*Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 189, No. 2 (1995) 325–331*

# SIMULTANEOUS DETERMINATION OF TRACE URANIUM AND THORIUM BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

L. BENEDIK, A. R. BYRNE

*"Jožef Stefan" Institute, University of Ljubljana, Jamova 39, P.O. 100, SLO-61111 Ljubljana (Slovenia)*

(Received October 21, 1994)

A method for the simultaneous, radiochemical neutron activation analysis of uranium and thorium at trace levels in biological materials is described, based on a technique known as LICSIR, in which a double neutron irradiation is employed. In the first, long irradiation $^{233}$Pa (27.0 d) is induced by neutron capture on $^{232}$Th and then the sample is cooled for several weeks. A second short irradiation to induce $^{239}$U (23.5 m) is followed by a rapid sequential radiochemical separation by solvent extraction of $^{239}$U with TBP and $^{233}$Pa with TOPO. Chemical yields of $^{239}$U and $^{233}$Pa were measured for each sample aliquot using added $^{235}$U and $^{231}$Pa tracers from the $\gamma$-spectra of the separated fractions. The technique was validated by quality control analyses.

Data on the low levels of uranium and especially thorium present in different biological samples are scarce 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 U and Th due to its high sensitivity and virtual freedom from blank problems.

Thorium is almost always determined in NAA from $^{233}$Pa (27.0 d) produced on neutron irradiation by $^{232}$Th(n, $\gamma$)$^{233}$Th$\rightarrow$$^{233}$Pa, since $^{233}$Th (22.3 m) offers lower sensitivity and a short half-life. Uranium, and uranium with thorium, is often determined via $^{239}$Np (2.35 d) via the reaction $^{238}$U(n, $\gamma$)$^{239}$U (23.5 m)$\rightarrow$$^{239}$Np. However, difficulties in determining the chemical yields of $^{239}$Np and $^{233}$Pa remain due to lack of suitable $\gamma$-emitting radioisotopes of Np and Pa. Thus they are usually measured in prior tracer experiments and assumed to remain constant, which can lead to errors. On the other hand, for determination of uranium, $^{239}$U offers increased sensitivity under normal irradiation conditions, especially if a well-type detector is used for the 74.7 keV $\gamma$-rays of $^{239}$U, as well as being more rapid. For example, using $^{239}$U, nanogram[2–5] and picogram[5,6] (L.o.D. 1–2 pg $\cdot$ g$^{-1}$) quantities can be determined.

In the present work, this $^{239}$U approach using selective TBP extraction ($F^-$ is used as a masking reagent) and determination of the chemical yield from the 185.7 keV peak of $^{235}$U from the added uranium carrier,[5,6] was combined with a determination of Th via a long prior irradiation to induce $^{233}$Pa. After cooling for 2–3 weeks, a second short

*Elsevier Science S. A., Lausanne*
*Akadémiai Kiadó, Budapest*

irradiation is followed immediately by a rapid sequential radiochemical separation of $^{239}U$ and then of $^{233}Pa$, from the solubilized sample. Chemical yields were measured in the two fractions using the tracers $^{235}U$ (185.7 keV $\gamma$-ray) and $^{231}Pa$ (27.4 keV or 283.6 keV $\gamma$-rays), their count rates being obtained from the $\gamma$-spectra of the separated fractions used for quantitation of $^{239}U$ (74.7 keV) and $^{233}Pa$ (311.8 keV).

## Experimental

On the basis of tracer experiments and our previous experience with radiochemical determinations for uranium,[5,6] a simple and rapid radiochemical separation for simultaneous sequential determination of uranium as $^{239}U$ and thorium as $^{233}Pa$ in different biological samples using solvent extraction was developed, using tri-n-butyl phosphate (TBP) for uranium while masking protactinium with added $F^-$ ion, followed by protactinium extraction with tri-n-octyl phosphine oxide (TOPO) after complexing $F^-$ with borate.

