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Radiochemical Techniques

Cation-Exchange Techniques in Radiochemistry

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Cation-Exchange Techniques in Radiochemistry

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Foreword

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences—National Research Council Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the radiochemical purity of reagents, the place of radiochemistry in college and university programs, and radiochemistry in environmental science

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique

Experts in the particular radiochemical technique have written the monographs The Atomic Energy Commission has sponsored the printing of the series

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems

Gregory R Choppin, *Chairman*
Subcommittee on Radiochemistry

Preface

This text covers the literature which appeared up to December 1970 in the more important journals or (as abstracts) in *Analytical Abstracts* Much use was made of the monographs which appeared in the series "Radiochemistry of the Elements "

The author wishes to thank Professor Dr Hoste Director of the Nuclear Institute at the University of Ghent, for the permission to use its library and for the hospitality extended on this occasion

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Cation-Exchange Techniques in Radiochemistry

by D. L. Massart

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Chapter 1 Introduction

1.1. Kinds of cation-exchange materials

The cation exchange materials now available for use in radiochemistry can be subdivided into several categories:

- polymeric resins
- celluloses such as carboxymethyl cellulose
- inorganic exchangers such as zirconium phosphate
- liquid cation exchangers such as dinonylnaphthalene sulphonic acid.

Only the radiochemical application of the first two categories will be discussed. At the moment resins are still the most widely used cation exchange materials. The other categories should however be kept in mind as possible alternatives.

In imitation of Inczedy (264) the following advantages of polymeric resins can be enumerated.

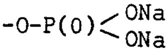
1° High capacity i.e. a large quantity of exchangeable ions per unit weight of resin.

2° A hydrophilic gel structure. The functional groups are easily reached by the ions to be adsorbed.

3° High resistance against acids and alkalis even at high temperature.

4° The ion exchange properties remain constant even after prolonged use.

Add to this that the spherical shape of the now available ion exchange particles allows very good column packings and high flow rates.
The present day ion exchangers are usually prepared by copolymerisation of styrene with a small percent of divinylbenzene. The percent of divinylbenzene can be varied so that resins with variable degrees of cross-linking are obtained. The commercial resins are usually prepared by suspension polymerisation. This yields spherical particles.
The matrix thus obtained is treated in different ways to introduce functional groups i.e. the groups which give the resin its ion exchange properties. Strong, monofunctional cation exchangers are obtained by introducing -SO_3H groups. This resin is so widely used that in the following paragraphs a resin will be supposed to possess this functional group unless stated otherwise. Other cation exchange resins with, for example, carboxylic (-COOH) or phosphoric acid (-$PO(OH)_2$) groups, have been used in a few instances (see for example paragraph 6.5.3.). They have weak acidic properties. Resins with chelating groups often contain groups with a H^+ that can undergo ionisation and can therefore be regarded as weak acidic cation exchangers. Since this is not the purpose for which they are used they will not be discussed further in this review.
There is a large variety of commercially available resins, often of a very similar nature. Inczedy (264) tabulated not less than 46 different kinds or brands. Saville (526) lists the same number. His list however contains no exchangers prepared in the USSR or the COMECON countries.
For many separations described in the literature the kind of resin used is not important (as long as the functional group is the same). This does not mean that distribution coefficients, determined on one resin will be exactly the same on another resin with the same functional group. As a matter of fact, until a few years ago small differences could be observed from batches of the same resin that were bought within a few months' interval.
An interesting property of sulphonic acid exchangers on a polystyrene base is that these resins are much more radiation resistant than the usually employed anion exchange resins (101, 557).
Cellulose-based ion exchangers with the following functional groups are now also available: sulphoethyl -O-$C_2H_4SO_3Na$ (SE), phosphonic acid

 $-O-P(O)<^{ONa}_{ONa}$ (P) and carboxymethyl $-O-CH_2COONa$ (CM). They have been used for the separation of isotopes on columns in a few instances, for example by Muzzarelli and Marcotrigiano (422, 423, 424, 425, 426) or in sheet techniques (see chapter 3).

1.2. Definitions

1.2.1. Distribution constants

The chromatographic literature has a regrettable lack of uniformity in the symbols used for the different sorts of distribution coefficients. Kraus and Moore's (334) method seems to have the most followers. They define D, the distribution coefficient (sometimes called equilibrium or weight distribution coefficient or constant) as:

$$D = \frac{\text{amount of substance per kilogram dry resin}}{\text{amount of substance per liter of solution}}$$

and D_V, the volume distribution coefficient (sometimes called the column distribution coefficient) as:

$$D_V = \frac{\text{amount of substance per liter of exchanger bed}}{\text{amount of substance per liter of solution}}$$

It should be noted that the symbol K_D was used by many authors both for D and for D_V (and even for the selectivity coefficient) , but this should be avoided now.

D and D_V are related by equation (1):

$$D_V = D\rho \qquad (1)$$

where ρ is the bed density (kilograms dry exchanger per liter of bed). Kraus and Moore also define E (the elution constant) as a measure of the migration rate of a band:

$$E = \frac{dA}{V} \qquad (2)$$

where d is the distance the adsorption band travels on addition of V ml eluent in a column with a cross-section area of A.

E is related to D by:

$$E = 1 / (i + D_V) \tag{3}$$

where i is the fractional interstitial volume of the column and also

$$D_V = \frac{V_{max}}{dA} - i \tag{4}$$

where V_{max} is the volume necessary to elute the maximum of a chromatographic band.

1.2.2. Separation coefficient

The separation coefficient, β , is defined as the ratio of the distribution coefficients. It is usual to divide the larger constant by the smaller. **Therefore, the larger β is, the easier and the more complete the separation will be.**

1.2.3. Selectivity coefficient

Consider the exchange reaction:

$$\bar{A}^+ + B^+ \rightleftarrows A^+ + \bar{B}^+$$

$\bar{A}^+$ and $\bar{B}^+$ are ions in the stationary phase and A^+ and B^+ in the mobile phase. The selectivity constant or coefficient is then given by

$$K_A^B = \frac{[A]\,[\bar{B}]}{[\bar{A}]\,[B]} \tag{5}$$

It should be noted that in the literature several other symbols such as K_{AB}, $K_{A/B}$ etc. are employed. K_A^B is a measure of the degree to which one ion is preferred to the other by the exchanger. The determination of a number of selectivity coefficients permits the elaboration of affinity- or selectivity sequences, such as

$$A > B > C$$

This means that the resin shows a higher affinity for A than for B and lowest of all for C.

The selectivity coefficient derives from the law of mass action. Therefore, for the general case of the exchange of two ions A^{a+} and B^{b+}

$$aB^{b+} \quad + \quad b\bar{A}^{a+} \quad \rightleftharpoons \quad a\bar{B}^{b+} \quad + \quad bA^{a+}$$

the selectivity coefficient is given by

$$K_A^B = \frac{[A]^b \; [\bar{B}]^a}{[B]^a \; [\bar{A}]^b} \qquad (6)$$

1.2.4. Theoretical plate

Earlier chromatographic theories represented the column as a large number of small discrete segments. The solvent leaving each segment was considered to be in equilibrium with the stationary phase of that segment. In analogy with distillation such a segment was called a theoretical plate and its height the height equivalent to one theoretical plate or HETP. The larger the number of theoretical plates in a column for a given length, the smaller HETP is and the more efficient the column.

