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THE X-RAY SPECTROMETRIC DETERMINATION
OF URANIUM IN SOLUTION

by

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ABSTRACT

An X-ray spectrometric method has been developed for the determination of milligram quantities of uranium in solution. In speed, sensitivity and accuracy it is comparable to spectrophotometric methods. Its freedom from interferences other than gross concentrations of other elements makes it notably superior for many applications.

INTRODUCTION

In the development of separation processes for nuclear reactor fuels, it is necessary to assay a wide variety of solutions for uranium. In addition to uranium these solutions often contain high concentrations of such anions as nitrate, sulfate, fluoride, chloride and bromide and varying concentrations of cations from the metals used to alloy the uranium, clad the fuel elements and make up the process equipment. Spectrophotometric methods had been satisfactory for large numbers of samples of a single type, e.g., those from the Purex and Redox solvent extraction processes, but recurring difficulties on solutions whose ionic composition had not been established prompted a search for a method which was less subject to interference by low concentrations of other ions. The X-ray spectrometric method described in this report has proved to be free from interferences of this type. Interferences from the high concentrations of process materials known to be present in the sample can be removed usually with little difficulty.

There have been several reports in the recent literature describing the use of the X-ray spectrograph in analyzing solid specimens for such elements as barium,¹ thorium² and uranium.² Pish and Huffman³ have described an X-ray spectrometric method for the analysis of thorium and uranium-containing solutions of appreciable concentrations, 10^{-2} to 1.0 M, by the use of a suitable internal standard. However, there has been no work reported in which an analysis for a single component has been made in the 10^{-3} M concentration range with a standard deviation approaching $\pm$ one per cent.

¹L. B. Gulbransen, Anal. Chem., 27, 1181 (1955).

²W. J. Campbell and H. F. Carl, Anal. Chem., 27, 1884 (1955).

³G. Pish and A. A. Huffman Anal. Chem., 27, 1875 (1955).

Apparatus

The X-ray equipment used in this work is the basic Norelco (North American Philips Co.) diffractometer with spectrograph accessories. Primary X-radiation is provided by a Machlett OEG-50T tungsten target tube operated at maximum rating, 50 kilovolts peak and 50 milliamperes.* The fluorescent beam defined by an open source-collimator tube is analyzed by diffraction from the cleavage plane (200) of lithium fluoride whose interplanar spacing is 2.014 angstroms. This diffracted radiation is collimated with a set of parallel plates, four inches long, spaced 0.005 inch apart (ratio 800 to 1), and the remaining almost parallel rays are detected by a Geiger counter. Counting is done with the counter tube positioned at a two-theta value of 26.15 degrees, the angular location of the uranium $L\alpha_1$ emission line for the lithium fluoride analyzer.

In order to obtain the desired analytical precision it was found necessary to decrease fluctuations in the primary X-ray intensity and in the counter tube operating voltage. The X-ray tube current control was replaced with a ten-turn Helipot and modifications were made in the original circuits of the tube current stabilizer and the DC high voltage supply, including replacement of the carbon resistors in the sensing section of each circuit with precision wire-wound resistors, and relocation of these sensing resistor strings away from localized heat sources. After these and other changes shown in Figures 1 and 2, the assembly was tested for stability, first on an undisturbed metal specimen and then on a solution with all the manipulations involved in repetitive analyses for a single component. With the metal specimen, twenty-two determinations, at irregular intervals during five hours, of the time required for 102,400 counts showed a standard deviation of $\pm 0.25\%$; during these determinations the position of the specimen was not changed. With the solution, nine determinations during four hours resulted in a standard deviation of $\pm 0.34\%$. For 102,400 counts the standard deviation expected is 0.31%.

These and other comparable tests demonstrate that the modified equipment can generate and measure X-ray intensities as precisely as is possible in reasonable counting times with a single Geiger tube detector. Day-to-day shifts can be corrected by adjusting the high voltage setting to a given counting rate on a properly selected "standard"; the necessary fine adjustment is provided by superposing the output of a variac-controlled 0/6.3 volt, 10-ampere filament transformer on the 0/250 volt variable transformer of the kvp control.

