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Determination of molybdenum and uranium in biological materials by radiochemical neutron activation analysis

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Recently developed radiochemical separation scheme for the simultaneous determination of trace amounts of molybdenum and uranium in biological materials by NAA has been further refined and used for the determination of these elements in several certified reference materials. The method assures very selective and quantitative separation of the indicator radionuclides: ^{99}Mo–^{99m}Tc and ^{239}Np from practically all accompanying activities followed by almost interference-free measurement by gamma ray spectrometry. The method can be applied to materials of both animal and plant origin and enables correcting the molybdenum results for uranium fission interference reaction thus assuring good accuracy for both elements down to ppb levels. The detection limits amount to 2.5 ppb (Mo) and 0.15 ppb (U) for ca. 200 mg samples.

Introduction

Accurate determination of molybdenum in biological materials especially at low (sub ppm) levels still poses problems[1,2] and Mo is as a rule classified among those elements for which the state of the art of analysis is unsatisfactory.[3,4] As Mo is an essential element for all forms of life and may be toxic at higher concentrations[1,5] its determination is of importance for biomedical sciences, nutrition considerations etc.

Neutron activation analysis (NAA) in its radiochemical version is quoted among most suitable methods for the determination of low levels of molybdenum in biological materials.[1,4,6] Contamination during sampling and sample handling prior to neutron irradiation as well as residual blank from irradiaton containers are most often mentioned potential sources of error when determining molybdenum.[1,2,7] Surprisingly enough another serious potential source of error i.e. uranium fission reaction yielding the same indicator radionuclide (^{99}Mo) which is used for molybdenum quantification has been overlooked or neglected by most of the analysts using NAA for the determination of traces in biological materials. While those workers who dealt with the analysis of geological materials have usually been aware of the necessity of determining uranium and introducing appropriate corrections for those elements that are formed as a result of uranium fission reaction,[8–10] the reverse seems to be true in the case of NAA of biological materials. An overwhelming number of radiochemical separation schemes that can be found in literature, both the old ones as well as those recently developed and designed for NAA of biological materials (including determination of Mo), do not foresee simultaneous determination of uranium.[11–20] This is equivalent to tacitly assuming that uranium contents in biological materials are always so small that their presence cannot significantly affect results of molybdenum determination. However, uranium content in many materials of biological origin is not negligible. So, although in many cases the methods were validated by analysis of reference materials, e.g., Bovine Liver and/or Bowen's Kale[14–20] with Mo contents of a few ppm, similarly as we did in our earlier work,[21] all those methods cannot be considered as universal, unbiased tools for the determination of Mo in biological materials. As was shown by us recently,[22] not taking into account the contribution of radiomolybdenum from uranium fission may in certain cases lead to serious systematic errors. The logical conclusion is that truly unbiased method for the determination of molybdenum traces should include also the determination of uranium and establishing of appropriate correction factor.

To confirm the above statement, in this paper the selective and quantitative separation scheme for the simultaneous determination of Mo and U by NAA in biological materials developed previously[22] has been further refined and used for the analysis of several reference materials.

Experimental

Ion exchange resins, adsorbents and columns

Aluminium oxide 90 active acidic (AAO), 0.063–0.200 mm (Merck) was used as received. Dowex 1-X8[Cl^-] (100–200 mesh) (Serva) was transformed into [NO_3^-] form by passing through the column an excess of 1M NaOH, doubly distilled water, and 1M HNO_3 solutions followed by rinsing with doubly distilled water. Dowex 50W-X4[H^+] (100–200 mesh) (Serva) was used as

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received. Water content in the above mentioned materials was determined by drying at 105 °C to constant weight. Bio-Beads SM-2 (200–400 mesh) (Bio Rad Laboratories) was dried at 105 °C to constant weight. Column filling for extraction chromatography was prepared as follows: 2 g of dry Bio-Beads SM-2 were suspended in a solution of 1 g of α-benzoinoxime in acetone.The suspension was heated to ca. 80 °C and stirred with a glass rod until the acetone evaporated, and free-flowing whiet powder was obtained. Dismountable glass columns of the type described in our earlier work[23] and i.d. of ca. 0.52 cm were employed.

