Pure & Appl. Chem., Vol.54, No.4, pp.755-767, 1982.
Printed in Great Britain.

0033-4545/82/040755-13$03.00/0
Pergamon Press Ltd
©1982 IUPAC

PRECONCENTRATION AND DECONTAMINATION IN RADIOANALYSIS

H.A. Das

Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN (N.H.)

Abstract - The scope of radioanalysis can be enlarged substantially by preconcentration. The minimal concentration factor required depends on the concentration to be determined, the limit of determination of the analytical technique and the maximal acceptable sample-weight. Simultaneously, the preconcentration step may cause a decontamination. In post-irradiation chemistry this is usually the crucial parameter.

The present paper proposes the classification of (pre-) concentration techniques by the relation between the concentration-factor X and the decontamination-factor Y.
In addition, three other criteria here are used to judge the applicability in combination with the analytical technique chosen. They stem from the minimal representative and the maximal acceptable sample-weights and the maximal acceptable dose-rate. The features of a particular combination of (pre-)concentration and analytical technique can be visualized in an X-Y graph.

The possibilities of the various concentration-techniques are discussed in terms of the mentioned criteria. Additionally, the economic aspects are considered.
It appears that an inorganic scavenger like active carbon or automatized liquid-liquid extraction is in general the best choise. More laborious techniques should be reserved for separate determinations of single elements.

1. ANALYTICAL CRITERIA FOR PRECONCENTRATION IN ELEMENTAL ANALYSIS

1.1. General. The scope of any analytical method may be enhanced by preconcentration of the compound of interest and the elimination of interferences. Often these steps may be combined. Obviously, preconcentration makes sense only if the sample material cannot be analysed as such. This depends on (a) the limit of determination, $(L_Q)_m$, expressed in µg, (b) the maximal volume or weight, V_1 or G_1, which can be handled, in ml or g, (c) the expected concentration level $\bar{C}_o$, expressed in $\mu g.ml^{-1}$ or $\mu g.g^{-1}$.
If the limit of determination for the untreated material is $(L_Q)_m$, the scope of the analysis without preconcentration is given by

$$V_1 \cdot \bar{C}_o > (L_Q)_m \qquad (1^a)$$

$$\text{or } G_1 \cdot \bar{C}_o > (L_Q)_m \qquad (1^b)$$

If this condition is not fulfilled it may be reached by
(a) increasing the concentration or (b) lowering the limit of determination.

The preconcentration-step may be defined by four criteria: (a) Concentration factor; (b) Decontamination factor; (c) Recovery; (d) Specificity.

1.2. Concentration factor. A concentration procedure reduces the original volume or weight, V_o or G_o, to new values V_1 or G_1, under constant, preferably quantitative, recovery of the compound of interest.
It thus follows from equations (1) that

$$X.V_1 \cdot \bar{C}_o = V_1\bar{C}_1 \geq (L_Q)_m \qquad (2^a)$$

$$\text{or } X.G_1 \cdot \bar{C}_o = G_1\bar{C}_1 \geq (L_Q)_m \qquad (2^b)$$

where X stands for the concentration factor and $\bar{C}_1$ for the average concentration in the preconcentrated aliquots.

The actual concentrations of the individual samples will vary around the estimated average. If this variation follows a Poisson-distribution, $\sigma(\bar{C}_o) = \sqrt{\bar{C}_o}$ and 99% of the samples will be covered by the analysis if equations (2^c) or (2^d) hold.

$$X.V_1 \cdot (\bar{C}_o - 2.5\sqrt{\bar{C}_o}) \geq (L_Q)_m \qquad (2^c)$$

$$X.G_1 \cdot (\bar{C}_o - 2.5\sqrt{\bar{C}_o}) \geq (L_Q)_m \qquad (2^d)$$

The blank caused by the preconcentration step poses a third condition:

$$\frac{\text{blank}}{[\text{mass of analyte}]} = \frac{\text{blank (in } \mu g)}{X.V_1 \cdot \bar{C}_o} \text{ or } \frac{\text{blank (in } \mu g)}{X.G_1 \cdot \bar{C}_o} \leq \frac{1}{r} \qquad (3)$$

The minimal acceptable value of r depends on the uncertainty in the blank. A reasonable practical choice is r = 2. When the blank is caused by the reagents solely it is obvious that

$$\frac{1}{r} \geq (\text{blank concentration}) \cdot \frac{[\text{mass of reagent}]}{[\text{mass of analyte}]} \qquad (4^a)$$

1.2. Decontamination factor. The elimination of interferences which is caused by the preconcentration step may be expressed in terms of the decontamination factor Y, defined as the double ratio

$$Y = \left(\frac{\text{concentration element of interest}}{\text{concentration interference}}\right) \text{ after/before} \qquad (5)$$

In general the value of $(L_Q)_m$ depends on that of Y. In spectrometric techniques a net peak-area is obtained by subtraction of a background which is due to the interferences. Moreover, the peak involved may be interfered by a similar peak of the interfering compound. Separation by a numerical technique will cause an extra uncertainty and thus increase $(L_Q)_m$. If it is required that the peak of interest is at least as strong as that of the interference a minimal value of Y can be defined.
The relation between X and Y and the minimal value of Y is "the X-Y-line" in an X-Y graph. The shape of this line depends on the preconcentration procedure.

For each material there exists a minimal representative sample-weight which imposes a minimal X-value depending on the maximal sample-weight or volume which can be handled. This is represented by a vertical line in the X-Y graph.

Finally the maximal weight which can be handled in activation analysis due to counting limitations depends on Y. In trace analysis this relation is usually a simple proportionality. In the X-Y diagram this becomes "the decontamination line". Its shape depends on the sampled material and the irradiation.

1.3. Recovery. The recovery, R, is defined as 100.[amount collected]/[amount present]. One may consider R as a function of the ratio $p = \frac{[\text{mass of reagent}]}{[\text{mass of analyte}]}$ as shown in figure 1. In the ideal case of a complete reaction and with a stoichiometric ratio α one has

$$R = \frac{100}{\alpha} \cdot p \qquad (6)$$

Then equation (4^a) becomes

$$\frac{1}{r} \geq (\text{blank concentration}) \cdot \frac{\alpha \cdot R}{100} \qquad (4^b)$$

Thus for a quantitative recovery and a given value of α the choice of r sets the maximal acceptable value of the blank concentration in the reagent.

1.4. Specificity. The determination of the isolated compound should be free of an appreciable bias due to interferences. The specifity for compound t, S_i, may thus be defined as

$$S_i = 100 \cdot \frac{k_i[A]_i}{\Sigma k_i[A]_i} \qquad (7)$$

where A_i is the mass of the analyte i and k_i the corresponding specific sensitivity.

