Journal of Chromatography, 600 (1992) 17–36
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 008

Review

Role of ion-exchange and extraction chromatography in neutron activation analysis

Rajmund Dybczyński

Department of Analytical Chemistry, Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw (Poland)

ABSTRACT

The role and uses of ion-exchange chromatography and extraction chromatography in neutron activation analysis are surveyed. Examples of post-irradiation group separations and isolation of individual radionuclides and also pre-irradiation separations are presented and their significance for achieving the best detection limits and the highest accuracy are emphasized, including the contribution of column chromatography to the construction of "definitive" methods of analysis. Special emphasis is given to difficult cases such as micro–macro separations of ions with similar properties (*e.g.*, rare earth elements, alkali metals). The importance of the proper choice of the chromatographic system, including such factors as the kind of ion exchanger–solution combination, resin cross-linking and temperature, is pointed out.

CONTENTS

1. INTRODUCTION

Most of the papers presented at this Symposium were devoted to the demonstration of merits of various types of chromatography used as individual and self-dependent method of quantitative analysis. This paper presents a brief survey of selected applications of ion-exchange and extraction chromatography used mainly as a separation tool in conjunction with neutron activation for the deter-

0021-9673/92/$05.00

mination of elements in inorganic trace analysis.

Neutron activation analysis (NAA) is one of the most powerful techniques available for the determination of trace amounts of elements. The principles of the method are such that typically samples and standards are irradiated in a high flux of thermal neutrons in a nuclear reactor, then the characteristic radiation of the radionuclides formed as a result of the nuclear reactions is measured with a suitable detection system, most often with a γ-ray spectrometer [1–5].

The general scheme of analysis is shown in Fig. 1. The purely instrumental (non-destructive) version of the method is indicated with thick arrows, whereas thin arrows show the radiochemical (destructive) variant of the method.

NAA occupies a unique position among other methods of inorganic trace analysis owing to several features. First, it is a nuclear method and so the induced radioactivity does not depend on the chemical form of an element. Hence NAA to a much lesser extent than other methods of analysis is vulnerable to the so-called matrix effects, which is in turn reflected in the generally good accuracy of the method. Second, once the sample had been irradiated, any subsequent contamination with elements from the ambient atmosphere, reagents, container walls, etc., does not influence the signal measured (*i.e.*, the radioactivity of a given radionuclide). In analytical terms, the blank is eliminated or drastically reduced. Finally, the method shows very favourable detection limits with respect to a large number of elements (Table 1).

The detection limits shown in Table 1 are the so-called "interference-free detection limits", *i.e.*, those attainable when the activity in question is measured in the absence of other radionuclides. For real samples the detection limits may be worse by several orders of magnitude, owing to spectral interferences, the necessity for measuring small photopeaks on a high and varying Compton background, interfering nuclear reactions, etc. [1–5]. At the same time, the accuracy of determinations is adversely affected by phenomena such as the count losses due to pile-up and dead-time effects [5,6]. Therefore, although the great progress observed

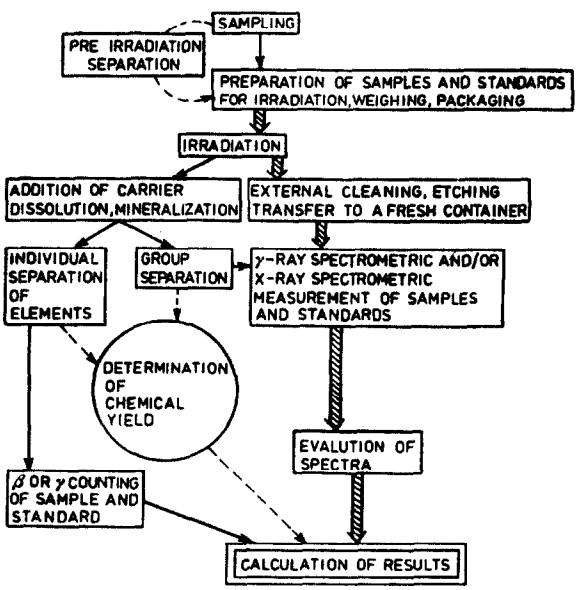

Fig. 1. General scheme of NAA method. Thick arrows, purely instrumental version; thin arrows, radiochemical version. (After Dybczyński [4]).

TABLE 1

CALCULATED BEST DETECTION SENSITIVITIES FOR 68 ELEMENTS IN THE ABSENCE OF INTERFERING ACTIVITIES

For $\Phi_{th} = 10^{13}$ n/cm^2 · s; $t_i = 5h$ maximum; $t_d = 0$; $t_c = 100$ min maximum; 40 cm^3 Ge(Li) detector; 2 cm distance; largest photopeak. (After Guinn and Hoste [2]).

Detection limit (μg)	Elements[a]
$1–3 \times 10^{-7}$	In, Eu, Dy
$4–9 \times 10^{-7}$	Ho
$1–3 \times 10^{-6}$	Mn, Sm, Au
$4–9 \times 10^{-6}$	Rh, Lu, Re, Ir
$1–3 \times 10^{-5}$	Co, Cu, Ga, As, I, Cs, La, Er, W, Hg, U
$4–9 \times 10^{-5}$	Na, V, Br, Ru, Pd, Sb, Yb, Th
$1–3 \times 10^{-4}$	Sc, Ge, Sr, Te, Ba, Nd, Ta
$4–9 \times 10^{-4}$	Cl, Se, Cd, Gd, Tb, Tm, Hf, Pt
$1–3 \times 10^{-3}$	Al, Zn, Mo, Ag, Sn, Ce, Os
$4–9 \times 10^{-3}$	K, Ti, Cr, Ni, Rb, Y, Pr
$1–3 \times 10^{-2}$	Mg
$4–9 \times 10^{-2}$	Zr
$1–3 \times 10^{-1}$	F, Ca, Nb
1–3	Fe
4–9	Si
10–30	S, Pb

[a] In addition to the above 68 elements, three can be determined by β^- counting: P (5×10^{-4} μg), Bi (1×10^{-2} μg) and Tl (2×10^{-2} μg).

over the past two decades in the technology of semiconductor detectors, pulse-height analysers and associated electronics has made possible the use of γ-ray spectrometry for the purely instrumental determination of several elements in a variety of matrices, nevertheless to achieve the best detection limits the use of separation methods is indispensable.

2. THE PLACE OF ION-EXCHANGE CHROMATOGRAPHY AMONG OTHER METHODS USED FOR RADIOCHEMICAL SEPARATIONS

Of the various separation methods used in NAA, such as distillation, precipitation and coprecipitation, solvent extraction, ion exchange and electrochemical deposition, ion exchange shows several advantages. The availability of several types of ion exchangers with different exchange groups provides a wide range of selectivities which can be further augmented by the proper choice of the composition of the mobile phase, including the use of complexing agents.

The broad literature on the subject [7–12], containing many tabulations of distribution coefficients for different elements in a variety of ion exchanger–solution systems, facilitates the planning of ion-exchange separation schemes. In most instances it is possible to find an ion-exchange system with sufficiently large differences in selectivities of the ions in question that quantitative separation can be achieved by stepwise elution from relatively short columns with simple gravity flow.

Good selectivity, quantitativeness and simplicity of operation have made ion-exchange chromatography (IEC) the leading separation technique employed in the radiochemical version of NAA.

IEC is often complemented by extraction chromatography, *i.e.*, the technique in which a porous hydrophobic support such as polytetrafluoroethylene, styrene–divinylbenzene copolymer or silanized silica gel is coated with a suitable extractant and used in columns similarly to ion exchangers [7,13–16]. Many of the extractants employed in this technique, such as tri-*n*-octylamine and di-(2-ethylhexyl)orthophosphoric acid, extract ions by an ion-exchange mechanism. In the following, selected examples of the use of ion-exchange and extraction chromatography in the determination of several elements by radiochemical NAA will be given. This review is not intended to give a comprehensive coverage of the field but rather to demonstrate the salient role of chromatography in cases when the determination of trace elements by the purely instrumental version of NAA is impossible.

3. REMOVAL OF MACROCONSTITUENTS (PREVAILING ACTIVITIES) AND GROUP SEPARATIONS

As was mentioned in section 1, despite the progress in instrumentation for γ-ray spectrometry, the measurement of weak γ lines is often impossible in the presence of high activity originating from activatable macro-constituents of the sample or even from trace elements with especially high activation cross-sections.

3.1. Analysis of biological materials

A common interference in the determination of trace elements in biological materials is the preponderant activity of radiosodium (^{24}Na). Girardi and Sabbioni [17] showed that sodium can be effectively separated from nearly all other elements by retention on a column with hydrated antimony pentoxide (HAP) from concentrated acid solutions, *e.g.*, 8 *M* HCl. This principle, among others, was used by Tijoe *et al.* [19] in a method for the determination of some elements essential for life or toxic in biological materials (see Fig. 2). Here the removal of ^{24}Na matrix activity on an HAP column is combined with further separation of trace elements into groups by stepwise elution from anion-exchange columns, permitting their interference-free determination in ensuing fractions by γ-ray spectrometry. HAP is still widely in use for the elimination of interference from ^{24}Na in NAA [19].

The use of crystalline hydrated antimony pentoxide in columns is often cumbersome because of its poor mechanical stability and tendency to clog the column. Recently, a "composite ion exchanger" containing HAP incorporated into a phenolsulphonic–formaldehyde resin matrix was prepared [20]. Its use in columns eliminates most of the problems mentioned above. Several other separation schemes for multi-element determination of trace components in biological materials by NAA have been devised [21–24].