Reagents and radioactive tracers

Alpha-benzoinoxime p.a. (POCh, Poland) was used as received. All reagents and acids were of Analytical Grade. Doubly distilled water from quartz apparatus was used for preparation of solutions. Stock solution of molybdenum (1 mg/ml) was prepared by dissolving appropriate amount of MoO_3 (Puratronic JMC) in aqua regia and diluting with distilled water. Stock solution of uranium (1 mg/ml) was prepared by dissolving appropriate amount of U_3O_8 uranium chemical standard No. 950a (NBS) in conc. HNO_3 and diluting with distilled water. Solutions of lower concentration were prepared from stock solutions by diluting with distilled water immediately before use. Radioactive tracers: ^{99}Mo–^{99m}Tc ($T_{1/2}$ = 66 h–6 h) and ^{239}Np ($T_{1/2}$ = 2.35 d) were prepared by irradiation in EWA reactor of appropriate amounts of the above solutions evaporated to dryness in a quartz ampoule. ^{32}P tracer was prepared by irradiating appropriate amount of NaH_2PO_4 $2H_2O$ solution evaporated to dryness in a quartz ampoule.

Standards and reference materials

Standards for NAA determination of both elements were prepared from the same solutions as described in the preceding section by evaporation of aliquots of standard solutions containing 5 μg Mo and 1 μg U, respectively, onto a strips of very pure Al foil and evaporated to dryness. The following certified reference materials (CRMs) were used in this study: NIST 1547 Peach Leaves, NBS 1566 Oyster Tissue, NIST 1566a Oyster Tissue, NBS 1570 Spinach, IAEA-331 Spinach (NIST 1570a Spinach Leaves), CTA-OTL-1 Oriental Tobacco Leaves, ICHTJ, Poland, and CTA-VTL-2 Virginia Tobacco Leaves, ICHTJ, Poland. Water content in CRMs was determined according to instructions given by manufacturers in separate portions (not those taken for analysis).

Gamma-ray spectrometry

Measurements were performed with the aid of 213 cm^3 HPGe coaxial ORTEC detector (47% relative efficiency) coupled via ORTEC analog line to the multichannel analyser SWAN-3 of the "plug in card" type, cooperating with an IBM/AT microcomputer. Detector resolution was 1.9 keV for 1332.5 keV ^{60}Co line. Measurements were performed in clock time, using pulser technique to account for possible losses due to dead time and pile up effects. In recent experiments also the well type HPGe detector (ORTEC) 180 cm^3 nominal volume, 35% relative efficiency, well depth 38 mm, well diameter 22 mm, resolution 2.3 keV for 1332.5 keV ^{60}Co line was used.

Molybdenum was determied via 140.5 keV line of ^{99}Mo–^{99m}Tc after establishment of radioactive equilibrium. Uranium was determined through measurement of 277.6 keV line of ^{239}Np.

Tracer studies

Weight distribution coefficients, λ (amount per g of stationary phase/amount per ml of the solution) were determined by contacting 200–300 mg of the resin or adsorbent of known moisture content with 10 ml of the solution of desired composition containing radioactive tracer(s) for 24 hours with occasional shaking. After separation of phases the concentration of individual tracer (A_s) was determined in an aliquot of the solution by γ-ray spectromery and compared with that in the initial solution (A_0). The distribution coefficient was calculated from the relation:

$$\lambda = \frac{(A_0 - A_s)}{A_s} \cdot \frac{V}{m_j} \qquad (1)$$

where m_j is the mass of dry ion exchanger (g), and V is the volume of the solution (ml).

