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PRELIMINARY INVESTIGATION OF MONOCHROMATIC X-RAY ABSORPTION AS A METHOD OF ANALYSIS FOR URANIUM

By

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Preliminary Investigation of Monochromatic X-Ray Absorption As a Method of Analysis for Uranium

W. F. Peed and H. W. Dunn

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Stable Isotope Research and Production Division

C. P. Keim, Director

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Preliminary Investigation of Monochromatic X-Ray Absorption As a Method of Analysis for Uranium

W. F. Peed and H. W. Dunn

ABSTRACT

Preliminary data have been taken to evaluate X-ray absorption at the L III edge of uranium as a method of detection of uranium in solution. Uranium concentrations in water from 150 ppm to 30,000 ppm have been investigated. The effect of copper as a typical contaminant in the range of 737 ppm of copper to 36,850 ppm of copper has been investigated for a representative uranium solution. Instrumentation has been constantly improved and suggestions for further improvements in amplifying and counting equipment are included. Comparison of experimental data with theory indicates that the derived equations are adequate.

HISTORICAL

A series of annual survey articles[1] on X-ray absorption and X-ray spectroscopy include numerous references to X-ray methods applied to analysis of samples for elemental constituents. More recent articles by Bartlett and by Friedman discuss applications of polychromatic X-ray absorption[2] and fluorescent X-rays[3] to analysis for uranium. Both of these methods have certain disadvantages, particularly the polychromatic

1. Liebhafsky, Anal. Chem. (Jan. 1949, 1950, 1951).
2. Bartlett, Anal. Chem. 72, 702 (1951).
3. Friedman, Anal. Chem. 72, 705 (1951).

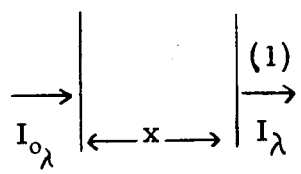
[redacted]

absorption method which is especially sensitive to impurity elements. It was the purpose of this preliminary research to investigate the precision of uranium determination by means of monochromatic X-ray absorption for the case of (a) pure uranyl nitrate solutions and (b) the effects of light element (e. g., Cu29) impurity on these solutions.

THEORY

The equation for absorption of X-rays passing through an absorption cell of length x (in cm) is

$$I_\lambda = I_{o_\lambda} e^{-\Sigma_i \mu_{m_i} x C_i} \tag{1}$$



where μ_{m_i} is the mass absorption coefficient in cm^2/gm, C_i is the concentration in gm/cm^3 of component i, and the sum is taken over all components in the absorbing material.

Let us choose λ_1 and λ_2 as wavelengths pre and post an absorption edge of uranium. We then obtain

$$\frac{I_{\lambda_1}}{I_{\lambda_2}} \frac{I_{o_{\lambda_2}}}{I_{o_{\lambda_1}}} = e^{-\Sigma_i x \left[(\mu_{m_i} C_i)_{\lambda_1} - (\mu_{m_i} C_i)_{\lambda_2}\right]} . \tag{2}$$

The summation extends over the solvent, the uranium and the impurities. Since I_o is difficult to measure directly and since solvent concentration will remain approximately constant for all uranium concentrations, we can measure I_w, the radiation transmitted by the cell containing only water. Hence, we can write in terms of the uranium and the

impurities

$$\frac{I_{\lambda_1}}{I_{\lambda_2}} \frac{I_{w_{\lambda_2}}}{I_{w_{\lambda_1}}} = e^{-x\left[C_u(\Delta\mu_u) + \sum_{imp} C_{imp}(\Delta\mu_{imp})\right]} , \tag{3}$$

where $\Delta\mu$ is the difference in the absorption coefficient at λ_1 and λ_2.

We may consider first the special case of no impurities (actually the presence of atoms other than uranium in the uranyl nitrate introduces an impurity effect proportional to the concentration of uranium). Here, $C_{imp} = 0$ and

$$C_u = \frac{1}{\Delta_{\mu_u}} \ln\left(\frac{I_{\lambda_2}}{I_{\lambda_1}} \frac{I_{w_{\lambda_1}}}{I_{w_{\lambda_2}}}\right) . \tag{4}$$

Thus, for each absorption cell we can construct a straight working curve of C_u from standard samples versus the logarithm of measureable intensity ratios.