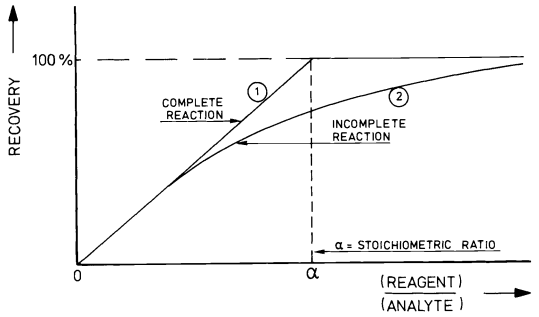


Fig.1. The recovery as a function mass of reagent/mass of analyte.

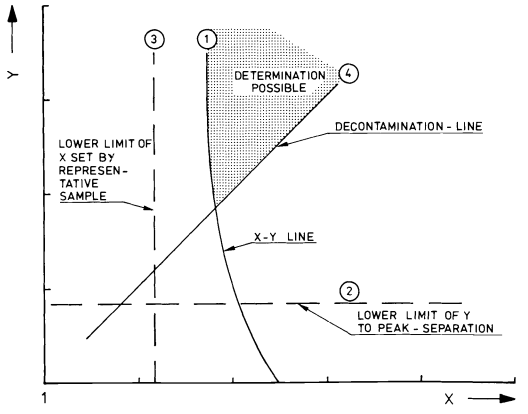


Fig.2. Principle of the X-Y diagram.

1.5. The X-Y diagram. Figure 2 summarizes the features of the X-Y diagram. The area which represents the analytical possibilities lies right of the lines 1 and 3 and above the lines 2 and 4. In addition to these requirements equation (3) has to be fulfilled.

1.6. Chemical speciation. A special case is presented by the separate determination of the different chemical forms of one element. This may sometimes be done by separate procedures for each species. More often it is achieved by some sort of chromatography. Then the peak-width is proportional to the amount of material. This implies that the required column length, needed to obtain a certain separation factor, is proportional to $(L_Q)_m^2$.

For a given separation technique the R- and S-values may be calculated from the experimentally observed separation factors and peak-widths.

2. APPLICATION TO RADIOANALYSIS

2.1. Choice of the procedure. The procedure which is followed in choosing a preconcentration/purification step is shown schematically in table 1. It is iterative by nature as $(L_Q)_m$ depends on Y. Whether the chosen procedure is feasible or not depends on the blank.

In activation analysis two additional, closely related, factors have to be considered: (a) the half-life of the radionuclide involved; (b) the dose-rate at the time of handling. In practice one gets the eight combinations shown in table 2. In cases 6 - 8 the analyst is in a conflicting situation. His choice depends on the local circumstances.

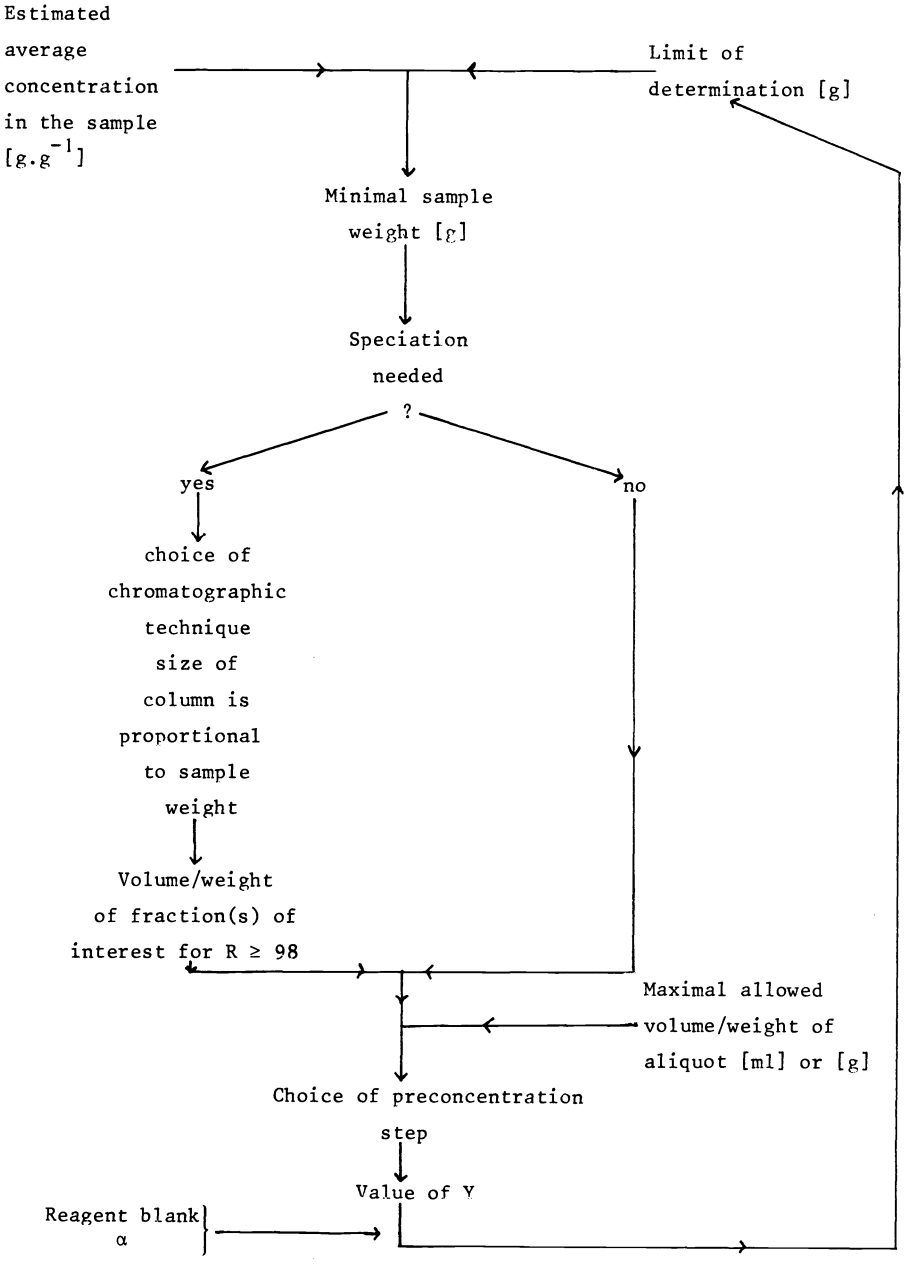
2.2. The limit of determination. The value of $(L_Q)_m$ follows from the total standard deviation in the final result of the analysis of the preconcentrated aliquot. One may write:

$$(L_Q)_m \geq k_Q \cdot G_1 \cdot \Sigma\, \sigma(\bar{C}_1) \qquad (8^a)$$

$$\text{or } (L_Q)_m \geq k_Q \cdot V_1 \cdot \Sigma\, \sigma(\bar{C}_1) \qquad (8^b)$$

where G_1 and V_1 are the maximal processable weight and volume of the preconcentrated aliquot. To cover 99% of all samples $\bar{C}_1$ has to be replaced by $\bar{C}_1 - 2.5\sqrt{\bar{C}_1}$ (cf. equation 2^c and 2^d). The factor k_Q is a matter of personal appreciation [1]; often one sets $k_Q = 10$. Inserting