Some of these methods employ, in addition to

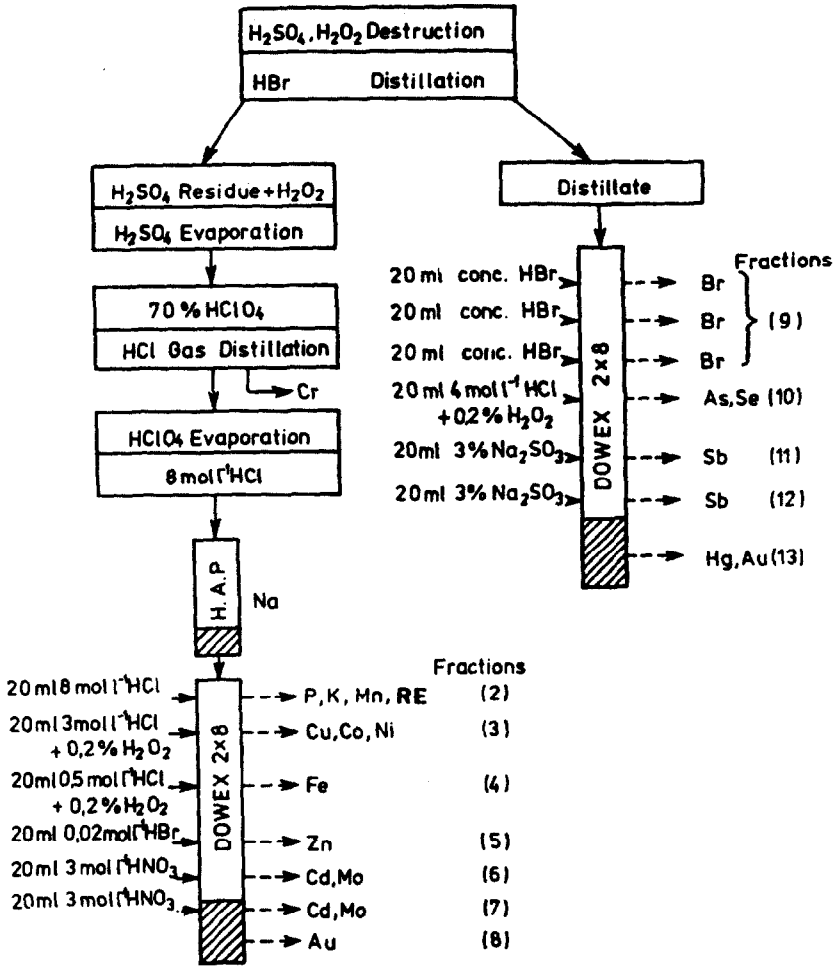

Fig. 2. Separation scheme devised for the determination of some toxic and/or essential trace elements in biological materials by NAA. (After Tijóe *et al.* [18]).

conventional strongly acidic cation exchangers and strongly basic anion exchangers, also the chelating resin Chelex 100 with iminodiacetic exchange groups and extractants such as di(2-ethylhexyl) orthophosphoric acid (HDEHP) adsorbed on a hydrophobic support.

The separation schemes are based either on stepwise elution or on selective fixation of a radionuclide or group of radionuclides with differing γ-ray energies on particular columns.

Other, less extensive, chromatographic procedures have been proposed for the determination of a single element or group of elements that are especially difficult to determine in neutron-irradiated biological materials.

Several rare earth elements (La, Ce, Nd, Eu, Gd, Yb and Lu) were determined, after wet ashing of the irradiated sample, by retention on a Dowex 50-X8 column followed by sequential elution of impurities. Rare earths were finally eluted with 6 *M* HCl and determined by γ-ray spectrometry [25].

The use of inorganic ion exchangers as selective sorbents for some elements in NAA procedures should be noted. For example, zinc hexacyanoferrate(II) was used for the selective retention of cadmium [26].

Tin dioxide (TDO) was used for the isolation of selenium from 1 *M* nitric acid solution, while hydrated manganese dioxide (HMD) served as a sorbent selective for chromium [27]. In another study HMD was employed as an effective sorbent for the whole group of elements of interest, namely Cr, As, Se, Mo, Ag, Sb and Sn [28]. Molybdenum and tungsten were separated from most other elements by extraction chromatography with a stationary phase consisting of α-benzoin oxime supported on Bio-Beads SM-2 [29].

New separation possibilities were revealed when studying the properties of an amphoteric resin, Retardion 11A8, containing both quaternary ammonium and carboxylic acid exchange groups. Selective separation of zinc [30] and cadmium [31] from nearly all other elements can be achieved with a single column of Retardion 11A8 by exploiting both anion and cation functions of the resin.

An interesting example of another kind of chromatography employed in NAA is a recently proposed procedure in which some elements, *e.g.*, Mn(II), Cu(II) and Zn(II) but also Se(IV), Hg(II), As(III) and Sb(III), are first complexed with a chelating agent such as 8-hydroxyquinoline, pyrrolidine dithicarbamate or diethylammonium diethyldithiocarbamate and then retained on columns of C_{19}-bonded silica gel [32,33].

3.2. Analysis of high-purity materials and geological samples

Chromatographic methods have been widely used in radiochemical NAA for the determination of trace elements in a variety of other matrices such as semiconductor materials, high-purity metals and geological materials.

When the technique of γ-ray spectrometry still relied on the use of NaI(Tl) detectors, but sometimes also in a later period very elaborate schemes of ion-exchange separation, *e.g.*, for the determination of trace elements in silica, were devised [34,35]. With the introduction of Ge(Li) and HPGe detectors, many more elements could be determined in Si or SiO_2 matrices non-destructively, but in several instances ion-exchange separations are still necessary. This may be exemplified by the procedure for the determination of indium, in which short-lived ^{116m}In was selectively retained on an inorganic ion exchanger, cerium oxalate, from hydrofluoric acid solution with 92–95% yield [36]. Another example is the determination of uranium and thorium in silica and aluminium where the activation products of both elements, *i.e.*, ^{239}Np and ^{233}Pa, were separated by retention on Dowex 1-X8 (Cl^-), followed by selective elution with 3 *M* HF–9 *M* HCl, coprecipitation with LaF_3 and measurement by γ-ray spectrometry [37].

Tantalum is an example of a material in which the determination of any impurity by instrumental NAA is virtually impossible owing to the high activity of the matrix due to both short-lived (^{182m}Ta) and long-lived (^{182g}Ta and ^{183}Ta) radionuclides. The separation scheme [38] devised for the determination of several trace impurities in tantalum metal (Fig. 3) makes use of the high affinity of tantalum to an anion-exchange resin in HF medium. Elements that do not form stable fluoride complexes (Co, Cr, Cu, K, La, Mn, Ni) are quantitatively eluted from a Dowex 1-X8 (F^-) column with 1–2 *M* HF. Elements taken up by the resin (Hf, Mo, Re, Sc and W) can be selectively eluted from the column with 40–50 *M* HF, leaving macro amounts of tantalum on the column (Fig. 4).

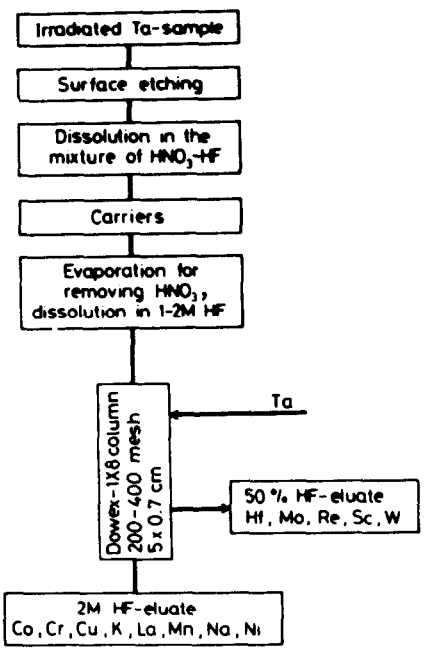

Fig. 3. Flow-scheme of the procedure for the post-irradiation separation of impurities from Ta metal matrix. (After Caletka *et al.* [38]).

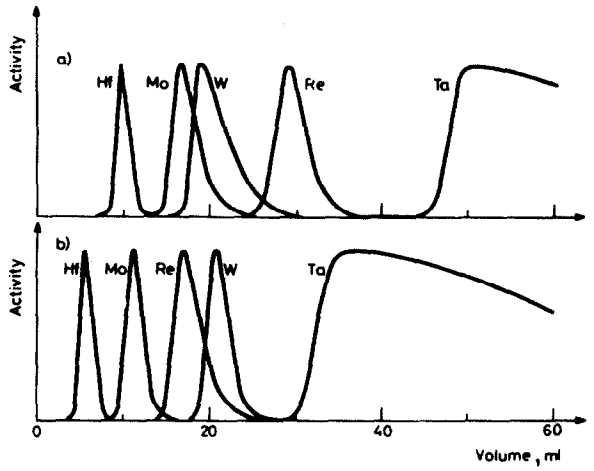

Fig. 4. Separation of Hf, Mo, W and Re from macro amounts of Ta. (a) Column, 12 cm × 0.38 cm^2 Dowex 1-X8 (F^-) (200–400 mesh); adsorption stage, 5 ml of 2 *M* HF containing 500 mg of Ta and respective tracers followed by 10 ml of 2 *M* HF washing solution; elution stage, 40% HF (22.5 mol/l); flow-rate, 0.4–0.5 ml/min. (b) Column, 13 cm × 0.38 cm^2 Dowex 1-X8 (F^-) (200–400 mesh); adsorption stage, as above; elution stage, 50% HF (31.2 mol/l); flow-rate, 0.4–0.5 ml/min. (After Caletka *et al.* [38]).

Similar methods also based on anion exchange in HF were used for the determination of several impurities in tungsten metal [39]. Another separation scheme for the determination of impurities in molybdenum metal employed first a Dowex 50W-X8 (H^+) column, which made it possible to isolate a group of several elements (Sm, Cr, Cs, Rb, Zr, Fe, Zn, Co, La), and then a Dowex 1-X8 (NO_3^-) anion-exchange column to retain ^{239}Np and ^{233}Pa for the determination of uranium and thorium [40].

Extraction chromatography was used for the determination of trace elements in high-purity tellurium [41]. After irradiation, dissolution and distillation of ^{131}I, tellurium was reduced to Te(IV) with hydrazine and retained from 12 *M* HCl on a column with TBP supported on polytetrafluoroethylene. The impurities (Na, K, Cr, Mn, Co, Cu, Zn, As, Ag, Cd and La) were recovered in the eluate and determined by γ-ray spectrometry.

A similar method with the use of an additional anion-exchange column in the bromide form to retain cadmium was used for the determination of impurities in cadmium telluride [42]. A modified version of the method served also for the determination of trace elements in the ternary compound $Pb_xSn_{1-x}Te$ [43].

In the analysis of geological materials, a strongly basic anion-exchange resin in the chloride form [44] or newly synthesized chelating resins [45] were used for the group separation of noble metals. Low levels of iridium in sedimentary rocks were determined by separating cationic interfering elements from the anionic $IrCl_6^-$ complex on a Bio-Rad AG 50W-X8 sulphonic cation exchanger [46].