Now let us consider the effect of impurities such as the nitrate (NO_3) or any other impurities contained in the uranium material. The general expression for the mass absorption coefficient is[4]

$$\mu_m = \frac{N}{C} (\tau_a + \sigma_a),$$

where N is Avogadro's number, A the atomic weight, τ_a the fluorescence absorption coefficient, and σ_a the scattering coefficient. This is approximately

$$\mu_m = \frac{NC_\lambda{}^3 Z^4}{A} + \frac{8\pi}{3} \frac{Ne^4}{Am^2c^4} Z.$$

4. Compton, A. H. and S. K. Allison, "X-Rays in Theory and Experiment," pp. 511-515. D. Van Nostrand (1935).

The relative effect of the second term will be

$$\frac{\sigma_a}{\tau_a} = \frac{8\pi}{3} \cdot \frac{e^4}{m^2 c^4 C\lambda^3 Z^3} \cong \frac{0.018}{CZ^3}$$

at wavelength 0.72 A. For K electrons, C = 0.018, so that for hydrogen we have $\sigma_a = \tau_a$, for oxygen $\sigma_a \cong 0.002\ \tau_a$, and for copper $\sigma_a = 4 \times 10^{-5} \tau_a$. Hence, except for the very light elements (for which absorption is also very small) we can safely assume that

$$\mu_m = CZ^4\lambda^3 \frac{N}{A}. \tag{5}$$

From equation (1) we have for the uranium, plus impurities (other than solvent)

$$I_{\lambda_1} = I_{w_{\lambda_1}} e^{-(\mu_{m_{\lambda_1}} Cx)_u - \Sigma(\mu_{m_{\lambda_1}} Cx)_{imps}}, \tag{6}$$

and we obtain

$$\ln \frac{I_{w_{\lambda_1}}}{I_{\lambda_1}} = (\mu_{m_{\lambda_1}} Cx)_u + \Sigma(\mu_{m_{\lambda_1}} Cx)_{imp}, \tag{7}$$

also

$$\ln \frac{I_{w_{\lambda_2}}}{I_{\lambda_2}} = (\mu_{m_{\lambda_2}} Cx)_u + \Sigma(\mu_{m_{\lambda_2}} Cx)_{imp}. \tag{8}$$

Impurity effects can now be minimized since

$$\mu_{imp} \cong \frac{CZ^4 \lambda^3 N}{A} \cong \text{const. } \lambda^3$$

for any one impurity. Combining (7) and (8), we find

$$\frac{1}{\lambda_1^3} \ln\left(\frac{I_{w_{\lambda_1}}}{I_{\lambda_1}}\right) - \frac{1}{\lambda_2^3} \ln\left(\frac{I_{w_{\lambda_2}}}{I_{\lambda_2}}\right) = \left(\frac{\mu_{m_{\lambda_1}} Cx}{\lambda_1^3} - \frac{\mu_{m_{\lambda_2}} Cx}{\lambda_2^3}\right)_u$$

or

$$C_u = \frac{\frac{1}{\lambda_1^3} \ln\left(\frac{I_{w_{\lambda_1}}}{I_{\lambda_1}}\right) - \frac{1}{\lambda_2^3} \ln\left(\frac{I_{w_{\lambda_2}}}{I_{\lambda_2}}\right)}{x \; \frac{\mu_{m\lambda_1}}{\lambda_1^3} - \frac{\mu_{m\lambda_2}}{\lambda_2^3}} .$$

This equation* is of the form

$$C_u = k_1 \log\left(\frac{I_{w_{\lambda_1}}}{I_{\lambda_1}}\right) - k_2 \log\left(\frac{I_{w_{\lambda_2}}}{I_{\lambda_2}}\right) , \qquad (9)$$

where k_1 and k_2 are constants for a given cell length and selected wavelengths λ_1, λ_2.

It should be pointed out that in the case of yttrium whose K edge occurs near 0.72 and polonium whose L II edge occurs near 0.73 A that the above equation is not applicable and these elements, when present, will prohibit analysis for uranium content. However, all other elements which have no absorption edge at 0.72 A can be treated by the above analysis.

* Derived by D. M. Bennett, Research Participant from University of Louisville, summer, 1950.

