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QUANTITATIVE ANALYSIS OF URANIUM AND THORIUM SOLUTIONS WITH A SEMICONDUCTOR X-RAY EMISSION SPECTROMETER

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INTRODUCTION

Recent improvements in the energy resolution performance of photon detectors made of lithium-drifted silicon and germanium semiconductors has made possible the construction of an improved non-dispersive X-ray emission spectrograph. A recent article by Bowman, Hyde, Thompson, and Jared[1] discusses the capabilities and usefulness of such a system. A later report by Hyde, Bowman, and Sisson[2] discusses some details in the quantitative analysis of certain elements. The present report is an extension of these studies with the intent of exploring the feasibility of rapid analysis of uranium- or thorium-containing solutions. A study of the analysis of such solutions has been carried out before by Forburg and De Ruvo[3] by non-dispersive X-ray fluorescence analysis but these workers used scintillation counters for analysis of the uranium and thorium X-rays. The work was done at the Lawrence Radiation Laboratory under a National Science Foundation Summer Research Grant for Undergraduate Students.

The basic principles of the analysis and the equipment were the same as used by Bowman et al.[1] and Hyde et al.[2] and will not be discussed in detail here. In this preliminary study of thorium and uranium analysis the silicon detector rather than the germanium detector was used and L X-rays rather than K X-rays were excited and measured, since the sensitivity for excitation and

recording of the L X-rays was greater. The study was restricted to simple solutions in which the resolutions of the L X-rays of these heavy elements from the K X-rays of light elements was not a problem.

The 60.2-day I^{125} was used as the primary source of radiation for excitation of the L X-rays of thorium or uranium. This isotope decays by electron capture to a 35-keV level in Te^{125} which in turn decays to the ground state by a highly converted transition. Hence the major radiations in an I^{125} source are the X-rays of tellurium: Te K_α 27.5 keV and Te K_β 31.0 keV. These X-rays are well suited to the excitation of the K X-rays of elements below tellurium or of the L X-rays of heavy elements. For these purposes I^{125} is superior to the Am^{241} sources used in the previously-cited papers. When I^{125} is substituted for Am^{241} the background radiations in the energy region below 20 keV are greatly reduced. The 60-day half life is a disadvantage, but the preparation of new sources at 2 or 3 month intervals is not particularly troublesome. We are indebted to Dr. Barclay Jones of the Technical Measurements Corporation, Menlo Park, California, for pointing out to us the superior merits of I^{125}.

EXPERIMENTAL PROCEDURE

Preparation of Solutions

Solutions were prepared from weighed amounts of reagent-grade uranium nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, and thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$. The original solutions, called standard solutions, had concentrations of ~ 0.26 gm/ml uranium in the uranium standard solution and ~ 0.026 gm/ml thorium in the thorium standard solution. These solutions were later found to contain 0.2652 ± 0.1% gm of uranium per ml and 0.02604 ± 0.1% gm of thorium per ml

by precipitating the corresponding oxalates, igniting them to the corresponding oxides, U_3O_8 and ThO_2, and weighing.

Other solutions were made by taking aliquots of the standard solutions (or aliquots of subsequent dilutions) and diluting to the required volume in Class A volumetric flasks with distilled water. The range of solutions was about 10^{-1} to 10^{-4} grams of uranium or thorium per ml of solution.

For the uranium and thorium mixtures, solutions of approximately equal concentrations (0.002652 gm/ml of U and 0.002604 gm/ml of Th) were pipetted into three volumetric flasks to give mixtures with the ratio of uranium to thorium of 3/1, 1/1, and 1/3.

To estimate background effects some measurements were also made with blank solutions which consisted of nitric acid solutions with the same nitrate ion concentration as that of the uranium solutions. Tests were also made with pure distilled water and no appreciable difference from the nitric acid solution was observed.

Source Preparation

Two I^{125} sources of approximately 2-millicurie and 4-millicurie strength were prepared from stock solutions obtained from the New England Nuclear Corporation, Boston, Massachusetts. Appropriate amounts of solution were evaporated in the bottom of a depression drilled in a piece of 5-mm thick tin stock 1 cm × 4 cm and covered with Epon cement. Tin was chosen because of its strong absorption of tellurium X-rays. In the experiments the unshielded side of the I^{125} mount was placed to face the liquid sample holder. The tin metal base faced the detector housing and served as a shield of the detector from the tellurium X-rays.

