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DETERMINATION OF TRACE ELEMENTS IN BIOLOGICAL MATERIALS BY NEUTRON ACTIVATION AND EXTRACTION WITH TOPO

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Solvent extraction with TOPO from 6*M* hydrochloric acid is proposed as a method for the elimination of interfering activities in neutron activation analysis of biological material for trace elements. By this procedure ^{24}Na, ^{42}K, ^{32}P, ^{82}Br, and ^{47}Ca are efficiently removed, and a number of trace element activities can be measured by Ge(Li) spectrometry. Chemical yields are determined by re-activation. Data for Cu, Zn, Mo, and Cd in two biological standards are presented.

Introduction

Until recently, multi-element analyses of biological material by neutron activation had to be based on radiochemical separation schemes including a great number of individual groups.[1–4] After the advent of Ge(Li) detectors, the determination of a considerable number of elements can be carried out non-destructively,[5–6] but some essential trace elements like Cu, Mo, and Cd are left undetermined. Simple chemical steps separating the trace element nuclides from interfering matrix activities are therefore becoming exceedingly important. Removal of ^{24}Na from strong HCl media by means of hydrated antimony pentoxide (HAP) has shown to be a powerful method.[7–8] Another approach, demonstrated in the present work, is batch extraction of a group of trace elements into an organic phase by means of tri-octyl-phosphine oxide (TOPO). This separation, which is carried out from about 6*M* HCl, leaves in addition to ^{24}Na also ^{42}K, ^{32}P, ^{47}Ca, and ^{82}Br in the aqueous phase. TOPO has previously been applied in a neutron activation multi-group scheme for biological material based on column separations.[2]

TOPO has been extensively used for solvent extraction separations,[9] and distribution ratios for most elements in the system 5% TOPO–HCl have been determined in the range 1–12*N* HCl.[10]

Elements of interest to the present work, appreciably extracted with TOPO from 6*M* HCl, are Sc, Fe(III), Co, Cu, Zn, Ga, As(III), Zr, Mo, Cd, In, Sn, Sb(III), W, Au, Hg, Pa, and Np. In this investigation Cu, Zn, Mo, and Cd have been determined quantitatively, and the inclusion of several other elements appears to be feasible.

Experimental

Samples

Two international biological standards were used as test material, namely BOWEN's standard kale[11] and Animal Blood from IAEA, Vienna. Weighed samples of about 500 mg were wrapped in aluminium foil for irradiation. The samples were analyzed as received. For kale, drying loss was determined on separate portions as recommended by BOWEN,[11] and the correction was applied to the results.

Carrier solution

A 1*M* nitric acid solution containing the elements to be determined in the following concentrations: Cu, 1.00 mg/ml; Mo, 2.00 mg/ml; Zn, 10.0 mg/ml; Cd, 5.00 mg/ml.

Standard solution

Carrier solution diluted 1 : 100 with 0.1*M* HNO_3. For irradiation, about 0.5 ml was sealed in a silica ampoule.

Irradiation

Three days in the JEEP-II reactor (Kjeller, Norway) at a thermal neutron flux of about $1 \cdot 10^{13}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1}. The samples were left for 2 – 3 days depending on the ^{24}Na concentration, before the commencement of the chemical separation.

Counting equipment

A 1700 channel γ-spectrometer consisting of an Ortec 20 cm^3 Ge(Li) detector with associated electronics, a Hewlett – Packard 200 MHz ADC, and a NORD-I (4K, 16 bit) digital computer.

Separation procedure

The sample is transferred to a 250 ml beaker containing 2 ml conc. H_2SO_4, 5 ml conc. HNO_3, and 1 ml carrier solution, and decomposed by heating on a hot plate. If necessary, more HNO_3 is added portionwise. After evaporation to incipient fumes of SO_3, the solution is cooled, 1 ml of 30% H_2O_2 is added, and a new evaporation is performed. After cooling, 15 ml 6*M* HCl is added and the resulting mixture is extracted with 25 ml TOPO solution (5% w/w in cyclohexane). After 2 washings of the organic phase with 5 ml 6*M* HCl, back extraction is accomplished with 25 ml 6*M* HNO_3. The aqueous phase is transferred to a 100 ml bottle for γ-activity measurements.

From the irradiated standard solution 0.100 ml is withdrawn with a micropipette and diluted to 25 ml in the same type of bottle as used for the sample fractions.

