Technical paper

Development of the Procedure for Simultaneous Determination of Vanadium, Uranium and Manganese in Biological Materials Using RNAA

Urška Repinc[1]* and Ljudmila Benedik[1,2]

[1] *Jožef Stefan Institute, Department of Environmental Sciences, Jamova 39, 1000 Ljubljana, Slovenia*

[2] *EC JRC IRMM, Retieseweg 111, B-2440 Geel, Belgium*

** Corresponding author: E-mail: urska.repinc@ijs.si*
Tel.: +386 1 58 85 347, Fax: +386 1 58 85 346

Received: 12-11-2007

Abstract

Radiochemical neutron activation analysis (RNAA) for simultaneous determination of V, U and Mn at trace levels in biological materials is described. This method is based on short irradiation of the sample together with standards and sequential separations of the induced nuclides based on selective solvent extractions. According to the very short half-lives of the induced nuclides, it is necessary to complete the separation of V first, then U and finally Mn. The chemical yield of the radiochemical procedure for each radionuclide was determined spectrophotometrically or by a use of a suitable tracer. The method was tested by the analysis of available reference materials that are commonly used as quality control materials for the determination of trace element content in food samples.

Keywords*:* Vanadium, uranium, manganese, reference materials, RNAA, INAA

1. Introduction

In recent years it is becoming widely accepted that the trace element vanadium has an important and unique role to play in human metabolism. Though this trace element is known to be essential for a number of species and should be present in the diet in minute quantities, its role as a micronutrient in humans has yet to be established.[1] In spite of its low concentrations in most foods, diet is the major intake route of vanadium for the general population. Literature data estimate the average daily dietary intake of vanadium to be between 15 and 30 μg.[2] Uranium has been classified as a toxic chemical that affects the kidneys, with nephritis being the primary chemically-induced effect on animals and humans.[3] Given a consumed diet about 0.5 kg/day dry-weight, daily uranium intake would be in the range of 0.75 to 2.65 μg/day (mean 1.25 μg/day).[4] Manganese is an essential element with a wide range of metabolic functions, present in human diet at moderate amounts (daily intake of 2,5 do 5,0 mg).[5]

Although there is a continuing interest in the biological functions of these elements, analytical difficulties occur if they are present in biological samples at the nanogram level and below. Even if the methods are sensitive enough, they suffer from potential errors involved in sample preparation. Neutron activation analysis (NAA) is a multi-element analytical technique used for both qualitative and quantitative analysis of major, minor, and trace elements, that in comparison with other analytical techniques offers advantages in sensitivity and blank-free characteristics. Radiochemical neutron activation analysis (RNAA), with the addition of carrier at μg and mg levels after irradiation, avoids the problems of working at trace levels (both loss and contamination), but demands manipulation of a rather radioactive sample. Non-destructive or instrumental NAA (INAA) is capable of determining elements like vanadium down to the about 10 ng/g at best, depending on the matrix.[6] If samples contain appreciable levels of easily activated elements that are usually present at relatively high levels in biological materials, separation of elements is required to achieve nanogram sensitivity or better. For fast and selective separation of the elements under carefully selected experimental conditions by radiochemical neutron activation analysis, solvent extraction is often used. In our laboratory we have previously developed methods of carbamate extraction for the radiochemical separa-

tion of traces of heavy metals in various environmental samples (Cd, Co, Cu, Zn), vanadium separation using selective extraction with BPHA and selective separation of uranium using TPB extraction, that were applied to different biological and environmental samples.[7–9] Previously, if suitable longer-lived tracers were not available, experiments with irradiated standards producing short-lived tracers were usually used to test the usefulness, selectiveness and efficiency of the extractions, and the same yield was applied to the analysis of real samples. Since totally post-irradiation selective separation of short-lived isotopes, has to be rapid, they are not necessarily quantitative and its yield depends on the skills of the analyst.