Solution Sample Cell

Samples of the solutions to be analyzed were placed in plastic cells designed for use in conventional X-ray emission analysis. We used the G.E. liquid sample cell kit, A4960 GB, which is a plastic cell 30 cm in diameter, 0.8 cm deep, with a volume capacity of ~ 7 ml. An aliquot of the sample solution was pipetted into the cell, a quarter-mil sheet of Saran plastic was placed on top and an outer retaining ring was slipped over the top and pressed down. This ring held the Saran sheet in place and stretched it to form a flat cell face. The thin cover sheet does not contribute unwanted X-rays to the recorded spectrum nor does it scatter any appreciable number of the incident radiation back into the detector.

Counting Procedure

When the sample cell was filled it was placed vertically in a simple cardboard holder and positioned with its front surface about 2 cm away from the front surface of the semiconductor detector housing. The I^{125} source in its tin mounting was fastened directly to the lower front surface of the detector housing with the shielded side facing the detector. The cell holder was somewhat crude but experiments showed that the cell could be repeatedly repositioned to give readings reproducible within an error of about 2 percent. The geometric relationship of I^{125} source, sample cell, and semiconductor detector is sketched in Fig. 1.

The radiations excited in or scattered from the solution were measured by the detector for periods of 2 to 10 minutes and recorded as 100-channel energy spectra in one portion of a RIDL 400-channel analyzer. Typical spectra are shown in Fig. 2. Suitable gain and bias settings on the amplifier were chosen by preliminary calibration runs in the same manner as described in

Ref. 2. The 100-channel spectra were printed out on paper tape and the integrated counts under the L_α and L_β X-ray peaks of thorium or uranium were determined. From this was subtracted the background count rate in the same energy region when a nitric acid blank solution was substituted for the heavy element solution. The corrected count was then reduced to a value in counts per minute.

RESULTS AND CONCLUSIONS

The observed count rates with L_α peaks for the various concentrations are given in Tables 1 and 2 and plotted in Figs. 3 and 4. The figures represent calibration curves which could be used for the analysis of solutions of unknown concentration with our apparatus. The curve is linear within the counting statistics below a concentration of about 2.6 mg/ml. Below a concentration of 0.1 mg/ml the ratio of L X-ray count to background becomes too small to give dependable results without a great increase in counting time. Above 2.6 mg/ml the curve bends over because of self absorption of uranium or thorium L X-rays in the heavy element solutions. Somewhat greater sensitivity and accuracy could be obtained by integrating under the L_β and L_γ peaks as well as the L_α and by use of a somewhat larger I^{125} source.

The attempt to analyze mixed solutions of thorium and uranium were not promising owing to the closeness in energy of the X-rays. The resolution of the detector system used was 1.2 keV (full width at half maximum) while the comparable X-rays are separated by only ~ 0.6 keV. This problem could be attacked by use of the better detectors now available with resolution characteristics of 0.6 keV or less (FWHM) or by use of critical absorption techniques. Another approach would be to use a higher energy primary γ-ray source to excite the K X-rays of these elements which are separated by several keV in energy

and hence easily resolved in the present spectrometer. The main disadvantage of this choice is a loss in sensitivity. Preliminary trials with a Co^{57} source of roughly the same strength as the I^{125} source indicated about a ten-fold decrease in counting rate.

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1. H. R. Bowman, E. K. Hyde, S. G. Thompson, and R. C. Jared, Science 151, 562 (1966).

2. E. K. Hyde, H. R. Bowman, and D. H. Sisson, University of California Lawrence Radiation Laboratory Report UCRL-16845, May 1966.

3. S. Forberg and A. R. de Ruvo, Analysis of Uranium Solutions by Scintillation Detection of X-Ray Fluorescence, in Proceedings of a Symposium on Radiochemical Methods of Analysis, Salzburg, Austria, October 1964 (International Atomic Energy Agency, Vienna), Vol. II, pp. 485-501.

Table 1. Count data on uranium L_α X-rays.

mg uranium per ml solution (± 0.1%)	Count time (min)	Mean counts/min in U L_α peak above background[a]	Statistical count error[b]	
			Counts/min	%
265.2	5.0	44800	95	0.2
106.1	5.0	40600	90	0.2
26.52	5.0	29400	77	0.3
10.61	5.0	18100	60	0.3
	5.0	18543	61	0.3
2.652	5.0	6320	36	0.6
	5.0	6283	35	0.6
	5.0	6140	35	0.6
1.061	5.0	2673	23	0.8
	5.0	2673	23	0.8
0.5093	5.0	1293	16	1.2
0.2652	5.0	672	11	1.6
0.1061	5.0	268	7.3	2.7
5.305	5.0	11329	48	0.4
1.698	5.0	4247	29	0.6

a. Mean background from blank run under U L_α peak = 1180. I^{125} source activity ≈ 1.5 Mc.

b. Positioning error of approximately 2% is also present in each run.