Measurements

The samples were counted immediately after the separation for the measurement of ^{64}Cu and ^{69m}Zn, via the 511 keV and 439 keV γ-rays, respectively. Measurements of Mo and Cd were postponed until ca. 40 hrs later, to reduce the ^{64}Cu activity and to allow radioactive equilibrium of ^{99}Mo – ^{99m}Tc and ^{115}Cd – ^{115m}In to be established. For Mo, the 140 keV γ-ray of ^{99m}Tc was made basis for the determination; for Cd, the 335 keV γ-ray of ^{115m}In as well as the 530 keV ^{115}Cd γ-ray were used. Peak areas were calculated by the computer according to a modified COVELL method using two channels on each side of the peak, instead of one, to establish the baseline. A γ-ray spectrum of an isolated fraction from a sample of kale, recorded 4 days after the irradiation, is shown in Fig. 1.

Chemical yield determination

After sufficient decay of the activities induced in the main irradiation, chemical yields were determined by re-activation. The sample solutions were diluted to 100 ml with water, whereafter aliquots of about 1.2 ml were sealed in polyethylene ampoules and irradiated for 20 min at a neutron flux of $1.5 \cdot 10^{13}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1}. Simultaneously, aliquots of the standard solution (carrier solution diluted 1 : 100) were irradiated. After 2 days' delay 1.00 ml solution from each ampoule was subjected to γ-spectrometry as previously described. The following chemical yields were observed: Cu, 20 – 50%; Mo, 60 – 80%; Zn, 89 ± 3%; Cd, 91 ± 4%.

Results and discussion

The results obtained on the two biological standards are shown in Table 1. For kale, the mean values for Zn and Mo are in good agreement with BOWEN's 'best values'.[13] The Cu results are significantly lower than the 'best value' assigned for that element. For Cd, the present results are higher than the 'best value', which seems not yet to be well established for Cd.

For animal blood, assigned values have not been issued so far. The present values for Cu and Zn are in good agreement with a set of data previously obtained by neutron activation in the authors' laboratory,[12] using a separation method based on anion exchange, and a NaI(Tl) detector for the γ-spectrometric measurements.

It appears that the extraction with TOPO is favourable for samples with an elemental composition approximating that of kale. From the γ-spectrum of Fig. 1, it is evident that in addition to the four elements determined in this work, the elements W, Au, Sb, Sc, and Fe might also be determined quantitatively. Calcium may also be determined via ^{47}Sc, if the Ca standard is extracted simultaneously with the sample. For samples with high iron content, such as animal blood, the method appears less promising. γ-Rays of ^{59}Fe at 143 keV and 340 keV in this case interfere seriously with the determination of Mo and Cd via the daughter isotopes.

