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THE DETERMINATION OF ULTRATRACE CONCENTRATIONS OF URANIUM AND THORIUM IN NATURAL WATERS BY X-RAY FLUORESCENCE

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ABSTRACT

An x-ray fluorescence method for the simultaneous determination of uranium and thorium at the less than 1-ppm level in natural waters is described. Uranium and thorium are coprecipitated with an internal standard, yttrium, and incorporated into an iron-aluminum hydroxide carrier. The hydroxide precipitate is filtered, and the filter disk is analyzed by the energy-dispersive x-ray fluorescence technique. Matrix interferences caused by the presence of unpredictable anions and cations are compensated for by the internal standard. The U/Y and Th/Y ratios are linear over the 5- to 100- μ g range of interest, and the detection limit of each element on the filter disk is 2 μ g (3 σ). Relative standard deviation was 17% at the 15- μ g and 4% at the 100- μ g level for thorium and 11% at the 11- μ g and 2% at the 100- μ g level for uranium. Analysis of spiked solutions showed a recovery of $19.6 \pm 0.3 \mu$ g for uranium and $19.8 \pm 0.3 \mu$ g for thorium at the 20- μ g level, and the normal lower reporting limit is 5 μ g. Fifty disks can be routinely measured during a normal working day.

INTRODUCTION

This procedure describes a multielement technique for the quantitative determination of uranium and thorium in aqueous solutions. The x-ray fluorescence (XRF) analyzer is used to simultaneously detect characteristic x rays for uranium, thorium, and yttrium generated in a prepared specimen and to compute the concentration of uranium and thorium.

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The accurate determination of trace levels of metallic elements in natural waters has become increasingly important in establishing the effects of metals on biological organisms and the human food chain. X-ray fluorescence methods for the analysis of stream and ground waters for environmental monitoring purposes and to assist in hydrogeological exploration have been reported.¹⁻³ The qualitative detection of U, Th, and Mo in water was reported by Pradzynski,⁴ while preconcentration and XRF analysis of heavy metals in dissolved pharmaceuticals were described by Linder.⁵ These methods require extraction on cellulose exchangers or coprecipitation with organic precipitants. Preparation of water specimens for the method described requires only a simple ammonia gas precipitation and filtration.

This procedure compensates for the inherent sources of error in x-ray fluorescence analysis, which are greatly magnified in microanalytical determinations. The matrix effects caused by unpredictable combinations of cations and anions in surface and ground waters from diverse sources are a particular concern in trace analysis. Requirements for successful quantitative analysis of ng/mL concentrations of uranium and thorium include preconcentration to increase the signal-noise ratio, presentation of a uniform sample to the x-ray beam, elimination of direct line interferences, and compensation for matrix effects. These requirements are met by a simple coprecipitation of the uranium and thorium with an iron-aluminum carrier that also contains yttrium as a demonstrated internal standard element.

EXPERIMENTAL

The carrier internal standard solution was prepared by dissolving appropriate amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and Y_2O_3 in 1 N HNO_3 to obtain a final concentration of 80 μg Y, 100 μg Al, and 300 μg Fe per mL. The calibration standards were prepared by pipetting appropriate volumes of uranium and thorium stock solutions into thoroughly cleaned and acid-rinsed 250-mL beakers that contained 100 mL of deionized water. For this procedure, total standard concentrations of uranium and thorium ranging from 2.6 to 102 μg were utilized. Because a total of 5 μg of uranium and thorium is necessary for analysis, the sample

volumes were adjusted accordingly; 0.5 mL of the carrier internal standard solution was added to each, and the solutions were made acid by addition of 10 drops of concentrated HCl. The specimens were boiled for 20 min to ensure the removal of CO₃, were covered, and were cooled in an ice bath to 40°C. Carbon dioxide-free ammonia gas was prepared by passing compressed air through an Ascarite scrubber and a bottle containing 20 mL of concentrated NH₄OH. This vapor was then bubbled through each specimen until a pH of 8 was obtained. Following the approximately 5 min required for precipitation, the precipitates were vacuum filtered through 25-mm-dia, 0.45- μ m-pore size Millipore membranes, rinsed with methanol, and briefly air dried. Each prepared specimen was placed on a 15- μ m-thick mylar film mounted on an x-ray fluorescence sample cup. A second 15- μ m-thick mylar film was then placed over the specimen filter and clamped in place with a plastic locking ring. The sandwiched specimen was arranged with the precipitate exposed to the x-ray source. The U L _{α 1} (13.613), Th L _{α 1} (12.966), and Y K _{α 1} (14.957) keV emission lines were utilized for analysis.