Table 2. Count data on thorium L_α X-rays.

mg Th/ml solution (± 0.1%)	Count time (min)	Mean counts/min in Th L_α peak above background[a]	Statistical count error[b]	
			Counts/min	%
26.04	5.0	59900	109	0.2
10.42	5.0	36400	85.4	0.2
5.208	5.0	21100	65.0	0.3
2.604	5.0	11580	48.2	0.4
1.042	5.0	4950	31.4	0.6
0.5208	5.0	2525	22.5	0.9
0.2604	5.0	1167	15.3	1.3
0.1042 (± 0.2%)	5.0	529	10.3	1.9

a. Mean background from blank run under Th L_α peak = 1900 c/min. I^{125} source activity ≈ 1.5 Mc.

b. Positioning error of approximately 2% is also present in each run.

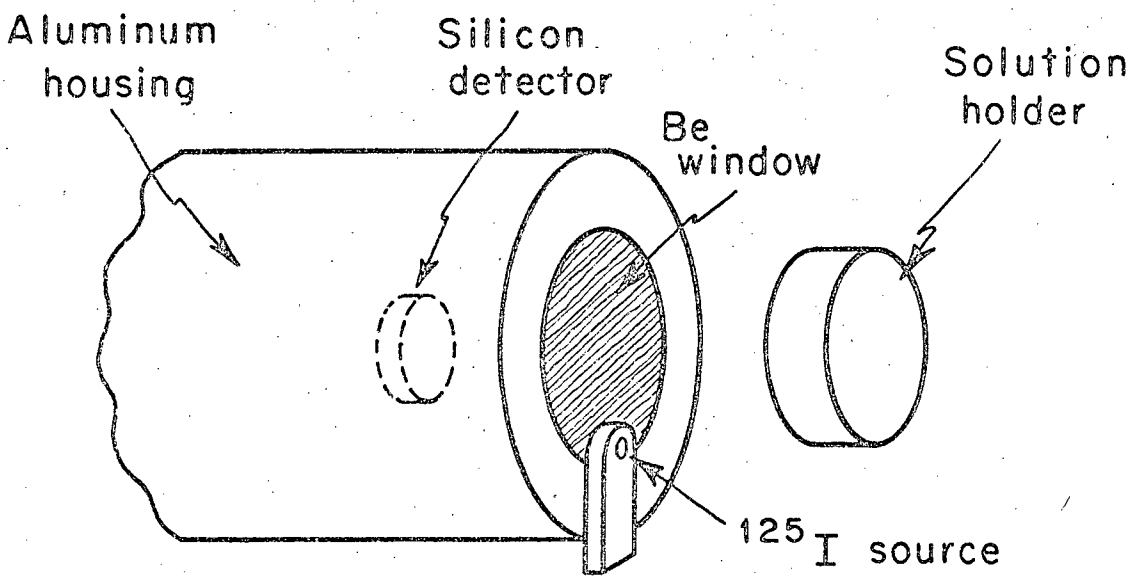
FIGURE CAPTIONS

Fig. 1 Sketch of geometrical relationship of silicon detector (in its housing) with the I^{125} exciting source, and the solution sample holder.

Fig. 2 Uranium L X-ray spectra excited in uranium solutions of three concentrations, 264 mg/cm^2 = 1.1 M, 26.4 mg/cm^2 = 0.11 M, and 2.64 mg/cm^2 = 0.011 M. Counting time = 2 minutes. Bottom curve shows background radiation excited or scattered by blank solution of dilute nitric acid during 2-minute period.

Fig. 3 Calibration curve for uranium analysis constructed from data in Table 1.

Fig. 4 Calibration curve for thorium analysis constructed from data in Table 2.



