation efforts resulting from R&D supported by that office.

In 1979, the concept¹ of using K-edge x-ray fluorescence analysis (K XRFA) for the analysis of actinide solution concentrations was first presented. K XRFA using small radioactive Co-57 sources has been shown to be a practical way to measure actinide solution concentrations in off-line, at-line, or on-line configurations. The experimental methodology is elegant and the hardware is simple. With little or no modifications, the same configurations can be used to measure solution concentrations of heavy elements. Since that first paper, a number of advancements have occurred and will be briefly reviewed here. Because of the brevity of this paper, the interested reader must seek details in the references.

Heavy element herein is defined as an element with atomic number (Z) greater than 72, hafnium. The K absorption edge, K_{ab} , for Hf is 65.3 keV; for Bi (Z=83) it is 90.5 keV. Elements Po, At, Rn, Fr, Ra, and Ac (Z=84-89) are rarely of industrial or trace interest. Thorium (Z=90) begins the actinide series and its K_{ab} is 109.6 keV; and Pu, the last major actinide of reprocessing interest, has a K_{ab} of 121.72 keV. The $K_{\alpha 1}$ x-ray energies of Hf to Bi, 72<Z<83, go from 55.8 to 77.1 keV, while for Th, U, Np, and Pu they extend from 93.35 to 103.75 keV. These are high energy x-rays and are very penetrating. In order to create x rays of the elements Hf to Pu, 72<Z<94, an excitation voltage in excess of 122 keV is needed. Such high energies can be obtained with massive and expensive x-ray machines; however, radioactive Co-57 emits a 122.05-keV gamma ray ideally suited to excite all of these heavy element x rays. It's available in high specific activities, which means very small sources can be

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made and its 270-d halflife means that sources need be replaced only once a year. The following sections discuss the experimental hardware required to do x-ray fluorescence analysis using radioactive source excitation, two examples of XRF systems used to monitor the concentration of heavy metals for process control, and the slight modifications required in the hardware when more accurate concentrations (inventory control) is needed.

EXPERIMENTAL GEOMETRY

Figure 1 shows the sophisticated, yet elegant geometry that allows K XRFA of all heavy elements with $^{72}\text{Zr}^{94}$. A Ge instead of a Si energy dispersive detector is required to detect x-ray energies above 50 keV. Sufficient shielding is required between detector and exciter sources and the exciting radiation must be collimated. An up-looking detector allows the analysis of horizontal pipes (on-line); or if we rotate this assembly 90° , a right-angle detector can analyze solutions in test tubes or in specially constructed cells (off-line or at-line).

The system shown in Fig. 1 was designed² to determine the concentration of solutions containing pure U, pure Pu, or mixtures of U+Pu. The top-view drawing shows two linear actuators that insert two shutters on command. The front shutter eclipses the exciter sources so that any radioactivity in the solution can be measured; the rear shutter composed of 1 mm Cd or Rh attenuates an intense 59.5-keV gamma ray from the decay of Am, a daughter activity of Pu-241. The purpose of the third, highly collimated, Co-57 source will be described below. The physical size of the entire source-collimator and detector shielding assembly is 3 inches in diameter by 2 in. long, which is considerably smaller and less expensive than an x-ray machine. More importantly, the assembly can be located anywhere the detector can and if there is no radioactivity in the solution, neither shutter is required. Industrial environments are often hostile, thus the detector can be located remote from the supporting computer-based electronics that operate the shutters and record the spectral data. Minor variations of this geometry will be described when the K XRFA systems developed over the past several years are described.

Fig. 1. Top view of one exciter-detector collimation assembly. Note the shutters and the very collimated 3rd Co-57 source opposite the detector.

Fig. 2. Partial XRF, passive, and net spectra from a mixed U+Pu solution.

Figure 2 shows a 500s XRF spectrum (top) of a 20/1::Pu/U mixture with 9.55 gU+Pu/l. The center spectrum is taken with the front shutter closed so that the emitted radioactivity is counted. The U and Np x rays result from the alpha decay of Pu and Am; the gamma rays result from the nuclear decay of various Pu isotopes. Their contribution is removed by subtracting the passive from the active spectrum to yield the net fluoresced x-ray spectrum (bottom). Note that the observed Pu/U ratio of 18.4 is less than the stated 20/1 value. The U x rays are enhanced by the emission of Pu K β x rays and a strong 129 keV Pu-239 gamma ray within the solution.