The aim of the present work was to extend a procedure for simultaneous determination of vanadium and uranium by radiochemical neutron activation analysis described elsewhere, to determine manganese from the same sample aliquot with little extra effort.[10] According to the half-lives of the induced nuclides, it is necessary to complete the extractive separation of vanadium first (^{52}V, $t_{1/2}$ = 3.75 min), then separate uranium (^{239}U, $t_{1/2}$ = 23.5 min), and from the remaining aqueous phase perform the separation of manganese (^{56}Mn, $t_{1/2}$ = 2.58 h). Due to the high cross-section of ^{55}Mn for thermal neutrons, manganese can be determined very sensitively via its short-lived gamma emitting isotope ^{56}Mn. The basis for the separation is the formation of the brown, chloroform-soluble Mn(III) diethyldithiocarbamate complex ($Mn(DDTC)_3$), suitable not only for the extractive separation of manganese but also for its spectrophotometrical determination. Due to the unsatisfactory stability of the complex, this relatively insensitive spectrometric method ($\varepsilon = 3.8 \times 10^3$ at $\lambda_{max} = 400$ nm) was not applied in this study. One of less sensitive spectrometric methods for determination of manganese in the form of $KMnO_4$ ($\varepsilon = 2.4 \times 10^3$ at $\lambda_{max} = 528$ nm) is more favourable.[11] The manganese separation procedure was modified by applying a long-lived gamma emitting tracer ^{54}Mn to evaluate the chemical yield. The results for manganese determination with the proposed method in reference materials of biological origin were compared with the results obtained in the present study by INAA, where matrix effects are significant. The separation procedure for sequential separation of vanadium, uranium and manganese using RNAA is presented and evaluated in the light of the results of certified reference materials, that are routinely applied for quality control purposes before analysis of food and other biological samples is performed.

2. Experimental

2. 1. Reagents, Standards and Reference Materials Analyzed

The following reagents are required: HNO_3, 70% $HClO_4$, 96% H_2SO_4, 5M and 10M HCl, 5M HNO_3/0.2% HF, 50% (v/v) solution of tri-n-butyl phosphate (TBP) in toluene, 0.2% (w/v) N-benzoyl-N-phenyl-hydroxylamine (BPHA) in toluene, 1% (w/v) aqueous solution of sodium diethyldithiocarbamate ($C_5H_{10}NNa\ S_2 \cdot 3\ H_2O$), Thymol Blue indicator. 10% (w/v) solution of Na-citrate was prepared by dissolution of 10 g of $C_6H_5Na_3O_7 \cdot 2\ H_2O$ in 100 mL of deionised water. Ammoniacal cyanide buffer, pH = 9.8, was prepared by dissolution of 10.5 g NH_4Cl in deionised water, addition of 60 mL conc. NH_4OH, 0.75 g of KCN and dilution to 500 mL mark with deionised water.

A 5 μg V/g irradiation standard solution was prepared by dilution of a vanadium standard solution of 1 mg V/g (Merck, Lot.No.K24914066). A vanadium carrier of 158 μg/g solution was prepared from ammonium vanadate. A natural uranium carrier solution of 50 mg/g U and a stock solution of 5 mg/g U were prepared from uranyl nitrate hexahydrate (natural isotopic composition). A working standard of 2.25 μg/g U was prepared by dilution of the uranium stock solution. A 11 μg Mn/g irradiation standard was prepared by dilution of a manganese carrier solution of 500 μg Mn/g, prepared from anhydrous $MnSO_4$.

Reference materials NIST-SRM 1549 (Non-fat Milk Powder), IAEA H-4 (Animal Muscle), NIST-RM 8433 (Corn Bran), NIST-SRM 1567a (Wheat Flour), NIST-SRM 1568a (Rice Flour), NIST-RM 8435 (Whole Milk Powder), NIST-RM 8415 (Whole Egg Powder), NIST-SRM 1548a (Typical Diet) were used for evaluation of the proposed procedure.