EXPERIMENTAL METHOD

All work discussed in this report was done on a General Electric XRD-3 X-ray unit using a type CA7 tungsten-target line-focus X-ray tube and a rock-salt crystal (diffraction from the 100 planes) as a source of monochromatic X-rays. A precision divided goniometer is used to select a Bragg angle such that radiation of a known wavelength is diffracted into the radiation detector. The X-ray tube high voltage is supplied from a circuit equipped with a "stabiline" regulator, while the X-ray tube current is maintained constant by a conventional current regulator circuit. This power supply arrangement results in a very stable source of X-radiation. Exact measurements of stability are not available, but generally, statistics of the counting process limit the reproducibility of repeated readings even when 10^6 counts are accumulated.

For detection of X-radiation at the intensity level desired and with the statistical limitations that were imposed by the precision of analysis, the counting equipment originally installed in the XRD-3 unit was inadequate. Since the instrumentation exerts a large influence on the data that are to be presented, it will be discussed in detail later (see section on Instrumentation).

The samples investigated were prepared from pure uranium oxide (U_3O_8) dissolved in nitric acid and diluted to volume. Solutions with concentration of approximately 30 gm of U/l and 8 gm of U/l were

prepared and then analyzed by the Analytical Chemistry Division of ORNL. Less concentrated solutions were prepared from these standard solutions by careful dilution using volumetric pipettes and volumetric flasks. A cell with 1.0 cm path length was constructed of stainless steel with thin (approx. 0.015") beryllium metal windows. These windows were held in the body of the cell with picein wax. Suitable clamps and brackets were added to the XRD-3 unit to insure reproducible location of the cell. The voltmeter on the X-ray tube was calibrated by means of a plot of intensity as a function of voltage, and precautions were taken to prevent generation of radiation with wavelength of $\lambda/2$ which would introduce a large error in measurements.

The L III absorption edge of uranium at 0.72 A was chosen for investigation because air and water absorption are considerably smaller than at the M edge at 3.5 A for which the absorption discontinuity is much larger (i.e., $\Delta\mu_m \cong 1500$ at the M V edge versus $\Delta\mu_m = 50$ at the L III edge). The K edge was not used due to the small value of $\Delta\mu_m = \sim 6$, plus the high X-ray tube voltage required to give appreciable intensity. Air and water absorption at the M V edge would reduce the X-ray intensity by a factor of approximately e^{-150}.

The exact wavelengths λ_1 and λ_2 were selected by consideration of the variation in intensity of radiation after passing through a cell containing uranium in concentrations of 2000 to 8000 ppm as a function of the angle of the goniometer setting. Wavelengths of these points can be cal-

culated by the Bragg law ($n\lambda = 2d \sin \theta$), the wavelengths selected correspond to $2\theta = 14.53^{\circ}$ and 14.77°. These points were chosen so that errors in setting the goniometer of the order of a few hundredths of a degree would not introduce large errors in absorption coefficient values. The wavelength of the absorption edge disagrees with published values by approximately 0.5 per cent, but a similar discrepancy in the measurements of wavelengths of tungsten L lines indicates that the error may be inherent in the instrument as presently aligned.

EXPERIMENTAL DATA

The data shown in Table 1 are representative of instrumental stability that is usually experienced. These two sets of twenty measurements each are repetitive readings of intensity with no changes made in goniometer settings or X-ray intensity controls. It will be noticed that the limit of error of a given measurement is almost twice that expected for the number of counts observed. Recent oscilloscope studies of pulses appearing at the output of the pulse amplifier show that pulses of two energies were being observed. Assuming that one pulse originates from 17 KV photons, the other pulse appears to be 6-8 KV energy. This does not correspond to the energy of the krypton K X-ray which would be expected from the gas in the counter tube. Since this effect was observed, changes have been made in amplifier settings to discriminate against this lower energy pulse.

