TRACE DETERMINATION OF URANIUM AND THORIUM IN BIOLOGICAL SAMPLES BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

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Abstract

Radiochemical neutron activation analysis (RNAA) is an excellent method for determining uranium and thorium; it offers unique possibilities for their ultratrace analysis using selective radiochemical separations. Regarding the favourably sensitive nuclear characteristics of uranium and of thorium with respect to RNAA, but the different half-lives of their induced nuclides, two different approaches were used. In the first approach uranium and thorium were determined separately via ^{239}U, ^{239}Np and ^{233}Pa. In the second approach these elements were determined simultaneously in a single sample using ^{239}U and/or ^{239}Np and ^{233}Pa. Isolation of induced nuclides was based on separation by extraction and/or anion exchange chromatography. Chemical yields were measured in each sample aliquot using added ^{235}U, ^{238}Np and ^{231}Pa radioisotopic tracers.

Introduction

Accurate and reliable data on microgram and nanogram quantities of some essential and toxic elements in most environmental samples are still scarce. Neutron activation analysis (NAA) offers important advantages for analysis of trace and minor elements due to its inherent characteristics, such as matrix independence, virtual freedom from blank problems and specificity. Data on the low levels of uranium and especially thorium present in different biological samples are few and variable. Radiometric methods based on alpha spectrometry are very time-consuming, need large samples and are limited by reagent blanks. Radiochemical neutron activation analysis (RNAA) is an excellent method for determining low concentrations of uranium and thorium due to its high sensitivity and virtual freedom from blank problems.

When uranium and thorium are irradiated in a reactor the following capture reactions are induced:

$$^{238}\mathrm{U}(n,\gamma)\,^{239}\mathrm{U}\ (t_{1/2} = 23.5\ \mathrm{min}) \rightarrow\ ^{239}\mathrm{Np}\ (t_{1/2} = 2.35\ \mathrm{d}) \rightarrow$$

$$^{232}\mathrm{Th}(n,\gamma)\,^{233}\mathrm{Th}\ (t_{1/2} = 22.3\ \mathrm{min}) \rightarrow\ ^{233}\mathrm{Pa}\ (t_{1/2} = 27.0\ \mathrm{d}) \rightarrow$$

Non-destructive simultaneous analysis of uranium and thorium by gamma spectrometry of ^{239}Np and ^{233}Pa in biological samples is possible if the sample contains more than about 30 μg kg^{-1} of uranium and more than 50 μg kg^{-1} thorium, depending on the matrix. For trace concentrations radiochemical separations of the induced nuclides ^{239}U and ^{233}Th or their daughters ^{239}Np and ^{233}Pa are necessary. In this work radiochemical separations following wet-ashing were based on solvent extraction and ion-exchange. The destruction of samples and the separation conditions were experimentally studied by the use of radioactive tracers. These were also used in every analysis, allowing the chemical yield to be determined for each

sample. The recovery factor often makes the most important contribution to the uncertainties of the result, so an accurate and precise recovery is of great importance to the quality of the results.

Experimental

Sample preparation:

Materials were weighed and sealed into polythene ampoules that had been cleaned by soaking for several hours in 7M nitric acid, rinsing well, and then dried. The sealed ampoules were further encapsulated in polythene foil to avoid superficial contamination during irradiation and handling. The sample weights ranged from 250 mg to 1 g for the lowest uranium and/or thorium concentration.

For the lowest thorium concentration (< 1 μg kg^{-1} dry weight) the samples were pre-ashed at 500°C in porcelain crucibles. The weight of the sample used was approximately 4-5 g dry weight.

Irradiations:

Samples were irradiated in the Institute's TRIGA Mark II reactor at different neutron fluence rates. For uranium determination via the short-lived radionuclide ^{239}U samples were irradiated in the pneumatic tube (rabbit system) at a neutron fluence rate of 4×10^{12}n cm^{-2} s^{-1} for a few minutes (exceptionally up to 30 min) with a uranium standard. For uranium and thorium determination (> 1 μg kg^{-1}) via the long-lived radionuclides ^{239}Np and ^{233}Pa dried samples were irradiated at a thermal fluence rate of 2×10^{12}n cm^{-2} s^{-1} for up to 40 h with uranium and thorium standards. Ashed samples with a low concentration of thorium (< 1 μg kg^{-1}) were irradiated for up to 200 h with an evaporated thorium standard at a neutron fluence rate of 4×10^{12}n cm^{-2} s^{-1}, or 1×10^{13}n cm^{-2} s^{-1} in the central channel of the reactor.