Table I. Scheme for the iterative choice of a preconcentration (-purification) procedure



$$\Sigma\,\sigma(\bar{C}_1) = \bar{C}_1 \cdot \Sigma\,\sigma_{rel}(\bar{C}_1) \qquad (9)$$

into (8), one obtains $(L_Q)_m$ as a function of the total relative standard deviation in $\bar{C}_1$:

$$L_Q \quad k_Q \cdot G_1 \cdot \bar{C}_1 \cdot \Sigma\,\sigma_{rel}(\bar{C}_1) \qquad (10)$$

Now $\Sigma\,\sigma_{rel}(\bar{C}_1)$ increases with decreasing $\bar{C}_1$ [2,3]. The minimal acceptable $\bar{C}_1$-value and thus $(L_Q)_m$ follows then from the relation

$$\Sigma\,\sigma_{rel}(\bar{C}_1) \leq \frac{1}{k_Q} \qquad (11)$$

The total relative standard deviation is built up from the relative σ's in the peak-area determinations for sample and standard, in the relative flux- or beam-intensity measurements and in the electronic correction factors.
In X-ray and γ-ray spectrometry these correction factors are usually obtained by way of peak-area determination as well. The relative standard deviation in an individual photopeak can be calculated from the specific count-rate in the peak, the ratio compton background/peak, the counting time and the number of channels in the peaks [2,3].
The second parameter decreases with increasing Y. One may write the compton background as the sum of two or more terms, each with a characteristic half-life. The elimination of interfering radionuclides will reduce one or more of these contributions.

Equally the maximal amount of sample which can be handled may increase by elimination of interfering radionuclides, if the dose-rate during handling is the governing factor. This is often the case when short-lived radionuclides have to be measured.

2.3. The use of the X-Y diagram. The use of the quantities X and Y may be demonstrated on two extreme cases. In the first example, the value of X is of primordial importance while in the second the improvement is due to a large Y-value. In both cases the recovery is (nearly) quantitative.

The first case deals with the determination of mercury in unpolluted air by thermal neutron activation [4]. Typical concentrations vary from 1 to 10 $ng.m^{-3}$. The available $(L_Q)_m$-value for instrumental neutron activation is ≃ 10 ng while the maximal acceptable volume V_1 = 5 ml. Thus, according to (1^a), X must be ≥ 2.10^6.
The metal is present in elemental form and as organomercurials; it is collected by pumping ≃ 5 m^3 air through ≃ 2 g (= 5 ml) active carbon. Air dust is removed by a 0.20 μm membrane filter. This eliminates the interfering elements sodium and bromine; Y ≃ 10^3.
The carbon contains < 1 $ng.g^{-1}$. Thus the ratio blank/collected mass is thus well below 0.5 as required by equation (3). Determination is based on activation to ^{197}Hg ($T_{\frac{1}{2}}$ = 66 h) and assayed by way of the 77 keV photopeak. Due to the removal of ^{24}Na and ^{82}Br the compton-background is reduced by two orders of magnitude which decreases $(L_Q)_m$ by a factor of ~ 10. Consequently one needs X ≃ 2.10^5 now. The actual X-value obtained is X = 4.10^5 - 10^6. Figure 3^a gives an account of the situation. The lines of the minimal X- and Y-values coincide the X- and Y-axis.

The second example refers to the determination by thermal neutron activation of arsenic in the NBS Standard Reference Material "Orchard Leaves" [5].
The relatively short-lived radionuclide ^{76}As ($T_{\frac{1}{2}}$ = 26.4 h) is measured by its 556 keV photopeak. It is interfered by the 559 keV line of ^{82}Br ($T_{\frac{1}{2}}$ = 35.6 h). The concentrations of arsenic and bromine in Orchard Leaves are ≃ 10 ppm [6]. Table 3 gives the values of $(L_Q)_m$ and the minimal determinable concentration $\bar{C}_1$ as a function of the cooling time. Without separation the maximal acceptable weight due to the dose-rate after 48 hrs of cooling is G_1 ≃ 1 mg. This maximal weight increases proportional with the decontamination factor against ^{24}Na and ^{82}Br: G_1 (in mg) ≃ Y. With an average mass of the concentrated aliquot of one gram, one has thus Y ≃ 10^3 X as the equation for the decontamination line.
The irradiation facility accepts sample weights up to ~ 0.5 g. A representative sample should be 100 mg at least. Thus the minimal X-value is ≃ 0.5. The ratio of the specific count rates in the ^{76}As- and ^{82}Br-peaks is 1.5. This sets the minimal Y-value at ≃ 2.

The arsenic is isolated by coprecipitation with $Fe(OH)_3$. For the decontamination from ^{24}Na and ^{82}Br Y ≥ 5.10^2. The equation of the X-Y line is a horizontal.

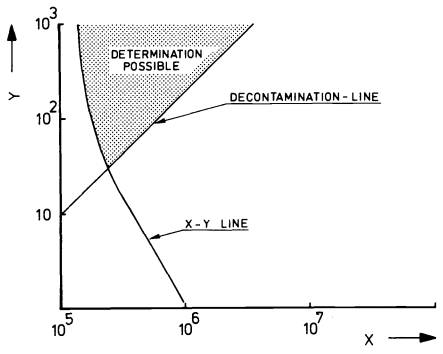


Fig. 3a

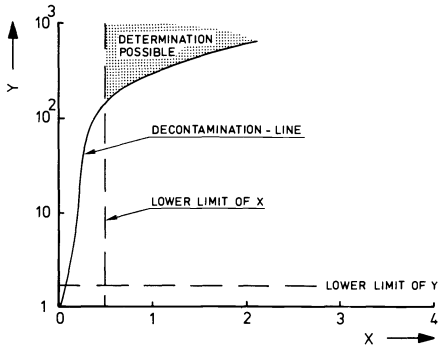


Fig. 3b

Fig.3a. The X-Y graph for the determination of mercury in air.