*Reagents and materials:* Standard solutions: 1 $\mu g \cdot g^{-1}$ uranium in 1% v/v nitric acid; 7 $\mu g \cdot g^{-1}$ thorium in 1% v/v nitric acid; 50% (v/v) solution of tri-n-butyl phosphate (TBP) in toluene; 5% (w/v) solution of tri-n-octylphosphine oxide (TOPO) in toluene; 6M $HNO_3$, 6M $HNO_3$/0.2% HF; conc. $HNO_3$, $HClO_4$, 9M $H_2SO_4$; $^{235}U$ solution (50 mg of natural $U \cdot ml^{-1}$ gives ~6.5 cps in the 185.7 keV peak on a well-type HP Ge detector); $^{231}Pa$ tracer solution; purchased from AEA Technology, Harwell, UK. This was diluted to give a solution containing about 10 cps per gram at the 283.6 keV peak in the well-type detector.

*Sample preparation:* Materials in the as-received state 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 longer, higher fluence irradiations (if the concentration of thorium in the sample was around or less than 1 $\mu g \cdot kg^{-1}$), samples were weighed into cleaned silica vials and pre-ashed before irradiation in the same vial. The temperature of the furnace was raised slowly over several hours to 500 °C and left for 2 days. The weight of the sample used was approximately 1.5–2 g dry weight.

*Irradiations:* Samples were irradiated in our TRIGA Mark II reactor at different neutron fluence rates depending on the uranium and thorium concentration.

Normally samples were irradiated in polythene ampoules at a thermal neutron fluence rate of $2 \cdot 10^{12}$ n $\cdot$ cm$^{-2} \cdot$ s$^{-1}$ for up to 40 hours with thorium standard (~700 ng). The irradiated sample was cooled for several weeks.

Ashed samples with a low concentration of thorium were irradiated in quartz for 1 week at a neutron fluence of $4 \cdot 10^{12}$ n $\cdot$ cm$^{-2} \cdot$ s$^{-1}$ or $1 \cdot 10^{13}$ n $\cdot$ cm$^{-2} \cdot$ s$^{-1}$ and also cooled for several weeks

Then the cooled samples were irradiated at a neutron fluence rate of $4 \cdot 10^{12}$ n $\cdot$ cm$^{-2} \cdot$ $\cdot$ s$^{-1}$ for up to 30 minutes with a uranium standard (~100 ng) to induce the neutron capture product $^{239}$U. The samples which had been weighed 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.

*Radiochemical procedure:* The irradiated sample was rapidly wet-ashed over a gas flame in a 100 ml long-necked silica Kjeldahl flask already containing 3 ml of 9M sulphuric acid, 50 mg of U and $^{231}$Pa tracer solution, by heating with repeated addition of concentrated nitric acid until a pale yellow-green colour was obtained which did not darken on heating. The flask was then cooled by plunging into water, 1-2 ml of concentrated perchloric acid was added, and the flask reheated to evaporate the perchloric acid as dense white fumes. If the use of perchloric acid is precluded by the fume-hood design or safety regulations, the wet-ashing can also be satisfactorily completed by dropwise addition of 30% hydrogen peroxide at this stage, and the excess destroyed by boiling. If total dissolution with the aid of hydrofluoric acid was to be used, the irradiated sample was transferred to a 100 ml Teflon beaker, and dissolved in $HNO_3$, $HNO_3 + HClO_4$, $HClO_4 + HF$, and finally fumed with $HClO_4$ to small volume. After dissolution the contents were transfered to a 50-ml separatory funnel with 19 ml of 6M nitric acid containing 2 ml of hydrofluoric acid per litre, and uranium extracted with 6 ml TBP solution in toluene. The aqueous phase was run off into a second 50 ml separatory funnel. The organic phase was washed briefly with 5 ml 6M nitric acid containing 2 ml of hydrofluoric acid per litre. The aqueous phase was run off into the second separatory funnel. The organic phase was washed once again with 5 ml 6M nitric acid. The aqueous phase was run off and discarded. 5 ml of the organic phase was drawn off by pipette, run into a 6 ml vial and measured directly in a Ge well-type detector ($^{239}$U at 74.7 keV, $^{235}$U at 185.7 keV) followed by measurement of the $^{239}$U standard.