For simultaneous determination of uranium and thorium using the double irradiation, LICSIR technique [1], samples were first irradiated (40 - 200 h) with a thorium standard. The irradiated sample was "cooled" for up to a month. Those samples which had been weighed and irradiated in polythene ampoules, were re-irradiated in the same ampoules. Ashed samples irradiated in quartz ampoules were transferred to polythene ampoules for the second, short irradiation. In this the ash or sample was irradiated up to 30 min with a uranium standard.

Radiochemical procedure:

Determination of uranium via the short-lived ^{239}U ($t_{1/2}$= 23.5 min, Eγ = 74.7 keV) nuclide was based on solvent extraction with 50 % tri-n-butyl phosphate (TBP) in toluene from 5 M HNO_3 following rapid conventional wet-ashing [2,3,4]. The organic phase was cleaned up with two washes of 5 M HNO_3 containing 0.2 % HF [5]. This small amount of HF was very effective in improving the radiochemical purity by removing traces of radionuclides other than those of uranium. The clean-up washes containing HF not only substantially reduce the Compton background but are also very effective in stripping REE nuclides, ^{234}Th, ^{231}Th and ^{234}Pa, the γ-emitting progeny in radioactive equilibrium with the added natural uranium carrier. The chemical yield was measured from the 185.7 keV peak of ^{235}U in the carrier.

Determination of uranium via the long-lived ^{239}Np ($t_{1/2}$= 2.35 d, Eγ = 277.6 keV) daughter was based on separation by anion exchange. This nuclide allowed use of lengthier dissolution procedures employing total decomposition with hydrofluoric acid. Nanogram quantities of ^{237}Np were irradiated simultaneously with the sample and an aliquot of the resulting solution

containing ^{237}Np and ^{238}Np ($t_{1/2}$ = 2.2 d, Eγ = 984.4, 1026 and 1028.5 keV) was added prior to sample destruction, these isotopes serving as carrier and yield tracer, respectively [6].
For Th, after three weeks cooling, irradiated samples were quantitatively transferred to Kejdahl flasks and then samples were dissolved in nitric and perchloric acid, and in the case of botanical samples, with addition of hydrofluoric acid. Pa extraction was carried out with 5 % tri-n-octyl phosphine oxide (TOPO) in toluene from 6 M HNO_3. The chemical yield of ^{233}Pa for thorium determination was measured from the γ-spectrum of the separated protactinium fraction via the 283.6 or 329 keV peaks of the added ^{231}Pa radioisotopic tracer [6].

Counting:
Gamma ray spectrometry was performed in a HP Ge well-type detector connected to Canberra MCA by Genie-2000 Software.

Results and discussion
The neutron-capture reaction ^{238}U(n,γ) ^{239}U $\rightarrow$ ^{239}Np $\rightarrow$ and successive beta decay offer two possibilities for RNAA of uranium, by use of either the short-lived ^{239}U or its longer lived ^{239}Np daughter. The methods for uranium alone, based on a single short (^{239}U) and long irradiation (^{239}Np) of the sample, have been thoroughly tested by the analysis of certified reference materials are shown in Table 1.

Table 1: Concentration of uranium in μg kg^{-1}dry weight in biological materials

Sample	U (μg kg^{-1})		Certified or literature[ ] value
	via ^{239}U*	via ^{239}Np*	
NBS SRM-1571 Orchard Leaves	24 ± 2 (6)	29 ± 2 (6)	29 ± 5
NBS SRM-1575 Pine Needles	15 ± 1 (6)	18 ± 1 (6)	20 ± 4
NBS SRM-1566 Oyster Tissue	114 ± 2 (6)	123 ± 7 (6)	116 ± 6
IAEA H-5 Animal Bone	12 ± 1	12 ± 1 (6)	-
IAEA CRM H-9 Mixed Human Diet	4.9 ± 0.2 (5)	5.3 ± 0.2 (5)	5.0 ± 0.6[8]
NBS SRM-1577a New Bovine Liver	0.70 ± 0.04		0.71 ± 0.03
IAEA CRM H-13 Animal Blood	0.19 ± 0.03 (6)		
NBS RM 8414 Bovine Muscle	0.085 ± 0.007 (6)		

* mean ± standard deviation, number of determination in parentheses

Due to weak gamma ray emission of the ^{233}Th nuclide, the neutron-capture reaction ^{232}Th(n,γ) ^{233}Th $\rightarrow$ ^{233}Pa $\rightarrow$ represents the most sensitive method of determination at trace levels of thorium via the long-lived ^{233}Pa nuclide. The limit of detection for a 200 h irradiation is about 20 ng kg^{-1}. The method for Th alone, based on a long irradiation of the sample, has been tested by the analysis of certified reference materials, as shown in Table 2.