2. 2. Preparation of ^{54}Mn Tracer Solution

2 g of Fe_2O_3 were irradiated for 40 h in the carousel facility of the TRIGA MK II reactor in Ljubljana at a neutron fuence rate of 1×10^{12} n cm^{-2} s^{-1} to induce ^{54}Mn by the reaction ^{54}Fe(n,p)^{54}Mn ($t_{1/2}$ = 312.5 d). The radionuclide ^{54}Mn was separated using ion exchange chromatography. After irradiation and 1 month cooling, Fe_2O_3 was dissolved in conc. HCl, evaporated till dryness and dissolved in 7M HCl. The solution was loaded on an anion-exchange column (Dowex 1X8, 50–100 mesh) in 7M HCl and ^{54}Mn eluted with 7M HCl. The obtained solution was evaporated till dryness, loaded on a second column, eluted with 7M HCl and evaporated. ^{54}Mn was transferred with 2 mL HNO_3 to a 100 mL flask and diluted to the mark with deionised water to give approximately 6000 counts/g of solution during a 600 s measurement on a well-type HPGe detector.

2. 3. Irradiations

Samples were irradiated in the pneumatic transfer system (rabbit facility) of the TRIGA MK II reactor in Ljubljana normally for 4 min, though irradiation up to 10 min was used near the limit of detection, at a neutron fluence rate of 4×10^{12} n cm^{-2} s^{-1} to induce ^{52}V by the reaction ^{51}V(n,γ)^{52}V ($t_{1/2}$ = 3.75 min), ^{239}U by the reaction

$^{238}U(n,\gamma)^{239}U(t_{1/2}$ = 23.5 min) and ^{56}Mn by the reaction $^{55}Mn(n,\gamma)$ ^{56}Mn ($t_{1/2}$ = 2.58 h). Vanadium, uranium and manganese irradiation standards (3 μg V/g, 2 μg U/g, 11 μg Mn/g) consisted of about 200 mg solution sealed in a polyethene tube of 2 mm i.d. and taped alongside the sample. Up to 0.25 g of sample was sealed in a polyethene tube. Both sample and standards were encapsulated in polyethene foil.

2. 4. V, U and Mn Sequential Separation Procedure

The irradiated sample was weighed before irradiation. After irradiation it was quickly transferred to a long-necked silica Kjeldahl flask and using a large gas flame, wet-ashed vigorously in 3 mL of conc. sulphuric acid containing 100 μg V-carrier, 25 mg U-carrier, 300 μg Mn-carrier and 0.5 g ^{54}Mn tracer solution, by repeated additions of nitric acid, until a pale yellow-green solution was obtained. Then 2 mL of 70% perchloric acid was added and the mixture heated until perchloric acid was fumed off. The flask was cooled, 8 mL of water and 3 mL of 10 M HCl were added to transfer the contents to a 50 mL separatory funnel. 6 mL of the BPHA reagent in toluene were added and the separator shaken for 5 s to extract vanadium. The organic phase was scrubbed for 5 s with 5 mL of 5 M HCl, and 5 mL of organic phase were pipetted into a counting vial for ^{52}V gamma activity measurement at 1434.2 keV. To the aqueous phase approximately 2 mL conc. HNO_3 were added, than uranium was extracted into 5.5 mL of TBP in toluene. The organic phase was scrubbed for 5 s with 20 mL 5M HNO_3/0.2% HF and then transferred to a counting vial for ^{239}U gamma activity measurement at 74.7 keV. The aqueous phase was transferred into the Kjeldahl flask, evaporated nearly till dryness, NH_4OH was added until Thymol Blue indicator turned blue (pH ~ 9). 1 mL of KCN solution, 1 mL of Na-citrate and approximately 3 mL of Na-DDTC solutions were added and manganese was extracted into 10 mL of $CHCl_3$. The organic phase was transferred into the Kjeldahl flask and evaporated till dryness. Finally 2 mL of HNO_3 were added, the solution evaporated nearly till dryness and transferred with deionised water into the 10 mL measuring vial for ^{56}Mn gamma activity measurement at 846 keV. The separation scheme is presented in Figure 1.