More recent theories (see for example 201) have abandoned the theoretical plate as a physicochemical concept but they still use HETP as a measure of zone spreading. The chromatographic band is considered to be a Gaussian distribution and HETP is defined as the variance of the distribution per unit of column length

$$\text{HETP} = \frac{\sigma^2}{d} \qquad (7)$$

The number of HETP's, N, is equal to the column length divided by HETP so that:

$$N = \left(\frac{d}{\sigma}\right)^2 \qquad (8)$$

Replacing the length of the column by V_{max}, σ is then the standard deviation of the zone as it emerges from the column. It can be shown that N can be determined from the graph of an elution curve by the following **equation (519):**

$$N = C_N \left(\frac{V_{max}}{W_N}\right)^2 \qquad (9)$$

where W_N is the band width at a fractional height h_N and C_N is a numerical constant. For $h_N = h_{1/2}$ (see figure 1), the equation becomes

$$N = 5{,}54 \left(\frac{V_{max}}{W_{1/2}}\right)^2 \qquad (10)$$

The distance W_B can also be measured between the tangents (figure 1) and N is then given by equation (11)

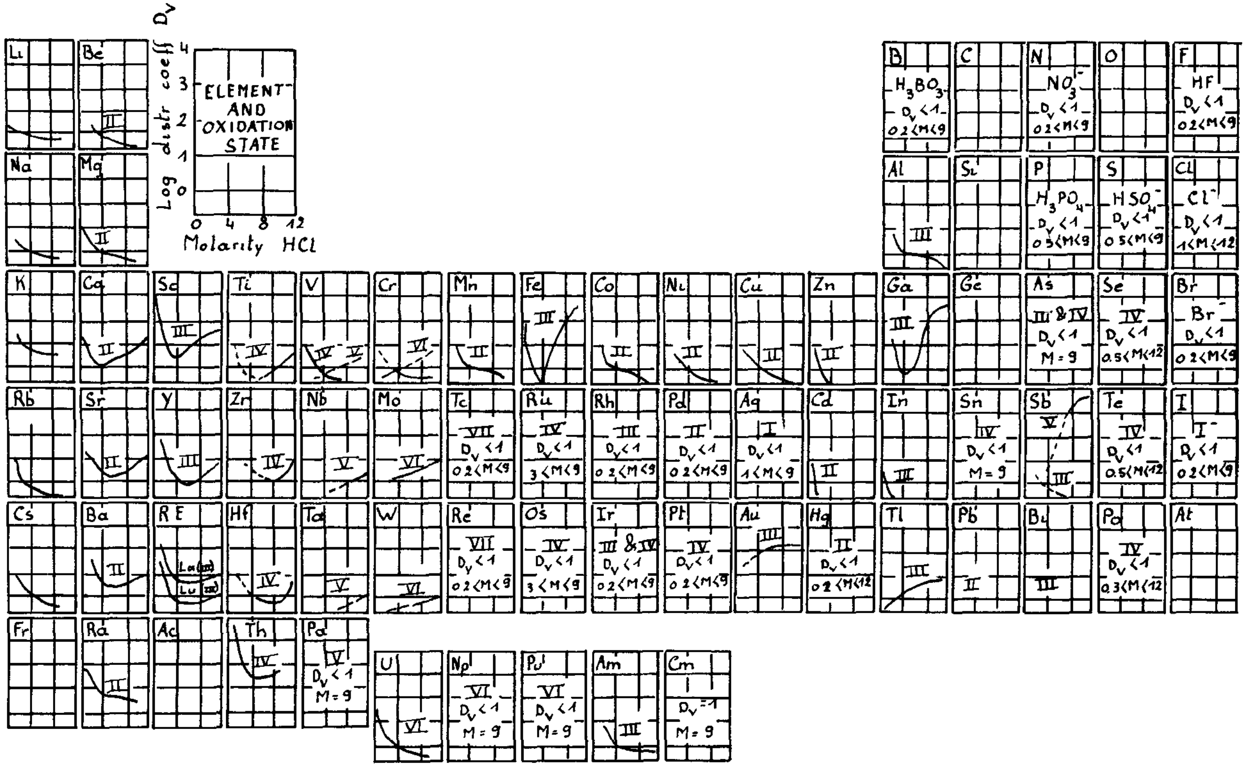
$$N = 16 \left(\frac{V_{max}}{W_B}\right)^2 \qquad (11)$$

1.3. General literature

A good introductory text to the whole field of chromatography is the collective book "Chromatography", edited by Heftmann (240). The theory of chromatographic migration is summarised by Giddings (201) and among many others, by Purnell (492). The theoretical aspects of ion exchange chromatography are discussed by Helfferich (242), by Marcus and Kertes (661) and in a series edited by Marinsky (380). The books by Samuelson (523) and Inczedy (264) contain a very valuable and detailed description of the chromatography of the elements. They are still very useful, although the most recent material that they contain dates from 1962. A more recent book by Korkisch (660) describes chromatographic and solvent extraction methods for the rarer metal ions.

Figure 1

Adsorption of the elements from HCl solutions by a cation exchange resin (Dowex 50 X4) (438)



Chapter 2 Theory

2.1. Chromatographic migration theory

2.1.1. Zone spreading

The discussion of this subject will be restricted to matters of practical interest. Detailed description of the theory and its consequences on separation efficiencies can be found in the monographs on ion exchange chromatography mentioned in the introductory chapter. A more general account is given in books by Purnell (492) and Giddings (201). The efficiency of a separation is a function of two parameters, namely the spreading of the elution zones of the ions to be separated and the difference in migration velocity. It is clear that to obtain optimal results the peaks should be as narrow as possible and the distance between the zones as large as possible. A measure of how narrow a chromatographic peak is, is the height of a theoretical plate, HETP, as measured from the elution curve (see 1.2.4.). Several equations which relate HETP to factors such as the flow rate have been developed.

$$\mathrm{HETP} = \gamma \frac{2\,D_l}{v} + d_p + \frac{1}{30}\,\frac{Dv}{(D+i)^2}\,\frac{d_p^2}{D_s} \qquad (12)$$

or

$$\mathrm{HETP} = 0.82\,d_p + \frac{D}{(D+i)^2}\,\frac{1}{28}\,v\,\frac{d_p^2}{D_s} + \left(\frac{D}{D+i}\right)^2 \frac{0.065\,d_p^2\,v}{D_l(1+35\,d_p\,v)} \qquad (13)$$

The first equation is an adaptation of the classical Van Deemter equation to ion exchange terminology and the second was developed by Glueckauf (214). γ is a numerical constant, d_p is the diameter of the ion exchange particles, v is the flow rate, D is a distribution constant (see section 1.2.1.), i is the interstitial volume of the column and D_l and D_s are the diffusion constants in the liquid and stationary phases.

The first term in equation (12) is due to longitudinal diffusion and is of no importance under the usual conditions of ion exchange chromatography.

It was not taken into consideration in equation (13). This equation contains, however, a term due to diffusion through the Nernst film (last term see 2.2.3.). The other terms in both equations are due to eddy diffusion and particle diffusion.
The equations (12) and (13) explain the influence of parameters such as the flow-rate, the diameter of the particles and the distribution constant on the HETP. Equation (12) yields, for example, HETP as a function of the flow rate (figure 2). The curve goes through a minimum.

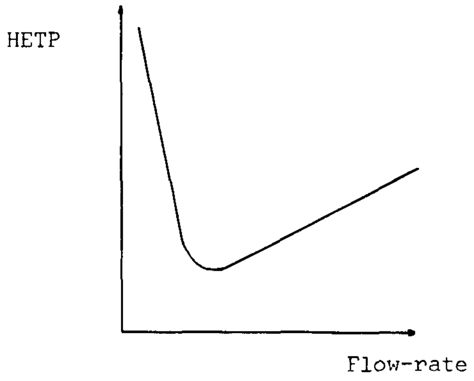


Figure 2
HETP as a function of the flow-rate

The increase of HETP at small flow rates is due to the longitudinal diffusion term whereas, at larger flow rates it is due to the particle diffusion term. It is also clear from both equations that HETP increases with increasing particle diameter. The effects of the particle size on the column performance are discussed further in paragraph 2.2.4.2. An increase of the distribution coefficient D causes a decrease in the HETP. Experimental evidence of this effect is shown in figure 3.
Some of the parameters which influence HETP are not incorporated explicitly in the plate equations (12) and (13). The **initial zone**

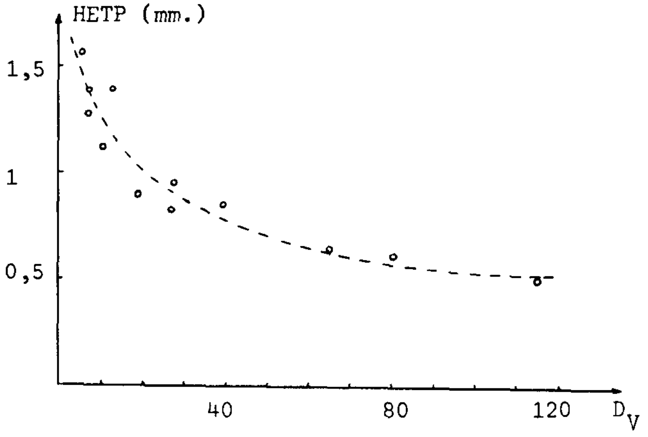


Figure 3
HETP as a function of the distribution coefficient (for the elution of rare earths with α-hydroxyisobutyric acid) (659)

as it is brought on the column should be as narrow as possible. The same is true for the volume between the end of the resin bed and the fraction collection or detection point. The diameter of the column must not be too large since this can lead to bad column packings and thus to large HETP-values. Nor are extremely narrow columns advisable because this can cause wall effects and channelling (71). The column diameter should be at least twenty times as large as the particle diameter.
The influence of the temperature is difficult to evaluate. D_I, D_S and D are all temperature dependent. Usually, an increase in temperature will yield a smaller HETP, but precautions have to be taken to avoid the formation of air bubbles in the column (see also 2.2.4.5.).