Fig.3b. The X-Y graph for the determination of arsenic in dry plant material.

Figure 3[b] visualizes the situation for a cooling time of 48 hours.

TABLE 2. Survey of the eight different situations encountered in the determination of total element concentrations by neutron activation analysis

No.	Volume	Blank	Dose rate and Time	Concentration/ purification prior or after the irradiation	Remarks	Example
1				after	Separation necessary for the elimination of interfering radionuclides	Cr in dry biological material
2		x		after		W in silicates
3			x	prior		Trace elements in metallic mercury
4	x			prior		Trace elements in airdust
5	x		x	prior		V in seawater
6	x	x	x	prior	Depends on the purification of the tools and reagents. Otherwise impossible	Mn in seawater
7	x	x		prior		Lanthanides in surface water
8		x	x	prior	Depends on the time needed for return to the laboratory and that used in dissolution and separation	Al in blood

The x sign indicates that the corresponding criterion is not met.

TABLE 3. The values of $(L_Q)_m$ and $\bar{C}_1$ as a function of the cooling time for the determination of arsenic in dry plant material by thermal neutron activation analysis

Cooling time in hours	G_1 = 1 Y = 1		G_1 = 10 Y = 10		G_1 = 100 Y = 100		G_1 = 400 Y = 400	
	$(L_Q)_m$ in µg	$\bar{C}_1$ in ppm	$(L_Q)_m$ in µg	$\bar{C}_1$ in ppm	$(L_Q)_m$ in µg	$\bar{C}_1$ in ppm	$(L_Q)_m$ in µg	$\bar{C}_1$ in ppm
12	0.025	25	0.015	1.5	0.015	0.2	0.015	0.05
24	0.03	30	0.015	1.5	0.015	0.2	0.02	0.05
36	0.04	40	0.025	2	0.02	0.2	0.025	0.1
48	0.05	50	0.02	2	0.025	0.3	0.035	0.1
60	0.07	70	0.025	2.5	0.03	0.3	0.045	0.15
72	0.09	85	0.035	3.5	0.04	0.4	0.06	0.15
84	0.12	115	0.045	4.5	0.05	0.5	0.08	0.2
96	0.15	150	0.055	5.5	0.07	0.7	0.11	0.3
108	0.21	205	0.075	7.5	0.09	0.9	0.14	0.35
120	0.28	280	0.10	10	0.12	1.2	0.19	0.5

G_1 = Mass of preconcentrated counting aliquot

Y = Decontamination factor from ^{24}Na and ^{82}Br, needed to make counting possible.

3. PRECONCENTRATION TECHNIQUES IN RADIOANALYSIS

3.1. General. Preconcentration is performed on a sample to get a suitable aliquot for the analysis. Thus preconcentration is subject to the sampling technique. The sample has to be regarded as being homogeneous and representative. If, for instance, water has been sampled including the suspended particulate matter an eventual preconcentration should be capable of collecting the compound of interest from both phases in the sample.

By the same token it is obvious that an eventual dissolution and mineralisation should be regarded as a separate step which, once again, by definition leads to a homogeneous material.

On the other hand the dissolution and destruction have to meet the suppositions on which the separation technique is based. If, for instance, it becomes manifest that the mineralisation has not been complete the whole analytical procedure has to be redressed.

If possible the (pre-)concentration technique should not be the limiting factor in the total analytical procedure with respect to time, costs or blank value. These three requirements narrow down the possibilities appreciably.

3.2. Preconcentration by evaporation, freeze-drying and dry ashing. Evaporation has been used frequently in the analysis of water samples by neutron activation analysis [7-9]. It only concentrates without any decontamination. The usual X-values are between 10^2 and 10^3.

Drying, especially of "nearly dry" biological material, has been recommended to obtain well-defined sample weights [10,11]. In general the temperature should not exceed ~ 90 °C [11]. The resulting X is ≤ 1.5.
Freeze-drying is generally applied for biological samples [12-15]. There is a slight influence of the freezing temperature on the weight loss [5]; usually the final weight is constant within 1%. The concentration factor may be as high as X = 10.

Dry ashing may lead to concentration factors of X ≤ 50. Volatile elements are easily lost but can be retained at a low temperature or trapped by a suitable agent. The recovery of lead from milk powder [16] and fluorine from plant material [17] can be quantitative.
An elegant technique is gradual dry oxidation with KNO_3 at a slowly increasing temperature [18].

3.3. Preconcentration by liquid-liquid extraction. Extraction from an aqueous solution into an immiscible organic phase is an obvious technique for preconcentration. Usually a chelating reagent is added. The recovery R is related to the concentration factor X and the distribution

coefficient D by

$$R = 100 \cdot \frac{D}{X + D} \tag{11a}$$

The value of D depends on the equilibrium constants of the compound involved and of competitive reactions, as on the ratio [mass of reagent]/[mass of analyte].
It follows from [11a] that D should be ≥ 49 X to obtain R ≥ 98.
Often part of the organic layer is left with the water to avoid contamination. The extraction may then be repeated to obtain a high R-value.

The resulting X can be enhanced still by evaporation of the organic solvent or by back extraction. The decontamination factor depends on the distribution constants of the compound of interest (D_1) and the interference (D_2). It is obvious that

$$Y = \frac{D_1}{D_2}\left(\frac{X + D_2}{X + D_1}\right) \tag{12}$$

An elegant procedure is the pulsating column technique [19,20]. The column consists of a syringe of ≥ 20 ml volume which contains a cylindrical plug of polyurethane foam impregnated with a hydrophobic organic reagent. Pressing and releasing the plunge causes a fixed volume of the sample to enter and come into contact with the reagent-loaded foam. It is obvious that

$$X = \frac{\text{Sample volume } (V_o)}{\text{Geometrical volume of the foam column } (V_1)}$$

If the porosity of the foam is ε and the distribution coefficient remains constant one has, for the recovery after n pumpings:

$$R = \left(\frac{D}{X + D}\right) \cdot \left[1 - \left\{\left(\frac{X - \varepsilon}{X}\right) \cdot \left(\frac{D}{1 + D}\right)\right\}^n\right] \tag{13}$$

It is obvious that at $n = \infty$, $R_\infty = D/(X + D)$.