2. 5. Measurements of ^{52}V, ^{239}U and ^{56}Mn

The separated fractions of vanadium, uranium and manganese and appropriate standards were counted using HPGe well-type detectors connected to a Canberra MCA by Genie 2000 software in 5 mL vials for vanadium and uranium and in a 10 mL measuring vial for manganese. The 1434.2 keV photons of ^{52}V (100% intensity), those of ^{239}U (74.7 keV, 59.3% intensity) and of ^{56}Mn (846.6 keV, 99%) were counted for 400 s, 1200 s and 600 s, respectively.

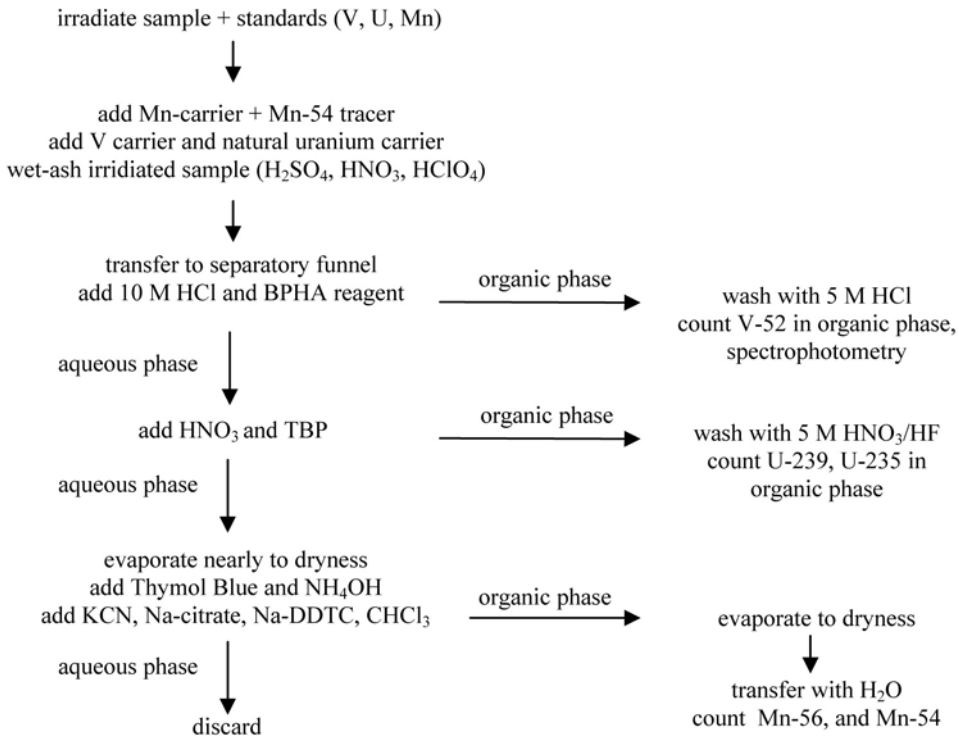

Fig. 1: Separation scheme for simultaneous determination of V, U and Mn using RNAA

2. 6. Chemical Yield Determination

Spectrophotometrically for vanadium: The absorbance of the organic phase of vanadium after extraction was measured at λ = 525 nm using an ISKRA MA 9525 – SPEKOL 210 spectrophotometer, a single beam instrument, at a monochromator slit width of 3 nm, calibrated with a reference cell containing BPHA in toluene.

Gamma measurement of ^{235}U: From the gamma spectrum of the ^{239}U fraction the ^{235}U gamma peak at 185.7 keV (54%) was evaluated. The yield was obtained by a comparison with the peak area given by 50 mg of uranium carrier.

Gamma measurement of ^{54}Mn: From the gamma spectrum of the ^{56}Mn fraction the ^{54}Mn gamma peak at 834.8 keV (99.98%) was evaluated. The yield was obtained by a comparison with the peak area given by 1g of the ^{54}Mn tracer solution.

