Determination of Isotopic and Total Thorium at Ultra-trace Level in Water by α-Spectroscopy and Micro-injection ICP–AES*

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The analytical chemistry of thorium became of great interest for geochemists and environmentalists when it was recognized that Th isotopes could be used as sensitive tools to obtain information about migration processes in nature (e.g. disequilibrium between ^{238}U/^{230}Th as an indicator for U mobilization [1], ^{232}Th as a possible chemical analog for Pu(IV) [2, 3], etc.). Difficulties encountered in their determination are individually very different and depend, as in the case of α-spectroscopy, not only on the specific activity of the isotopes to be measured but also on their environmental 'history'. While it is normally an easy task to analyse ^{228}Th, genetically derived from ^{228}Ra/^{228}Ac, in natural waters, the same task is much more complicated for ^{232}Th for several reasons: (1) the isotope has a very low specific activity (0.0041 Bq per μg); (2) the solubility of Th(IV) can be extremely low (<0.1 ppb [3]); (3) strong radioactive disequilibria between ^{232}Th and ^{228}Th frequently observed in water, cause a significant loss in power of detection for ^{232}Th determination by α-spectrometry, because of the increase in background of the ^{232}Th spectral region due to the presence of ^{228}Th.

Based on the above a proposed new method will be discussed. More details about the experimental protocol, of interest primarily to radioanalytical chemists and emission spectroscopists, will be published elsewhere [4].

Experimental

Preconcentration of Thorium

After collection and filtration (0.45 μm) the water sample (10 to 20 l) is acidified and spiked with ^{234}Th or ^{229}Th tracer. The volume is reduced by evaporation in large glass beakers up to approximately 500 ml and the remaining fraction carefully transferred to a Teflon beaker. After further evaporation and decomposition with $HF/HNO_3/HClO_4$, the residue is dissolved in 20 to 50 ml of HNO_3 (1 M). Thorium is then extracted with 10 ml of TOPO/cyclohexane (0.1 M) and afterwards re-extracted 3 times with 10 ml of H_2SO_4 (0.3 M). From this solution Th(IV) can be directly coprecipitated with lanthanum fluoride (50 μg of La^{3+}) and separated by membrane filtration on a filter (0.2 μm), where previously 100 μg of LaF_3 had been deposited to enable better spectrum resolution. When ^{234}Th has been used as tracer, the β-counting rate of the filter is measured by means of a suitable detector for determination of the overall chemical recovery. An analytical flow-sheet of the procedure, which includes also indications for the analysis of some other elements and samples types, is shown in Fig. 1.

α-Spectrometric Determination of Thorium

The filters are measured by α-spectrometry with the use of surface barrier detectors (300 or 450 mm^2 nominal area) and their activities evaluated by comparison with standard filters, prepared by direct coprecipitation of thorium. Energy resolution (*FWHM*) of the ^{232}Th peak is <80 keV and counting efficiency (2π) typically between 15 and 20%. Examples of spectra are shown in Figs. 2 and 3.

Determination of Thorium by ICP–AES

After α-counting, the filter is carefully calcinated in a platinum crucible, and the residue wet-ashed with some drops of a mixture of $HF/HNO_3/HClO_4$, which is then evaporated to dryness. 1.00 ml of HNO_3 (1 M) is pipetted into the cold crucible, which is then immersed into an ultrasonic bath to promote better Th dissolution. 200 μl aliquots of this solution are injected into an ICP by means of a GMK nebulizer, connected to a peristaltic pump and a small Teflon cup. The analog signal from the analytical emission peak (Th(II) 439.1 nm) is registered by a line recorder. The equipment used in this part of the work was a simultaneous 2m Paschen-Runge spectrometer (Analymat 2502 RSV), optically coupled to a Kontron-1000 ICP source (1.5 kW). Before analysis, all relevant plasma and spectrometer parameters had been carefully optimized [4].