For polyurethane foam $\varepsilon \simeq 0.99$.
The required number of pumpings pulses, needed to reach R_∞ within one percent follows from (14)

$$n \geq \frac{-2}{\log\left[\left(\frac{X - \varepsilon}{X} \cdot \frac{D}{1 + D}\right)\right]} \tag{14}$$

For $X = 10^2$ and $D = 10^4$ one needs $n \geq 460$. With a fixed pumping rate of $\sim 8.\text{min}^{-1}$ [20] one reaches $X = 10^2$ in one hour.

The practical procedures for preconcentration by extraction usually consist of three steps:
(a) The extraction itself, sometimes performed in several successive stages; (b) Evaporation;
(c) Mineralisation.
Two representative examples of this approach are given here.
(a) Using pyrrolidine-dithiocarbamate or diethylammonium-dithiocarbamate as the chelating reagents and extraction into chloroform, values of R ≥ 98, $X = 10^2 - 2.10^2$ and $Y \geq 10^2$ are obtained [21, 22].
(b) The application of pyridine ketoximes as a reagent for the determination of ultra trace amounts of cobalt leads to R ≥ 98, $X = 10^2 - 3.10^2$ and $Y \geq 10^2$ [23].

The application of the pulsating column to the determination in water samples of ^{131}I ($T_{\frac{1}{2}}$ = 8.1 d), present as iodide, and ^{203}Hg ($T_{\frac{1}{2}}$ = 45.1 d), probably present as Hg^{II}, has been reported [20].

The use of extraction in post-irradiation chemistry is well known. The analysis of the NBS environmental Standard Reference Materials for copper and cadmium was performed by extraction of the DDC-compounds [24]; Zn $(DDC)_2$ is used as the reagent. The resulting Y-values with respect to ^{24}Na and ^{82}Br are $\simeq 10^3$. The concentration factor is $X \simeq 0.1$. A system for multi-element solvent extraction based on DDC was developed by several groups [25,26]. The elements which are indeterminable by neutron activation are used as subsequent scavengers at increasing pH-values. The time needed is ≃ 2 hours. Starting with 40 ml sample solution it leads to R ≥ 98 and Y (against ^{24}Na) ≥ 10^4 at $X \simeq 2$.
Extraction is often applied in the elaborate group separation schemes for irradiated samples. Here the sole aim is decontamination.
Examples are found in the schemes of Samsahl [27] and its modification by Schramel [28] for biological material and that of Smet for rocks and minerals [29].

3.4. Preconcentration by ion exchange. Ion exchange is often used for preconcentration. Moreover it is the backbone of many separation schemes which are applied in post-irradiation chemistry. The use for the isolation of single elements is restricted to a few cases where no other, more rapid, techniques are available.

The application in preconcentration is almost entirely restricted to water samples. Moreover the trend is towards those types of ion exchangers which can be used directly in multi-element determinations. Thus resin-loaded papers have become popular as collectors in the determination of trace elements by X-ray fluorescence or instrumental neutron activation analysis in filtered fresh water. Preliminary work [30-34] led to procedures, based on cellulose-phosphate paper which contains DDC-groups (8 $\mu Mol.cm^{-2}$) at the surface [35] and on anionic resin loaded filters [36]. The DDC-filters have to be prepared afresh. Samples of 200 - 1000 ml are pH-adjusted and pumped through at a specific flow-rate of $\simeq$ 10 $ml.cm^{-1}$. The observed capacities of 13 mm diameter filters range from 20 to 100 µg metal.

Usually one has R $\geq$ 98, X = 10^2 - 10^3 with Y $\geq$ 10^2 against sodium, chlorine and bromine. The possibilities can be summarized as below. The collection from alkaline medium is of limited use due to the risk of hydroxide precipitations.

	Cellulose phosphate	Quaternary ammonium		Immobilized dithiocarbamate
Optimum pH	1	1		6 - 8
Medium	HNO_3 or HCl	HCl	CN^- (10^{-4}M)	HNO_3
Preconcentrated elements	Th, U, lanthanides	Au, Hg, Sb, Cd, W, U	Hg, Au, Zn, Cd, Cu, Co, U	Hg, Cu, Zn, W, U

Paper loaded with anion-exchange resin was used for the collection of mercury ions as $HgCl_4''$ [37], leading to R $\geq$ 95, X = 50 and Y $\geq$ 100 from alkali-ions.

The use of chelating resins opens up the possibility of preconcentration followed by atomic absorption spectrophotometry [38] or neutron activation analysis [39]. Usually the chelating compounds are grafted on a cellulose support which may be a filter or a small column [40,41]. If a column is used the elements are eluted with 1 M HCl. Results are: R $\geq$ 98, X = 10^2 - 2.10^2 (column) or $\geq$ 10^3 (filter) and Y $\geq$ 10^3 against sodium.
The obvious drawback of the filter is their low capacity ($\simeq$ 5.10^{-2} m Mol).

The application of small columns of Chelex-100 resin for preconcentration in multi-element neutron activation [42] is hampered by their blank value [43]. For some single elements it may be feasible. Examply are uranium [44], the lanthanides, copper and zinc [45]. For uranium the resin is irradiated. For the lanthanides are eluted with 2.5 M HNO_3. At R $\geq$ 98 and Y $\geq$ 10^3 for the decontamination from the alkalis and earth alkalis, one has X $\simeq$ 10^3 for uranium and X $\simeq$ 10^2 - 5.10^2 for the lanthanides, copper and zinc.

Single element preconcentration with columns of other chelating resins are based on mixed anionic-cationic resins, eventually combined with a chelating reagent [46] or some specialized resin like the aniline sulfur ASH for mercury [47], Srafion NMRR [48-50] for the noble metals and XAD-7 for cesium [51].
Usually R is $\geq$ 95, X $\geq$ 10^2 and Y $\geq$ 10^3 against the major interferences. The elimination of interfering elements prior to the irradiation in case of determination by short-lived radionuclides belongs to this class also. An example is the assay of vanadium in biological material by ^{52}C ($T_{\frac{1}{2}}$ = 3.8 min). The element can be concentrated on a cation-resin with R = 93, X $\simeq$ 0.5 and Y $\simeq$ 20 [52]. Eventually the adsorbed elements may be eluted prior to the counting to avoid most of the resin's blank.