2.2. Properties of resin ion exchangers

2.2.1. Swelling

When an ion exchange resin becomes wet, it absorbs water and increases in volume. For most commercial products, the wet volume can be as much as two to three times the dry one. The phenomenon is reversible and a consequence of the strongly hydrophilic nature of the groups that give the resin its ion exchange properties. The degree to which swelling occurs is controlled by two opposing forces namely the osmotic pressure in the resin (due to differences in concentration of the solution in and out of the resin) and the strain to which the elastic polymeric network is submitted (219). Therefore the amount of swelling depends on:

1° The cross-linking of the resin: an increase in cross-linking causes a loss of elasticity of the polymer network and thus diminishes the possibility of swelling.

2° The nature of the counterions: the osmotic pressure depends to a large degree on the nature of the counterions. Indeed, the swelling will be larger when the number of osmotically active ions is higher. This means that monovalent ions will cause more swelling than higher charged cations. Boyd and Myers (70, 427) have shown that, under certain conditions the logarithm of the selectivity coefficient is linearly related to the swelling of the resin. It appears that the stronger an ion is bound, the less swelling occurs (220). Swelling decreases for example in the order

$$H^+ > Li^+ > Na^+ > NH_4^+ > K^+ > Cs^+ > Ag^+$$

for strong sulphonic acid type exchangers.

3° The concentration of the external solution: an increase in the external solution decreases the difference between internal and external solutions and therefore causes the resin to shrink (33).

4° The nature of the solvent: it was already stated that swelling is caused by solvation of the hydrophilic functional groups. The degree of solvation depends on the polarity of the solvent. When the dipole moment is small, the affinity of the solvent for the ionic groups decreases and the swelling diminishes. Complications can arise, however, through affinity of the solvent for the resin itself. Furthermore, swelling equilibrium is reached much more slowly in nonaqueous solvents.

Changes in the external solution, either in the nature of the cation or in its concentration during a cation exchange run should be avoided. A sudden shrinking of the column will lead to air pockets in the ion exchange bed while swelling can cause breakage of glass columns.

2.2.2. Selectivity

There is still a large amount of controversy about the reasons for selectivity. This subject was reviewed by Kitchener (308), by Helfferich (242) and more recently by Reichenberg (503) and by Diamond and Whitney (144). Although the last two reviews appear in the same book both authors defend different theories. Reichenberg supports theories such as those developed by Rice (505), Eisenmen (164) and Ling (357). The two parameters that determine selectivity are thought to be the strength of the electrostatic ion bond between the functional group and the counterion and the hydrostatic energies of both. Diamond and Whitney describe ion exchange as a process of competitive solvation. The resin phase and the external phase compete for the solvation of the two exchanging ions. Solvation must be understood in its broadest sense i.e. a mechanism that permits spreading of the ionic charge and lowering of the free energy.

In general one can make the following conclusions about selectivity:

1° The higher the ionic charge of the cation, the stronger it is bound to the resin.

2° For ions of the same charge, the following affinity series were found for resins with sulphonic acid functional groups:

$\mathrm{Tl} > \mathrm{Ag} > \mathrm{Cs} > \mathrm{Rb} > \mathrm{NH_4} \approx \mathrm{K} > \mathrm{Na} > \mathrm{H} > \mathrm{Li}$

$\mathrm{Ba} > \mathrm{Pb} > \mathrm{Sr} > \mathrm{Ca} > \mathrm{Co} > \mathrm{Ni} \approx \mathrm{Cu} > \mathrm{Zn} \approx \mathrm{Mg} > \mathrm{Mn} > \mathrm{Be}$

On resins with carboxylic acid groups the affinity series for monovalent cations is the inverse of the series for sulphonic acid groups.

3° The values of the selectivity coefficients increase with increasing cross-linking.

4° The nature of the solvent has a very large influence on the selectivity coefficients. In many instances the selectivity is larger in mixed or nonaqueous solvents than in water (318, 192).

2.2.3. Kinetics

The exchange reaction

$$A + \bar{B} \rightleftharpoons B + \bar{A}$$

can be divided into 3 steps

1) Diffusion of A through the external solution up to the surface of the exchanger particle. Simultaneously, B diffuses from the surface to the bulk of the solution.

2) Diffusion of A through the exchanger particle up to the site of exchange and simultaneous diffusion of B from the ion exchange site to the surface of the particle (particle diffusion).

3) Chemical exchange between A and B

Step 1 would be negligible if perfect mixing existed. This is impossible since the aqueous phase of a slurry cannot be homogeneous up to the surface of a particle, and a concentration gradient exists around the particle. For the sake of simplicity one assumes perfect mixing up to a certain distance from the particle. This stationary film around the particle is called the Nernst film. Diffusion through it is called film diffusion and can be represented by equations (14) and (15).

$$F = 1 - e^{-Rt} \tag{14}$$

$$R = 3\ D_l / d_p D\ \Delta d_p \tag{15}$$

t = time

F = fractional attainment of equilibrium

D_l = diffusion constant in solution

d_p = diameter of particle

Δd_p = thickness of the Nernst film

Particle diffusion is represented by equation (16):

$$F = \frac{-6}{d_p} \sqrt{\frac{D_S t}{\pi}} \tag{16}$$

where D_S is the diffusion coefficient in the solid phase.

From these equations it is clear that in both cases the attainment of equilibrium will be faster for particles with a small diameter (because d_p appears in the denominator) and at higher temperatures (because the values of D_S and D_1 increase). When particle diffusion is the rate controlling step the charge and the size of the diffusing ions are very important. The diffusion coefficients decrease with increasing ionic charge and size. Large ions have more difficulties in diffusing through the network of the exchanger. This also explains why particle diffusion tends to become the rate controlling step at higher cross-linkages.

Chemical exchange has never proved to be the rate controlling step in cation exchange.

A detailed account of modern kinetic theories can be found in a chapter written by Helfferich (243).

2.2.4. Practical parameters

2.2.4.1. Capacity

The total capacity of the resin i.e. the capacity specified by the manufacturer, indicates the total quantity of exchangeable ions per unit weight of dry resin or per unit volume of wet resin. It is given as milliequivalents per gram or milliliter. From a table published by Inczedy (264) the summarising table I was compiled for a number of commercial resins

Table I

Capacity of a number of commercial resins

Type of resin	Functional group	meq/gr	meq/ml	number of resins
Phenolcondensation	$-SO_3H$	1.9-4.0	0.3-1.2	8
	$-COOH$	2.0-4.0	2.0	2
Polystyrene	$-SO_3H$	4.2-5.5	0.4-2.4	25
	$-PO(OH)_2$	6.6-6.8	3.1	2
Polyacrylic acid	$-COOH$	7.0-11.0	1.2-1.4	9

The total capacity is usually determined by titration. For strong acid groups it is nearly equal to the capacity calculated from the sulfur content which proves that all the functional groups can undergo exchange. The total capacity is thus a fundamental property of the resin. This is not the case for the so-called "breakthrough" capacity. This quantity is smaller than the total capacity and depends not only on the sort of resin but also on other factors such as the composition of the solution and the flowrate. In radiochemistry it is an important quantity because it constitutes the upper limit on the quantity of substance that can be sorbed on a resin in separations where one ion is sorbed completely and the other eluted.

2.2.4.2. Particle diameter

Resins prepared by condensation usually take on the form of irregularly formed particles, while resins prepared by polymerisation can be obtained as spherical beads.

The diameter of the beads is of importance mostly for the time necessary for a separation. There are two reasons for this. One is kinetic: the smaller the particles, the easier an equilibrium between resin and solution will be attained. The second is of a more technical nature: small particles limit the flow rate. In practice most radiochemical separations use mesh-sizes of 50-100, 100-200, 200-400, which is equivalent to particle diameters of 0.3 mm to 0.04 mm. Of special importance on the column performance is the particle diameter distribution. The more narrow the range in which these particle diameters fall, the smaller HETP will be. This is due to better column packing with particles of the same diameter than with particles of largely differing diameters.