About 200 mg of boric acid was added to the second separatory funnel to complex fluoride. Protactinium was extracted by vigorous shaking with 10 ml of 5% tri-n-octylphosphine oxide (TOPO) in toluene. The aqueous phase was run off and discarded. The organic phase was washed with 10 ml 6M nitric acid and drawn off by pipette, then put into a 50 ml polythene measuring bottle and counted directly on the top of an HP Ge low energy photon detector (LEPD) ($^{233}$Pa at 311.8 keV, $^{231}$Pa at 27.4 or 283.6 keV), followed by measurement of the $^{233}$Pa standard. In an alternative approach an HP Ge well-type detector was used, which improves the sensitivity of measurement by a factor of about five compared with the LEPD. In this case protactinium was

extracted with 6 ml of 5% TOPO following the procedure just described. The organic phase was drawn off by pipette, run into 6 ml measuring vial and counted in the well-type detector ($^{233}$Pa at 311.8 keV, $^{231}$Pa at 283.6 keV).

## Results and discussion

The chemical yield for uranium was measured in the γ-spectrum of $^{239}$U from the 185.7 keV peak of $^{235}$U from the 50 mg of natural U carrier added to the sample before destruction (as described previously,[5,6]) and was typically around 80%. The radiochemical purity of this U fraction was excellent (Fig. 1), and the method allows pg amount to be determined.

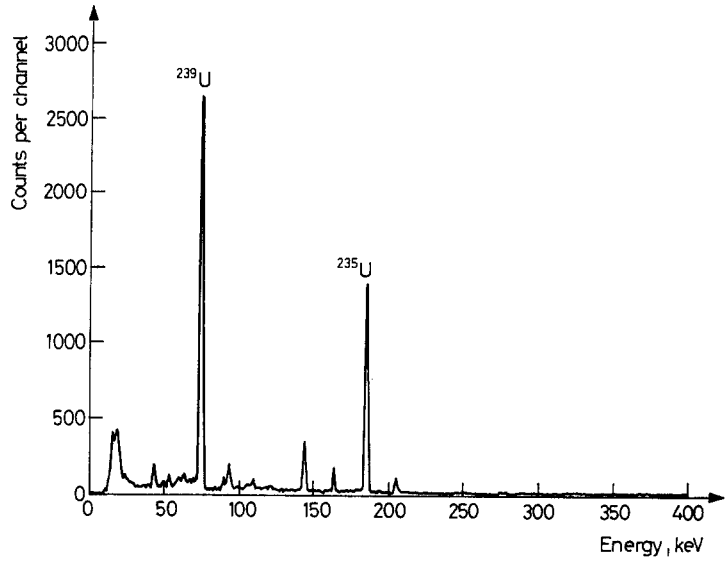


Fig. 1. Gamma-spectrum (well-type HP Ge detector) of uranium fraction from neutron-irradiated IAEA CRM H-9, Mixed Human Diet, counted for 20 minutes

The chemical yield of $^{233}$Pa for thorium determination was measured from the γ-spectrum of the separated protactinium fraction via the 27.4 or 283.6 keV peaks of the added $^{231}$Pa radioisotopic tracer. The yield was very high ($\geq 95\%$) and the radiochemical purity good. When determining the chemical yield of $^{233}$Pa using $^{231}$Pa two possibilities are open, depending on the detectors available, and the sensitivity requirements. If somewhat larger amounts of $^{231}$Pa tracer are used, the weak 283.6 keV

peak can be measured in a well-type detector, resulting in the highest sensitivity for thorium determination on measuring $^{233}$Pa at 311.8 keV (Fig. 2). However, the original solution of $^{231}$Pa as supplied contains decay products, particularly $^{227}$Th at 286.1 keV, which should be removed before use (anion exchange in hydrochloric acid achieves this simply and rapidly). The well-type detector cannot be used to measure the 27.4 keV line