In post-irradiation chemistry ion-exchange is the base of most of the laborious schemes for group separation which were developed for NaI-counting [53]. The development of the Ge(Li) detector and the increasing labour costs have tended to reduce the number and complexity of the separation steps and to automatize the whole procedure.
The modifications of Samsahl's scheme for dry biological material [27] by Schramel [28] and Tjioe et al. [54] feature still 7 - 10 fractions. That of Smet et al. for the determination of 24 elements in rocks and minerals [29] implies 21 fractions. The alternative to these

systems is a combination of rapid scavenging procedure for all trace elements, like that with active carbon (see below), with a few elements specific determination must be done in terms of the analytical criteria mentioned above and of the costs involved.

For some separations of single elements or one group, ion-exchange remains the best technique. The anion-exchanger "Srafion NMRR" which is specific for noble metals can be used for a group separation of the noble metals [55]. It leads to $R \geq 95$ (except for Pt^{IV}) and $X \simeq 0.1$ with $Y > 10^3$ from ^{24}Na, ^{32}P and ^{82}Br. The application to the determination of copper [49] and molybdenum [50] in dry biological material, silicates and coal yields the same R, X and Y-values.

3.5. Preconcentration by coprecipitation, isotopic exchange and adsorption. Collection of a microcomponent by coprecipitation belongs to the oldest part of radiochemistry [56]. In its ideal form, coprecipitation becomes cocrystallisation and it follows Hahn's rule: "A microcomponent is carried down by a solid formed by crystallisation of precipitation if it enters into the normal lattice formation".
Often however, the collecting precipitates acts as a scavenger by the combined actions of coprecipitation, inclusion, adsorption and ion-exchange.
Distribution between a suitable solid phase and a solution may be used as an alternative.
Finally isotopic exchange may be applied in radiochemistry.
In practice the behaviour of the collector can best be described by the empirically determined relation between the recovery R and the ratio p = [mass of precipitate]/[mass of analyte] as shown in figure 1. In the ideal case of cocrystallisation the two straight lines are obtained.

Cocrystallisation may yield impressive concentration factors. A determination of copper and manganese by cocrystallisation with oxine [27] yields $R = 100$, $X = 10^3$ and $Y \geq 10^3$ with respect to ^{24}Na and ^{82}Br. The distribution of cesium and strontium between the hexacyanoferrates and an aqueous solution may be used to separate the fission products ^{137}Cs and ^{90}Sr from water samples, yielding X-values of $10^2 - 10^4$ [57].

Isotopic exchange is of interest in post-irradiation chemistry. It depends on the application of a large excess of the inactive element in a suitable form. The collection of ^{203}Hg from an acid solution by adding a droplet of mercury metal [58] and that of ^{128}I by exchange with a solution of iodine in carbon tetrachloride [59] work well. The collection of the lanthanide ions by isomorphic exchange with La-oxalate [60] is another example. In all cases $R \simeq 100$ and $Y \geq 10^2$ from the interfering radionuclides.

The collection of trace elements by scavenging has become important with the development of multi-element analytical techniques [61]. The scavenger is either formed "in situ" by precipitation or it is added.
Iron hydroxide is often used as an "in situ" scavenger; hydroxides of metals of the third and fourth group like aluminium or lead are applicable also [62].
The agent is characterized by determining the R versus p diagram. The pH, ionic strength and precipitation rate are used as parameters [63].
Applications of ferric hydroxide are the determination of arsenic in water [64] and thorium in large samples of soft tissues [65] leading both to $X \simeq 10^2$. The collection of fall-out radionuclides from river water by flocculation of aluminium hydroxide gives $X \simeq 4.10^4$ [66].

The action of an added solid scavenger is based on adsorption and ion-exchange at one hand and collection of precipitate particulates at the other.
Van der Sloot et al. [67,68], Jackworth [69,70], Lieser [71,72] and van Grieken [73] developed the use of active carbon for preconcentration of trace elements from sea- and surface-water. The ions are chelated and scavenged into a small aliquot. The carbon may be stirred through the sample and filtered off or the water may be filtered through a carbon layer.
The carbon is submitted to neutron activation [67] or, in the case of uranium, to delayed neutron counting [74]. Alternatively the elements are desorbed into dilute nitric acid and determined optically [70]. Commercial active carbon may be used [67] but it is possible to prepare a purer brand [75], The best procedure is found by separate variation of the concentration of the chelating agent, amount of carbon, pH and stirring-time or rate of filtration.
Results are: $R \geq 95$, $X = 10^2 - 10^3$ and $Y \geq 10^2$ from ^{24}Na, ^{32}P and ^{82}Br.
Active carbon is used for collection from the gas phase, notably for the halogens [77] and mercury [4], resulting in X-values of 10^4 or more. An elegant application is the determination of uranium by way of ^{222}Rn ($T_{\frac{1}{2}} = 3.8$ d) [78].

The use of active carbon for the collection of trace elements from a neutron irradiated sample leads to a rapid multi-element determination [5,79].

Figure 4 summarizes the effect in the case of "Orchard Leaves". The features of this technique are: $R \geq 95$, $X \simeq 5$, $Y \geq 2.10^2$ from ^{24}Na, ^{32}P and ^{82}Br.

3.6. Volatilization techniques. Trace constituents which are volatile or can be transformed into volatile compounds may be isolated by evaporation and subsequent ad- or absorption. This principle is applied in post-irradiation chemistry primarily. Mutual separation has been restricted to the fractionation of the halides [80] and the hydrides [81].

The primordial importance of the technique lies in a few determinations which cannot be matched by other procedures and which yield Y-values well above 10^3 at $R \simeq 100$. These are: (a) The distillation of chromium as $CrOCl_2$ [54]; (b) The isolation of osmium and ruthenium as their oxides [82]; (c) Hydride formation of arsenic, antimony and germanium [83,84]; (d) Hydride formation and fractionation of organotin compounds [81].