*Note: The signal-to-noise ratio can be improved by filtering out the tungsten L characteristic radiation with a nickel foil over the tube window. The ratio can be doubled by using molybdenum K characteristic radiation instead of the unfiltered tungsten continuum for excitation.

FIGURE 1

MODIFICATION OF TUBE CURRENT STABILIZER FOR NORELCO X-RAY DIFFRACTOMETER AND SPECTROGRAPH

FIGURE 2

MODIFICATION OF DC HIGH VOLTAGE SUPPLY FOR NORELCO GEIGER COUNTER X-RAY DIFFRACTOMETER AND SPECTROGRAPH

Sample Cells

A sample cell of the type used in this method* is shown in Figure 3. The cell is constructed from standard-wall Pyrex glass tubing with a 0.075-mm Pyrex window sealed directly to the cell. Two side arms rather than one greatly facilitate the filling, emptying, washing, and drying cycle necessary in each analysis. The arms are attached to the side of the cell and tilted upward from horizontal to prevent return of air bubbles to the cell proper. The cell is permanently fixed with deKhotinsky cement to a 0.04-in. aluminum plate which is held in place by a pair of aluminum springs as shown in Figure 4. Filling the cell is easily done by holding it vertically and introducing the sample with a syringe-controlled transfer pipette.

For the occasional sample which contains as little as 0.5 mg of uranium, 2×10^{-3} M in one ml, a smaller cell has been built. This cell, which has a volume of 0.75 ml, is about half the height and diameter of the cell shown in Figure 3 and has only one side arm. The filling, emptying, cleaning and drying cycle is more troublesome because of the single port, and the counting rate for a solution of given molarity is about half that for the larger cell.

Sealing the glass window directly to the cell gives several advantages over both a gasketed mechanical seal and a cemented window. The simplicity of the all-glass cell makes it particularly preferable to a gasketed cell in handling operations, its resistance to chemical attack makes it preferable to both gasketed and cemented cells. Further, it was found that the high intensity irradiation embrittled the available cements and caused leaks to develop. An anticipated advantage of notably increased fluorescent intensity from the use of very thin Mylar or mica windows, 0.025 mm or less, was not realized. The durability of the glass window cells has been surprisingly good, with only one cell being lost by window fracture in six months of work.

Interferences

Negative interferences arise from the absorption of fluorescent uranium radiation by other atoms in the matrix. Negative errors of about one per cent were found when the interference-to-uranium molar ratio was 50 for aluminum, 25 for chlorine, 10 for iron, and one for bromine. Increasing the nitric acid concentration from 1.5 to 3.0 M also caused the uranium result to be about one per cent low, although this effect was not explainable by mass absorption.

*Now obtainable from W. H. Kessel and Co., Chicago, Illinois.

FIGURE 3

AN ALL-GLASS X-RAY SPECTROMETER CELL

Diameter: 2.5 cm Height: 1.0 cm
Window thickness: 0.007 cm

FIGURE 4

X-RAY SPECTROMETER CELL ASSEMBLY

Positive interferences occur when a characteristic emission line of the interference and the $L\alpha_1$ line of uranium are not well resolved and when the energy of a characteristic X-ray of the interference is sufficient to excite additional uranium fluorescence. Only rubidium and strontium gave interferences of the former type at interference-to-uranium molar ratios of one or less; at a ratio of one and a uranium concentration of 4×10^{-3} M these interferences were 5 and 3 per cent, respectively. For barium, platinum, gold, mercury, lead and bismuth, which have less proximate lines, positive interference of this type is more than cancelled by the mass absorption effect.

Molybdenum, whose $K\alpha$ emission wavelength ($0.710 \text{ \AA}$) is slightly less than the L_{III} absorption edge of uranium ($0.722 \text{ \AA}$), should give the largest interference of the latter type. At a molybdenum-to-uranium molar ratio of one and concentrations of 4×10^{-3} M enhancement was not noticeable, i.e., the excitation effect was balanced by the mass absorption effect. For elements of higher atomic number, any enhancement will be more than offset by mass absorption and the errors will be negative.