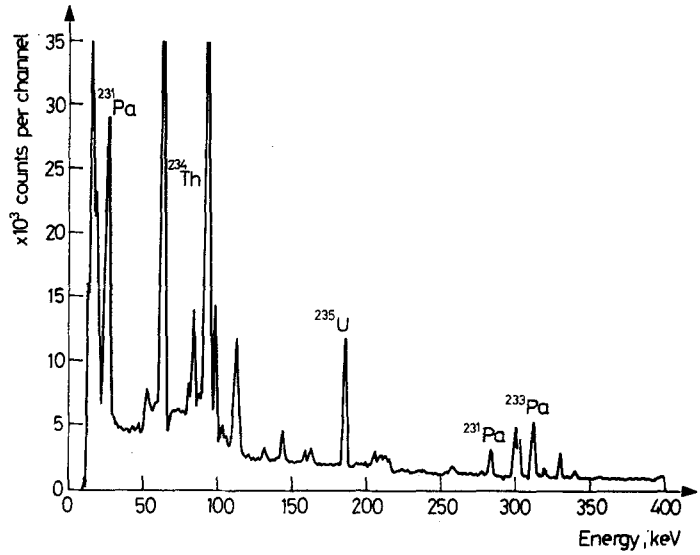


Fig. 2. Gamma-spectrum (well-type HP Ge detector) of protactinium fraction from neutron irradiated IAEA CRM H-9, Mixed Human Diet, counted for 90 000 seconds (background not subtracted)

of $^{231}$Pa because of interference from the 25.6 keV peak of $^{231}$Th, the daughter of $^{235}$U which is added as uranium carrier and radioisotopic tracer. The second possibility is to measure the 27.4 keV peak of $^{231}$Pa on the LEPD; in this case $^{231}$Th need not be removed from the tracer, due to the high resolution of the LEPD. This detector also has a very low Compton continuum at low energies so that the presence of $^{234}$Th (from the added uranium tracer) does not represent any problem. These points are illustrated in Fig. 3. Thus the use of $^{231}$Pa appears to be a succesful and original solution to the problem of determining the chemical yield of $^{233}$Pa. Previously MORGAN and LOVERING[7] used $^{231}$Pa for this purpose but with separate total alpha counting for quantitation.

The method developed in this work was tested by the analysis of biological reference materials, and the results are shown in Table 1. From those materials which are certified or for which literature data on U and Th concentrations exist, it is clear that our method

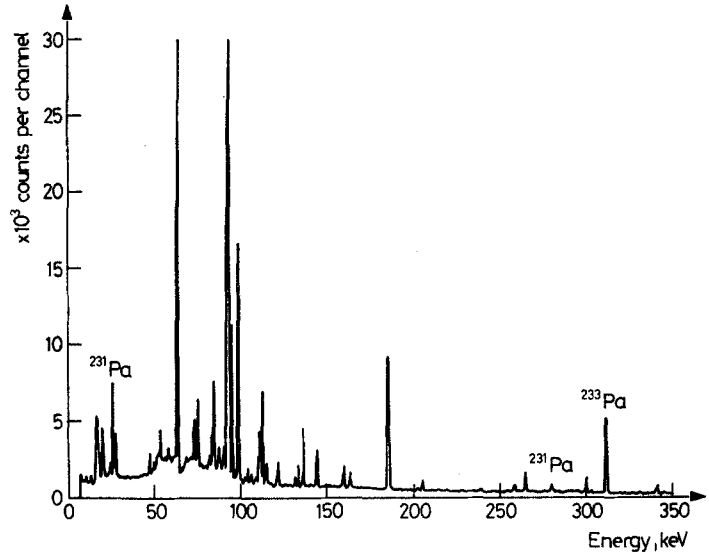


Fig. 3. Gamma-spectrum (LEPD detector) of protactinium fraction from neutron-irradiated NBS SRM-1570 Spinach, counted for 100 000 seconds