3.3. Unconventional separations

In ion-exchange separations, sometimes unusual selectivities occurring in concentrated electrolyte solutions are exploited. In Fig. 5, a flow scheme of the separation procedure [47] devised for the determination by NAA of La, Ga, Hf and Sc in chamotte brick and related refractory materials is presented. These elements were studied and employed as "internal isotopic tracers" for the investigation of metallurgical processes. In this method gallium and scandium were separated from most of the other elements by retaining them on a column with a low

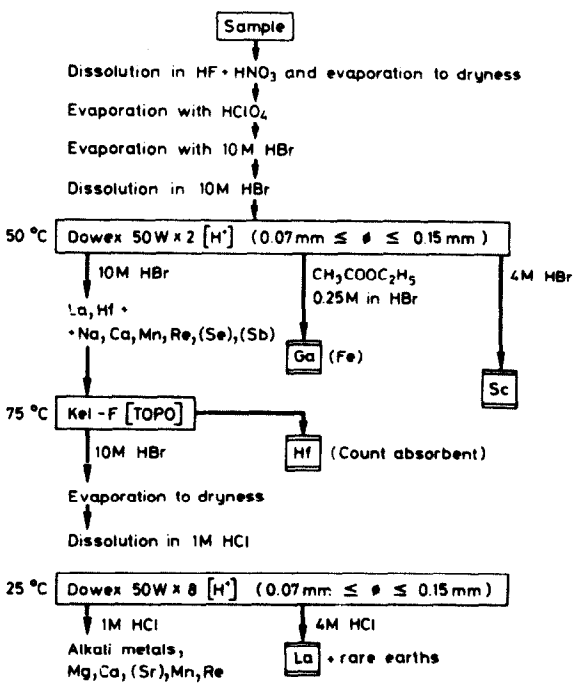

Fig. 5. Radiochemical separation scheme for the quantitative isolation of Ga, Sc, Hf and La from refractory materials. (After Fołdzińska and Dybczyński [47]).

cross-linked strongly acidic sulphonic cation exchanger, following by selective stepwise elution (Fig. 6).

It is interesting that the retention of both elements from 10 *M* HBr seemingly contradicts the mass-action law of a cation-exchange reaction. In reality, gallium, which is known to form a negatively charged bromide complex, is probably taken up by the resin owing to some kind of complex formation between the undissociated $HGaBr_4$ (or ion pair $H^+ GaBr_4^-$) and the benzene rings of the resin network. Consequently, it can be eluted with an organic extractant containing a small amount of HBr.

Scandium, which does not form negative bromide complexes, is apparently at least partially dehydrated in 10 *M* HBr and fulfills its solvation needs via sulphonate groups of the resin. When the concentration of the acid is diminished to 4 *M*, scandium elutes easily, as could be expected on the basis of the mass-action law of an ion-exchange reaction. Lanthanum, hafnium and other elements were eluted with 10 *M* HBr at 50°C because the elevated temperature reduced tailing. Hafnium was selectively retained from the same solution at 75°C on a column with tri-*n*-octylphosphine oxide (TOPO) supported on Kel-F powder and measured on the bed by γ-ray spectrometer. Lanthanum (together with other lanthanides) was finally separated from accompanying elements by stepwise elution from a Dowex 50W-X8 column.

This separation scheme ensured virtually quantitative ($\geq 96\%$) recovery of the elements in question and good radiochemical purity of the respective fractions so that a γ-ray spectrometer with only moderate energy resolution [NaI(Tl) detector] could be used for determination. Amounts of the order of mg/kg (ppm) for all four elements could be conveniently determined by this method in a variety of refractory materials.

3.4. Problems with micro–macro separations of ions with similar chemical properties

The separation procedures and schemes discussed above and based on stepwise elution or selective fixation on the column exploit large differences in the selectivities of individual ions occurring in various ion-exchange and extraction systems. Sometimes, however, it is necessary to separate elements with very similar chemical properties.

A classical example is the group of rare earth elements. While the separation of lanthanide ions present in trace amounts can be relatively easily achieved, the realization of macro–micro separations may create serious problems. This will be

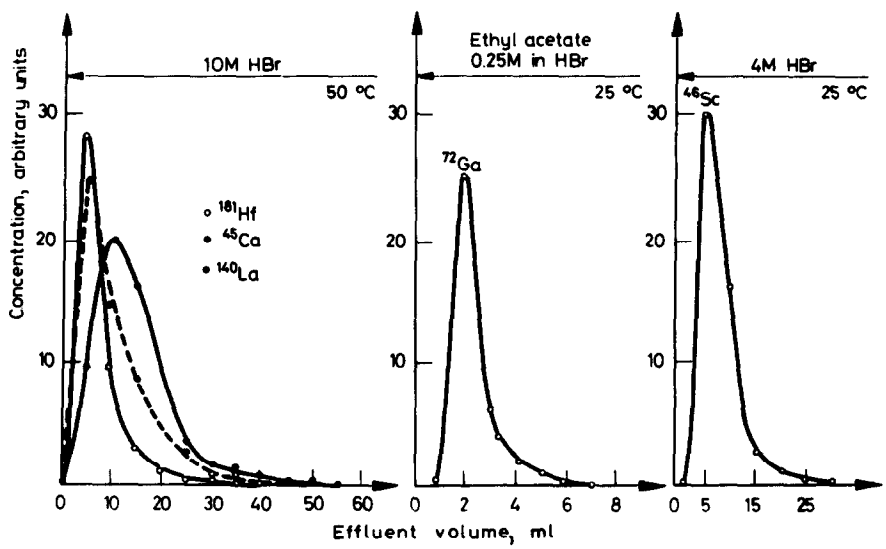

Fig. 6. Isolation of Ga and Sc by ion-exchange chromatography. Column, 10.0 cm × 0.18 cm^2 Dowex 50W-X2 (H^+) (0.07 mm $\leq \phi \leq$ 0.15 mm); flow-rate, 5 cm/min. (After Fołdzińska and Dybczyński [47]).

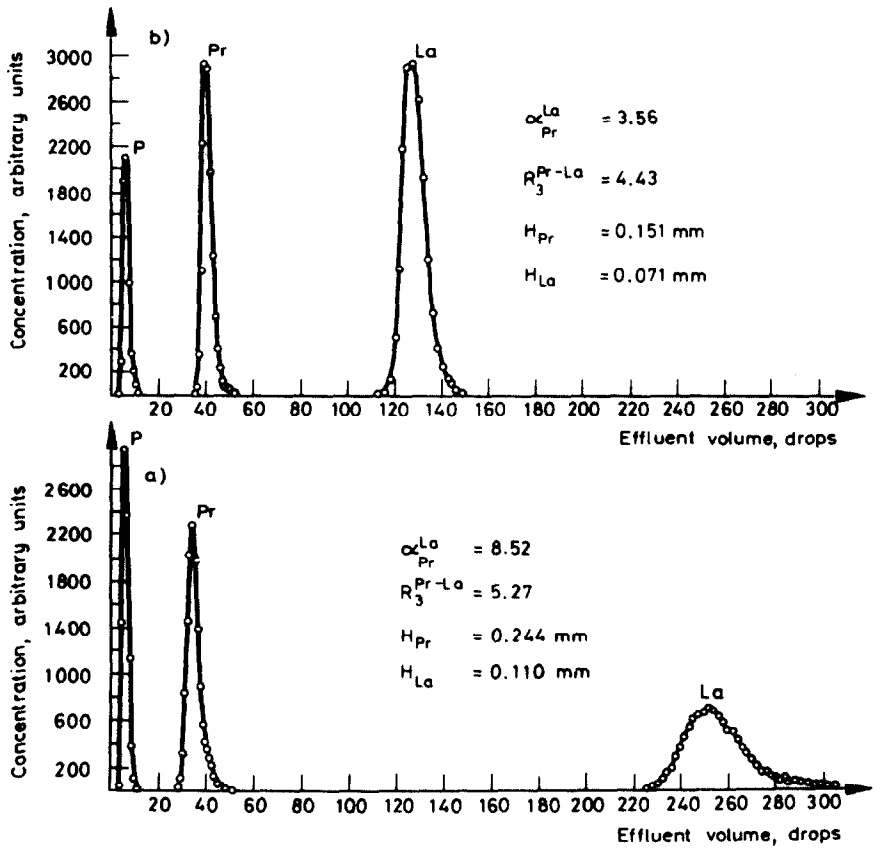

Fig. 7. Comparison of elution curves for trace amounts of La and Pr in various systems. Column, 5.0 cm × 0.0306 cm² Dowex 50W-X8 (11 μm $\leq \phi \leq$ 23 μm). (a) Eluent, 0.2 *M* iminodiacetate (pH 6.3); flow-rate, 0.87 cm/min. (b) Eluent, 0.5 *M* lactate (pH 3.6); flow-rate, 0.76 cm/min. (After Dybczyński [49]).

illustrated by the example of developing a separation method for the NAA determination of lanthanum in Pr_6O_{11} [48,49].

During the search for suitable separation system, elution of rare earth elements (trace amounts) from cation-exchange columns with various complexing agents was studied with the aid of radioactive tracers. Some results are shown in Fig. 7.

Separation factors, α_1^2, theoretical plate heights, H, and resolutions, R_3^{1-2}, were calculated from the following equations:

$$\alpha_1^2 = \frac{\lambda_2}{\lambda_1} = \frac{U_{\max(2)} - (U_0 + V)}{U_{\max(1)} - (U_0 + V)} \tag{1}$$

$$H = \frac{L}{N} = \frac{L\sigma^2}{(U_{\max} - U_0)^2} \tag{2}$$

$$R_3^{1-2} = \frac{U_{\max(2)} - U_{\max(1)}}{3(\sigma_1 + \sigma_2)} = \frac{(\alpha_1^2 - 1)\sqrt{L}}{3(\alpha_1^2 + 1)\sqrt{H}} \tag{3}$$

where:

λ = distribution coefficient;
$U_{\max}$ = retention volume (ml);
U_0 = dead volume of the column;
V = free volume of the resin bed;
L = length of the resin bed;
N = number of theoretical plates;
σ = standard deviation of chromatographic peak.

As can be seen from Fig. 7a, the separation of trace amounts of lanthanum and praseodymium on a micro-column employing 0.2 *M* ammonium iminodiacetate (pH 6.3) as eluent seemed to be

especially promising, better than that obtained with ammonium lactate (Fig. 7b).