TABLE 1

REPRODUCIBILITY OF INTENSITY MEASUREMENTS
AT DIFFERENT COUNTING RATES

	Time for 1,048,576 Counts at 31 KVP-10 ma Attenuated by 1.0 CmH_2O	Time for 131,072 Counts at 31 KVP-10 ma Attenuated by 1.0 CmH_2O and 0.003 Inches Ni Foil
	109.55 sec	102.23 sec
	109.42	102.19
	109.25	102.56
	109.53	102.18
	109.60	101.79
	109.68	101.82
	109.77	102.28
	109.71	102.23
	109.72	102.10
	109.70	101.63
	109.73	103.00
	109.44	102.61
	109.55	102.71
	109.48	103.18
	109.39	103.22
	109.27	102.74
	109.31	102.47
	109.11	102.49
	109.48	103.30
	109.23	102.55
Average	109.50 sec	102.46 sec
Average Counts per second	9576 sec^{-1}	1279 sec^{-1}
L. E.	0.37 sec	0.963 sec
% L. E.	0.34	0.93
Predicted % L. E.	0.20	0.55

Data of the type shown in Table 1 are taken at frequent intervals as it is the best test available in this laboratory for checking stability of X-ray generating and counting equipment.

Table 11 shows data taken in the measurement of three different concentrations of uranium solutions. To minimize the effects of long term changes in X-ray intensity or counting equipment, measurements were made alternately at $2\theta = 14.53°$ (corresponding to λ_1) and $2\theta = 14.77°$ (corresponding to λ_2). These data, therefore, include errors introduced in setting the goniometer as well as errors which are introduced in changes in X-ray intensity, amplifier instability, and other instrumental effects, with thirty measurements being made at each wavelength for each solution. It will be observed that the percent limit of error is not much larger than that experienced from counting statistics as shown in Table 1, indicating that statistical considerations in counting are the major source of uncertainty.

TABLE II

REPRODUCIBILITY OF DATA INCLUDING ERRORS FROM RESETTING GONIOMETER DATA ON TIME FOR 1,048,576 COUNTS OF X-RAY ABOVE AND BELOW L III ABSORPTION EDGE AS A FUNCTION OF URANIUM CONCENTRATION IN ABSORPTION CELL

Concentration (ppm)	7371.8	7371.8	3685.9	3685.9	294.9	294.9
Setting 2θ	14.53°	14.77°	14.53°	14.77°	14.53°	14.77°
Average Time of Counting (sec)	210.18	156.03	148.54	132.16	109.92	114.44
L. E. (sec)	0.96	0.75	0.61	0.53	0.29	0.41
% L. E.	0.46	0.48	0.48	0.40	0.26	0.35
Pred. % L. E.	0.20	0.20	0.20	0.20	0.20	0.20

Table III A shows measurements of a series of solutions with concentration varying from 14,774 ppm to 147.9 ppm. It is reasonable to assume that the concentration of the strongest solution, 29,570 ppm, is most accurately known since all other solutions were prepared by dilution of this standard. The constant in equation 4 was, therefore, evaluated from measurements of this solution. This table clearly shows the increasing error that is introduced as concentration is decreased. The source of this error appears to be in instrumentation and is discussed later in this report. Table III B shows precision to be expected from this method of analysis. This table was calculated from data in Table II.

TABLE III (A)

ACCURACY OF MEASURED URANIUM CONCENTRATION

Known Concentration of Uranium	Average* Measured Concentration of Uranium	Limit of Error 95% Confidence Internal	% Error
14774 ppm	14803 ppm	± 17 ppm	+ 0.2 %
7372	7274	± 80	- 1.3
3686	3546	± 9	- 3.8
1843	1749	± 53	- 5.1
737	686	± 6	- 7.0
295	265	± 34	-10.1
147	122	± 41	-17.6

* Average of 3 measurements for each concentration.

TABLE III (B)

PRECISION* OF MEASURED URANIUM CONCENTRATION

Concentration of Uranium	Limit of Error Any One Measurement	Limit of Error of Mean*
7372 ppm	86 ppm	16 ppm
3686	114	21
295	63	11
147	27	5

* Based on 30 measurements for each concentration.

Table IV shows data calculated from measurements of a series of solutions with varying amounts of copper which was chosen as an impurity typical of its atomic number range (iron, nickel, zinc, calcium and other elements in this atomic number range would have approximately the same effect).