3. Results and Discussion

Adequate sensitivity for vanadium and uranium is obtained from short irradiation with thermal neutrons only if the easily activated elements (Na, K, Mn, Cl and Br) are removed by the use of suitable separation techniques. The procedures for determination of vanadium and uranium by radiochemical neutron activation analysis have been shown to give good radiochemical purity of the separated fractions and are sufficiently rapid to allow detection limits at the ng-level to be achieved. The chemical yield of the separation procedure for each sample aliquot being analyzed is evaluated using spectrophotometry for vanadium or with ^{235}U tracer for uranium. Oxidative reagents (for example $KMnO_4$) have to be avoided if spectrophotometry is used for vanadium chemical yield evaluation. Variable extraction efficiencies (in the range of 70 to 100%) were probably obtained due to partial reduction of V(V) to V(IV) in warm solution after HCl addition. The detection limit for vanadium can be improved by reducing the time necessary to perform the separation. Therefore, time necessary for the separation was considerably shortened from 10 to typically less than 6 minutes for up to 0.25 g of dry biological material. The details of both procedures are described in the literature.[8–10] In the present work the procedure for simultaneous determination of vanadium and uranium was extended to be able to determine manganese from the same sample aliquot.

3. 1. Separation of Manganese with Sodium Diethyldithiocarbamate (Na-DDTC)

The use of dithiocarbamates (DDTC) for separation of metals was described by Minczewski *et al.*[12] In acid solutions manganese is probably found in the thermodynamically favoured oxidation state of Mn(II). Contact with air and excess of Na-DDTC converts the yellow pale precipitate of $Mn(DDTC)_2$ into brown-violet $Mn(DDTC)_3$.[11] At a pH value of 9 and with the use of KCN and Na-citrate as masking agents, manganese can be selectively extracted as $Mn(DDTC)_3$ complex into chloroform. $Mn(DDTC)_3$ due to its unsatisfactory stability, eventually precipitates from the chloroform solution. If gamma ray measurements are not performed immediately after separation, homogeneity has to be assured using an additional wet-ashing step to convert the organic phase to an aqueous one, as described in the separation procedure.

Though spectrophotometry provides information about the chemical yield with adequate precision, the same information could be obtained in much more elegant way with a use of a suitable tracer. ^{54}Mn offers a unique possibility, because it is a long-lived isotope with half-life of 312 days and a suitable γ-ray energy (E_γ = 834.8 keV, 99.98%). The manganese fraction can be measured immediately after separation in the organic phase or can be measured in the form of an aqueous solution as described in the above V, U and Mn sequential separation procedure.

3. 2. Comparison of INAA and RNAA for Determination of Manganese

Instrumental neutron activation analysis is a technique frequently used for obtaining multielement profiles in various samples. Neutron activation of biological mate-

Table 1: Comparison of the results obtained using RNAA and INAA for determination of manganese in selected reference materials (uncertainty reported as expanded uncertainty, a coverage factor k = 2, number of analyzed samples in parentheses)

Sample	RNAA	INAA	reference values
		Mn, ng/g	
NIST-SRM 1549, Non-fat Milk Powder	246 ± 18 (4)	268 ± 9 (7)	260 ± 60
IAEA H-4, Animal Muscle	456 ± 11 (4)	481 ± 56 (4)	466 ± 42
NIST-RM 8433, Corn Bran	2494 ± 384 (4)	2568 ± 229 (4)	2550 ± 290
NIST-SRM 1567a, Wheat Flour	9437 ± 595 (4)	9439 ± 944 (4)	9400 ± 900
NIST-SRM 1568a, Rice Flour	18379 ± 698 (4)	18181 ± 382 (4)	20000 ± 1600
NIST-RM 8435, Whole Milk Powder	170 ± 22 (5)	192 ± 131 (5)	170 ± 50
NIST-RM 8415, Whole Egg Powder	1673 ± 64 (3)	1857 ± 349 (3)	1780 ± 380
NIST-SRM 1548a, Typical Diet	5997 ± 546 (7)	5779 ± 1422 (4)	5750 ± 170

rials yields intense radioactivity of several radionuclides (^{24}Na, ^{42}K, ^{56}Mn, ^{38}Cl and ^{82}Br) which complicate the gamma ray spectrum. These problems may be overcome by the use of radiochemical neutron activation analysis, which results in favourable detection limits for many elements.