For scaling up the separation to amounts of praseodymium up to fractions of milligram, the use of larger columns and a coarser mesh size of the resin to maintain a reasonable flow-rate was necessary. This adversely influenced the column performance but the separation was still fairly good (Fig. 8a). A further increase in the amount of praseodymium in the sample, however, resulted in rapid deterioration of the separation and with 10 mg of praseodymium no separation could be achieved (Fig. 8b).

Hence this system was shown to be very sensitive to overloading. On the other hand, separation of the lanthanides on an anion exchanger, after converting them into anionic complexes with disodium ethylenediaminetetraacetate (Na_2H_2Y), proved to be very insensitive to loading effects. One can see from Fig. 9 that, despite the moderate separation factor ($\alpha_{La}^{Pr} = 3.28$), much smaller than that observed in the cation-exchange system discussed previously, an excellent separation of trace amounts of lanthanum from 1 mg of praseodymium could be easily accomplished.

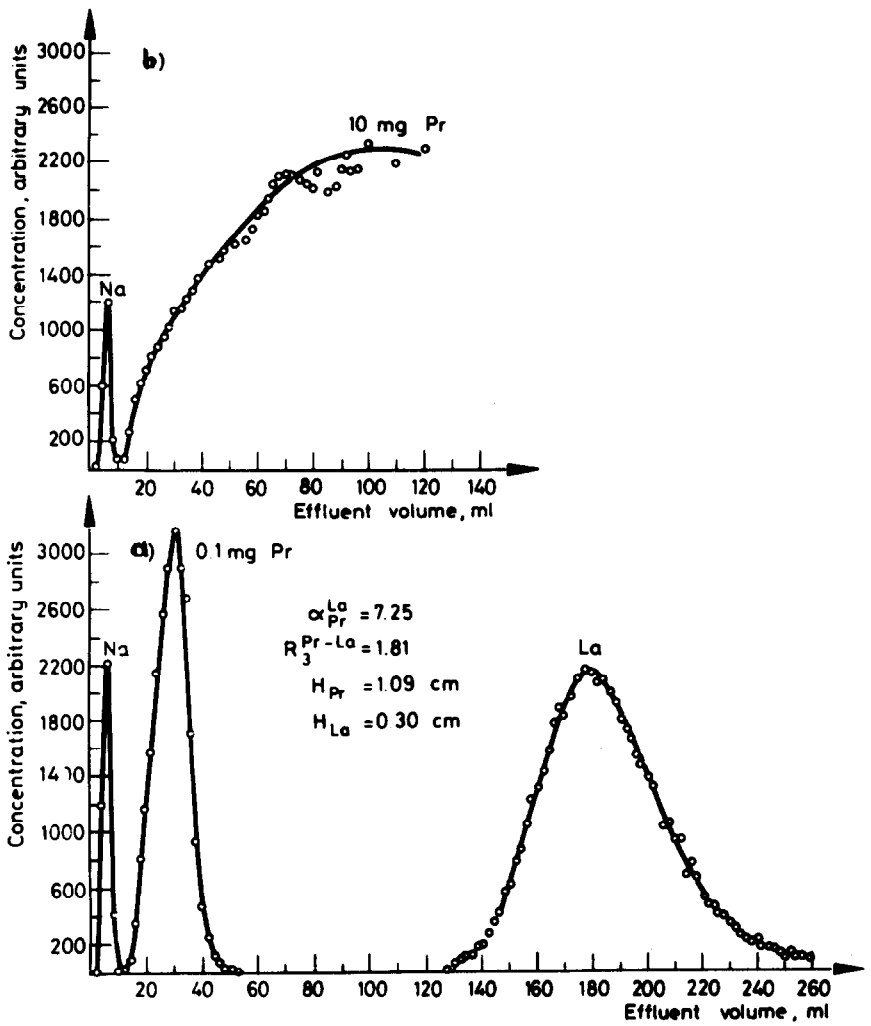

Fig. 8. Effect of loading on the separation of trace amounts of La from Pr by cation-exchange chromatography. Column, 19.6 cm × 0.392 cm^2 Dowex 50W-X8 (0.10 mm $\leq \phi <$ 0.20 mm); eluent, 0.2 *M* iminodiacetate (pH 6.4); room temperature; flow-rate, 2 cm/min. (a) 0.1 mg Pr; (b) 10 mg Pr. (After Dybczyński [49]).

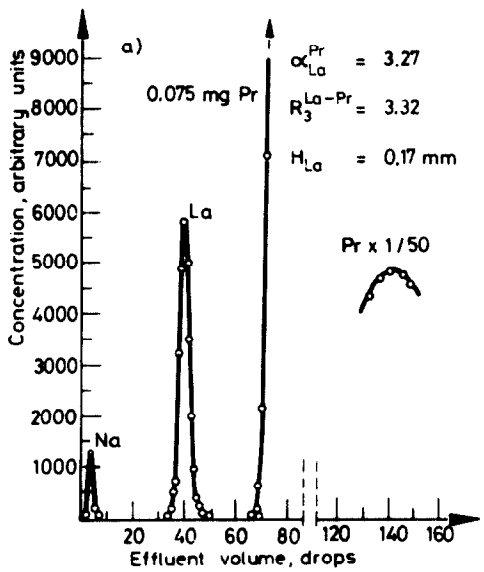

Fig. 9. Effect of loading on the separation of trace amounts of La from Pr by anion-exchange chromatography. (a) Column, 5.8 cm × 0.0306 cm² Dowex 1-X4 (H_2Y^{2-}) (11 μm ≤ ϕ ≤ 42 μm); eluent, 0.05 *M* Na_2H_2Y; temperature, 50°C; flow-rate, 1 cm/min; load, 0.075 mg Pr. (b) Column, 6 cm × 0.116 cm² Dowex 1-X4 (H_2Y^{2-}) (15 μm ≤ ϕ ≤ 48 μm); eluent, 0.03 *M* Na_2H_2Y; temperature, 50°C; flow-rate, 0.91 cm/min; load, 1 mg Pr. (After Dybczyński [49]).

It is interesting that the proper choice of temperature played an important role here in optimization of the separation conditions. In Fig. 10 the temperature dependence of the selectivity coefficients $k_{H_2Y^{2-}}^{LnY^-}$ for the two lanthanides (Ln) in the system Dowex 1-X4 (H_2Y^{2-})–Na_2H_2Y (aq.) is presented. The selectivity coefficient for an ion-exchange reaction:

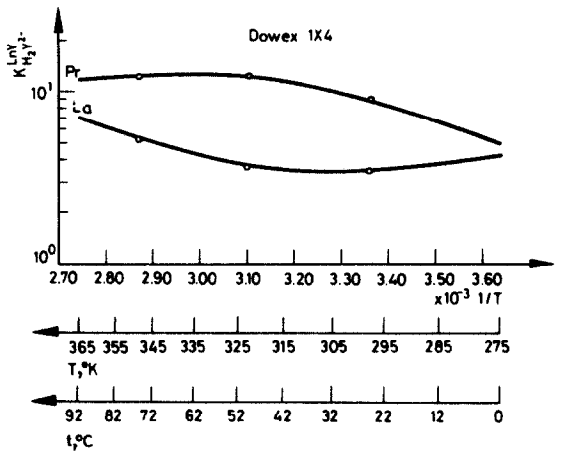

Fig. 10. Temperature dependence of selectivity coefficients for an ion-exchange reaction: $\frac{1}{2}R_2H_2Y + LnY^- = RLnY + \frac{1}{2}H_2Y^{2-}$. (After Dybczyński [49]).

$$\frac{1}{2}R_2H_2Y + LnY^- = RLnY + \frac{1}{2}H_2Y^{2-} \qquad (4)$$

where R denotes a structural unit of the ion exchanger and Y^{4-} is the anion of ethylenediaminetetraacetic acid (H_4Y), may be expressed as [50]

$$k_{H_2Y^{2-}}^{LnY^-} = \frac{\lambda_{LnY^-} m_{H_2Y^{2-}}^{1/2} d}{C_r} \qquad (5)$$

where

λ_{LnY^-} = distribution coefficient of the lanthanide complex;
m = molality of eluent (Na_2H_2Y) solution;
d = density of eluent solution;
C_r = concentration of the resin phase (mmol per g of dry resin [H_2Y^{2-}]),

and so is directly proportional to the distribution coefficient. One can easily note from Fig. 10 that the highest ratio of distribution coefficients, *i.e.*, separation factor, may be expected at 50°C. Both lower and higher temperatures would result in deterioration of the separation conditions.

The significance of the resin cross-linking should

also be emphasized. As was shown in earlier studies [50], the theoretical plate height when separating complex ions of large dimensions may vary considerably. When separating rare earth ethylenediaminetetraacetates on strongly basic anion-exchange resins, Dowex 1 (H_2Y^{2-}), the plate height varies by two orders of magnitude within the cross-linkings X2 and X16, reaching a minimum for Dowex 1-X4 [50]. Hence the proper choice of temperature, resin cross-linking and also the flow-rate is a key factor when aiming at successful separations.