Table 2: Concentration of thorium in μg kg^{-1}dry weight in biological materials

Sample	Th (μg kg^{-1})*	Certified or literature value
NBS SRM 1570 Spinach	102 ± 13 (8)	120 ± 30
NBS SRM-1571 Orchard Leaves	60 ± 2 (5)	64 ± 6
NBS SRM-1575 Pine Needles	34 ± 3 (6)	37 ± 3
IAEA CRM H-9 Mixed human diet	1.2 ± 0.3 (5)	1.9 ± 0.9[8]
IAEA CRM H-13 Animal Blood	0.54 ± 0.02 (3)	
NBS SRM-1567a Wheat Flour	1.4 ± 0.5 (3)	

* mean ± standard deviation, number of determination in parentheses

Simultaneous determination of uranium and thorium in a single sample is possible via the long lived ^{239}Np and ^{233}Pa nuclides. Separation of the induced nuclides was based on ion exchange and solvent extraction. The chemical yield was determined by the isotopic tracers ^{238}Np and ^{231}Pa. Determination of uranium via long-lived ^{239}Np offers lower sensitivity and the limit of detection is higher than whwn using ^{239}U. The problem in the case of this method (^{239}Np) is overlapping the peaks of protactinium isotopes and ^{239}Np. ^{239}Np gamma lines at 285.4 keV (0.77%), 315.8 keV (1.6 %) and 334.3 (2.0 %) interfere with ^{233}Pa line at 311.7 keV and ^{231}Pa lines at 283.6 and 329 keV. Another possibility is to measure twice; first for neptunium and then the protactinium fraction after one month of cooling.

The nuclear characteristics of uranium and thorium are favourable, but the half-lives of their induced nuclides ^{239}U ($t_{1/2}$ = 23.5 min) and ^{233}Pa ($t_{1/2}$ = 27.0 d) are very different. For their simultaneous determination in a single sample, a method was developed based on a technique known LICSIR (**L**ong **I**rradiation, **C**ooling, **S**hort **I**rradiation, **R**adiochemistry) in which a double neutron irradiation is employed. In the first long irradiation ^{233}Pa is induced by neutron capture on ^{232}Th and then the samples "cooled"for several weeks. A second short irradiation to induce ^{239}U is followed by a rapid sequential radiochemical separation by solvent extraction of uranium with TBP and protactinium with TOPO. Chemical yields of ^{239}U and ^{233}Pa were measured in each sample aliquot using added ^{235}U and ^{231}Pa radioisotopic tracers. Table 3 shows results obtained from the combined method for uranium and thorium simultaneously in a single sample. As is evident from the table, the results from the combined approach are in good agreement with the certified values and the results obtained for uranium or thorium when determined alone (Table 1, 2).

Table 3: Concentration of uranium and thorium found in biological samples by LICSIR technique in μg kg^{-1} dry weight

Sample	Uranium		Thorium	
	Found*	Certified value	Found*	Certified value
NBS SRM-1571 Orchard Leaves	26 ± 1 (3)	25 ± 5	59 ± 5 (3)	64 ± 6
NBS SRM-1575 Pine Needles	18 ± 1 (6)	20 ± 4	32 ± 2 (69	37 ± 3
NBS SRM-1547 Peach Leaves	14 ± 1 (4)	(15)	50 ± 4 (4)	(50)
NBS SRM-1515 Apple Leaves	7 ± 1 (6)	(6)	37 ± 3 (6)	(30)
NBS SRM-1577a New Bovine Liver	0.68 ± 0.03 (3)	0.71 ± 0.03	0.64 ± 0.05	
NBS SRM-1567a Wheat Flour	0.28 ± 0.05 (6)		1.7 ± 0.3 (6)	
IAEA CRM H-9 Mixed human diet	4.8 ± 0.1 (4)	5.0 ± 0.6[8]	1.8 ± 0.8 (4)	1.9 ± 0.9 [8]

* mean ± standard deviation, number of determination in parentheses

All the methods developed were validated by quality control analysis with standard reference materials. The high chemical yields, more than adequate purity of the gamma spectra and good reproducibility of the results show the suitaibility of the methods developed for the single and simultaneous determinations of uranium and thorium. Using ^{239}U nanogram and picogram (L.o.D. 1-2 pg g^{-1}) quantities can be determined [9,10,11].The methods was also tested by the standard addition techniques at ultra trace level [12].

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