Aubouin and Laverlochère (21) investigated the influence of the homogeneity of the resin particles on the separation of alkali metals and alkaline earths with HCl as the eluting agent. The time necessary for a separation on a column of Dowex 50WX12 (-400 mesh) was 31 hours. By using only the 10-25 μ fraction they were able to obtain the same result in 4.5 hours. In the same way, the time for a rare earth separation was reduced from 19 hours to 4 hours. See also the results of Höhlein et alii (252).

2.2.4.3. Cross-linkage

An increase in the degree of cross-linkage has the following consequences on the properties of the resin:

1° the swelling of the resin is less and therefore a higher capacity per bed volume is obtained.

2° the selectivity is higher

3° the diffusion rate in the resin is lower and therefore the attainment of equilibrium is slower.

It is clear that a high cross-linkage has both advantages and disadvantages. Therefore in most applications resins with intermediate cross-linking percentages are employed. For radioanalytical separations one usually works with percentages of cross-linking ranging from 4 to 12 %.

2.2.4.4. Porosity

According to Griessbach (221) the pore diameter of polymerisation resins is of the order of 10 Å. When working with large ions or in circumstances where particle diffusion is the rate controlling step, resins with larger pore diameter possess better kinetic properties. Macroreticular resins with pore diameters of 100-1000 Å are now available. No radiochemical applications seem to exist.

2.2.4.5. Temperature

The influence of the temperature on tracer-level separations was investigated by Dybczynski (157). An increase in temperature causes an increase in the diffusion coefficients in the resin as well as in the solution. Therefore (see 2.1.1.) narrower zones, smaller HETP's and more efficient separations are generally obtained.

Originally it was thought that selectivity coefficients always diminish with a rise in temperature (221). In most cases however, the temperature seems to have a rather small effect on the separation coefficients. This would lead to the conclusion that an increase in temperature will nearly always have a beneficial effect on the separation and in practice this seems to be the case, too.

According to Dybczynski (157) however the effect of the temperature on a separation should be investigated in each case. Indeed, this author proved theoretically that both HETP and the selectivity coefficient can increase with an increase in temperature. The author illustrates this with a study of the effect of the temperature on the separation of the alkali metals on Amberlite IR-120 and on MK3 (a phenolsulphonic resin) with HCl. With a rise in temperature the plate height increases and the separation factors of the pairs Na-K and K-Rb decrease. As a result the resolution decreases sharply.

With increasing temperature, the viscosity of the liquid phase decreases so that the hydraulic resistance of the resin becomes smaller and a larger flow rate is obtained.

There is one practical difficulty in work at higher temperatures, namely the formation of air bubbles in the columns. This can cause a disruption of the column so that a possible beneficial effect of the increase of the temperature on HETP is counteracted by a bad column packing. To avoid this a careful degassing of the eluting agent at a temperature equal to or higher than the column temperature can be carried out.

2.2.4.6. Concentration of the eluted components

The elution of traces is not the only application of interest to the radiochemist. In many instances traces must be separated from macroquantities. The elution of macroquantities has a twofold influence:

1° The peaks are larger (i.e. HETP is larger)

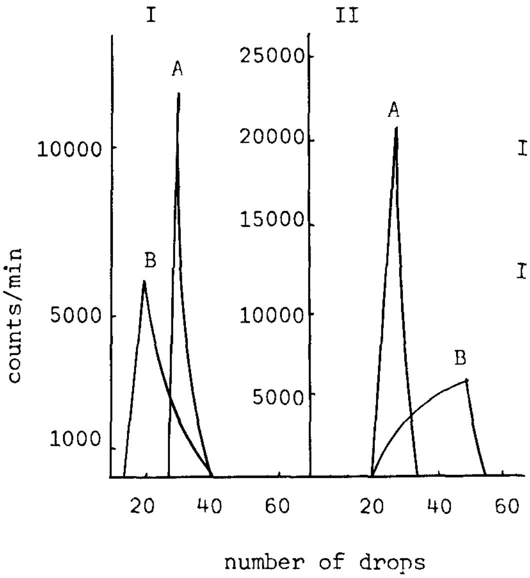
2° A shift of the elution peak maximum takes place, accompanied by an assymetry of the peak.

The influence of the concentration on the position of the chromatographic band was investigated by Russian authors. The conclusions of Geinar and Geinar (198) were corrected later by Preobrazhenski and Lilova (490). According to these authors a speedup of the elution is caused by a decrease in affinity. Consider the elution of a macroquantity of multivalent ions on a NH_4^+-form resin. The multivalent ions possess a much larger affinity for the resin than the NH_4^+-ion. In the zone in which the macrocomponent is situated, many exchange positions are already taken up by the multivalent ions so that less affinity exists and further sorption is reduced. In this case the ions to be chromatographed travel a longer distance before a new adsorption takes place (example: see figure 4, I).

Slowing down of the migration rate occurs when a strong eluting agent is used in a dilute solution. The eluting agent is not present in sufficient quantity and the exchange process is disturbed (fig. 4, II). The last effect is of special importance in the elution with strong complexing agents (hydroxycarboxylic acids, EDTA, cfr. 6.3.).

Figure 4 Dependence of elution on quantity of eluted substance (490)

Resin: KU-2, column: 80 mm x 2 mm



I. Elution of Ba by ammoniumacetate

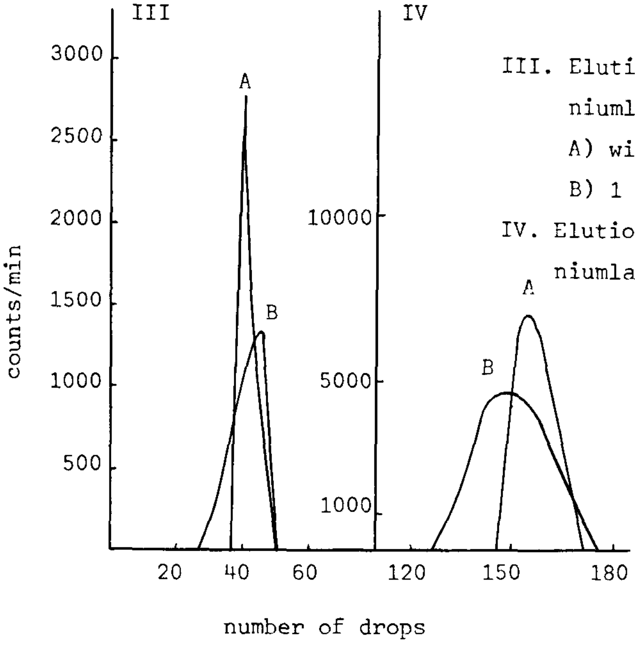
A) without carrier

B) with 8.24 mg carrier

II. Elution of Ca with 0.3 N $BaCl_2$

A) 0.08 mg Ca

B) 1.2 mg Ca



III. Elution of La with 0.5 M ammoniumlactate

A) without carrier

B) 1 mg carrier

IV. Elution of La with 0.35 M ammoniumlactate

A) without carrier

B) 5 mg carrier

In some instances the two effects compete. This is demonstrated to be the case in the elution of La with lactate (fig. 4, III and IV).

Chapter 3 Techniques

The purpose of this chapter is not an exhaustive discussion on the techniques used in ion exchange chromatography, but rather a study on some points of special interest to the radiochemist. For a general survey of ion exchange techniques, books such as those written by Samuelson (523) and Inczedy (264) should be consulted.