In the present study we compared the results for reference materials of biological origin obtained by non-destructive NAA with the proposed RNAA technique for the determination of manganese. Comparison of the results for determination of manganese in different biological reference materials analysed by RNAA and INAA is presented in Table 1. In general the results obtained by RNAA and INAA agree with the certified or literature values. However, RNAA offers a significant improvement in uncertainty of manganese determination at concentrations bellow 1 μg/g, as presented in Figure 2.

surements of ^{54}Mn tracer indicated that manganese was not extracted into the V-BPHA fraction. Since manganese is present in acid solutions in its thermodynamically favoured oxidation form of Mn(II), it does not effect the spectrophotometrical determination of vanadium and is not extracted into BPHA/toluene in the conditions used for vanadium extraction.

3. 4. Nuclear Interferences

Possible nuclear interferences for vanadium determination from the reaction ^{55}Mn(n,α)^{52}V were tested experimentally at our reactor earlier. Negligible interference for biological materials was found.[8] Possible interferences from the reactions ^{56}Fe(n,p)^{56}Mn and ^{58}Co(n,α)^{56}Mn were tested in the present study. The results obtained showed that the interference contributions are negligible in compa-

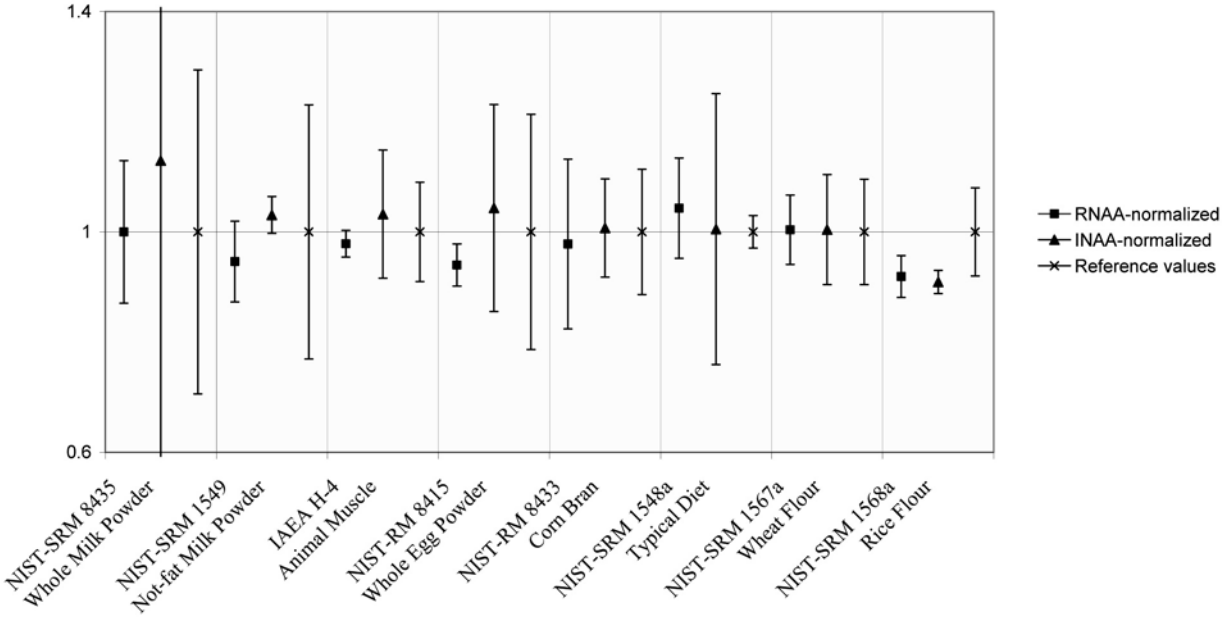

Figure 2: Normalized results for Mn with corresponding uncertainties, obtained using RNAA and INAA