Table 1
Concentration of uranium and thorium found in biological samples

| Material | Uranium concentration, ng · g$^{-1}$ | | Thorium concentration, ng · g$^{-1}$ | |
|---|---|---|---|---|
| | This work | Certified value | This work | Certified value |
| Tomato Leaves SRM 1573a | 35.8 ± 2.0 (8) | – | 114 ± 4 (5) | (125 ± 3)** |
| Spinach NBS SRM-1570 | 35.7 ± 5.0 (4) | 46 ± 9 | 100 ± 13(9) | 120 ± 30 |
| Pine Needles NBS SRM-1575 | 17.8 ± 0.9 (6) | 20 ± 4 | 31.7 ± 1.6 (5) | (37)* |
| Peach Leaves NBS SRM-1547 | 14.2 ± 1.2 (4) | (15)* | 50 ± 4 (4) | (50)* |
| Orchard Leaves NBS SRM-1571 | 26 ± 1 (3) | 25 ± 5 | 59 ± 5 (3) | 64 ± 6 |
| Wheat flour NBS SRM-1567a | 0.28 ± 0.05 (6) | – | 1.7 ± 0.3 (6) | – |
| Bovine Liver NBS SRM-1577a | 0.68 ± 0.03 (3) | 0.71 ± 0.03 | 0.64 ± 0.05 (3) | – |
| Mixed human diet IAEA CRM H-9 | 4.8 ± 0.1 (4) | (5.0 ± 0.6)*** | 1.8 ± 0.8 (4) | (1.9 ± 0.9)*** |

*Information value only.
**Literature value.[13]
***Literature value.[14]

gives results in good agreement, and can be considered reliable. It should also be mentioned that the results obtained for the botanical materials listed in Table 1 were obtained using total dissolution of the sample with HF (the two dissolution procedures were given in the section Radiochemical Procedure). As we have found previously,[5] without HF part of the uranium (probably that associated with silicaceous materials on or in the leaves, eg. soil) remains undissolved.

As mentioned in the introduction, a number of previous authors have determined U and Th simultaneously by RNAA, but always on the basis of $^{239}$Np and $^{233}$Pa.[7-9] Use of $^{239}$U offers higher sensitivity for uranium, and a very simple yet accurate yield determination using $^{235}$U. If $^{239}$Np is used, the chemical yield measurement is again troublesome. The only feasible $\gamma$-spectrometric Np radioisotope is $^{238}$Np (2.2 days), which must be prepared immediately before the analysis, or during irradiation of the sample, by neutron irradiation of $^{237}$Np, as used by some previous workers.[5,10,11]

In conclusion, the method developed has some advantages: sensitivity, high chemical yields and good purity of the $\gamma$-spectra, and above all, simple but accurate measurement of the chemical yields, the lack of which has been a weakness of most previous methods.

In spite of the need for a double irradiation in the so-called LICSIR technique[1] (Long Irradiation, Cooling, Short Irradiation, Radiochemistry), it appears that this method of combining together radionuclides with very different half-lives in a joint determination can be very useful. This was also demonstrated[12] recently in a LICSIR joint determination of iodine ($^{128}$I) with selenium ($^{75}$Se).

*

We thank the National Institute of Science and Technology, Washington, and the Slovenian Ministry of Science and Technology for partial financial support.

## References

1. A. R. BYRNE, Radiochem. Radioanal. Letters, 52 (1982) 99.
2. E. STEINNES, Talanta, 22 (1975) 1041.
3. E. STEINNES, Anal. Chim. Acta, 76 (1975) 461.
4. M. DERMELJ, J. NOVAK, V. RAVNIK, L. KOSTA, J. Radioanal. Chem., 44 (1978) 271.
5. A. R. BYRNE, L. BENEDIK, Talanta, 35 (1988) 161.
6. A. R. BYRNE, L. BENEDIK, Sci. Total Environ., 107 (1991) 143.
7. J. W. MORGAN, J. F. LOVERING, Anal. Chim. Acta, 28 (1963) 405.
8. D. N. EDGINGTON, Int. J. Appl. Radiation Isotopes, 18 (1967) 11.
9. H. S. DANG, D. D. JAISWAL, C. M. SUNTA, S. D. SOMAN, Health Phys., 57 (1989) 393.
10. U. NIESE, J. Trace Microprobe Techniques, 1 (1983–82) 339.
11. U. NIESE, S. NIESE, J. Radioanal. Nucl. Chem., 91 (1985) 17.
12. M. DERMELJ, V. STIBILJ, J. STEKAR, A. R. BYRNE, Fresen. Z. Anal. Chem., 340 ((1991) 258.
13. B. SMODIŠ, J. Stefan Institute Report, US DP-9493 (1991), Ljubljana, Slovenia.
14. A. CHATT, H. S. DANG, B. B. JAYAWICKREME, L. S. McDOWELL, D. L. PEGG, J. Radioanal. Nucl. Chem., 124 (1988) 65.