Results and Discussion

Preconcentration of Thorium

All preconcentration steps were separately evaluated by radioactive tracer methods and only some results can be summarized here, 'Extraction' and 'Reextraction' of thorium is nearly quantitative as previously reported by White and Ross [5] and

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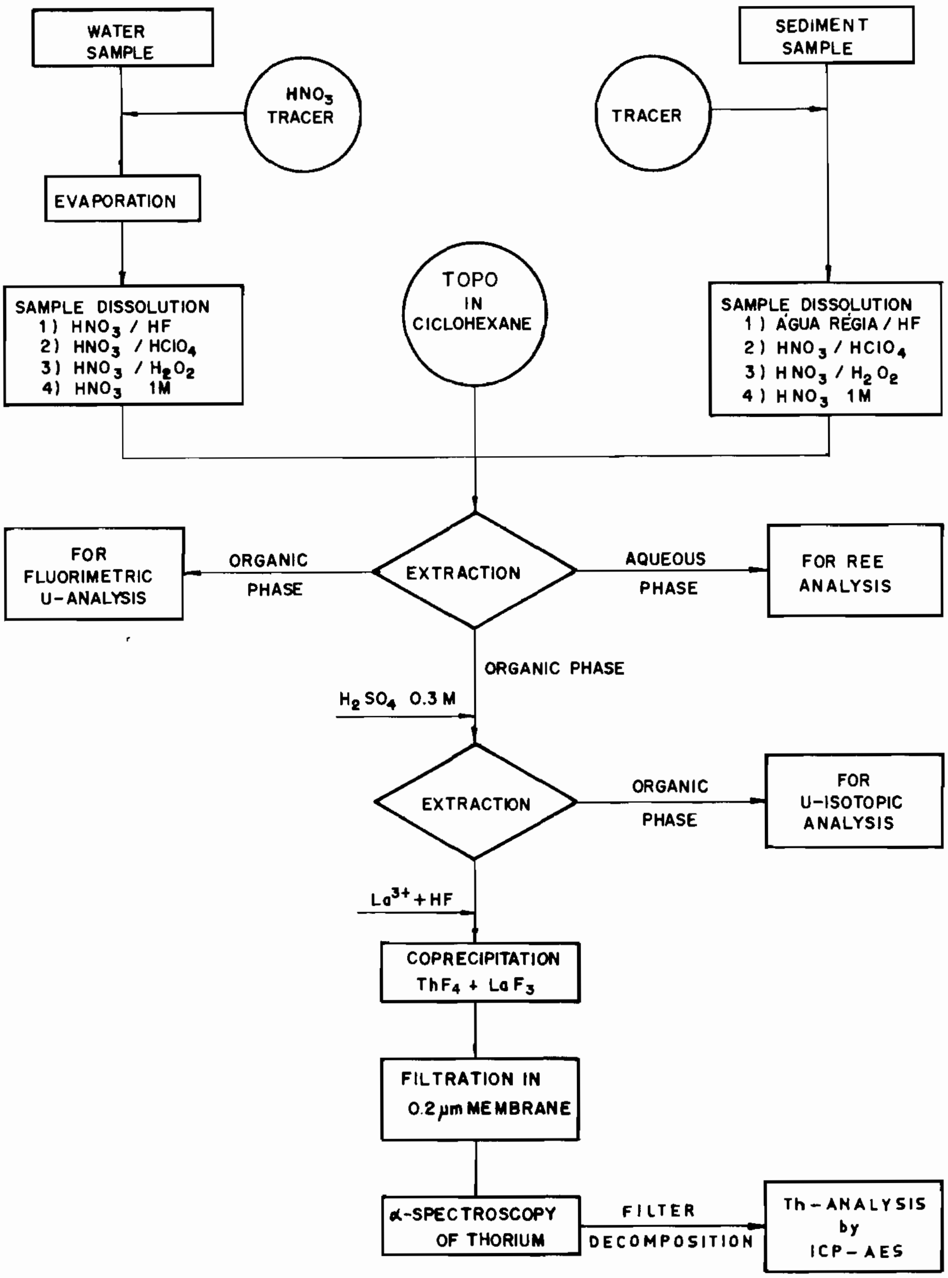

Fig. 1. Flow-sheet of the analytical procedure used for the separation and purification of thorium from water.