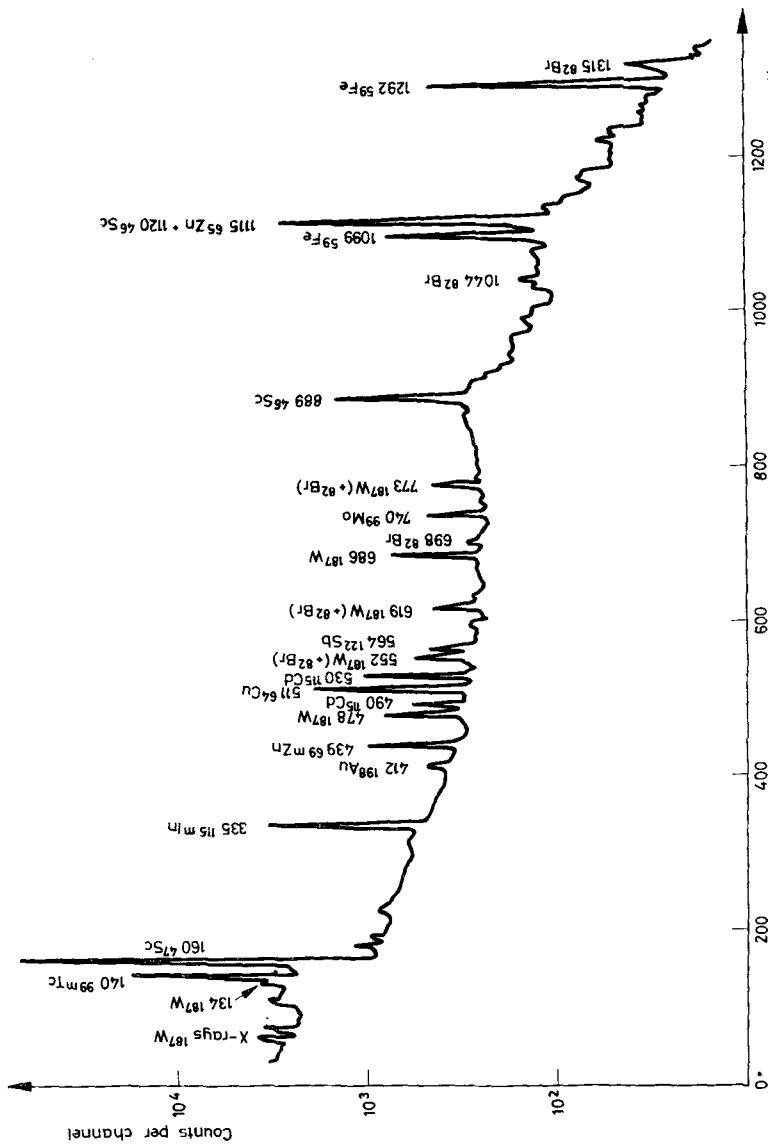

Fig. 1. γ-Spectrum from an isolated fraction of BOWEN's kale, recorded with a 20 cm^3 Ge(Li) detector 4 days after the end of the irradiation

Table 1

Content of Cu, Zn, Mo, and Cd in two biological standards, ppm

Standard	Present work	Anion exchange method[12]	'Best value'[13]
Kale	Cu 3.96 4.26 4.55 4.15 4.55		
	mean 4.29		5.0
	Zn 32.8 32.5 33.6 33.1 34.0		
	mean 33.2		32
	Mo 2.09 2.16 2.07 2.22 2.36		
	mean 2.16		2.3
	Cd 1.05 1.03 (^{115m}In)		
	1.07 1.08 (^{115}Cd)		
	mean 1.06		0.74
Animal blood	Cu 1.90 1.87 1.69 1.84 1.52	1.70 1.72 1.66 1.63 1.61 1.68	
	mean 1.76	mean 1.67	
	Zn 19.6 19.5 22.0 20.6 21.3	20.8 18.6 19.0 18.6 20.7 18.6	
	mean 20.2	mean 19.4	
	Mo <0.04		
	Cd <0.1		

In the kale samples traces of ^{82}Br were observed in the separated fractions, as indicated in Fig. 1. Kale, with its high Br content (24.3 ppm[11]) should probably represent an especially unfavourable case in this respect. Addition of an extra evaporation step with H_2O_2 should facilitate additional decontamination from ^{82}Br.

The chemical yield determination by multiple carrier addition and re-activation seems to be a convenient technique to be used in connection with Ge(Li) spectrometry. If the amount of carrier for each element is adequately chosen, there seems to be no reason why the number of elements determined in the same chemical fraction could not be extended to 8–10 without appreciable loss in accuracy for each individual element.

The chemical yields for Zn and Cd appear to be high and reproducible, indicating that chemical yield determination may be excluded for these elements using the present method, if aliquots of the standard are treated chemically in the same manner as the samples.

References

1. K. SAMSAHL, P. O. WESTER, O. LANDSTRØM, *Anal. Chem.*, 40 (1968) 181.
2. F. GIRARDI, M. MERLINI, J. PAULY, R. PIETRA, Proc. IAEA Symp. Radiochemical Methods of Analysis, Vol. 2, Salzburg, 1964, p. 3.

3. R. E. JERVIS, K. Y. WONG, Proc. IAEA Symp. Nuclear Activation Techniques in the Life Sciences, Amsterdam, 1967, p. 137.
4. P. VAN DEN WINKEL, A. SPEECKE, J. HOSTE, Proc. IAEA Symp. Nuclear Activation Techniques in the Life Sciences, Amsterdam, 1967, p. 159.
5. R. W. PERKINS, W. A. HALLER, Proc. IAEA Symp. Nuclear Activation Techniques in the Life Sciences, Amsterdam, 1967, p. 557.
6. R. A. NADKARNI, W. D. EHMANN, *J. Radioanal. Chem.*, 3 (1969) 175.
7. F. GIRARDI, E. SABBIONI, *J. Radioanal. Chem.*, 1 (1968) 169.
8. W. A. HALLER, R. H. FILBY, L. A. RANTICELLI, *Nucl. Appl.*, 6 (1969) 365.
9. J. C. WHITE, W. J. ROSS, NAS-NS 3102, 1961.
10. T. ISHIMORI, E. NAKAMURA (Eds), Data of Inorganic Solvent Extraction (1). JAERI-1047, 1963.
11. H. J. M. BOWEN, *Analyst*, 92 (1967) 124.
12. O. JOHANSEN, E. STEINNES, Unpublished work.
13. H. J. M. BOWEN in J. M. A. LENIHAN, S. J. THOMSON (Eds), Advances in Activation Analysis, Vol. 1, Academic Press, London 1969, p. 101.