Column experiments were performed using glass columns of ca. 0.52 cm I.D. with fritted glass disc or glass wool plug and a stopcock at the bottom. Effluent was collected in fractions and measured with 2″ × 2″ well type NaI(Tl) detector coupled to a scaler or by γ-ray spectrometry. ^{32}P was mesured using GM counter.

Analytical procedure

The radiochemical separation scheme used in this work and schematically presented in Fig. 1 was essentially the one described in the previous paper[22] with slight modifications. Samples of biological materials (100–200 mg) were weighed into Al foil bags made of foil of low Mo and U contents, previously washed with concentrated nitric acid and distilled water. Four samples and 2 Mo and 2 U standards (also wrapped in Al foil) and empty Al foil bag were irradiated in reactors EWA (24 h at a flux of $\Phi = 10^{14}$ n · cm^{-2} · s^{-1}) or MARIA (6 h at a flux of $\Phi = 4 \cdot 10^{14}$ n · cm^{-2} · s^{-1}) and cooled ca. 5 days. The irradiated material was gently crushed and after opening

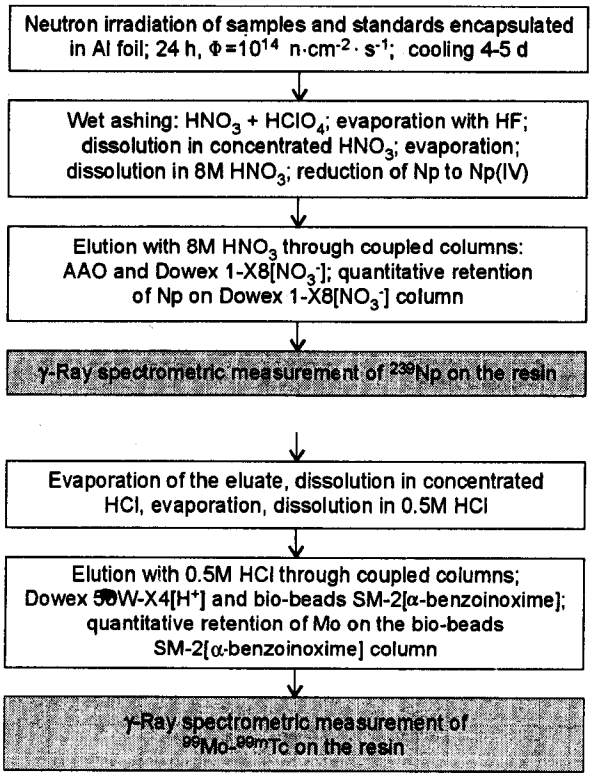

Fig. 1. Flow chart of the analytical procedure

the foil bag quantitatively transferred into 150 ml conical flask containing 50 μg of Mo carrier and the inner surface of unfolded Al foil bag was washed with 6–10 ml of conc. HNO_3, adding the washings to the sample. The sample was heated under watch glass cover until fumes of nitrogen oxide ceased to appear. After cooling, 2 ml of conc. $HClO_4$ was added and the heating continued up to complete decolorization of the solution. The solution was then transferred to a teflon beaker, the flask washed with conc. $HClO_4$ and washings added to the sample solution. 15 ml of conc. HF were added to remove silica and solution evaporated gently to dryness. Dry residue was dissolved in conc. HNO_3 on heating under the watch glass cover, evaporated nearly to dryness and dissolved in 2 ml 8M HNO_3. After cooling to room temperature 100 μl of H_2O_2 was added with gentle stirring and the solution quantitatively transferred without delay onto the top of first of the two columns connected in series. The first one (column A) was filled with AAO (bed dimensions: 7 cm × × 0.22 cm^2) and the second (column B) with Dowex 1-X8 [NO_3^-] (5 cm × 0.22 cm^2), respectively. Both columns were previously washed with 8M HNO_3. After the sample and washings passed through the columns, elution with 30 ml of 8M HNO_3 at 70 °C was performed. The eluate was evaporated to dryness, dissolved in conc. HCl, evaporated again and the residue dissolved in ca. 2 ml 0.5M HCl. This solution was quantitatively transferred onto the second series of coupled columns the first of which (column C) contained Dowex 50W-X4 [H^+] (bed dimensions: 7 cm × × 0.22 cm^2) and the second one: Bio-Beads SM-2 [α-benzoinoxime] (2 cm × 0.22 cm^2) (column D). The columns were previously equilibrated