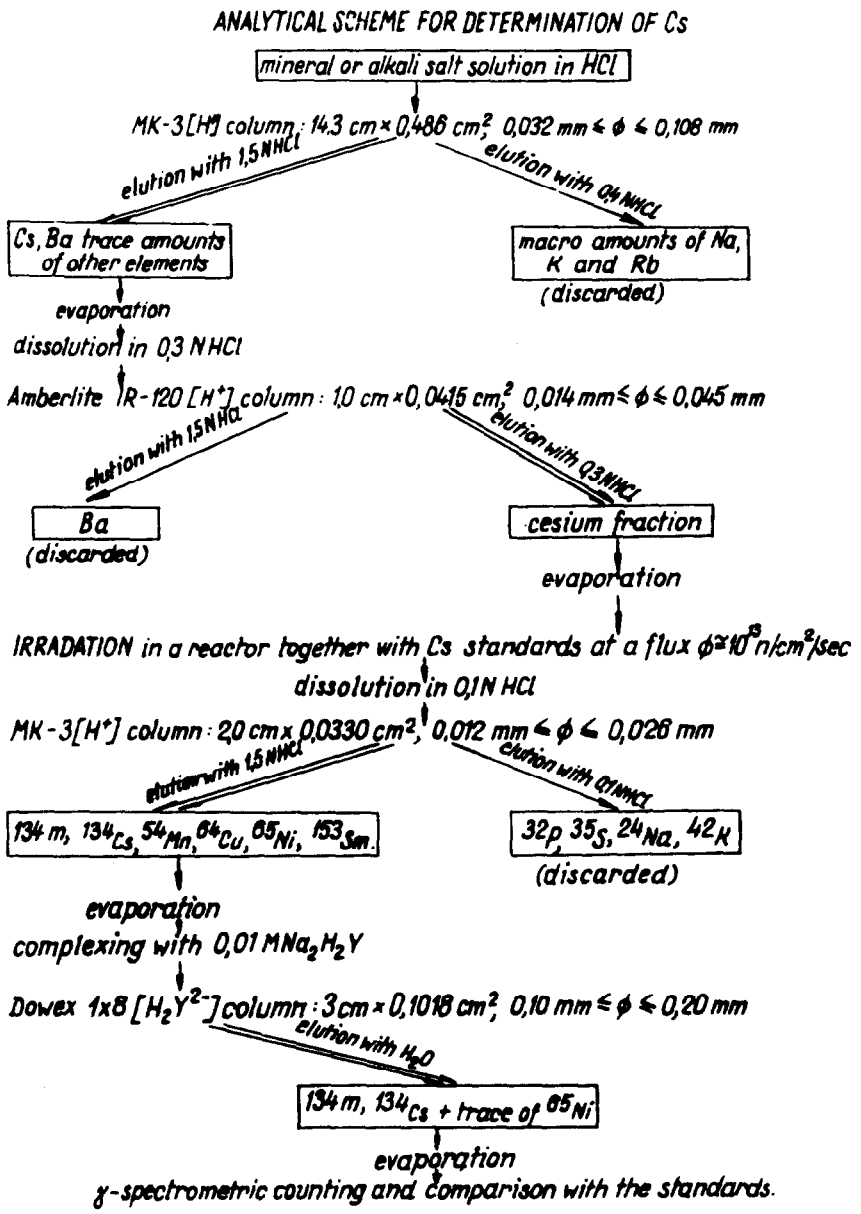

Fig. 11. Analytical scheme for the determination of traces of Cs in mineral salts by NAA, involving pre- and post-irradiation ion-exchange separations. (After Dybczyński and Sterliński [52]).

Somewhat similar to the case of rare earth elements is the problem of micro–macro separations of alkali metals. Some inorganic ion exchangers, such as hexacyanoferrates and salts of heteropoly acids, show high selectivity towards heavier alkali metals, especially caesium [51]. However, the elution of

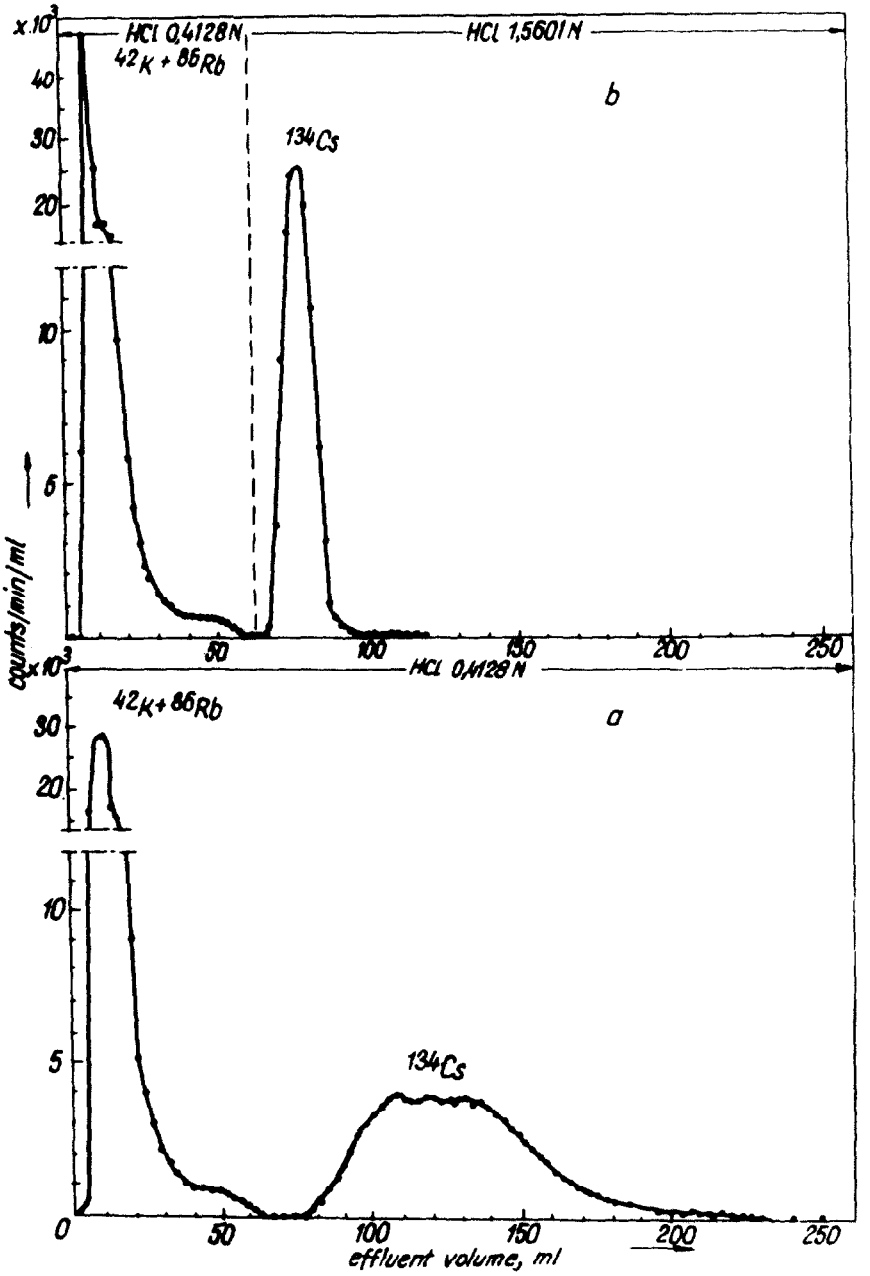

Fig. 12. Typical elution curve illustrating the separation of trace amounts of Cs from macro amounts of potassium (0.5 g KCl) and rubidium impurity. Column, 14.3 cm × 0.486 cm^2 MK-3 (H^+) (phenolsulphonic cation exchanger) (0.032 mm $\leq \phi \leq$ 0.108 mm); temperature, 25°C. Eluent: (a) 0.4128 *M* HCl; (b) 0.4128 *M* HCl until collection of 61 ml of the eluate, then 1.56 *M* HCl; flow-rate, *ca.* 2 ml/cm^2 · min. (After Dybczyński and Sterliński [52]).

caesium from these sorbents is difficult and inorganic ion exchangers are not completely insoluble in aqueous solutions, which may cause problems especially when preconcentration of caesium before irradiation is desired. In such instances the use of organic ion-exchange resins for micro–macro separations may be preferred.

A flow scheme of the analytical procedure for the determination of traces of caesium in mineral salts (NaCl, KCl, etc.) is shown in Fig. 11. In this method, a large sample (0.5 g) is taken and caesium is separated from other elements by stepwise elution from two cation-exchange columns [52]. The first is filled with phenolsulphonic resin, MK-3 (H^+), which shows increased selectivity towards caesium owing to the complexing properties of the phenolic groups, which permits the separation of traces of caesium from macro amounts of sodium, potassium and rubidium (Fig. 12). The other column is filled with a conventional sulphonic-type resin [Amberlite IR-120 (H^+)] on which it is relatively easy to achieve separation of univalent metal ions from those of higher valency.

The combination of pre-irradiation isolation of caesium with post-irradiation separation from impurities and measuring the 31-keV gamma line of the short-lived ^{134m}Cs isotope ($t_{1/2}$ = 3.1 h) with an NaI(Tl) wafer coupled to a pulse-height analyser made it possible to achieve a detection limit as low as 0.08 ppb.

4. PRECONCENTRATION OF TRACE ELEMENTS BEFORE NEUTRON IRRADIATION

All the examples quoted above except the last one concerned radiochemical separations, *i.e.*, procedures in which the sample is first irradiated with neutrons and then, after dissolution, IEC and/or extraction chromatography are employed to isolate the nuclide(s) of interest and to permit the interference-free measurement of its (their) characteristic radiation.

Sometimes, however, it may appear necessary to remove matrix elements before irradiation. Certain types of samples activate too strongly to permit their safe handling with moderate shielding, *i.e.*, without the use of hot chambers. Especially difficult is the situation when the radionuclide to be measured is short-lived and emits γ-rays of low energy. A typical example is shown in Fig. 11. Another typical case is the determination of very low concentrations of elements in large volumes of solution (*e.g.*, water, wastes), where it is necessary to perform preconcentration and to bring the element(s) in question into the form compatible with the requirements set for irradiation in a nuclear reactor.

Therefore, although performing the separation before irradiation eliminates one of unique advantages of NAA, *viz.*, the lack of a blank, there are cases where such an approach is the only possible solution.

4.1. Rare earth elements

Several rare earth elements (REE), *e.g.*, Sm, Gd, Ho, Yb and Lu, form in (n,γ) reactions isotopes that emit γ-rays lying exclusively or mostly in the low-energy region of the γ-ray spectrum. Hence their determination in the presence of a high activity of matrix elements is usually impossible. REE are usually preconcentrated as a group, and this procedure may also be combined in case of need with post-irradiation separation.

Trace amounts of REE in briny groundwaters were preconcentrated by coprecipitation with $Fe(OH)_3$ followed by separation of iron on a Dowex 1-X8 (Cl^-) column from 10 *M* HCl. REE were recovered in the eluate, and sent for irradiation in a reactor [53].

In determine REE at ultratrace abundance levels in geological materials, the samples were decomposed with HF–$HClO_4$ and, after evaporation and removal of fluorides, REE were coprecipitated with calcium oxalate. The precipitate was ignited, dissolved in HNO_3 and REE were purified by several adsorption–elution cycles using Dowex 1-X8 (NO_3^-) anion exchanger and nitric acid mixtures with acetic acid, propanol and methanol. The REE were finally eluted with dilute HNO_3 and subjected to irradiation with neutrons [54].

In another study, REE were preconcentrated from 1.8 *M* HCl solution (obtained after dissolution of rocks in HF–$HClO_4$–HNO_3, evaporation and dissolution in HCl) by retention on a Dowex 50W-X8 (H^+) column. Macro constituents were removed with 2 *M* HCl, then REE were eluted with 6 *M* HCl, converted into nitrates and sent for irradiation [55].