RESULTS AND DISCUSSION

X-ray tubes or radioisotopic sources can be utilized as the method of excitation. In a test for sensitivity, approximately 2500 net counts were obtained for both 2.6 μ g U and 5.0 μ g Th in 200 s when the exciting source was a 27-kV, 0.37-MA molybdenum x-ray tube. A comparison test using a 50-mCi ¹⁰⁹Cd radioisotope source required 1200 s to accumulate 3000 net uranium or thorium counts. As shown in Table 1, both excitation sources yield comparable results. For improved precision at lowest concentrations, longer counting times or a combination of longer counting times and precipitation of a larger volume of sample may be desirable.

The set of standards provided a linear relationship of U/Y and Th/Y over the 2.6- to 102.0- μ g range for uranium and 5.0- to 98.9- μ g range for thorium. Fig. 1 shows a plot of U/Y and Th/Y standard data using molybdenum tube excitation; a pooled-data uranium and thorium calibration curve is plotted for simplicity. Estimated uranium and thorium values are compared with theoretical values in Table 1. The relative standard deviation was 17%

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Table 1. Comparison of U/Th standards using molybdenum x-ray tube and ^{109}Cd isotopic source excitation

Uranium, μg^a	Uranium concentration estimated from calibration curve, μg^b	
	Mo transmission tube	^{109}Cd isotopic source
2.6	2.2 \pm 1.17	2.3 \pm 1.51
5.1	5.1 \pm 1.16	5.4 \pm 1.50
10.2	10.9 \pm 1.14	11.0 \pm 1.48
20.4	20.7 \pm 1.12	20.9 \pm 1.45
51.0	48.8 \pm 1.11	48.1 \pm 1.44
76.5	77.0 \pm 1.18	76.2 \pm 1.52
102.0	101.5 \pm 1.29	102.5 \pm 1.69

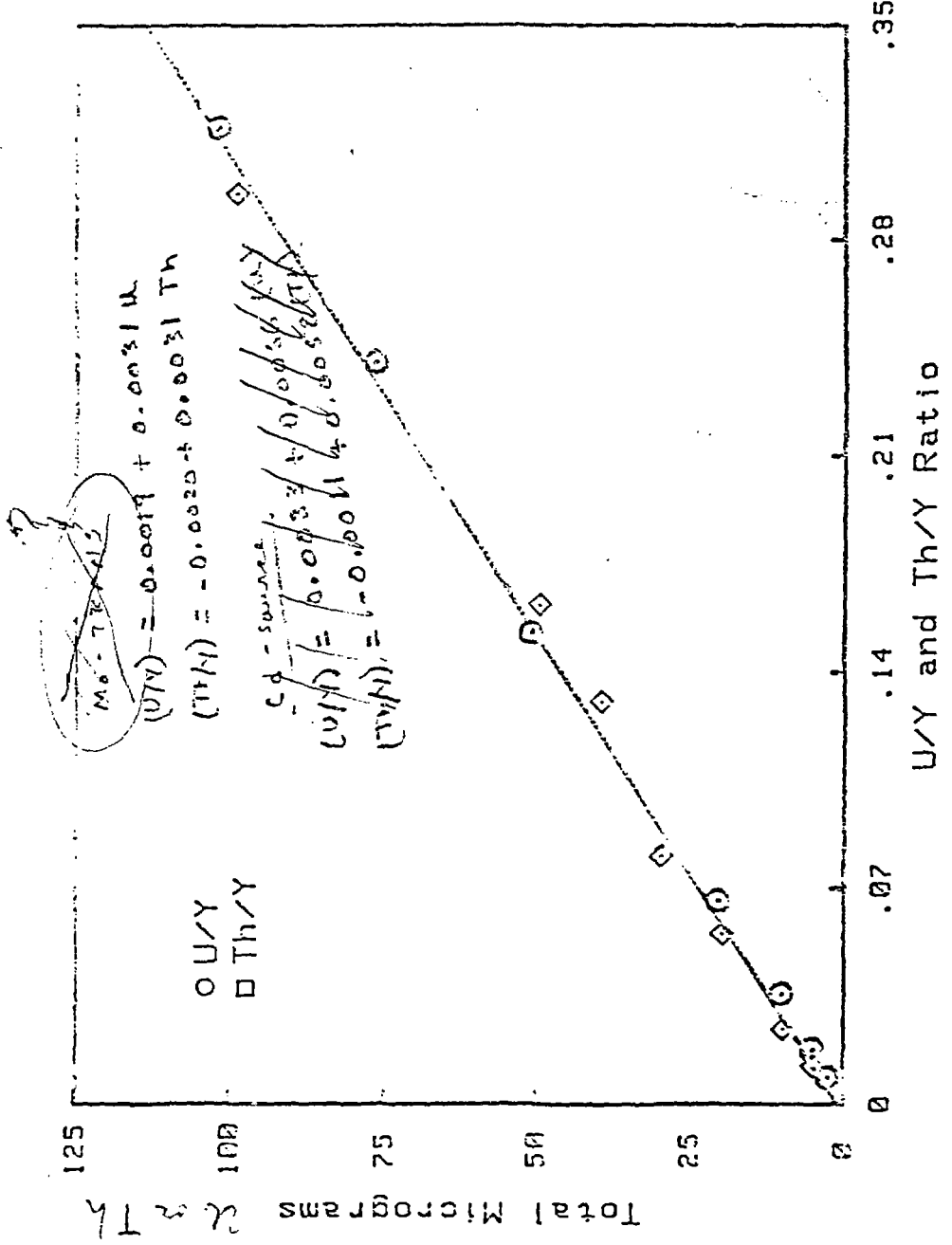
Thorium, μg^a	Thorium concentration estimated from calibration curve, μg^b	
	Mo transmission tube	^{109}Cd isotopic source
5.0	4.7 \pm 3.41	4.5 \pm 3.96
9.9	8.5 \pm 3.37	8.4 \pm 3.89
19.8	18.6 \pm 3.27	18.2 \pm 3.78
29.7	26.7 \pm 3.22	27.3 \pm 3.72
39.6	42.9 \pm 3.21	44.7 \pm 3.72
49.5	53.1 \pm 3.26	53.8 \pm 3.78
98.9	95.9 \pm 3.93	96.7 \pm 4.57