3.1. Determination of distribution coefficients

Distribution coefficients can be determined by shaking a known weight of dry resin with known volume of a solution of the metal ion in the solvent under study (batch experiments) or by chromatographing a small quantity of metal ion on a column and applying equation (4). These methods are the most generally used. A few other methods have been applied by Kraus et alii (337, 339). In the frontal analysis method a solution of the metal ion is percolated through the column until the concentration in the effluent becomes constant. The quantity C_R removed from the solution and the equilibrium concentration in the solution are determined. If the breakthrough curve is not distorted then $V_R . C_M = C_R$ (see figure 5) so that

$$D = V_R / m_h \qquad (17)$$

where m_h = weight of the resin

For D-values of the order of unity, a radioactive tracer solution can be passed through a small column until the inflowing and the outflowing solutions have the same composition. The column is centrifuged to remove the interstitial liquid and the bed is counted. D is then obtained from this measurement together with the known concentration of the solution and the weight of the resin.

$$D = A_{resin} / A_{sp} . m_h \qquad (18)$$

A_{resin} = activity of the resin

A_{sp} = specific activity of the solution

The "preloaded column" method can be used for the determination of very

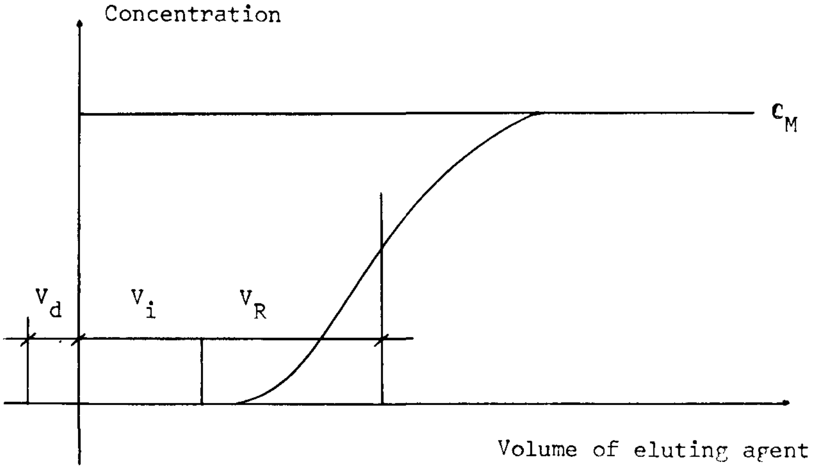


Figure 5

Determination of distribution coefficient according to the frontal analysis method. V_d = dead volume of column, V_i = interstitial volume of column

high distribution coefficients. A tracer solution is preequilibrated with a known quantity of resin and a column is packed with the loaded resin. The solution for which D must be determined is then passed through the bed. A small fraction of the tracer adsorbed on the bed is eluted and its activity determined in the effluent. D is then calculated according to equation (18).

3.2. Special column techniques

3.2.1. Gradient elution

Gradient elution consists in the gradual and continuous increase of the eluting power of the eluting agent. Its use is dictated by the following considerations:

1°) When tailing occurs, the tail is eluted with a more powerful eluting agent so that the peak is narrower. The same effect occurs with normally Gaussian peaks and leads to a substantial decrease of the HETP. The present author found that when the rare earths are separated with a continuous gradient the HETP is 5 to 25 times smaller than when the separation is carried out at constant concentration on an equivalent column.

2°) The time needed to carry out a separation of complex mixtures can be considerably shortened although gradient elution leads to a considerable decrease in separation coefficients. However, the adverse effect on the separation is balanced by the decrease in HETP.

The separation coefficient between each pair of rare earths is nearly constant. Nervik (439) showed that as a consequence, when these elements are separated with lactate at constant ligand concentration, the separation of the first two elements Lu and Yb takes 22 minutes, while the separation of Eu and Sm takes nearly 9 hours. By using the gradient elution method, this author was able to separate Eu and Sm in 19 minutes, while Lu and Yb are still sufficiently separated.

3°) A continuous gradient elution constitutes a means for automation since it can eliminate the need for changing eluting agents during the elution.

From this enumeration it appears that gradient elution will be used mainly for the separation of mixtures of several ions when this separation is carried out with one eluting agent at different concentrations. This should be the case for the alkali metals, the alkaline earths and the rare earths and the actinides. In fact, in radiochemistry, gradient elution is used nearly exclusively for the separation of the rare earths (see 6.3.). Nonradiochemical procedures for the separation of the alkali metals (152, 174) have, however, been reported.

To obtain a continuous gradient one needs at least one mixing chamber in which an initial eluting agent is present, and one reservoir from which eluting agent with another concentration is added to the mixing chamber. The simplest and most frequently employed gradient uses a mixing chamber with constant volume of eluting agent. The mathematical treatment for this gradient was given by many different authors such as (60, 106, 239bis, 350). It leads to equation (19):

$$C = C_o - (C_o - C_1)\, e^{-v/V} \qquad (19)$$

C_o = concentration in the reservoir

C_1 = initial concentration in the mixing chamber

C = concentration

v = volume

V = volume of the mixing chamber

A simple way to realise such a gradient consists in filling a chamber with the initial eluting agent, connecting one end to the column and one to the reservoir (see fig. 6) and closing other outlets. Eluting agent from the mixing chamber is fed by gravity to the column and is continuously replaced by eluting agent from the reservoir. Simple apparatus was described among others by Vobecky (632), Clanet (114), Katz (287) and Donaldson (148).

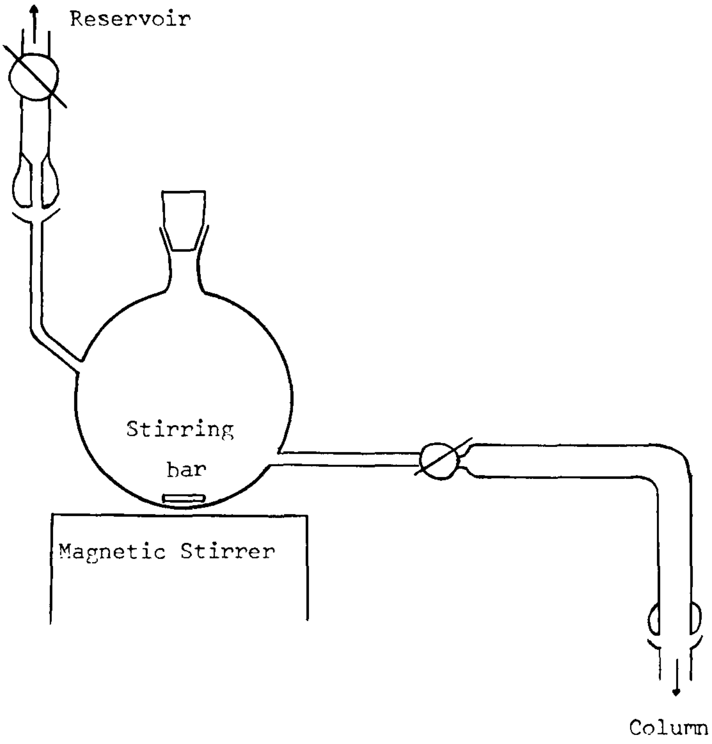


Figure 6

Apparatus for gradient elution (exponential gradient)

A more versatile way of obtaining gradients consists in connecting the reservoir and the mixing chamber, so that they form a system of communicating vessels. In this case the gradient is given by equation (20) (60, 153, 313, 350, 469):

$$C = C_o - (C_o - C_1)\left(1 - \frac{v}{V_t} \right)^{\kappa} \qquad (20)$$

where V_t = total initial volume

$\kappa = Q_o/Q_1$

where Q_o and Q_1 are the cross sections of the two communicating vessels. When $\kappa = 1$ the gradient is linear, for $\kappa > 1$ it is concave and for $\kappa < 1$ convex. This equation is only correct when the densities in both vessels do not differ too much (313).

An apparatus for the production of a linear gradient is shown in figure 7.

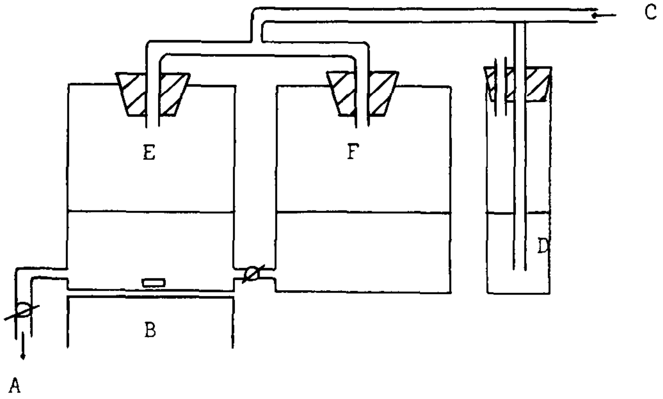


Figure 7

Apparatus for gradient elution (linear gradient)

A: to column
B: magnetic stirrer
C: pressure
D: mercury
E: mixing chamber
F: reservoir

More complex gradients (fig. 8) can be obtained with other systems. One of these is available commercially under the name of Varigrad. It consists of a series of communicating vessels (9 in the commercial apparatus). A different concentration of eluting agent can be obtained in each of these vessels. The general equation for the concentration of the eluting agent in such a system was given by Sober and Peterson (559). No applications in radiochemistry seem to exist.