REE in environmental samples were preconcen-

trated on a column with HDEHP adsorbed on porous PTFE powder. Other metals were removed by stepwise elution and the fraction was analysed by NAA [56]. Similarly, extraction chromatography with TOPO adsorbed on Wofatit EP-60 as a stationary phase was used for the separation of REE by stepwise elution from virtually all other elements, including scandium [57].

4.2. Noble metals

Preconcentration is often used when determining noble metals, the contents of which in most of materials are very low. Trace amounts [in the ng/g (ppb) range] of gold and iridium in steel were determined by retention of the two metals on an anion exchanger, elution of most of the impurities and ashing the resin before irradiation [58].

A newly synthesized chelating ion exchanger was used for selective retention of the group of noble metals, *viz.*, Ru, Pd, Os, Ir, Pt and Au [59]. The resin was then ashed and irradiated in a nuclear reactor. This method was employed for the determination of some of these elements in an ore and in high-purity copper metal.

The determination of ultratrace amounts of palladium and platinum may be hindered by the presence of even trace amounts of gold in the sample sent for irradiation. A new method for the determination of palladium and platinum in ores, concentrates and other products of the copper industry consisted in removal of most of cations on a column of Dowex 50W-X8 (H^+) from 0.5 *M* HCl solution, selective retention of gold by "anomalous" sorption on a column of Dowex 50W-X4 (H^+) from 3 M HCl–Cl_2 solution, followed by adsorption of anionic complexes of palladium and platinum on a Dowex 1-X8 (Cl^-) column. The resin was irradiated and wet ashed and post-irradiation separation also by ion-exchange chromatography was used to obtain palladium and platinum fractions of high radiochemical purity with almost 100% yield [60].

Gold, palladium and platinum together with uranium and tungsten were determined in natural water samples by complexation with pyrrolidine-carbodithioate and retention on the column with C_{19}-bonded silica gel at pH 2 followed by neutron irradiation and γ-ray spectrometry [61].

4.3. Other elements

Several elements (Al, Ba, Ca, Ce, Cr, Cu, Fe, La, Mg, Mn, Sc, Sm, V and Zn) can be retained as a group on the chelating resin Chelex 100 at pH 5–6 with simultaneous separation from macro amounts of sodium and chlorine. The resin can then be irradiated with neutrons and measured by high-resolution γ-ray spectrometry, thus permitting the determination of many elements from one sample. This approach was used for the analysis of rain water [62], sea water [63], etc. In a similar way, Al, Cu, Mn and V were determined in solutions obtained from the wet-ashing of biological materials [64].

Another method of group separation before irradiation consisted in retaining Ag, Cd, Co, Cr, Cu, Fe, Hg, Mo, Se and Zn from water and waste on Dowex 1-X2 containing 8-hydroxyquinoline-5-sulphonate as a counter ion [65].

Some preconcentration methods were designed for the determination of selected single elements. For example, vanadium was determined in biological tissues by wet-ashing, retention of vanadium on Dowex 1-X8 from ammoniacal solution, elution of vanadium with 1 *M* HNO_3 and irradiating the eluate [66]. Copper in biological materials was determined via short-lived ^{66}Cu using extraction chromatography with LIX 64 (active component 2-hydroxy-5-nonylbenzophenone oxime) supported on Bio-Beads SM-1. After selective retention of copper from the solution obtained by wet-ashing of the sample in HNO_3–$HClO_4$ and neutralization to pH 4.4, the resin was irradiated in a reactor and measured by γ-ray spectrometry [67].

Two variants of ion-exchange preconcentration were proposed for the determination of several trace elements in tantalum metal [38]. In the first, tantalum solution in HF was passed through Dowex 50W-X8 (H^+) cation exchanger. Tantalum, which forms negatively charged fluoride complexes, passed to the eluate and trace elements were retained on the resin, which was subsequently dried and irradiated with neutrons. The second method consisted in retention of tantalum on Dowex 1-X8 (F^-) anion exchanger and elution of groups of trace elements with HF of various concentrations. The eluates were evaporated and irradiated in a reactor.

Other workers preconcentrated trace amounts of uranium and thorium in tantalum metal by reten-

tion on Dowex 50W-X8 (H^+) from HF–H_3BO_3 solution in which the affinity of tantalum to the resin is low, followed by elution of uranium and thorium with 0.5 *M* HF. As the elution curve of tantalum showed considerable tailing, multiple column operation was used to achieve the desired decontamination factor ($\geqslant 10^6$) (Fig. 13) [68].

It is perhaps worth mentioning that although ion-exchange chromatography is usually used as an auxiliary tool in NAA, sometimes the reverse is also true. For example, NAA has been used for studying the speciation of some elements in biological tissues. In particular, NAA was employed to monitor the separation of protein-bound trace elements (Cu, Mn, Zn, Cd, etc.) as performed by ion-exchange chromatography and other techniques (size-exclusion chromatography, electrofocusing, etc.) [69,70].

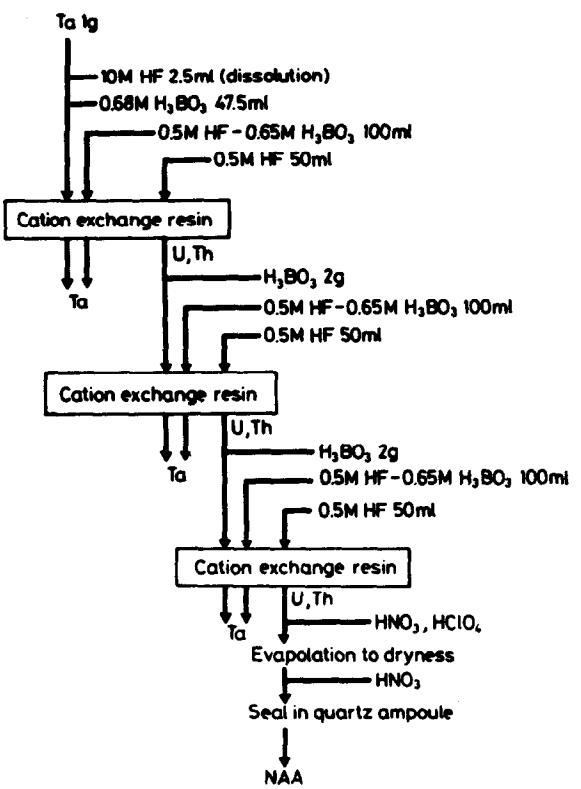

Fig. 13. Scheme for the separation of trace amounts of U and Th from macro amounts of Ta employing multiple column operation. (After Sasaki *et al.* [68]).

5. COLUMN CHROMATOGRAPHY AS A COMPONENT OF "DEFINITIVE" METHODS OF ANALYSIS

In inorganic trace analysis, accuracy is still a problem, as evidenced by the results of numerous interlaboratory comparisons in which results provided by individual laboratories sometimes differed by several orders of magnitude [71–73].

Analytical difficulties tend to increase, often drastically, on going to analyses of materials with very low contents of trace elements [74]. Therefore, there is an obvious need to devise very reliable methods for the determination of individual trace elements, whose status would be close to that of "definitive" methods.

As formulated by Uriano and Gravatt [75], "definitive" methods of chemical analysis are those that have a valid and well described theoretical foundation, have been experimentally evaluated so that reported results have negligible systematic error and have high levels of precision".

Definitive methods reported so far are not numerous. Isotope dilution mass spectrometry has almost exclusively been used to devise definitive methods for the determination of trace amounts of elements [75].

Recently, the first definitive method based on a combination of NAA and column chromatography, intended for the determination of trace amounts of copper in biological materials, was devised in our laboratory [76]. The flow scheme of the method is shown in Fig. 14. The most important step is the highly selective and quantitative separation of radiocopper formed as a result of the $^{63}Cu(n,\gamma)^{64}Cu$ reaction from virtually all other radionuclides present in a neutron-irradiated biological sample. This separation is accomplished with the use of a relatively short column with stationary phase consisting of LIX 70 (active component 2-hydroxy-3-chloro-5-nonylbenzophenone oxime) supported on Bio-Beads SM-1 (styrene–divinylbenzene copolymer) (Fig. 15) [77]. Almost all matrix and accompanying trace elements are eluted with 0.1 *M* glycine buffer (pH 2.8), 0.2 *M* in sodium hypophosphite and 1 *M* in $NaNO_3$, followed by elution of copper with 4 *M* HCl. As can be seen from Fig. 16, the copper fraction is virtually radiochemically pure.

Definitive methods are not intended for routine determinations, but rather for verification of results

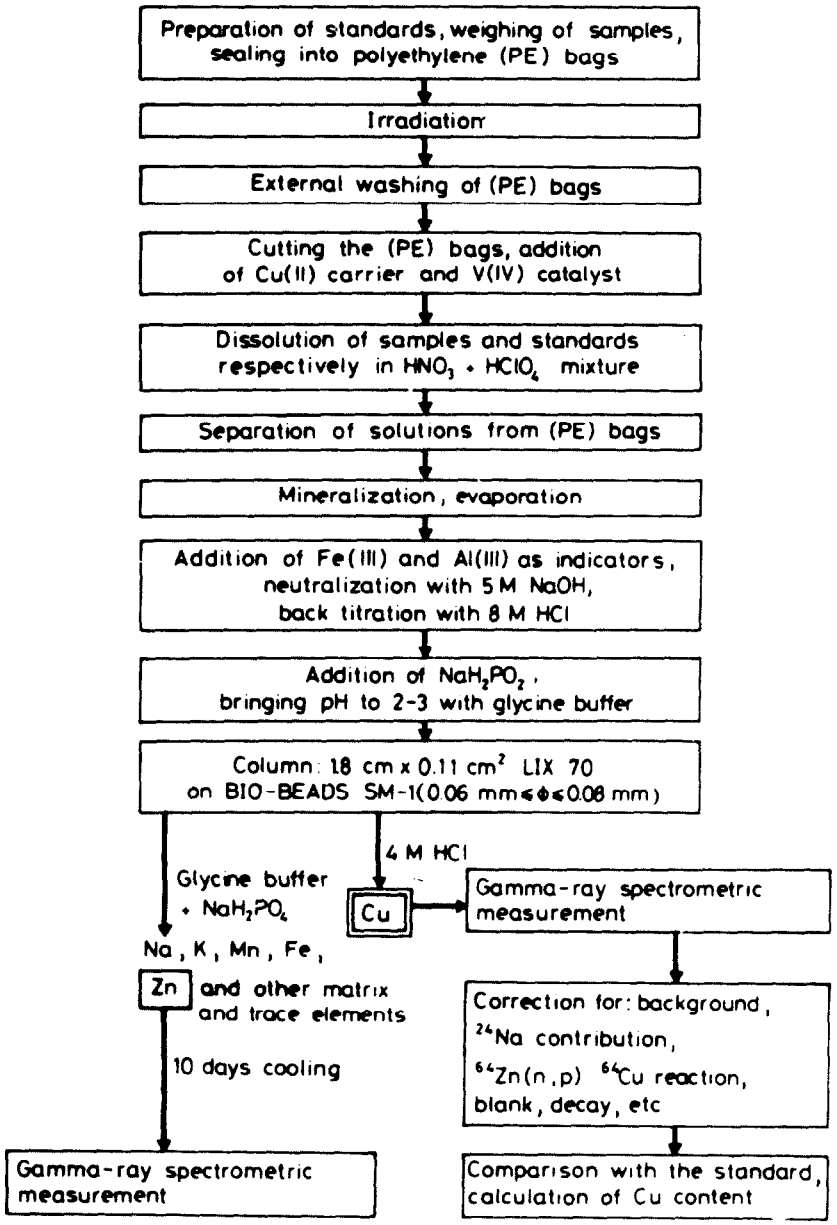

Fig. 14. Flow scheme of the analytical procedure for the determination of Cu in biological materials by NAA, involving selective and quantitative separation of Cu from other elements by extraction chromatography. (After Dybczyński *et al.* [76]).