Since the inside lining of the detector collimator is Cd or Rh, its K α x rays are always recorded. Similarly, the 122-keV transmission gamma ray is always recorded. Thus, the Cd K α and 122-keV peaks are used to zero and gain stabilize the pulse height analysis system against voltage shifts or gain drifts during accumulation of either the active or passive spectra. This ensures accurate quantitative data from their difference.

INDUSTRIAL PROCESS CONTROL OF HEAVY ELEMENTS

Energy dispersive X RFPA is ideal to monitor the process chemistry of heavy metals. Usually the solution concentrations need not be determined accurately (<10%). Two on-line X RFPA systems have been installed to monitor U concentrations. Figure 3 show cross-sectional and top views of the hardware installed on-line at the Idaho Chemical Processing Plant (ICPP).³ A U bearing organic solution is air lifted from 3 floors below, flows through an air de-entrainer into a reservoir, which fills a side stream stainless steel cell where the analysis is performed. Three collimators, small (2.6 mm ϕ), medium (7.0 mm ϕ), and large (12.2 mm ϕ) limit the amount of fission product radiation seen by the detector. The entire assembly is enclosed in a lead enclosure, roof and sides.

Two Co-57 sources are located at the ends of the two foot-long rods (top view). These rods allow source changes without disassembly of the lead house. The two shutters are computer controlled; the inner one eclipses the exciter sources so that passive fission product activity can be measured; the outer one inserts a Ni-coated, 5-mil thick, U foil that is used to periodically monitor system performance, or calibrate the system when new sources are installed.

Figure 4 shows a 500s livetime XRF spectrum of a 93% dodecane plus 7% tributylphosphate (TBP) containing 5 gU/l using the medium collimator with two 50 mCi Co-57 exciter sources. The U concentrations are determined by ratioing the net K α x-ray area (NK α) to the gross incoherent (GI) area. This ratio is independent of the Co-57 half life and only slightly sensitive (<3%) to variations in the organic matrix. Normally, spent nuclear fuel is reprocessed in long campaigns, hence fission product levels reach an equilibrium value. After the appropriate sized collimator is chosen, the activity level need be measured only once/hr. If fission product activity within the GI window (shutter closed) is less than 4% of the shutter open GI value, then it is ignored. Otherwise, the NK α /GI ratio is obtained from the (active - passive) difference spectrum. U concentration results are printed every 10 min.; then each hour 5 or 6 results are listed along with a calculated mean value for the past hour. Finally, once each day the past 24 hourly mean values are listed. The Cd K α and 122-keV coherent scatter peaks are used to stabilize the spectrum.

Fig. 3. Cross section and top view of the ICPP on-line K RFPA hardware. One of three different size collimators limits fission product count rate. The long rods allow source change without disassembly of the Pb enclosure.

Fig. 4. XRFA of a 5 gU/l organic solution as measured thru a steel cell. The region where the K α x rays occur for heavy metals is shown. The simulated fission background was recorded with the front shutter closed.

Figure 4 indicates the region where the K α x ray for the heavy elements occur. The background for this region is about the same as that for the region in which the actinide x rays fall. However, there is some loss in sensitivity. The fluorescence efficiency will decrease as we go to lower Z elements because of the increasing separation between the 122-keV exciting radiation energy and the 90- to 65-keV binding energies of the heavy metals, Bi to Hf. In fact, for Hf, the required analysis time is about 300 s to obtain 1% counting statistics on a solution containing 25 g Hf/l compared to only 100 s for Pu. A 25 gAu/l solution would only require 200 s to obtain 1% counting statistics. The time required to obtain 10% counting statistics on a 1 g/l solution would be 80 s for Hf and 55 s for Au. The minimum concentrations detectable by the K XRFA methodology described in this paper approaches 10-20 parts per million (ppm). 50 ppm can be measured to reasonable accuracies (~3%) in 1 to 3 hours.