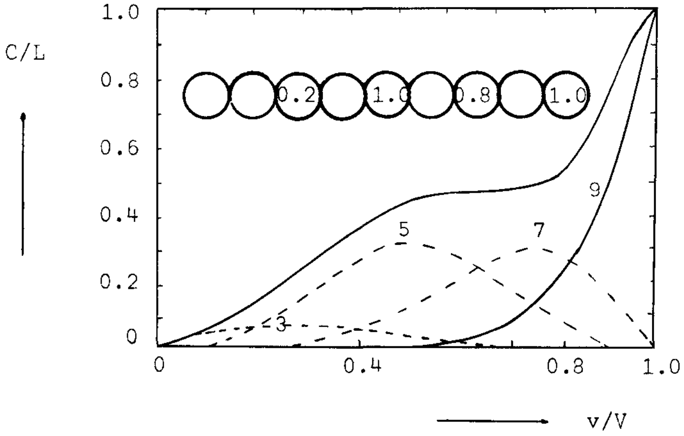


Figure 8

Complex gradient obtained with the Varigrad system (559)

Methods for the prediction of the apparent distribution coefficients obtained by gradient elution have been described by Freiling (175, 176), Ohashi (450) and Molnar (412).

3.2.2. Rapid separations

Optimal conditions for rapid separations are:

1°) High temperatures: this leads usually to higher resolution and allows higher flow rates (see 2.2.4.5.).

2°) Small column dimensions: Rengan and Meinke (504) for example used a column of 2 mm internal diameter and 2.8 cm long to separate certain pairs of rare earth elements (see fig. 9).

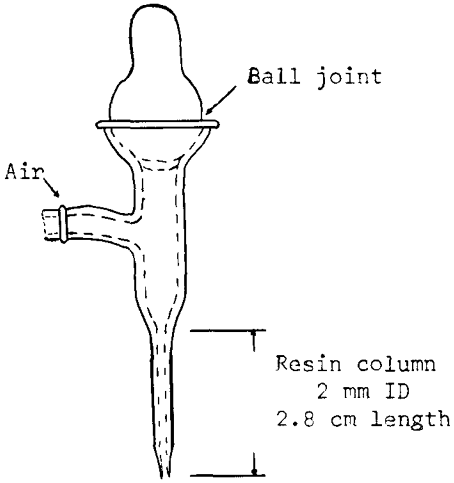


Figure 9

Column for rapid radiochemical separations (504)

3°) Small ion exchange particles (see 2.2.4.2.): Farrar et alii (167) for example describe the use of a very fine grained resin (20 to 40 μ diameter) for the separation of ^{249}Bk from fission products.

4°) Particles with a narrow diameter distribution (see 2.2.4.2.)

5°) High flow rates. These can be obtained by forcing the solutions through the columns under pressure. Both articles cited in this paragraph

use this method. Farrar et alii use a high-pressure pump(1800 to 2500 psi) while Rengan and Meinke use air pressure.
A rapid method for the elimination of matrix activities in activation analysis, the so-called "isotopic ion exchange method", was developed by Tera, Morrison and Peterson (458, 623). Isotopic exchange of the matrix activity with a cation exchanger column in the stable form of the cation delays breakthrough of the activity, while radioactive trace species are rapidly eluted. In acetone-water-HCl mixtures separations of Mg^{2+}, Sr^{2+}, Cu^{2+} matrix activities from many trace species is possible in 5 minutes.

3.2.3. Automation

A review on the automation of radiochemical separations in general is contained in a paper presented by Girardi at the Symposium on Nuclear Activation Techniques in the Life Sciences (208) at Amsterdam. The same author described (207) an apparatus for the automatic sequential elution from ion exchange resins (see figure 10). The eluting solutions are contained in the separatory funnels, A, mounted on a turntable. When the stopcocks hit against rod B, the solution flows into the reservoir of the pump (peristaltic type). The electrodes D are then shorted and the turntable stops. The pump starts and forces the solution at a predetermined flow rate through the column. When the liquid descends below the level of the electrodes D, the pump stops and the turntable rotates until the stopcock of the next funnel opens. The cycle is then repeated. A waiting time can be introduced between sucessive elutions by means of timer F. A more sophisticated system suitable for the simultaneous treatment of 4 samples was described later, also by the same author (209). This equipment consists of two independent units: a programming unit and an operating unit. The programmer supplies a D.C voltage to the various elements of the operating unit according to a predetermined time sequence. This sequence is programmed by means of a printed circuit card. When it operates a pump, the program also determines the flow rate. The operating unit contains the pump and the valves to start, regulate and stop the flow of reagents along the analytical line. Mathers and Hoelke (394) describe an elution scheme in which fission product radioelements are divided into five groups. An automatic machine feeds the sample and the elutriants from 10 ml disposable

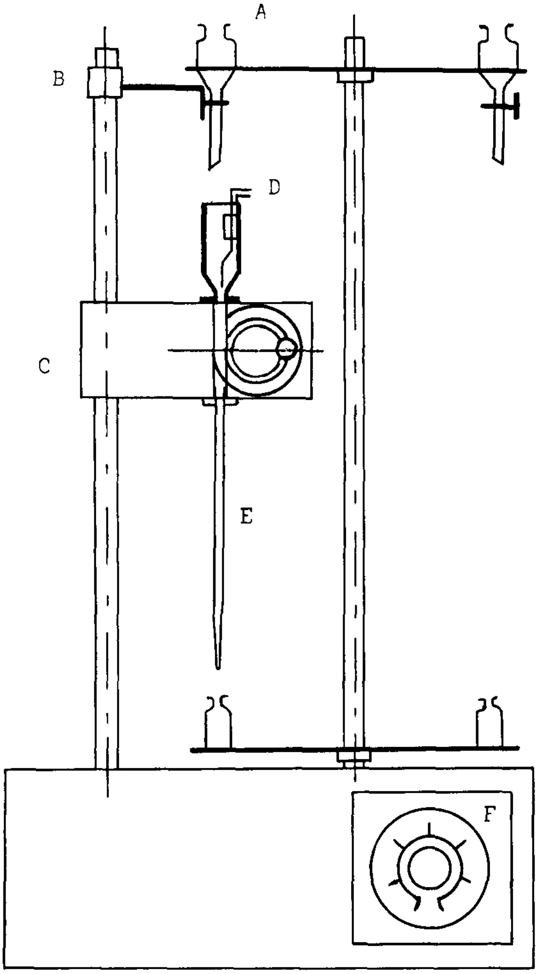


Figure 10

Apparatus for automatic sequential elutions from ion exchange resins (207). The explanation of the symbols is given in the text plastic syringes to a battery of columns. The effluents are collected and evaporated simultaneously on counting trays. When this method is used in conjunction with an automatic β-counting system, one technician can separate 12 samples into 5 fractions and count the fractions in one 8-hour day.

Fourcy et alii (173) described an automatic apparatus built for the sequential elution of activated samples on 8 columns simultaneously. Electric peristaltic valves dispense at the proper times the solutions that are pushed through the column by a peristaltic pump.

Comar and Le Poec (116) constructed an automatic chemical treatment system for the determination of iodine by activation analysis in biological samples. An ion exchange step was incorporated in this system. A turntable is fitted with small polyethylene columns. Onto a stand are fixed three ground cones through which pass the sample and the two eluting agents. An electromagnet brings these cones into contact with the columns or else detaches them, thereby leaving the rack to rotate freely. The cones are made of teflon and neoprene o-rings seal the column to the reagent input tubes.

A method for the automated neutron activation analysis of biological material with high radiation levels is described by Samsahl (522) (fig. 11). The sample is sent over six successive columns by a peristaltic pump. Each column adsorbs selectively one element or a group of elements. Mixing coils between the column make it possible to change the medium in which the elements are percolated through the successive columns. The time needed for one separation (preparation of sample not included) is 40 minutes.

A rather special technique was described by Burnett and Cohan (657). They constructed modular units which can be joined together. One of the units is a chromatographic column in which the traditional bed was replaced by a stack of ion exchange paper discs (fig. 12). This makes it possible to dismantle the column and to select for counting the paper discs that contain the element to be determined.