confirmed, even for carrier-free radioactive tracer amounts, in this work. 'Coprecipitation' of thorium with LaF_3 is also practically complete (>95%). La^{3+} was used for coprecipitation instead of other more suitable carriers (Ce^{3+}, Nd^{3+}) because of the absence of spectral interferences of this element with the Th(II) 439.1 nm line [6]. Extraction as well as reextraction and coprecipitation steps provide sufficient separation of Th^{4+} from other elements normally present in environmental samples, to exclude interferences in α-spectroscopy (e.g. by U) and ICP–AES (e.g. REE [6]). The precision of the whole procedure, including α-spectrometric determination of Th, was determined with 20 l-aliquots of a 'real' water sample and the results are summarized in Table I. Taking into account the very low ^{232}Th concentration of the sample (0.076 μg/l) and the complex nature of the analytical procedure, the relative standard deviation (*RSD*) obtained of 11% can be considered as very satisfactory. Analysing four other water aliquots by use of an entirely different and much more time consuming procedure for Th

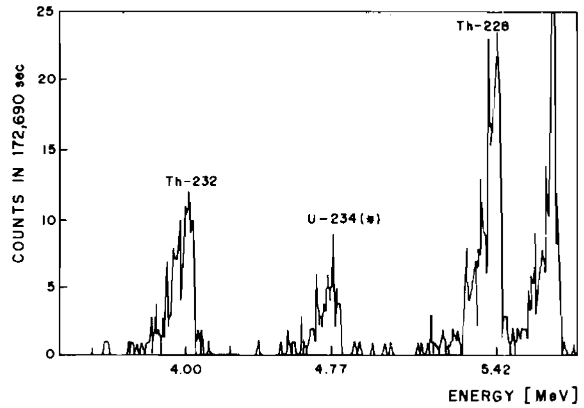

Fig. 2. Example of an α-spectrum of a processed water sample with low $^{228}Th/^{232}Th$ activity ratio (1.8), showing low background near the ^{232}Th peak region. (Sample: Morro do Ferro, Brazil, 0.055 μg/l of ^{232}Th; *contribution from the tracer.)

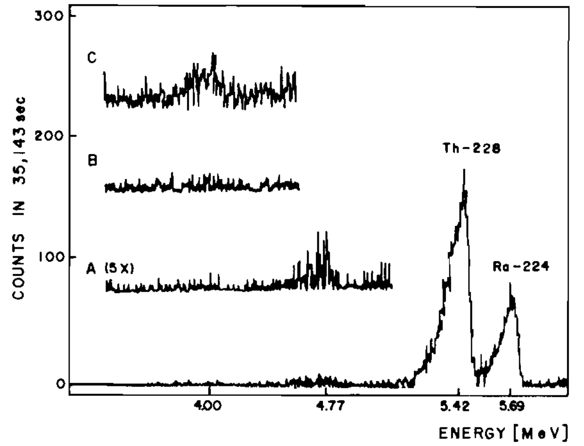

Fig. 3. Examples of α-spectra of processed water samples with high $^{228}Th/^{232}Th$ activity ratios, showing the increase in 'background' due to ^{228}Th. (Samples from the Morro do Ferro, Brazil.) (A) Ground water; activity ratio (*AR*) of ^{228}Th to ^{232}Th 298; 1.2 μg of ^{232}Th on the filter; water volume 19.6 l; counting time 35 143 s. (B) Ground water; *AR* = 325; volume 15 l, 1.9 μg of ^{232}Th on the filter; counting time 15 828 s. (C) Ultraconcentrate of a ground water sample; *AR* = 295; 4.0 μg of ^{232}Th on the filter; counting time 84 425 s.

separation and purification [7], the results agreed within the limits of *RSD*, indicating that the accuracy of our simplified method is also acceptable.

α-Spectrometric Determination of Thorium

Coprecipitation with LaF_3 was shown to be an excellent method for final concentration of Th^{4+} and counting sample preparation. This technique was first proposed by Lieberman [8] for α-spectroscopy. Figure 2 represents a typical α-spectrum of a surface water sample processed by our method, showing well defined peaks and permitting unambiguous determination of the corresponding activities.