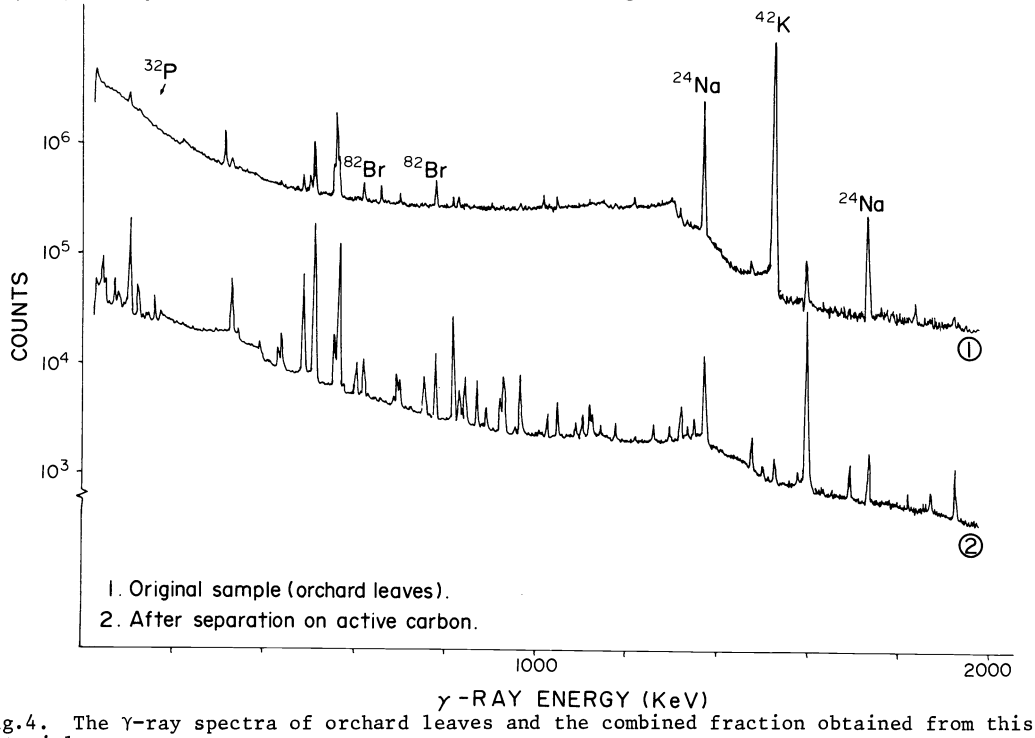


Fig.4. The γ-ray spectra of orchard leaves and the combined fraction obtained from this material.

3.7. Electrochemical preconcentration. Electrolysis and amalgamation are primarily applied in post-irradiation chemistry. An exception is the collection of mercury from a gas stream. Electro deposition on pyrolitic graphite is applied for the determination of heavy metals in seawater by atomic absorption [85,86]. The procedure is slow and concentration factors do not exceed $X = 10^2$ at complete recovery. The blank of the graphite limits the applicability in neutron activation.

Simple electrochemical displacement can be used in post-irradiation chemistry for quantitative collection of the noble metals except ruthenium, osium and iridium, on copper powder [87]. The technique is rapid and gives $X \simeq 10^2 - 10^3$.

4. PRACTICAL CONCLUSIONS

Preconcentration comes between sampling and analysis. It should be able to keep pace with the sampling and eventually be carried out in the field. This presses for simple, rapid and reliable techniques. Moreover it should be possible to store the resulting aliquots without risk of contamination or deterioration. If the preconcentration is performed in the laboratory it is possible to use slow but easily controllable techniques. It should be realized that a longer processing time implies a longer exposure to contamination, notably by dust. Post-irradiation chemistry is restricted to the laboratory. Considerations of radiation burden and radioactive contamination again press for simple and rapid procedures. Here sample dissolution, radiation level and half-life of the radionuclide of interest set the limits. For preconcentration in the field the best general choice seems to be the scavenging with active carbon or liquid-liquid extraction with a pulsating column. The use of metal hydroxides as scavengers is more restricted due to blank values.

If a considerable time-gap may occur between the preconcentration and the analysis, the preconcentrated aliquots should not deteriorate during storage.
From this point of view liquid extraction seems somewhat less useful than ion-exchange or scavenging with active carbon.

The processing of irradiated samples in the radiochemical laboratory can best be based on the combination of a general scavenging technique with the separate determination of a few elements.
If too less sample material is present the general scavenging is usually preferable as it leads to more information.
If only one element is wanted the chemical separation may be slow and laborious. If the choice is possible one should prefer the procedure which is most open to automation.

The costs of preconcentration and post-irradiation chemical separation within the total analytical procedure may be estimated only. The following data apply to the Dutch situation. They are an illustration of the need for multi-element techniques.

	Preconcentration in the field No chemical separation	Preconcentration in the laboratory No chemical separation	No preconcentration Post-irradiation group separation	No preconcentration Single element determinations
Total costs per sample	$ 100 - 150	$ 150 - 175	$ 150 - 175	$ 175 - 225
Total costs per element	5 - 10	5 - 10	5 - 10	20 - 100
Sampling	20 - 35%	20 - 30%	20 - 30%	15 - 30%
Preconcentration	15 - 20	30	-	-
Irradiation	15 - 20	15	15	15
Post-irradiation separation	-	-	20 - 35	40 - 60
Counting	10	5 - 10	5 - 10	5 - 10
Calculation	10	10	10	10
Overhead	15 - 20	15	15	15

REFERENCES

[1] Currie, L.A., Anal. Chem. 40 (1968), 586.
[2] Faanhof, A. et al., J. Radioanal. Chem. 54 (1-2), (1979), 289.
[3] Faanhof, A. et al., J. Radioanal. Chem. 54 (1-2), (1979), 303.
[4] van der Sloot, H.A. et al., Anal. Chim. Acta 70 (1974), 439.
[5] Weers, C.A., Multi trace element analysis of dry biological material by neutron activation analysis including a chemical group separation. Report ECN-85; 1980, p. 126 - 137.
[6] NBS Certificate of Analysis Standard Reference Material No. 1571 "Orchard Leaves", Jan. 1971.
[7] Schutz, D.F. and K.K. Turekian, Geochim. Cosmochim. Acta 29 (1965), 259.
[8] Cawse, P.A., Report AERE-R7669 (1974).
[9] Bogen, J., Atmospheric Environment 8 (1974), 835.
[10] Bowen, H.J.M., Atomic Energy Review 13 (1975), 451.
[11] NBS Centificates of Analysis. Examples No. 1573 "Tomato leaves" and No. 1574 "Pine needles", Oct. 1876.
[12] De Soete, D. et al., Neutron activation analysis, Wiley Interscience, New York, (1972), p. 262.
[13] Ibbott, F.A., Accuracy in trace analysis 1974 (IV), 299 and 353.
[14] Wiseman, B.F.M., J. Radioanal. Chem. 24 (1975), 313.
[15] Heine, K., Milchwissenschaft 31 (1976), 65.
[16] Dutilh, C.E., Radiochem. Radioanal. Lett. 6 (3), (1971), 195
[17] Wals, G.D., Radiochem. Radioanal. Lett. 26 (5-6) (1976), 353.
[18] Fritze, K. and R. Robertson, J. Radioanal. Chem. 7 (1971), 213.
[19] Braun, T., Anal. Chim. Acta 99 (1978), 1.
[20] Palagyi, S. and T. Braun, J. Radioanal. Chem. 51 (2) (1979), 267.