with 0.5M HCl. The elution was carried out with 25 ml of 0.5M HCl at 50 °C. The filling from column B was transferred into flat-bottomed glass test tube (∅ = 1.5 cm) together with minimum amount of water wash, stirred to homogenize, and neptunium was measured by γ-ray spectrometry. The filling from column D was dried at 105 °C, homogenized by gentle shaking, and counted as above to determine molybdenum. One of uranium and one of molybdenum standards were dissolved in aqua regia, evaporated to dryness, dissolved in conc. HNO_3 evaporated again, dissolved in 8M HNO_3 and later on each of them was processed exactly as the samples. The molybdenum activity from that uranium standard was used to calculate the "correction factor" (apparent μg Mo/1 μg U). The second uranium standard after dissolution as above was dissolved in 2 ml 8M HNO_3, 100 μl of 30% hydrogen peroxide was added and the standard was introduced directly on column B. The second Mo standard after dissolution as above, evaporation to dryness from conc. HCl solution was dissolved in 0.5M HCl and introduced directly on column D.

The results for a given series of determinations were considered accurate if the standards of Mo and U which passed through the separation procedure agreed with the ones measured directly within ± 5%.

Residual blank was determined by washing the inside of empty Al foil bag (irradiated together with the samples) with conc. HNO_3 and processing the washings exactly as the samples. In our experiments the residual blank was as a rule below the detection limit both for uranium and molybdenum.

Results and discussion

Separation scheme

The general idea underlying the construction of separation scheme was to assure selective and quantitative isolation of both radiomolybdenum and ^{239}Np (for the determination of uranium) in their respective fractions in one run and in the state of high radiochemical purity. Such approach, together with the determination in each run the correction factor for uranium fission reaction, should guarantee both high accuracy and precision for the simultaneous determination of molybdenum and uranium. At the same time every care was taken to make the method truly universal in a sense of insensitivity to matrix composition variations (within the category of biological

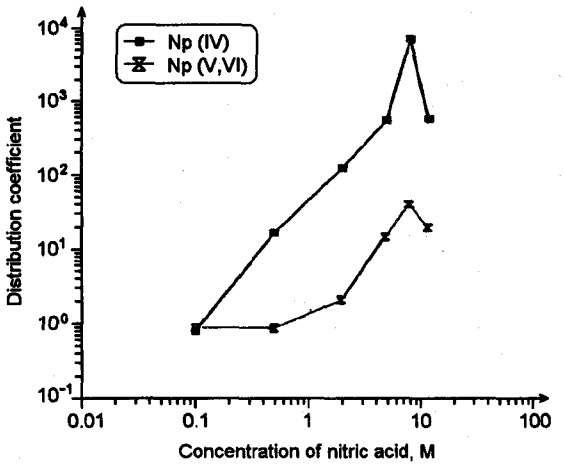

Fig. 2. Distribution coefficients of Np in the system: Dowex 1-X4[NO_3^-]–HNO_3 before and after reduction of tetravalent state

materials). The separation scheme as described above and schematically presented in Fig. 1 was extensively tested by experiments in which radiomolybdenum and neptunium tracers were added to various biological materials of both plant and animal origin and the separation executed as in the real NAA runs. The recoveries were invariably quantitative (100 ± 2% for neptunium, and 100 ± 2% for molybdenum).