obtained by other methods of trace analysis and for certification of candidate reference materials. Definitive methods are based on procedures comprehensively elaborated and tested in every detail. However, despite all the precautions taken, theoretically there is always a possibility that something may go wrong without being noticed by the analyst. Therefore, a definitive method should have some warning mechanisms incorporated into the procedure to safeguard against making gross errors.

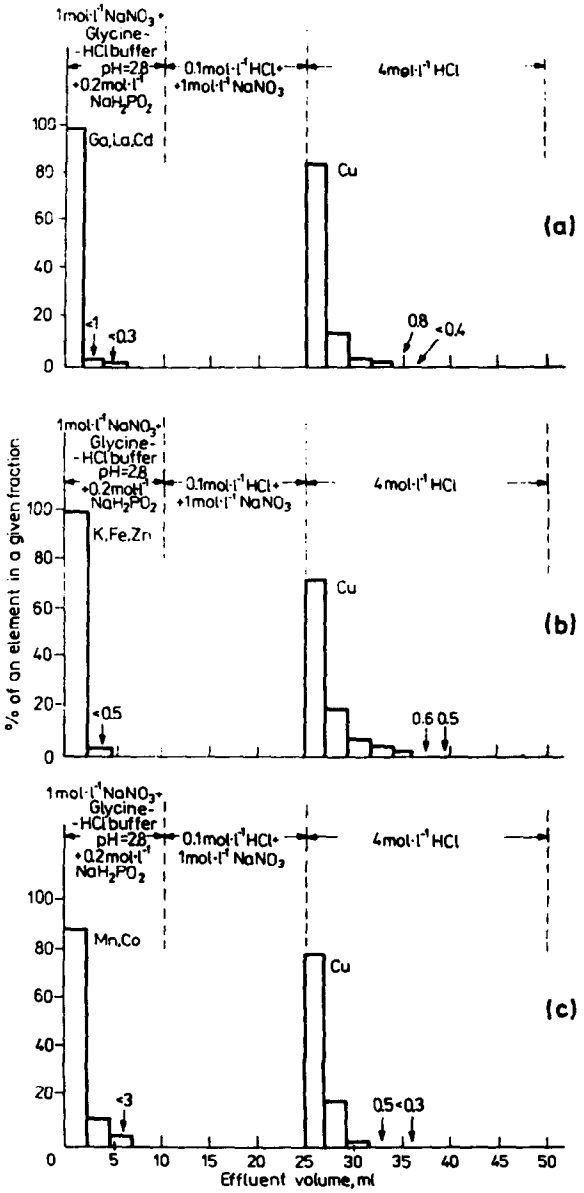

Fig. 15. Typical separations of Cu from various elements by extraction chromatography. Column, 2.3 cm × 0.116 cm² LIX 70 on Bio-Beads SM-1 (0.8 g/g); particle size, 0.06 mm $\leqslant \phi \leqslant$ 0.08 mm; flow-rate, 1.6–2.7 cm/min. (After Dybczyński and Maleszewska [77]).

In this method, the criteria for accepting the results of analysis, in addition to agreement of the normalized count rates of at least two standards, one of which has passed through the whole mineralization and separation procedure and the other is measured directly, low value of the residual blank, correct result for the parallel analysed reference material, etc., include also the visual inspection of the separation process.

Owing to the addition of 50 μg of inactive copper carrier to the sample at the beginning of the analysis, the movement of the greenish blue copper band with a sharp front can easily be followed visually. In the correctly performed procedure the band should not have travelled more than one to two thirds of the bed length by the end of the elution run. If this (and the other conditions mentioned above are not simultaneously fulfilled, then the results of this series of determinations are not considered to be obtained by a definitive method.

6. CONCLUSIONS

This review is intended to demonstrate the significance and important role that ion-exchange and extraction chromatography play in neutron activation analysis. Despite the current trend towards purely instrumental analysis, the use of chemical separations and in particular ion-exchange and extraction chromatography is still indispensable in many instances in NAA, especially when achieving the highest accuracy and interference-free detection limits is required.

A similar philosophy could be applied also to other methods of inorganic trace analysis with this reservation, but contrary to NAA, the problem of the blank is here of much greater significance.

7. ABBREVIATIONS AND SYMBOLS

HAP	hydrated antimony pentoxide (ion exchanger)
HDEHP	di(2-ethylhexyl)orthophosphoric acid
HMD	hydrated manganese dioxide (ion exchanger)
IEC	ion-exchange chromatography
NAA	neutron activation analysis
TBP	tributyl phosphate
TDO	tin dioxide (ion exchanger)
TOPO	tri-*n*-octylphosphine oxide
REE	rare earth elements
Na_2H_2Y	disodium ethylenediaminetetraacetate

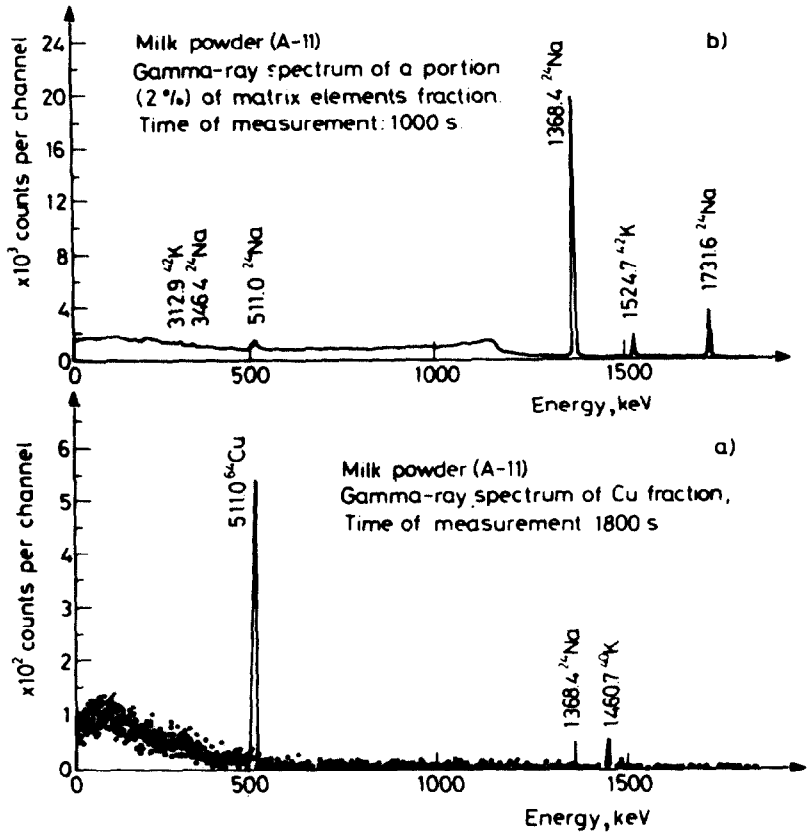

Fig. 16. Typical γ-ray spectra of (a) copper fraction from Milk Powder A-11 [reference material with very low copper content (0.33 mg/kg)] and (b) an aliquot from "matrix elements fraction" from the same material. (After Dybczyński *et al.* [76]).

Ge(Li) detector	lithium-drifted germanium detector
HPGe detector	high-purity germanium detector
NaI(Tl) detector	thallium-activated sodium iodide detector
α_1^2	separation factor
σ	standard deviation of chromatographic peak
λ	distribution coefficient
Φ_{th}	flux of thermal neutrons
C_r	concentration of resin phase
d	density of eluent solution
H	theoretical plate height
k	selectivity coefficient
L	length of the resin bed
m	molality of eluent solution
N	number of theoretical plates
R_3^{1-2}	resolution
$t_{1/2}$	half life
t_i	irradiation time
t_d	decay time
t_c	counting time
U_{max}	retention volume (ml)
U_0	dead volume of the column
V	free volume of the resin bed
ø	particle diameter

REFERENCES

1 D. De Soete, R. Gijbels and J. Hoste, *Neutron Activation Analysis*, Wiley, New York, 1972.
2 V. P. Guinn and J. Hoste, in *Elemental Analysis of Biological Materials (Technical Reports Series*, No. 197), International Atomic Energy Agency, Vienna, 1980.
3 V. Krivan, *Angew. Chem., Int. Ed. Engl.*, 18 (1979) 123.
4 R. Dybczyński, *Chem. Anal. (Warsaw)*, 30 (1985) 749.