[21] Weiss, H.V. et al., Anal. Chim. Acta 104 (1979), 337.
[22] Bruland, K.W. et al., Anal. Chim. Acta 105 (1979), 233.
[23] Beauport, P., Mikrochimica Acta (1978), II, 95.
[24] Gallorini, M., Anal. Chem. 50 (1978), 1479.
[25] Schubiger, P.A., Anal. Chim. Acta 106 (1979), 103.
[26] Ooms, P.C.A., Displacement and exchange reactions in radioanalysis. Report ECN-87, 1980.
[27] Samsahl, K. et al., Anal. Chem. 40 (1967), 181.
[28] Schramel, P., Mikrochim. Acta (1978), I, 287.
[29] Smet, T. et al., Anal. Chim. Acta 101 (1978), 45.
[30] Leyden, E. et al., Anal. Chem. 47 (9), (1975), 1512.
[31] Knapp, G. et al., Anal. Chim. Acta 77 (1975), 293.
[32] Head, A.J., J. Chem. Soc. 111 (1958), 3418.
[33] Kember, N.F., Analyst 85 (1960), 449.
[34] Bruce, T. et al., Analyst 97 (1967), 137.
[35] Gendre, G. et al., Int. J. Environ. Anal. Chem. 5 (1977), 63.
[36] Bergerioux, C. et al., J. Radioanal. Chem. 37 (1977), 823.
[37] Clechet, P. et al., Analysis 5 (1977), 366.
[38] Kingston, H.M. et al., Anal. Chem. 50 (1978), 2064.
[39] Hirose, A. et al., Anal. Chim. Acta 97 (1978), 303.
[40] Burba, P. et al., Z. Analyt. Chem. 284 (1977), 361.
[41] Liesser, K.H. et al., Mikrochimica Acta (1978), I, 363.
[42] Riley, J.P. and D. Taylor, Anal. Chim. Acta 40 (1968), 479.
[43] van der Sloot, H.A., Private Communication.
[44] Hirose, A. and Ishii, D., J. Radioanal. Chem. 46 (1978), 211.
[45] Hirose, A. et al., Anal. Chim. Acta 97 (1978), 303.
[46] Abe, M. et al., Bull. Chem. Soc. Japan 52 (1979), 2574.
[47] Krämer, H.J., J. Radioanal. Chem. 37 (1977), 835.
[48] Koster, G. and G. Schmuckler, Anal. Chim. Acta 38 (1967), 179.
[49] Gladney, E.S., Anal. Chim. Acta 91 (1977), 353.
[50] Nadkarni, R.A., Anal. Chem. 50 (1978), 294.
[51] Nakaoka, A. et al., J. Radioanal. Chem. 56 (1980), 13.
[52] Blotcky, A.J. et al., Anal. Chem. 51 (1979), 178.
[53] De Soete, D. et. al., Neutron activation analysis. Wiley Interscience, New York, 1972, p. 327 - 346.
[54] Tjioe, P.S. et al., J. Radioanal. Chem. 37 (1977), 511.
[55] Nadkarni, R.A. and G.H. Morrison, J. Radioanal. Chem. 38 (1977), 435.
[56] Haïssinsky, M., Nuclear chemistry and its applications Addison-Wesley, Reading, 1964, p. 597 - 605.
[57] Lieser, K.H., Radiochem. Radioanal. Lett. 42 (4-5) (1980), 329.
[58] de Voe, J.R. et al., Talanta 3 (1959), 298.
[59] Luten, J.B., J. Radioanal. Chem. 35 (1977), 147.
[60] Csajka, M., Radiochem. Radioanal. Lett. 13 (2) (1973), 151.
[61] Meinke, W.W. and B.F. Scribner (Eds), Trace characterization. NBS Monograhp 100, Washington D.C. 1967, p. 398 - 402.
[62] Plotnikov, V., Report KfK-tr-636, 1979 and KfK-tr-637, 1979.
[63] Darydov, Y.P., J. Radioanal. Chem. 51 (2) (1979), 325.
[64] Wals, G.D. et al., J. Radioanal. Chem. 57 (1) (1980), 215.
[65] Singh, N.P. et al., Anal. Chem. 51 (1979), 207.
[66] Roy, J.C. et al., Nucl. Inst. Meth. 160 (1979), 187.
[67] van der Sloot, H.A., Neutron activation analysis of trace elements in water samples after preconcentration on activated carbon. Report ECN-1, 1976.
[68] van der Sloot, H.A. et al., J. Radioanal. Chem. 25 (1) (1975), 99, and Proc. Modern Trends in Act. Anal. (1976), I, 466.
[69] Jackworth, E., Fresenius Z. Anal. Chem. 271 (1974), 120.
[70] Piperaki, E. et al., Anal. Chim. Acta 100 (1978), 589.
[71] Lieser, K.H. et al., J. Radioanal. Chem. 37 (1977), 717.
[72] Heuss, E. and K.H. Lieser, J. Radioanal. Chem. 50 (1-2), (1979), 289.
[73] Vanderborght, B. et al., Anal. Chem. 49 (1977), 311.
[74] Brits, R.J.N. et al., Radiochem. Radioanal. Lett. 36 (6) (1978), 313.
[75] van der Sloot, H.A., Preparation of very pure active carbon. Report ECN-80, 1980.
[76] Jackworth, E. et al., Anal. Chim. Acta 107 (1979), 177.
[77] Miller, D.H. et al., Radiochem. Radioanal. Lett. 30 (4) (1977), 235.
[78] Hambleton-Jones, B.B., Nuclear Active, Jan. 1980, 24
[79] van der Sloot, H.A. et al., Anal. Chem. 52 (1980), 112.
[80] Weers, C.A. et al., J. Radioanal. Chem. 42 (1978), 113.
[81] Braman, R.S. and M.A. Tompkins, Anal. Chem. 51 (1979), 12.
[82] Korkisch, J., Modern methods for the separation of rarer metal ions. Pergamon Press, Oxford. (1969), p. 546 - 551.
[83] Pallière, M. and G. Gernez, Analusis, 7 (1979), 46.
[84] van der Sloot, H.A. and D. Hoede, Anal. Chim. Acta 111 (1979), 321.
[85] Mark, H.B. and J. Berlandi, Anal. Chem. 36 (1964), 2062.
[86] Batley, G.E. and J.P. Matousek, Anal. Chem. 49 (1977), 2031.
[87] Furler, R., Contributions to activation analysis. Thesis Amsterdam 1974, p. 37.