Sample Preparation

To reduce the concentration of such anions as fluoride, chloride, bromide, and bromate below the interference level the sample is fumed to dryness with sulfuric acid. Up to 50 ml of solution containing from 7 to 15 mg of uranium is pipetted into a 100-ml beaker (quartz if the sample is high in fluoride), ten drops of concentrated sulfuric acid are added and the sample is taken to dryness on a sand bath. One ml of concentrated nitric is added, the sample is transferred to a 10-ml volumetric flask and diluted to volume with water.

In samples containing interfering concentrations of such metals as iron, nickel, chromium, aluminum, and zirconium, the uranium is extracted with ethyl acetate as solvent and aluminum nitrate as salting agent. The sample is pipetted into a 125-ml Erlenmeyer flask, excess nitric acid is added if chloride and/or bromide are present, and the sample is evaporated to about 3 ml. Dilute hydrogen peroxide is added to reduce chromium (VI) to (III). The sample is transferred to a separatory funnel with 20 ml of saturated aluminum nitrate and extracted twice with equal volumes of ethyl acetate. The ethyl acetate extracts are combined and stripped twice with half volumes of water. The water strips are combined and evaporated to dryness. Finally, the residue is dissolved in one ml of concentrated nitric acid, transferred to a 10-ml volumetric flask and diluted to volume with water.

For samples containing only 3 to 7 mg of uranium the residue is dissolved in 0.5 ml of concentrated nitric acid and the final dilution is made to 5 ml. For 0.5 to 3 mg of uranium, the sample is evaporated to

dryness in a centrifuge cone, dissolved in 0.5 ml of 1.6 N nitric acid, and diluted to volume with 1.6 N wash acid in a syringe-controlled 100- λ micro pipette. The sample is mixed by repeated delivery to and withdrawal from a clean centrifuge tube.

Calibration and Results

Five standard solutions: 1, 2, 3, 4 and 5 $\times 10^{-3}$ M, were prepared by dissolving N.B.S. U_3O_8 in nitric acid and diluting to the desired concentrations with 1.6 M nitric acid. From these five solutions and a 1.6 M nitric acid solution five series of determinations were made of count rate vs. concentration. In each case the recorded variable was the time required to accumulate 102,400 counts. These data are summarized in Table 1 and shown graphically in Figure 5.

Table 1
URANIUM CONCENTRATION VS. COUNT RATE AT
50 KVP AND 50 MA, 1.6 M NITRIC ACID

<u>Molarity</u> <u>($\times 10^3$)</u>	<u>Seconds for</u> <u>102,400 Counts</u>	<u>Counts per</u> <u>Second</u>	<u>Fraction of Total</u> <u>Counts Due to Uranium</u>
0	500	205	-
1.00	405	253	0.19
2.00	341	300	0.32
3.00	298	344	0.40
4.00	265	386	0.47
5.00	241	425	0.52

FIGURE 5

TYPICAL CALIBRATION CURVE FOR THE X-RAY
SPECTROMETRIC DETERMINATION OF URANIUM

In Table 2 a summary is given of errors in the analysis of 5 solutions which were prepared from N.B.S. U_3O_8 but whose compositions were unknown to the analyst. The per cent standard deviation for each of these solutions is compared with that expected from counting statistics for the same concentration.

Table 2

OBTAINED AND EXPECTED STANDARD DEVIATIONS
FOR X-RAY SPECTROMETRIC URANIUM
ANALYSES IN THE CONCENTRATION
RANGE 1 TO 5×10^{-3} M

Molarity ($\times 10^3$)	No. of Determinations	Per Cent Standard Deviation	
		Obtained	Statistical
1.09	3	0.4	1.3
2.19	6	1.0	1.0
3.24	4	1.2	0.8
4.38	6	0.6	0.7
5.48	7	0.7	0.6

In the calibration described above thirty individual determinations were made to arrive at a calibration curve. A less time-consuming method was contrived by assuming that the deviation from linearity in the calibration curve was proportional to the square of the count rate. Thus, a correction factor of 7.2 per cent per 100 counts per second was derived to give a "corrected" count rate linear with concentration. On this basis count rate determinations at only two uranium concentrations, 0 and 5×10^{-3} M, are sufficient for either a graphical or algebraic calibration. A series of tests has shown the two calibration methods to be equally reliable in the concentration range 3 to 6×10^{-3} M.

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