The first on-line XRF assemblies were installed⁴ on-line in 1981 at Allied General Nuclear Services Plant in Barnwell, SC (now closed). Solutions were flowed through steel cells, the U x-rays excited by Co-57, and the NK α /GI method used to obtain concentrations. Figure 5 shows the first on-line, near-real time, U concentration results ever reported.⁴

INVENTORY CONTROL CONCENTRATIONS

As mentioned above, the NK α /GI method is sufficiently accurate to

Fig. 5. The left graph shows results from input, output, and waste streams operating normally; the right plot shows data reported when the input stream was temporarily blocked. The blockage was immediately detected, communicated to the control room; then the stream was reopened.

be used when monitoring the concentration of one or more heavy metals in their process chemistry. The ratio eliminates the ever decreasing Co-57 source intensity due to its decay, and there is only the need to change the radioactive sources once per year. In the event that the concentration needs to be known more accurately (defined here as less than 0.5%), then the NKal/GI methodology is not sufficiently accurate. Nuclear safeguards material accountability has such a requirement; and it can be met using x-ray fluorescence analysis technique, but does not require slight modifications in the already elegant experimental hardware.

In the chemical process of heavy metals and in the reprocessing of nuclear fuels, the process chemistry is not able to control exactly the solution temperature, acid molarity, anion or cation content, or the extent of aqueous or organic impurities. Variations in any or all of these parameters cause density changes in the solution containing the heavy metal of interest. As the density increases, x-ray self-absorption increases and the measured x-ray intensity, NKal will decrease. Meanwhile, as density increases the Compton scattered peak, GI, will increase; hence, the ratio NKal/GI will decrease. This was confirmed in earlier work.⁵ So in fact, there are really two unknowns, solution concentration and density. However, the earlier work⁵ showed that transmission of the coherently scattered 122-keV radiation also decreased as the density increased. So elemental concentration is proportional to $NKal/\rho$; the solution transmissivity is proportional to $T(122)/\rho$, and then perhaps their ratio $(NKal/\rho)/(T(122)/\rho)$ will be independent of density (ρ).

This is exactly what happens. Heavy elements are usually dissolved in aqueous or organic solutions, which contain H, C, N, O, and other low Z elements such as Al, F or S necessary to customize the process chemistry. The mass absorption coefficients (μ) of these light elements are all nearly equal at 100 keV (the vicinity of the U and Pu K α x rays); and more importantly, the ratios of μ at 120 to 100 keV differ by less than 3.5% from H to S. Since the heavy metal concentrations are always being measured in solutions, variations in the minor aqueous or organic impurities or light element admixtures do not significantly alter the scattering, and hence the transmission. The relevant mass absorption coefficients for a selected few of the low Z elements are shown in Table 1.

Table 1. Mass Absorption Coefficients (μ) in cm^2/gm

Element symbol	Z	100 keV	120 keV	$\frac{\mu(120)}{\mu(100)}$
H	1	0.294	0.280	0.952
-	-	-	-	-
C	6	0.151	0.145	0.960
N	7	0.153	0.146	0.954
O	8	0.155	0.147	0.948
F	9	0.149	0.140	0.940
Al	13	0.170	0.153	0.900
-	-	(mean including H & S)		0.940 ± 0.024
S	16	0.201	0.175	0.871
-	-	(mean including H & S)		0.932 ± 0.033

In effect, the change in density as measured by 122-keV transmission is quantitatively representative of transmission changes in the actinide x-ray region. So $\text{NK}\alpha_1/\text{T}(122)$ is independent of density for U and Pu. This explains the need for the third, highly collimated, Co-57 source that is located opposite the detector and was mentioned above. It does fluoresce the solution, but only 10^{-4} as much as the exciter sources. The third source allows actinide solution concentrations to be measured independent of stream density and minor light element matrix impurities.

The exciter-detector collimation assembly shown in Fig. 1 was developed as an off-line, K XRFA system for Savannah River's Pu reprocessing Plant in 1981. Technician operators withdraw solution samples into small plastic test tubes from any of 34 different process or product storage tanks. These samples are transported to the K XRFA system and placed in between the exciting and transmission sources as shown in Fig. 1. A remote terminal links the XRFA system to a computer and disk-based PNA, that begins the analysis automatically, once seven simple questions are answered on a remote terminal. If the need is only for process control information, only an active fluorescence measurement is made. If instead an accountability measurement is desired, then the passive radioactivity spectrum must be recorded for the same lifetime as the active analysis, and the concentration determined from the active - passive spectrum. If both U and Pu concentrations are desired, then regardless of the analysis purpose, both active and passive spectra must be recorded to remove the contribution of U x-ray intensity that comes from the alpha decays of Pu.