Neptunium

Tetravalent neptunium is known to have high affinity to strongly basic anion exchange resins in nitric acid solutions and this reaction is quite selective, only thorium, protactinium and Pu(IV) are also strongly uptaken in these

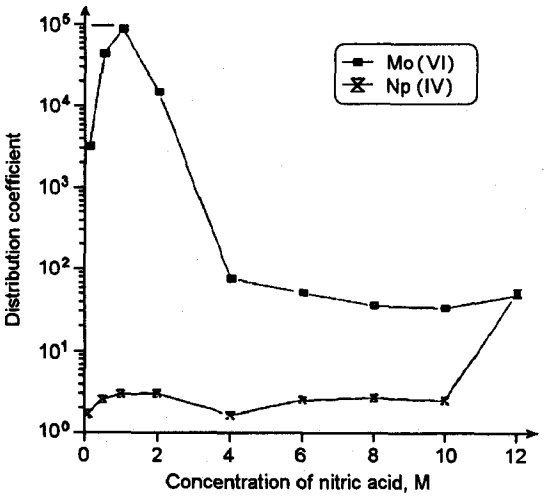

Fig. 3. Distribution coefficients of Mo(VI) and Np(IV) in the system: AAO–HNO_3 aq.

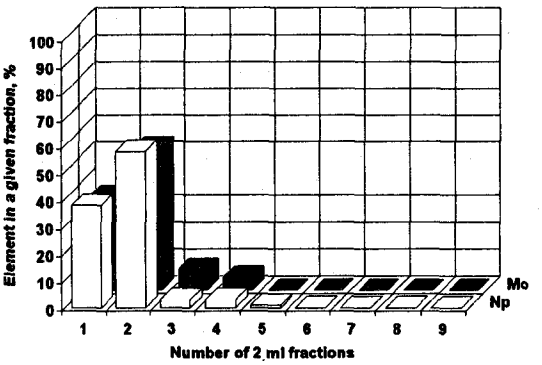

Fig. 4. Elution of Np(IV) and Mo(VI) tracers added to plant material sample from 7 cm × 0.22 cm^2 AAO column

conditions.[24] The necessary requirement for successful retention of Np is its quantitative reduction to Np(IV). This is illustrated in Fig. 2 where the distribution coefficients of neptunium prepared by dissolution of Np standard in aqua regia, evaporation to dryness, and dissolution in 8M HNO_3 {probably the mixture of Np(V) and Np(VI)}, are shown together with corresponding data after Np has been reduced to Np(IV) with hydrogen peroxide. It was found in the preliminary stage of our investigation, however, that macro amounts of certain anions like phosphates and fluorides, present, e.g., in Oyster Tissue can considerably affect the uptake of Np(IV) by the resin, lowering significantly the distribution coefficient of Np(IV). Acidic aluminium oxide (AAO) is known to sorb phosphates and not to retain neptunium[25] so its use as a precolumn for Dowex 1-X8[NO_3^-] seemed to be a logical choice. Sorption capacity of AAO is sufficiently high (5.83 mg PO_4^-/g AAO at 20 °C and 5.04mg PO_4^-/g AAO at 70 °C in 8M HNO_3 medium as determined by us by the method of break through curves). It was necessary, however, to check the behavior of molybdenum on this adsorbent, as some literature data suggested moderate or strong sorption of Mo on AAO.[25,26] Distribution coefficients of Np(IV) and Mo(VI) on AAO as a function of nitric acid concentration are shown on Fig. 3 and the elution curves of these elements from AAO column documenting quantitative recovery on Fig. 4, respectively. So, although molybdenum is indeed very strongly sorbed by AAO at lower concentrations of nitric acid reaching maximum at 1M HNO_3, it can be effectively eluted with 8M HNO_3 at 70 °C.

Molybdenum

Retention of molybdenum on the column with α-benzoinoxime supported on Bio-Beads SM-2 was studied and described by us in detail already previously[21,22] and the system was shown to be quite selective (cf. Fig. 5).