MUB 13850

Fig. 1

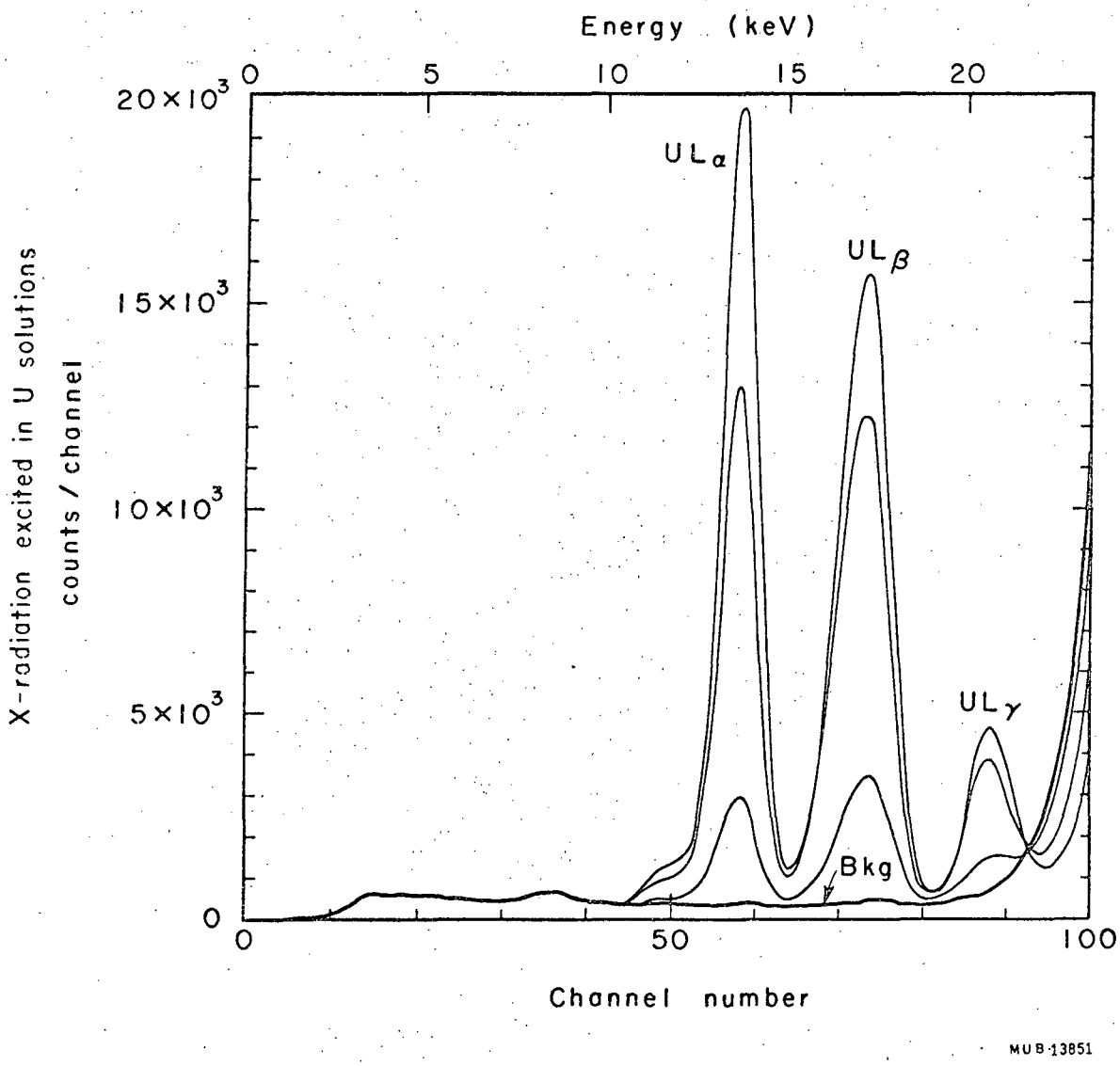
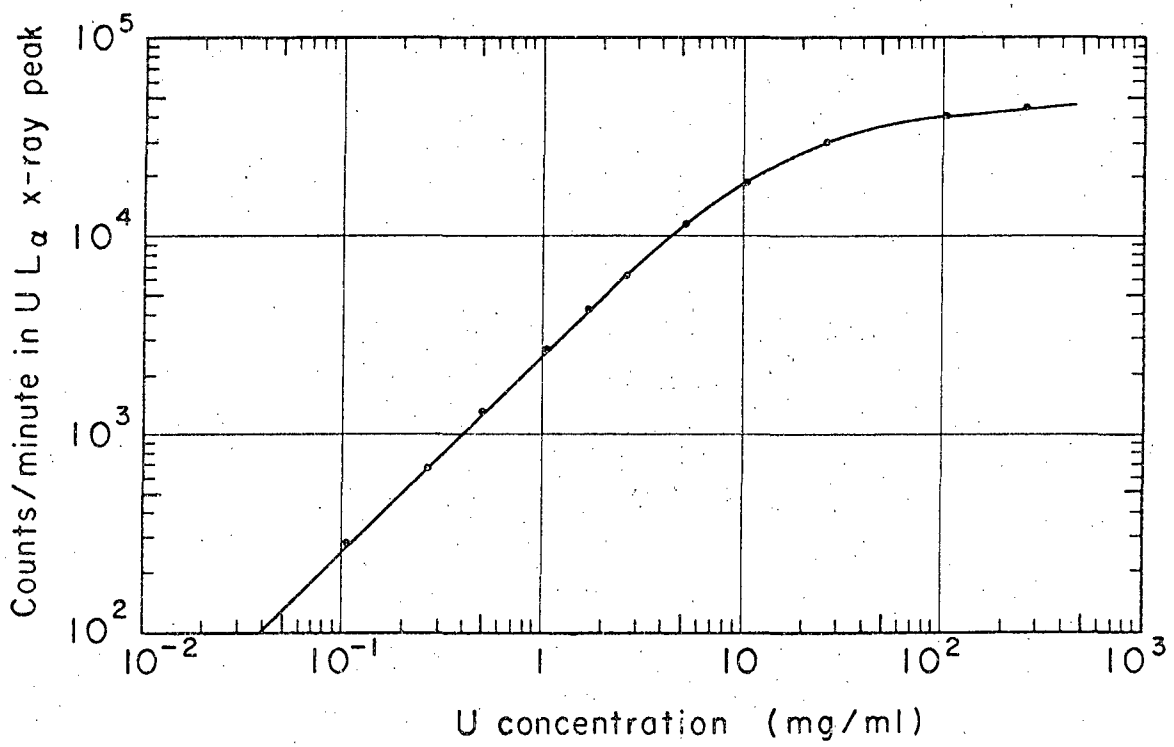