TABLE I. Analytical Results on Replicate Thorium Determinations in 20 l Aliquots of a Surface Water Sample from Morro do Ferro, Brazil

Aliquot No.	^{232}Th (μg/l ± (σ))	
	This method	Modified Sill method [7]
1	0.073(0.009)	0.064(0.010)
2	0.083(0.009)	0.064(0.004)
3	0.083(0.012)	0.050(0.009)
4	0.065(0.012)	0.074(0.009)
mean	0.076(0.009)	0.063(0.010)

The limit of detection (*LD*) for α-spectrometric determination of ^{232}Th depends not only on the detector/blank background (*BG*) (1–4 counts per 40 ks, in our case) but, also on the ^{228}Th to ^{232}Th ratio of the sample. This can be seen in Fig. 3, which represents spectra of three water samples with high ^{228}Th activities as compared with ^{232}Th. 'Background' in the ^{232}Th peak region increases as much as 60 times when the $^{228}Th/^{232}Th$ ratio increases from about 1.8 (Fig. 2) to 295 (Fig. 3, sample C), obscuring the ^{232}Th peak almost completely. Assuming that a 20 l sample was processed and considering other experimental parameters (e.g. chemical recovery 80%, sensitivity of the calibration curve (*S*): 24.1 counts per 40 ks and μg of ^{232}Th), this increase in 'background' causes a reduction of the *LD* (defined according to Currie [10]: $LD\ (\mu g) = (2.71 + 4.65\sqrt{BG})/S$) from 0.015 μg/l to 0.065 μg/l in the original water. (In this example *BG* was taken as 1 and 60 counts, respectively. *S* refers to an ORTEC BR-21-300-100 detector).

Determination of Thorium by ICP–AES

Filters with a known amount of ^{232}Th (2 μg), coprecipitated with LaF_3, were decomposed, dissolved in 1.00 ml of HNO_3 (1 M) and then analysed by the above mentioned ICP technique, together with standard Th solutions. Results are summarized in Fig. 4(a) and 4(b) and show that the dissolution procedure is reproducible (and quantitative) as well as the injection and signal generation procedure. A minor positive contribution from La to the Th emission peak was observed but, as this element is always in a constant concentration within the injected volume (30 μg/200 μl), its influence can be corrected by using Th standard solutions in which lathanum is present as the matrix element.

Figure 5 shows ICP signal recordings from two filters (A and B) whose α-spectra are presented in Fig. 3, as well as those from Th standards, which are injected consecutively to compensate for small