In 0.5M HCl molybdenum is strongly retained ($\lambda_{Mo} > 6 \cdot 10^3$ while the distribution coefficients for most of common elements are of the order 2–30) and quantitative separation of Mo from many elements may be achieved even with short columns. However, in order to remove the last traces of ^{47}Ca–^{47}Sc and $^{175,181}Hf$ it was necessary to include a precolumn with Dowex 50W-X4[H^+].[22]

Tungsten is also uptaken by the α-benzoinoxime column in these conditions but because of its low abundance in biological materials and also relatively long cooling time it was not observed in the spectrum of molybdenum.

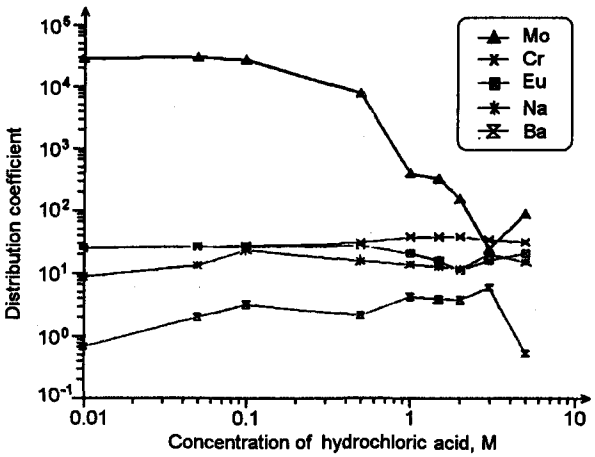

Fig. 5. Distribution coefficients of molybdenum and some other elements in the system: Bio Beads SM-2[α-benzoinoxime]–HCl aq.

Analytical results

Results of NAA determinations of molybdenum in several CRMs are presented in Table 1. One can easily note very good agreement with the certified values whenever they were available. However, in many CRMs, even those issued recently Mo was not certified. One can presume, that not considering the correction for uranium content (which in certain cases may exceed even 50%, cf. Table 1), could probably be one of the reasons of disagreement of NAA results for Mo with other analytical methods. This, in turn, might have prevented the certification of CRM for molybdenum. The results of this work demonstrate once again that without determining the correction for interfering uranium fission reaction, no NAA method, instrumental or radiochemical, can claim to be an unbiased tool for the determination of Mo in biological materials.

Table 1. Results of molybdenum determination before and after correction for uranium fission

Analyzed material	Molybdenum content*** ng · g^{-1} [$X \pm t_{0.05} \cdot s \cdot n^{-1/2}$ (n)]			Certified or information value, ng · g^{-1}
	Result without correction for uranium ($X_{app.}$)	Result after correction for uranium (X_{true})	Difference, % $\left(\frac{100(X_a - X_{true})}{X_{true}}\right)$	
1547 NIST Peach Leaves	76.3 ± 4.8 (10)	59.2 ± 4.0 (10)	+28.9	60 + 8*
1566 NBS Oyster Tissue	332.1 ± 22.9 (8)	207.9 ± 17.5 (8)	+59.3	(≤ 200)**
1566a NIST Oyster Tissue	367 ± 92 (3)	229 ± 51 (3)	+60.3	–
CTA-OTL-1 Oriental Tobacco Leaves ICHTJ, Poland	356.6 ± 47.6 (7)	251.1 ± 41.1 (7)	+42.0	(390) orig.** (260) now** (from 1994)
CTA-VTL-2 Virginia Tobacco Leaves ICHTJ, Poland	2110 ± 152 (6)	1933 ± 141 (6)	+9.2	2011 ± 151*
NBS 1570 Spinach	334 ± 97 (4)	293 ± 89 (4)	+14.0	
IAEA-331 Spinach (NIST 1570a Spinach Leaves)	530 ± 64 (4)	356 ± 45 (4)	+48.9	

*Certified value.
**Information value.
***Arithmetic mean ± confidence interval for significance level 0.05 (No. of results).