Energy (keV)
0
5
10
15
20
20×10³
15×10³
10×10³
5×10³
0
X-radiation excited in U solutions
counts / channel
ULα
ULβ
ULγ
Bkg
0
50
100
Channel number
MUB-13851

Fig. 2



MUB-13852

Fig. 3

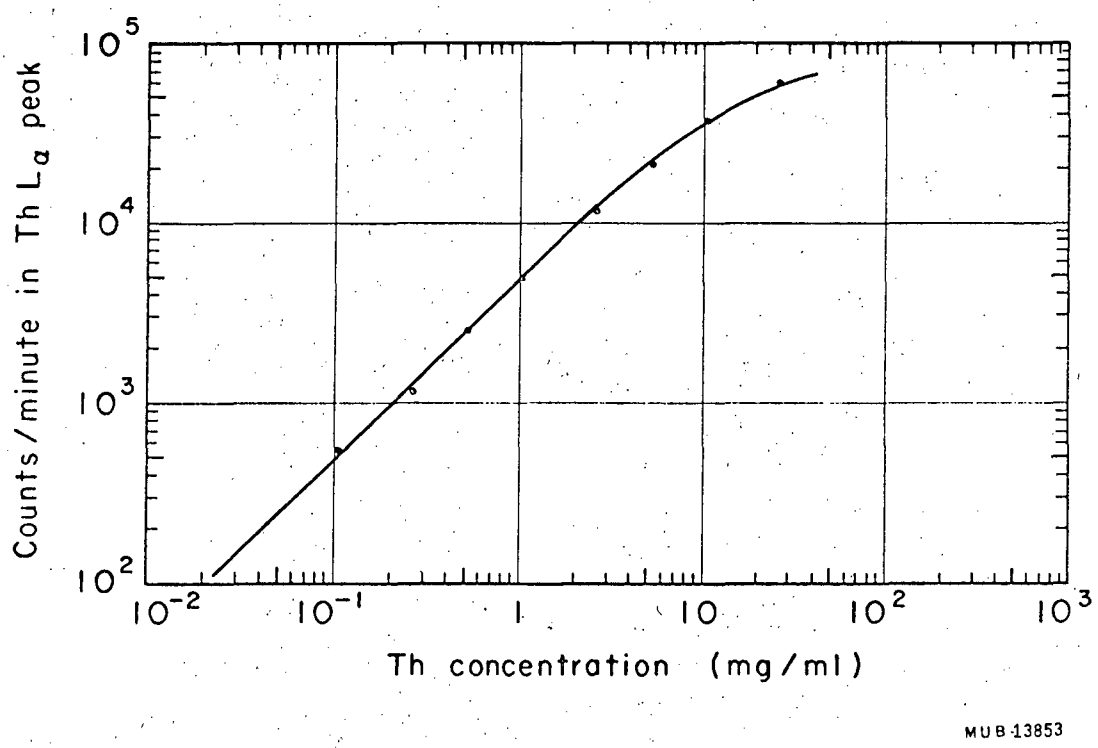

Counts/minute in Th Lα peak
10^5
10^4
10^3
10^2
10^-2
10^-1
1
10
10^2
10^3
Th concentration (mg/ml)
MUB-13853

Fig. 4

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