TABLE IV

ANALYSIS OF URANIUM IN SOLUTION
EFFECT OF COPPER AS A CONTAMINANT

Ratio Conc. Copper to Conc. Uranium	Conc. Copper in ppm	Actual Conc. Uranium in ppm	Calculated Conc. Uranium in ppm	% Deviation
10/1	36,860	3685.9	3900.7	+ 5.83
4/1	14,743.6	3685.9	3580.7	- 2.85
2/1	7,371.8	3685.9	3685.0	- 0.02
1/1	3,685.9	3685.9	3685.4	- 0.01
0.2/1	737.2	3685.9	3675.5	- 0.28

Constants in equation 9 were evaluated by solving the equation for data from two different concentrations of copper (2/1 and 1/1 copper/uranium) simultaneously. This may be regarded as experimental verification of the method of calculation developed by D. M. Bennett and, in general, indicates that for all but a few impurities, such as yttrium and probably polonium and radon, will have little effect on the accuracy of analysis by this method.

INSTRUMENTATION

Original radiation detection equipment on the XRD-3 unit consisted of a multi-chamber Geiger tube, a low-gain preamplifier, pulse-shaping and rate-meter circuits, a scale of 16,384 scalar, and an electric stop clock. Due to its short life, long dead time, and high cost, the Geiger tube was replaced with a proportional chamber.

The detector was designed specifically for this research by D. J. Knowles of the ORNL Instrument Division. The chamber is filled with a krypton - 10 per cent methane mixture at 2 atmospheres pressure in a cylindrical chamber equipped with a beryllium metal window. Calculations show that approximately 90 per cent of the radiation incident on the counter window should be detected. Since the pulse size from this chamber is much smaller than from the Geiger counter, the low gain preamplifier was replaced with an A1A preamplifier and an A1 linear amplifier. To discriminate against amplifier noise, the output from the pulse height selector of the A1 amplifier is fed into the pulse-forming

circuit of the XRD-3 unit. To extend the scale range, a Nuclear Instrument and Chemical Company model 161S scalar with scale of 256 is connected ahead of the existing General Electric equipment. Suitable interconnections have been made so that both scalars are operated from one start-stop-reset switch. Scaling factors from 1024 counts to over 4×10^6 counts are available on a preset count basis. Average counting rates as high as 10,000/second are used in measuring I_W. Consideration of counting statistics shows that 10^6 counts are needed for each intensity measurement to attain a useful limit of error. For this reason, high counting rates are desirable so that the time required for one analysis is not excessively long.

Since the first data were taken of a series of solutions with decreasing uranium content, it was noticed that the measured uranium concentration was consistently lower than that known to be present. As the uranium concentration became less, the difference percentage-wise became greater (see, for example, Table III-A). Resolving time of the amplifying and counting equipment was measured and suitable corrections made. The discrepancy, although reduced, still was present. It has since been recognized that the X-ray tube high voltage is supplied from a full-wave rectified, unfiltered source. The wavelength of the X-rays used corresponds to approximately 17 KEV; therefore, a maximum high voltage (peak) of 34 KEV is used to eliminate radiation of wavelength $\lambda/2$. Since no X-rays of 17 KEV energy are generated unless the voltage across the

X-ray tube exceeds this value, no X-rays are being counted for almost 1/3 of the time as the voltage varies between 0 and 34 KEV 120 times a second. Counting rates assumed to be average are, therefore, 30 per cent low and resolving time corrections are correspondingly in error. In addition to this, the efficiency of X-ray generation varies in this case as $(E-17)^{1.8}$, where E is the instantaneous voltage across the X-ray tube. It is obvious when this factor is considered that the counting rates assumed to be average are invalid as far as resolving time corrections are concerned. It should be pointed out that data at low counting rates are but slightly affected by this factor, but all calculations involve the term $I_{w_{\lambda_1}}/I_{w_{\lambda_2}}$, so that absolute values of absorption coefficients that have been calculated are in error.

At the present time, a filter unit is being designed for the high voltage power supply which will eliminate this source of error in counting. Further improvements that are planned in instrumentation include (1) improvement in scaling equipment to minimize maintenance which, in the past, has been excessive; (2) addition of a printing time meter to permit at least semi-automatic collection of data; and (3) improved resolving time measurements when power supply changes are made.

All measurements made in the past have been made with a 1 cm path length cell. There is sufficient intensity available in the case of solution containing small amounts of contaminants, to permit use of a cell length of 3 or 4 cm. This should allow analysis of samples with

concentrations of the order of 50 ppm of uranium with an error of less than 10 ppm. More complete reports on theoretical considerations, sources of error, and experimental data will be issued in the future.

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