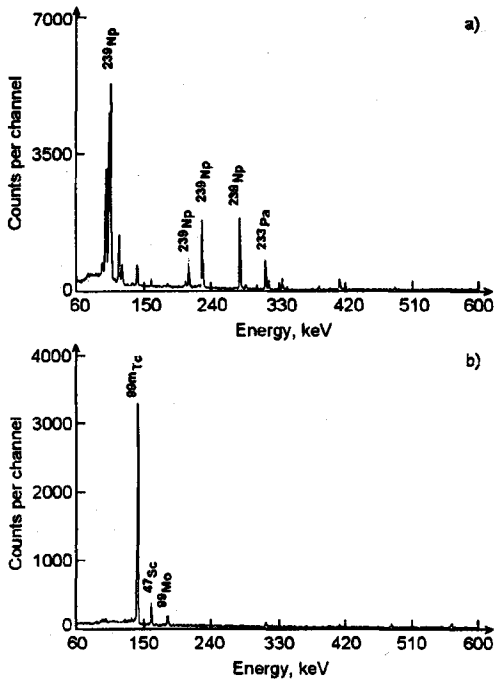

Fig. 6. Gamma-ray spectra of molybdenum and uranium fractions obtained when analysing Virginia Tobacco Leaves (CTA-VTL-2) sample; (a) Mo fraction, counting time: 2000s; (b) Np fraction, counting time: 500 s

Our results for uranium are shown in Table 2. Again, excellent agreement with the certified values should be noted.

Conclusions

The method for the simultaneous determination of Mo and U presented in this work enables interference-free analysis of all kinds of biological materials. Selective and quantitative separation scheme assures very high decontamination factors what can be easily seen from the spectra of neptunium and molybdenum fractions (cf. Fig. 6). The detection limits calculated according to CURRIE's convention[27,28] amounted to 0.03 ng for U and 0.5 ng for Mo, i.e., 0.15 ng · g^{-1} for U and 2.5 ng · g^{-1} for Mo (200 mg samples). The correction factor for the interfering uranium fission reaction as observed in this work varied from 0.7 to 1.5. Analogous data reported in literature are in the range: of 0.58–3.1 apparent μg Mo/1 μg U,[29–32] while the values calculated theoretically amounted to 0.9–3.[33] This means that for very accurate work this correction factor should be, in principle, determined in each irradiation run.

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Table 2. Results of uranium determination in biological materials

Analyzed material	Uranium content, ng · g^{-1} $[X \pm t_{0.05} \cdot s \cdot n^{-1/2}$ $(n)]$		Certified or information value, ng · g^{-1}
NIST 1547 Peach Leaves	161.1 ± 2.4	(8)	(15)**
NBS 1566 Oyster Tissue	114 ± 3.1	(6)	116 ± 6*
NIST 1566a Oyster Tissue	133.7 ± 4.8	(5)	132 ± 12*
CTA-OTL-1 Oriental Tobacco Leaves ICHTJ, Poland	103.0 ± 6.4	(7)	(100)**
CTA-VTL-2 Virginia Tobacco Leaves ICHTJ, Poland	164 ± 8.6	(10)	163 ± 8*
NBS 1570 Spinach	41.9 ± 6.7	(4)	46 ± 9*
IAEA-331 Spinach (NIST 1570a Spinach Leaves)	158 ± 22	(4)	(150 000?)**

*Certified value.
**Information value.

methods",[34,35] i.e., using always at least two standards for each element, one of which was passing through the whole radiochemical procedure and the other was measured directly, as well as including into each irradiation package appropriate CRMs with known Mo and U contents, were applied in this work contributing to its high accuracy.

The method constructed in such a way is a truly universal tool for the very accurate determination of molybdenum and uranium in biological materials of both animal and plant origin. The theoretically possible nuclear interference due to the threshold reaction: $^{102}Ru(n,\alpha)^{99}Mo$ can be safely neglected because of the small reaction cross section of this reaction (7 μb)[36] and very low levels of ruthenium content in not only biological, but also in environmental materials.[37]

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