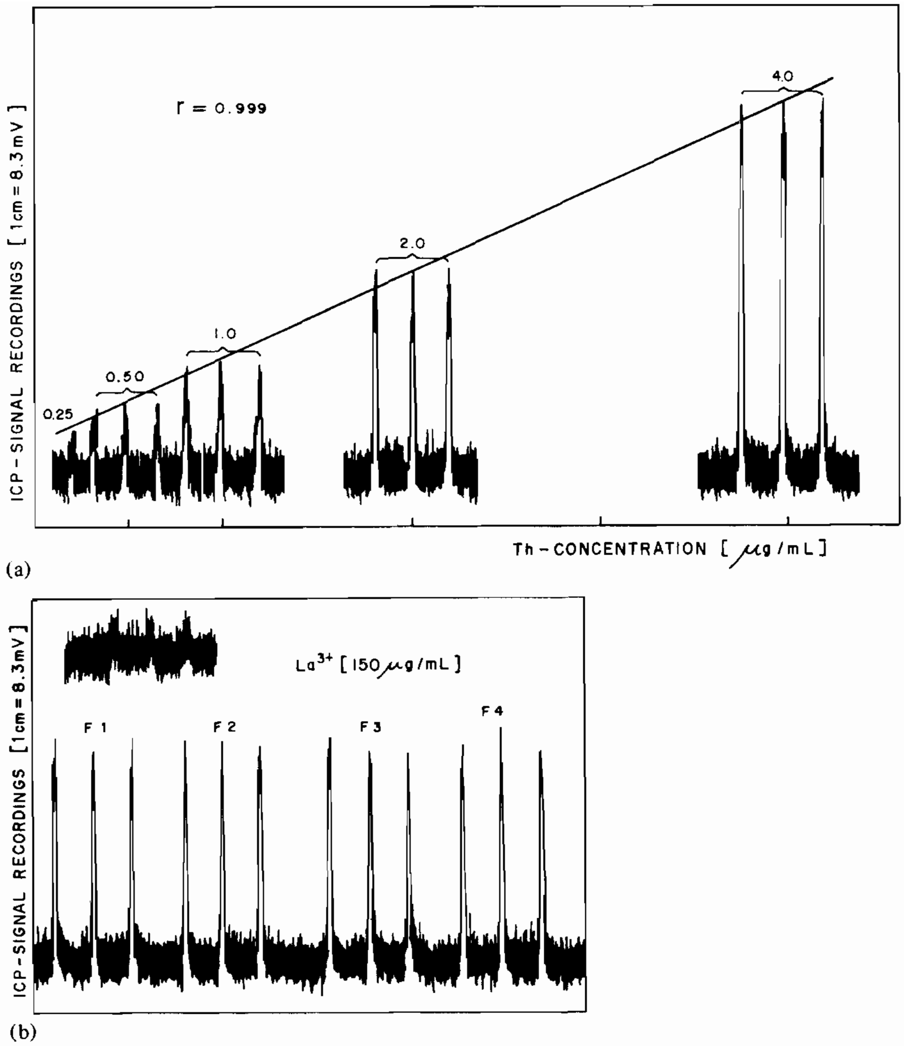

Fig. 4. Recordings of ICP signals caused by injection of 200 μl of solutions with different Th concentrations. (a) Repeated injections of standard Th solutions (μg/ml). (b) Signals from 4 dissolved filters (2 μg of Th) showing the reproducibility of the dissolution and injection procedure (*RSD* = 3%). In the left upper corner: signals when 150 μg/ml of La^{3+} are injected, causing a small positive contribution to Th peak height.

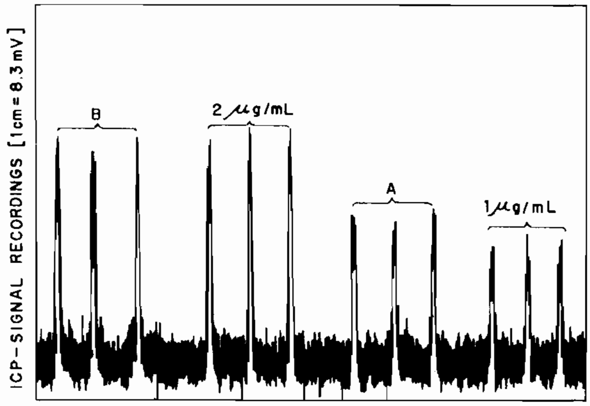

Fig. 5. Recordings of ICP signals from counting filter A and B (Fig. 3) and from standard Th soltuions.

variations in the plasma excitation conditions. The superiority of the signal to background ratio (*S*/*BG*) of the ICP technique as compared to α-spectroscopy can clearly be seen (e.g. sample C: *S*/*BG* (ICP) = 8; *S*/*BG* (α) = 2.4) and this feature, finally permitted accurate analysis of ^{232}Th in these samples. The 'practical' *LD* for thorium is at present 0.25 μg per filter (0.05 μg injected into the plasma), which corresponds to about 0.016 μg/l for the original water (20 l). This compares well with the *LD* of α-spectroscopy when a sample with low activity ratio of ^{228}Th/^{232}Th is analysed.

The method is being used also for different environmental matrices (e.g. plant ash) and presently adapted for the sequential analysis of other elements at ultra-trace level (e.g. U, REE).

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References

1 J. N. Rosholt, *J. Geophys. Res.*, *88* (B9), 7315 (1983).
2 D. G. Brookins, 'Geochemical Aspects of Radioactive Waste Disposal', Springer Verlag, New York, 1984, p. 2.
3 N. Miekeley and I. L. Küchler, *Inorg. Chim. Acta*, *140*, 315 (1987).
4 Manuscript in preparation.
5 J. C. White and W. J. Ross, *ORNL-2498*, 1968.
6 P. W. J. M. Boumans, 'Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectroscopy', Pergamon, Oxford, 1980, Table 726B.
7 M. G. R. Vale, *Masters Thesis*, Department of Chemistry, Pontifical Catholic University of Rio de Janeiro, Brazil, 1982.
8 R. Lieberman and A. A. Moghissi, *Health Phys.*, *15*, 359 (1968).
9 L. A. Currie, *Anal. Chem.*, *40* (3), 586 (1968).