Another aspect of automation resides in the continuous measurement of radioactivity in the eluate and the recording of the elution curve. Continuous analysis of the eluate can be carried out by forcing the eluate to run through a measuring cell coupled to a γ or a β counter. Several systems have been described in the literature. The elaboration of a γ counting system

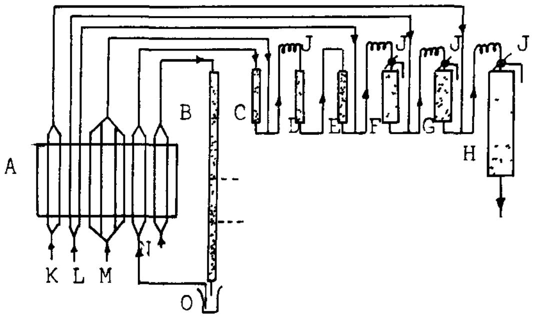


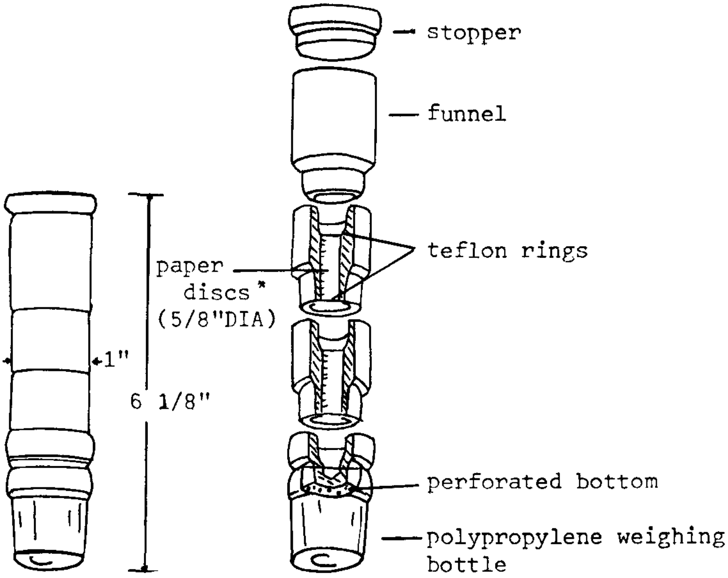
Figure 11

Automated system for neutron activation analysis of biological samples (522)

A = peristaltic pump B, C, D, E, F, G, H = ion exchange columns

J = mixing coils K, L, M, N = introduction point of eluting agents

O = test tube



*Amberlite IRA-400 resin - Cl form
Grade SB2

Figure 12

Plastic modular ion exchange column (657)

is of course easiest because almost no problems arise concerning the form of the measuring cell or the materials from which it is made. To avoid adsorption on glass walls other materials such as teflon can be used (54). For hard betas, some precautions must be taken to avoid too high a loss of counting efficiency. Thin walled Geiger Müller tubes built for these purposes are commercially available. The detection of weak betas is more difficult. The need for measuring weak betas arises rarely in radioanalysis and is nearly completely confined to biochemical work (^{14}C, ^{3}H, ^{35}S).
An example of a γ -counting system installed at the Nuclear institute of the University of Ghent, Belgium is shown in figure 13. The flow cell consists of a glass spiral. After passage through the cell, fractions are automatically collected for further analysis. Each time that the collection of a new fraction is begun an event marking system described by Geerinck and Hoste (197) makes an indication on the recording of the elution curve. Many other examples are present in the literature. A chamber for the simultaneous detection of γ and β rays was described by Tompkins (613).

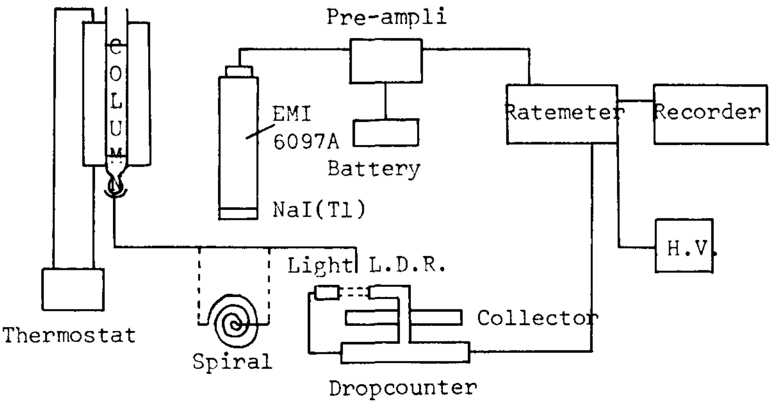


Figure 13
System for automatic γ -monitoring of column effluent

The elution can also be followed by automatically scanning the columns with a movable detector. Holm and Kraus (336) have described such a device.

3.2.4. Concentration

If a solution containing traces of metal ions is percolated through a cation exchange column in a suitable medium, the ions will be retained. They can be desorbed later with a smaller volume of an appropriate eluting agent and thus concentrated. Samuelson (523) devotes a chapter to this technique in his book on ion exchange, discussing more particularly work on the concentration of long-lived fission products from environmental samples (17, 165, 249, 278, 279, 280, 374). Analogous work is cited occasionally in this review in the chapters on the alkali metals, the alkaline earths, the rare earths and vanadium.

The determination of the fission products is often carried out by low-level counting. The use of ion exchangers for the concentration can lead to higher blank corrections because of the presence of ^{90}Sr in the resin (237).

Cation exchangers are most used in concentration procedures, but a mixed ion exchanger also offers advantages. Eichholz et alii (163) described its use for the concentration of Y-Ce-(Sr-Y)-(Ba-La) from aqueous fission product solutions.

Tera et alii (604) described a method for the concentration of trace elements by precipitation of the matrix (an alkali or alkaline earth element) as the chloride on a cation exchange column in strong HCl and elution of the trace with further HCl. Fig. 14 shows an application of this method to the concentration of Al, Cd, Zn, Cu, Ag, Mn, In and Mg traces in NaCl.

3.3. Sheet techniques

Organic ion exchange papers can be obtained by the impregnation of cellulose with classical ion exchange particles on a polystyrenedivinylbenzene base, or by introducing functional groups in the cellulose matrix. They can also be prepared by impregnation with liquid ion exchangers or inorganic exchangers. In the context of this review only the first two categories can be considered. Both are commercially available.

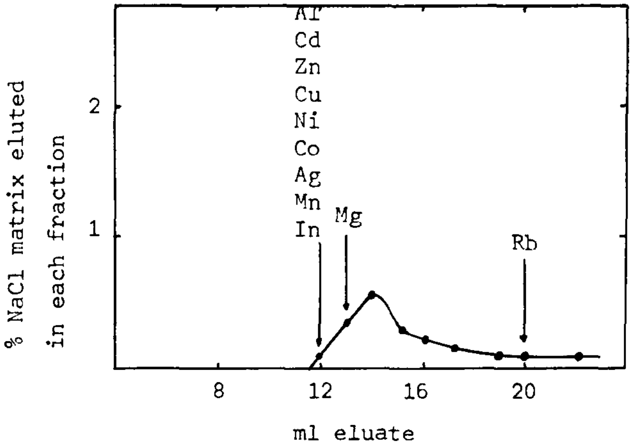


Figure 14

Separation of trace elements from NaCl matrix (604). Amount of matrix: 700 mg, eluent 12.2 M HCl. Arrows indicate volume of eluent containing yields of 90 % or higher of trace elements.

Lederer, Ossicini and coworkers (352) studied very extensively the chromatography of inorganic ions on anion- and cation-exchange papers of the cellulose and the polystyrene variety. Their work consists mostly in the gathering of R_f-data in the usual mineral acid media. These data are used to study problems of a more theoretical nature. Very few separations were actually studied but many seem possible. Sherma (544, 545, 548) reported several separations in organic solvent-acid media. One of these uses Korkisch's CIESE principle (see 5.9.); another consists in a separation of the alkali metals. A separation of the rare earths with an organic complexing agent (glycolic acid) was reported by Heininger and Lanzafame (241). This procedure is also interesting because of the use of a centrifugal force to accelerate the flow of solvent.

It can be seen that about every solvent system that can be used on columns can also be employed on papers. An exception is mineral acids with a molarity higher than 6 since these attack the cellulose base of the paper.
A radiochemical separation on Whatman P-20 of some uranium-fission products and U was reported by Getoff and Bildstein (199). The following separations were carried out: U from ^{95}Zr-^{95}Nb with 0.5 to 1.0 % HF, U-^{90}Sr-^{90}Y-^{140}Ba-^{140}La with 2 N HCl, ^{90}Sr-^{90}Y-^{137}Cs with 1 M α-hydroxyisobutyric acid (pH 5).
Another sheet technique which can be used is thin-layer chromatography (TLC). A recent review about TLC for inorganic ions was published by the present author (392). Sherma (546) separated As, Cd and Ba on a starch bound ion exchange layer with NaCl as the developing solvent. Berger et alii (41, 42, 43, 44) described a number of separations of radioactive tracers. These include alkali and alkaline-earth metals. An interesting application is the use of two neighbouring layers, the first one being an anion exchanger on which the anions are separated, the second one a cation exchanger on which the cations are separated. This method was applied to the separation of alkali halogenide salts (fig. 15).