^aConcentrations used to derive the calibration curves.

^bBased on least-squares fit of standard data.

Calibration Curves for Uranium and Thorium with Yttrium Internal Std.

Fig 1



at the 5- μg and 4% at the 100- μg level for thorium and 11% at the 11- μg and 2% at the 100- μg level for uranium. The method was then tested using surface and well water samples from a variety of sources. All samples were divided into two 100-mL sources. One portion was spiked with a known concentration of uranium and thorium (20 μg), and both portions were precipitated and analyzed. In all locations studied, uranium and thorium contents of the unspiked portion were below the detection limit (2 μg). Table 2 details the results obtained from one of these locations. Ten test aliquots were spiked and precipitated. The filter disks were analyzed on successive days. The pooled data showed a spike recovery of $19.6 \pm 0.3 \mu\text{g}$ for uranium and $19.8 \pm 0.3 \mu\text{g}$ for thorium at a 95% confidence interval.

The experiments show that a rapid, multielement XRF analysis of water samples for uranium and thorium is practical and cost effective. Standard filter disks, prepared with uranium and thorium both singly and in combination, demonstrated that there was no interelement effect. The precipitate is washed to remove anions and soluble cations, especially rubidium, to eliminate the possibility of interference by the 13.393 keV Rb $K_{\alpha 1}$ with the 13.612 keV U $L_{\alpha 1}$ line being measured. Should the specimens contain appreciable amounts of Pb, an interference of the Pb $L_{\beta 1}$ line with the Th $L_{\alpha 1}$ line will occur. Computer peak deconvolution will remove the Pb interferent. It is imperative that carbonate, which forms a stable, soluble complex with uranium, be eliminated prior to precipitation. Solubility of uranium and thorium hydroxides becomes significant when sample volumes greater than 500 mL are required to yield approximately 5 μg of heavy metal. When it is necessary to use larger volumes for increased sensitivity, a calibration curve should be prepared using the same volumes of water as will be used for the samples. The method is equally valid for isotopic or x-ray tube excitation and is applicable both to wavelength-dispersive and energy-dispersive instruments.

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 Table 2. U/Th spike recovery, 20 μg spike in well water obtained from one source and analyzed on successive days

Specimen number	Uranium recovered, μg		Thorium recovered, μg	
	Day 1 ^a	Day 2	Day 1 ^a	Day 2
1	19.4	19.6	19.3	19.8
2	18.3	19.7	19.3	21.3
3	19.3	20.1	19.5	19.7
4	19.5	20.2	19.2	20.3
5	19.7	20.6	19.2	20.9
6	18.1	20.0	19.4	20.7
7	19.4	20.8	19.7	20.4
8	19.5	19.3	19.8	20.6
9	19.6	19.7	19.1	19.8
10	19.9	20.1	19.4	18.3
Average	19.3	20.0	19.4	20.2
Standard error (S/\sqrt{N})	0.19	0.14	0.07	0.27
Pooled data average	19.6		19.8	
Pooled std error ($S_p/\sqrt{N_p}$)	0.14		0.16	
95% C.I. (pooled data)	19.6 \pm 0.3		19.8 \pm 0.3	

^aMeasurements between day 1 and day 2 were found to be statistically significant at the 95% level, but the differences were not considered to be of any practical difference.

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LIST OF FIGURES

Fig. 1. Calibration curves for uranium and thorium with yttrium internal standard