The use of mass produced plastic test tubes with their variable wall thicknesses and diameters leads to a limitation of the ultimate accuracy obtainable with this system. As a result of this and the steady need to make accountability grade measurements ($<0.5\%$); the next system⁶ was designed to be operated at-line. That is, solutions are drawn into a precision machined, stainless steel cell. The cell is located between the exciter and transmission sources as before. In addition, a third air controlled shutter was added which can insert a Ni-coated U foil behind the cell. It is used to monitor system performance and to facilitate updating the calibration equations when the Co-57 sources are changed.

The minimum detectable concentrations of Pu using two 10 mCi sources, a standard 12-mm deep, HPGc detector with 500 eV resolution (FWHM) at 122 keV with 0.48-in detector collimation and 0.75-in inside diameter steel cell in a 1000 s analysis is 0.05 g/l. This corresponds to a count rate

about 4X the background beneath the Pu K α 1 x-ray peak. If U is present in the solution, then Pu ($>0.05\text{g/l}$) would still be detectable at levels 1000X less than the U concentration because the Pu x rays fall above those of U. On the other hand, because the scattering background is higher beneath the U K α 1 peak, and because the Pu K α 2 x ray falls only 1.03 keV above U K α 1, the minimum concentration of U detectable in the presence of Pu is only one part in 200 (again with U $> 0.05\text{ g/l}$).

Clearly, ratioing one of the heavy metal K α 1 x-ray intensities to the transmission intensity at 122 keV would not be as good a correction for solution density variation as it is for the actinide K α x-ray region. If very accurate concentrations were needed for one of the heavy metals, say gold, then it would be better to use a Ta foil behind the cell instead of a transmission source. The Au K α 1 to Ta K α 1 ratio would correct for both solution density variations and source exciter half life. If accurate concentrations are not needed, then the NK α 1(Z)/GI corrects for source decay, and no shutters are needed if there is no solution radioactivity.

SUMMARY

The advantages of using Co-57 as an exciter for X XRFA include:

- a compact design that requires no x-ray tubes;
- the exciter-detector assembly locates remote from support electronics;
- on-line, at-line, or off-line configurations for monitor/measurements;
- systems that can be run by semi-skilled technicians, once programmed;
- and operated via remote terminals with results sent to control rooms;
- heavy element concentrations that are measurable thru industrial pipes
- independent of minor changes in solution matrix or source half life
- with concentration results reported in near-real-time;
- a dynamic range of measurable concentrations that is greater than 10^4 ;
- measurement times that are reasonable even at 1 gram/liter; and
- for nuclear safeguards, it provides the $<0.5\%$ accuracy required by DOE for the accountability of U, Pu, or both, once the system is calibrated.

REFERENCES

1. D. C. Camp and W. D. Ruhter, Nondestructive, Energy Dispersive X-Ray Fluorescence Analysis of Actinide Stream Concentrations from Reprocessed Nuclear Fuel, Adv. in X-Ray Analysis, 23:163 (1980).
2. D. C. Camp, W. D. Ruhter, and K. W. MacMurdo, Determination of Actinide Process and Product Stream Concentrations Off-Line or At-Line by Energy Dispersive X-Ray Fluorescence Analysis, Proc. of 3rd ESARDA Symposium on Safeguards and Nuclear Material Management, Karlsruhe, F. R. Germany, 6-8 May 1981, p. 155-159 (1981).
3. D. C. Camp, W. D. Ruhter, C. E. Johnson, and T. C. Piper, Near-Real-Time Actinide Concentrations Via Energy Dispersive XRFA for Process Control and Material Accountability, Proc. of Am. Nuc. Soc. and Inst. Nuc. Mat. Mgrs. Conf. (1984) and UCRL-90037 (1983).
4. B. G. Henderson, R. S. Lee, G. A. Huff, and D. C. Camp, Energy Dispersive XRFA for On-Line U Concentration Measurements, "Analytical Chemistry in Nuclear Technology," W. S. Lyon, ed., Ann Arbor Science, p. 253-260 (1982).
5. D. C. Camp, W. D. Ruhter, S. Benjamin, Nondestructive, Energy Dispersive XRFA of Product Stream Concentrations from Reprocessed LWR Fuels, UCRL-52616, LLNL Report (1979).
6. R. A. Johns, R. Parry, V. Walker, D. C. Camp, W. D. Ruhter, and D. Eccels, On-Line Analysis of Pu by Energy Dispersive X-Ray Fluorescence, Proc. of 25th Ann Mtg. of the Inst. Nuc. Mat. Mgrs. (1984).

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