5 *Quality Assurance in Biomedical Neutron Activation Analysis, IAEA-TECDOC-323*, International Atomic Energy Agency, Vienna, 1984.
6 S. Sterliński and W. Hammer, *J. Radioanal. Chem.*, 31 (1976) 235.
7 J. Minczewski, J. Chwastowska and R. Dybczyński, *Separation and Preconcentration Methods in Inorganic Trace Analysis*, Ellis Horwood, Chichester, 1982.
8 M. Marhol, *Ion Exchangers in Analytical Chemistry*, Academia, Prague, 1982.
9 E. Egorov and S. B. Makarova, *Ionnyĭ Obmien v Radiokhimii*, Atomizdat, Moscow, 1971.
10 K. Dorfner (Editor), *Ion Exchangers*, Walter de Gruyter, New York, 1991.
11 F. Girardi, R. Pietra and E. Sabbioni, *J. Radioanal. Chem.*, 5 (1970) 141.
12 F. Girardi and R. Pietra, *At. Energy Rev.*, 14 (1976) 521.
13 E. Cerrai, *Chromatogr.* Rev., 6 (1964) 129.
14 T. Braun and G. Ghersini (Editors), *Extraction Chromatography*, Akadémiai Kiadó, Budapest, 1975.
15 G. S. Katykhin, *Zh. Anal. Khim.*, 20 (1965) 615.
16 T. A. Bolshova and E. N. Shapovalova, *Zh. Anal. Khim.*, 38 (1983) 1489.
17 F. Girardi and E. Sabbioni, *J. Radioanal. Chem.*, 1 (1968) 169.
18 P. S. Tijoe, J. J. M. De Goeij and J. P. W. Houtman, *J. Radioanal. Chem.*, 37 (1977) 511.
19 N. Levi, F. Lux and Z. B. Alfassi, *J. Radioanal. Nucl. Chem.(Articles)*, 129 (1989) 93.
20 A. Bilewicz, B. Bartoś, J. Narbutt and H. Polkowska-Motrenko, *Anal. Chem.*, 59 (1987) 1737.
21 K. Samsahl, *Sci. Total Environ.*, 1 (1972) 65.
22 J. A. Velandia and A. K. Perkons, *J. Radioanal. Chem.*, 20 (1974) 743.
23 L. O. Plantin, *Nuclear Activation Techniques in the Life Sciences, Proceedings of Symposium, Bled, 1972*, International Atomic Energy Agency, Vienna, 1972, p. 73.
24 G. V. Iyengar, *J. Radioanal. Nucl. Chem. (Articles)*, 110 (1987) 503.
25 P. Collecchi, M. Esposito, S. Meloni and M. Oddone, *J. Radioanal. Nucl. Chem. (Articles)*, 112 (1987) 473.
26 A. Brandone, P. A. Borroni and N. Genova, *Radiochem. Radioanal. Lett.*, 57 (1983) 83.
27 M. B. A. Vasconcellos, V. A. Maihara, D. I. T. Fararo, M. J. A. Armelin, E. Cortes-Toro and R. Ogris, *J. Radioanal. Nucl. Chem. (Lett.)*, 153 (1991) 185.
28 R. Zeisler, R. R. Greenberg and S. F. Stone, *J. Radioanal. Nucl. Chem. (Articles)*, 124 (1988) 47.
29 B. Danko, R. Łobiński and R. Dybczyński, *J. Radioanal. Nucl. Chem. (Lett.)*, 137 (1989) 145.
30 R. Dybczyński and S. S. Aldabbagh, *Analyst (London)*, 112 (1987) 449.
31 R. Dybczyński and Z. Samczyński, *J. Radioanal. Nucl. Chem. (Articles)*, 150 (1991) 143.
32 J. J. Fardy, G. D. Meorist and T. M. Florence, *Anal. Chim. Acta*, 159 (1984) 199.
33 J. J. Fardy and M.-G. Tang, *J. Radioanal. Nucl. Chem. (Articles)*, 123 (1988) 573.
34 A. I. Kalinin, R. A. Kuztentsov, V. V. Moiseev and V. E. Tspepurnek, *Radiokhimicheskie Metody Opredeleniya Mikroelementov*, Nauka, Moscow, 1965, p. 161.
35 M. M. Ivanova, I. P. Oglobina, S. A. Genel, V. V. Mitina, A. I. Kalinin and V. G. Lambrev, *Zh. Anal. Khim.*, 32 (1977) 1066.
36 M. Gallorini, M. di Casa and G. F. Cerofolini, *Radiochem. Radioanal. Lett.*, 55 (1982) 77.
37 T. Mitsugashira, Y. Koma, S. Hirai, I. Okada, N. Kurashima and H. Sakurai, *J. Radioanal. Nucl. Chem. (Articles)*, 147 (1991) 69.
38 R. Caletka, R. Hausbeck and V. Krivan, *J. Radioanal. Nucl. Chem. (Articles)*, 120 (1988) 319.
39 R. Caletka, R. Hausbeck and V. Krivan, *J. Radioanal. Nucl. Chem. (Articles)*, 120 (1988) 305.
40 K. S. Park, N. M. Kim, Y. S. Kim, K. Y. Lee, H. W. Choi and Y. Y. Yoon, *J. Radioanal. Nucl. Chem. (Articles)*, 123 (1988) 585.
41 S. S. Grazhulene, V. K. Karandashev and Yu. V. Yakovlev, *Radiochem. Radioanal. Lett.*, 57 (1983) 273.
42 S. S. Grazhulene, V. K. Karandashev and Yu. V. Yakovlev, *Radiochem. Radioanal. Lett.*, 59 (1983) 225.
43 V. K. Karandashev, S. S. Grazhulene and Yu. V. Yakovlev, *J. Radioanal. Nucl. Chem. (Lett.)*, 106 (1986) 223.
44 M. Oddone, S. Meloni and R. Vanucci, *J. Radioanal. Nucl. Chem. (Articles)*, 142 (1990) 489.
45 C. F. Chai, S. L. Ma, X. Y. Mao, K. N. Liao and W. C. Liu, *J. Radioanal. Nucl. Chem. (Articles)*, 114 (1987) 281.
46 M. J. A. Armelin, M. B. A. Vasconcellos, E. B. Pereira and F. Sireilli Neto, *J. Radioanal. Nucl. Chem. (Articles)*, 132 (1989) 261.
47 A. Fołdzińska and R. Dybczyński, *J. Radioanal. Chem.*, 21 (1974) 507.
48 R. Dybczyński, S. Sterliński and C. Golian, *J. Radioanal. Chem.*, 16 (1973) 105.
49 R. Dybczyński, *J. Radioanal. Chem.*, 31 (1976) 115.
50 R. Dybczyński, *J. Chromatogr.*, 50 (1970) 487.
51 K. H. Lieser, in K. Dorfner (Editor), *Ion Exchangers*, Walter de Gruyter, New York, 1991, p. 519.
52 R. Dybczyński and S. Sterliński, in I. Buzas (Editor), *Proceedings of the Analytical Chemical Conference, Budapest, 20–23rd April 1966*, Technical University, Budapest, 1966, p. 398.
53 J. C. Laul, F. A. Lepel and H. R. Smith, *J. Radioanal. Nucl. Chem. (Articles)*, 123 (1988) 349.
54 C. Koeberl, F. Kluger and W. Kiesl, *J. Radioanal. Nucl. Chem. (Articles)*, 112 (1987) 481.
55 Y. Terakado, T. Fujitani and T. Takada, *J. Radioanal. Nucl. Chem. (Articles)*, 129 (1989) 23.
56 L. A. Smakhtin, L. I. Mekhryusheva, N. V. Filippova, N. V. Migalina and T. S. Sinitsyna, *J. Radioanal. Nucl. Chem. (Lett.)*, 154 (1991) 293.
57 B. Gorski, Yu. S. Korotkin and V. N. Kosyakov, *J. Radioanal. Nucl. Chem. (Lett.)*, 135 (1989) 27.
58 X.-L. Wang, Y.-L. Chen, X.-Y. Wang, Y. Sun, Y.-B. Fu and G.-P. Gao, *J. Radioanal. Nucl. Chem. (Articles)*, 147 (1991) 377.
59 K. Huang, G. S. Zhuang and Y. O. Cheng, *J. Radioanal. Nucl. Chem. (Articles)*, 112 (1987) 193.
60 R. Dybczyński, J. Majchrzak, H. Stokowska and H. Szyszko, *Chem. Anal. (Warsaw)*, 35 (1990) 609.

61 N. K. Shah and C. M. Wai, *J. Radioanal. Nucl. Chem. (Articles)*, 130 (1989) 451.
62 J. E. Milley and A. Chatt, *J. Radioanal. Nucl. Chem. (Articles)*, 110 (1987) 345.
63 R. R. Greenberg and H. M. Kingston, *Anal. Chem.*, 71 (1982) 147.
64 R. R. Greenberg, H. M. Kingston, R. Zeisler and J. Woittiez, *Biol. Trace Elem. Res.*, 26 (1990) 17.
65 W.Żmijewska, H. Polkowska-Motrenko and H. Stokowska, *J. Radioanal. Nucl. Chem. (Articles)*, 116 (1987) 243.
66 A. J. Blotcky, F. G. Hamel, A. Stranik, A. Ebrahim, R. B. Sharma, E. R. Rack and S. S. Solomon, *J. Radioanal. Nucl. Chem. (Articles)*, 131 (1989) 319.
67 R. Dybczyński, B. Danko and J. Kaczorowski, *Chem. Anal. (Warsaw)*, 34 (1989) 103.
68 Y. Sasaki, H. Takeishi, T. Adachi and K. Izawa, *J. Radioanal. Nucl. Chem. (Articles)*, 139 (1990) 143.
69 C. K. Jayawickreme and A. Chatt, *J. Radioanal. Nucl. Chem. (Articles)*, 124 (1988) 257.
70 C. K. Jayawickreme and A. Chatt, *Biol. Trace Elem. Res.*, 26 (1990) 503.
71 G. H. Morrison, *Anal. Chem.*, 43 (1971) 22A.
72 D. J. von Lehmden, R. H. Jungers and R. E. Lee, Jr., *Anal. Chem.*, 46 (1974) 239.
73 R. Dybczyński, A. Veglia and O. Suschny, in P. Bratter and P. Schramel (Editors), *Trace Element Analytical Chemistry in Medicine and Biology*. Walter de Gruyter, New York, 1980, p. 657.
74 R. Dybczyński, in *Nuclear Techniques for Analysis of Environmental Samples, IAEA/RL/135*, International Atomic Energy Agency, Vienna, 1986.
75 G. A. Uriano and C. C. Gravatt, *CRC Crit. Rev. Anal. Chem.*, 6 (1977) 361.
76 R. Dybczyński, M. Wasek and H. Maleszewska, *J. Radioanal. Nucl. Chem. (Articles)*, 130 (1989) 365.
77 R. Dybczyński and H. Maleszewska, *Chem. Anal. (Warsaw)*, 32 (1987) 619.