3. 3. Evaluation of the Procedure for Simultaneous Determination of V, U and Mn

Interferences of manganese on vanadium and uranium extraction were evaluated using an irradiated manganese standard solution (^{56}Mn) or ^{54}Mn tracer. Possible interferences of manganese on the spectrophotometrical determination of vanadium were evaluated using different additions of manganese carrier solution and observing the effects on the V-BPHA calibration curve.

Preliminary experiments with ^{56}Mn or ^{54}Mn tracer showed that manganese extraction into TBP in toluene was negligible (less than 1%). No effect of manganese was observed on the V-BPHA calibration curve and mea-

rison to the actual concentrations of manganese found in the analyzed reference materials. Possible interference from the reaction ^{54}Fe(n,p)^{54}Mn could cause overestimation of the chemical yield due to the production of ^{54}Mn during the irradiation. Since ^{54}Fe has a low abundance (5.8%) and a small cross section for fast neutrons (82.5 ± 5 mb), no interference would be expected from this reaction.

3. 5. Analysis of Biological Reference Materials

The procedure for simultaneous determination of vanadium, uranium and manganese was evaluated by analyses of the available low-level biological reference materials, to evaluate the reliability of the proposed proce-

Table 2: Results for simultaneous determination of vanadium, uranium and manganese in reference materials (uncertainty reported as expanded uncertainty, a coverage factor k = 2, number of analyzed samples in parentheses); certified or information values (in parentheses) were obtained from the literature.[13–16]

Sample	V, ng/g	U, ng/g	Mn, ng/g
NIST-SRM 1549, Non-fat Milk Powder	0.92 ± 0.15 (5)	0.28 ± 0.07 (5)	221 ± 16 (5)
reference values	(0.97 ± 0.09)	(0.17 ± 0.10)	260 ± 60
EA H-4, Animal Muscle	2.7 ± 0.5 (6)	3.3 ± 0.5 (6)	405 ± 24 (6)
reference values	(2.8 ± 0.2)	(3.3 ± 0.63)	466 ± 42
NIST-RM 8433, Corn Bran	5.1 ± 0.7 (5)	0.82 ± 0.24 (5)	2269 ± 150 (5)
reference values	5 ± 2	–	2550 ± 280
NIST-SRM 1567a, Wheat Flour	7.9 ± 0.8 (2)	0.29 ± 0.07(2)	8226 ± 420 (2)
reference values	(11)	(0.29 ± 0.04)	9400 ± 940
NIST-SRM 1568a, Rice Flour	5.4 ± 0.4 (2)	0.27 ± 0.05 (2)	18461 ± 740 (2)
reference values	(6.2 ± 0.8)	(0.27 ± 0.02)	20000 ± 1600
NIST-RM 8435, Whole Milk Powder	0.46 ± 0.05 (2)	3.5 ± 0.2 (2)	193 ± 80 (2)
reference values	–	–	170 ± 50
NIST-SRM 1548a, Typical Diet	18.5 ± 1.1 (2)	2.3 ± 0.1 (2)	5825 ± 291 (2)
reference values	–	–	5750 ± 173

dures and compare the sensitivity of RNAA in comparison to INAA. The chemical yields obtained during the analysis of different biological materials by RNAA did not exhibit any significant variations. The chemical yields, determined spectrophotometrically or by the use of a suitable radiotracer, were in the range 70 ± 8% for vanadium, 61 ± 11% for uranium and 80 ± 12% for manganese. Table 2 shows that the results for V, U and Mn in the analyzed reference materials are in agreement with the certified or literature values.

4. Conclusions

The sensitivity of NAA for elements like vanadium, uranium and manganese in combination with selective separation procedures offers a unique possibility to determine these elements from the same sample aliquot. As described, after the separation of short-lived ^{52}V and ^{239}U, separation of manganese was performed with very little extra effort. Since manganese is present in biological materials at the few 100 ng level or more, count times for gamma ray measurements were short, but can be increased if a lower detection limit is needed. If ^{54}Mn is used as a yield tracer, the yield can be easily evaluated from the same gamma spectrum, avoiding the time consuming determination by spectrophotometry. The developed procedure offers the possibility to extract as much information as possible, especially valuable in cases when samples are difficult to obtain or available in limited amounts.

The proposed method can be applied to the analysis of biological materials for elements vanadium, uranium and manganese, present as trace elements, especially when other analytical methods can not provide adequate sensitivity or when risk of sample contamination during the analysis is considerably high.

5. Acknowledgements

Financial support from the Slovenian Research Agency (P1-0143) is gratefully acknowledged.

6. References

1. A. M. Evangelou, *Critical Reviews in Oncology/Hematology* **2002**, *42*, 249–265.
2. R. J. French, P. J. H. Jones, *Life Sciences* **1992,** *52*, 339–346.
3. C. H. Zarkadas, A. G. Karydas, T. Paradellis, *Spectrochimica Acta Part B* **2001**, *56,* 2505–2511.
4. A. R. Byrne, L. Benedik, *Health Phys.* **1995**, *68*, 732–733.
5. A. Spencer, *Nutrition* **1999,** *15 (10)*, 731–734.
6. A. R. Byrne, J. Kučera, *Fresenius J. Anal.Chem.* **1991,** *340*, 48–52.
7. M. Dermelj, A. Vakselj, V. Ravnik, B. Smodiš, *Radiochem. Radioanal. Letters* **1979***, 41/2*, 149–160.
8. A. R. Byrne, L. Kosta, *J. Radioanal. Chem.* **1978,** *44*, 247–264.
9. A. R. Byrne, L. Benedik, *Talanta* **1988,** *35/3*, 161–166.
10. U. Repinc, L. Benedik, V. Stibilj, *J. Radioanal. Nucl. Chem.* **2005,** *264/1*, 39–43.
11. Z. Marczenko, Separation and Spectrophotometric Determination of Elements, John Wiley and Sons, New York, **1986**, p.p. 360–370.
12. J. Minczewski, J. Chwastowska, R. Dybczyñski, Separation and Preconcentration Methods in Inorganic Trace Analysis, Distributed by John Wiley & Sons, New York, Chichester, Brisbane, Toronto, **1982**, p.p. 209–210.
13. L. Benedik, A. R. Byrne, *Trace uranium determination in foodstuffs and diets by radiochemical neutron activation analysis,* Proceedings of the Seventh Symposium on Trace Elements in Man and Animals (TEMA7), ISBN 8681477021, Institute for Medical Research and Occupatio-

nal Health Zagreb, Croatia, **1991**, pp. 33–12 – 33–13.
14. A. R. Byrne, J. Versieck, *Biol. Trace El. Res.* **1990**, *27*, 529–540.
15. A. R. Byrne, M. Dermelj, L. Kosta, M. Tušek-Žnidarič, *Microchimica Acta I* **1984**, 119–126.
16. The IAEA Database of Natural Matrix Reference Materials, http://www-naweb.iaea.org/nahu/nmrm/nmrm2003/descript.htm

Povzetek

Opisan je postopek sočasnega določanja sledov elementov V, U in Mn v bioloških materialih. Metoda temelji na kratkem obsevanju vzorca skupaj s standardi in zaporedni ločitvi induciranih radionuklidov s solventno ekstrakcijo. Glede na razpolovne čase induciranih radionuklidov je potrebno najprej ločiti V, nato U in končno Mn. Kemijski izkoristek posamezne ločitve je bil določen spektrofotometrično ali z uporabo primernega radioaktivnega sledilca. Metoda je bila uporabljena za analizo referenčnih materialov, ki pogosto služijo za kontrolo kvalitete določitev elementov v sledovih v vzorcih hrane.