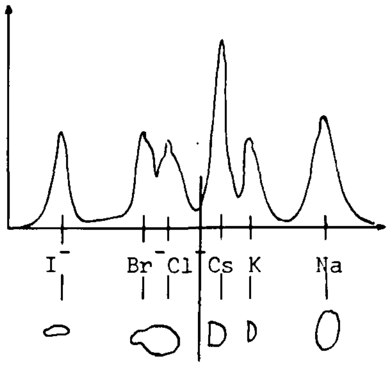


Figure 15

Radiochromatogram of a mixture of alkalihalogenides on adjacent thin layers of Dowex 1X10 and Dowex 50WX2 (41)

No radiochemical determinations with ion exchange sheets seem to have been carried out. The following alternatives could be used should the need arise:

- scraping of the stationary phase or cutting the paper and counting with conventional methods.
- scanning: with a movable G.M. tube and a stationary sheet or else with a moving sheet and a stationary G.M. tube. Many scanners (mostly built for biochemical use) are commercially available. The paper or thin layer can also be saturated with a liquid scintillator and moved under a photomultiplier tube.
- autoradiography and densitometry of the photographic plates.

Chapter 4 Physicochemical basis of separations

4.1. Separations based on selectivity

Selectivity differences can be used to separate cations from other cations. In practice this is achieved by eluting the mixture of the ions with a mineral acid or with a salt. Let us consider the separations of ions M^{m+} and N^{n+} with a monobasic strong acid HX. The selectivity coefficient for the exchange between M and H is given by:

$$K_H^M = \frac{[H]^m \cdot [\bar{M}]}{[\bar{H}]^m \cdot [M]} \qquad (21)$$

and since the distribution coefficient of M, D(M), is given by

$$D(M) = \frac{[\bar{M}]}{[M]} \qquad (22)$$

one obtains

$$D(M) = K_H^M \left(\frac{[\bar{H}]}{[H]} \right)^m \qquad (23)$$

and in the same manner

$$D(N) = K_H^N \left(\frac{[\bar{H}]}{[H]} \right)^n \qquad (24)$$

From equations (23) and (24) it is then possible to calculate the separation coefficient β :

$$\beta = D(M) \;/\; D(N) = (K_H^M \;/\; K_H^N) \; ([\bar{H}] \;/\; [H])^{m-n} \qquad (25)$$

When m=n, the separation coefficient is determined by the values of the selectivity coefficients and is theoretically independent of H^+. When $m \neq n$, the separation coefficient is a function of the concentration of H^+.

From equation (23) one can deduce the behaviour of D as a function of H^+. When H is present in a large excess and when M is present in tracer concentrations, the quantity $[\bar{H}]$ is not influenced by changes in the concentration of M and is equal to the capacity of the resin. Therefore

$$D(M) \;=\; \text{constant} \;/\; [H]^m \qquad (26)$$

or

$$d \log D(M) \;/\; d \log [HX] \;=\; -m \qquad (27)$$

Equation (27) means that D(M) is a function of the acid concentration. The theoretical treatment is highly idealised and holds true approximately only for noncomplexed elements at low concentrations of HX. At higher concentrations of the element an increase of D can occur (see fig. 16). A theoretical treatment to explain this phenomenon was given by Nelson et alii (438).

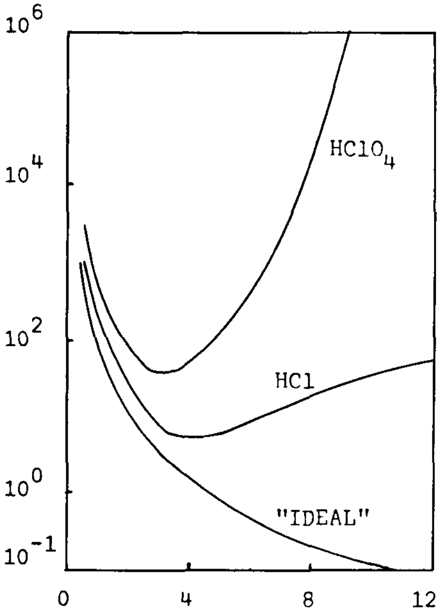


Figure 16

Non ideality at high ionic strenghth (Sc^{3+}, Dowex 50X4, 25°C) (438)

4.2. Separations based on complex formation

In many cases the ion exchange selectivity is not large enough to achieve sufficient separation. Complex formation may then be used to obtain better results.

A very important example is the separation of the rare earth and actinide groups. Neighbouring rare earths cannot be separated from each other with the common inorganic acids as eluting agents. Very good results are obtained, however, with (among other possibilities) hydroxycarboxylic acids such as α-hydroxyisobutyric acid. The anion of this acid forms stepwise complexes with the rare earth M according to the following scheme:

$M^{3+} + L^- \rightleftharpoons ML^{2+}$ stability constant k_1

$ML^{2+} + L^- \rightleftharpoons ML_2^+$ stability constant k_2

$ML_2^+ + L^- \rightleftharpoons ML_3$ stability constant k_3

$ML_3 + L^- \rightleftharpoons ML_4^-$ stability constant k_4

$$\text{where } k_1 = [ML^{2+}] / [M^{3+}][L^-] \quad \text{etc.} \qquad (28)$$

From the definition of D

$$D = [\bar{M}] / [M]$$

Since only positive ions are adsorbed by an ion exchanger one obtains:

$$[\bar{M}] = [\bar{M}^{3+}] + [\overline{ML}^{2+}] + [\overline{ML}_2^{+}]$$

If, as a first approximation, one neglects the adsorption of positively charged complexes because they have a lower charge and thus show less selectivity towards the resin, one may write:

$$[\bar{M}] = [\bar{M}^{3+}]$$

or

$$D = \frac{[\bar{M}^{3+}]}{[M^{3+}] + [ML^{2+}] + [ML_2^{+}] + [ML_3] + [ML_4^{-}]} \qquad (29)$$

and

$$D = \frac{[\bar{M}^{3+}]}{[M^{3+}]\ (1 + \sum_{n=1}^{n=4} K_n [L^-]^n\ )} \qquad (30)$$

K_n is here the total complex constant:

$$K = k_n . k_{n-1} \ldots k_1$$

From (30) it appears that when the ion is present in solution bound to n ligands, that:

$$d \log D \ / \ d \log L^- \ = \ -n \qquad (31)$$

For rare earths and α-hydroxyisobutyric acid one would expect for n a value between 3 and 4. Experimentally one finds indeed a linear relation between log D and log L with, however, a slope between -5.81 and -4.87. This deviation from the theoretical value is due to the approximations introduced in the derivation of equation (31).

The adsorbed species may not necessarily be M^{3+}. This was pointed out by Choppin (110). By taking into account constants for the reaction between the resin and the different positive ions, the following values (d log D / d log L) were obtained for the different possible combinations of species in the resin and in the solution.

Species in solution	Species in the resin phase		
	M^{3+}	ML^{2+}	ML_2^{+}
M^{3+}	-3	-1	1
ML^{2+}	-4	-2	0
ML_2^{+}	-5	-3	-1
ML_3	-6	-4	-2
ML_4^{-}	-7	-5	-3

In fact more than one species can be in the aqueous phase. Other studies in this context are due to Brücher and Szarvas (81), Powell (484) and Holm et alii (256).

Chapter 5 Applications of the principal resin eluting agent systems (*)

5.1. HCl

Strelow (571) has published a table of distribution constants for many elements in HCl of molarities ranging from 0.1 to 4 N. In this region D_V decreases continuously as a function of the molarity of the eluting agent. Nelson (438) and Diamond et alii (143) noted that several ions show a sharp increase in D_V after a minimum has been reached in 5-6 M HCl. In 9 N HCl the following ions are strongly adsorbed ($D_V > 10$): Au^{3+}, Fe^{3+}, Ga^{3+}, Sb^{5+}, Sc^{3+}, Th^{4+}. This permits us to separate those ions from most others in high molarity HCl. On the other hand, some ions show a very sharp decrease of D_V as a function of HCl. This is the case for ions that form strong chloride complexes such as Zn, Cd, Hg, Pb, In, Bi. The D_V-molarity function of some other ions contains only a shallow minimum followed by a slow increase at higher concentrations. This is due to complex formation as can be shown from a comparison with the adsorption from $HClO_4$. It is dangerous to make conclusions about the occurrence of negative complexes from cation exchange data obtained at high ionic strength. Indeed most negative complexes are not adsorbed on a cation exchanger, but Au and Fe are almost certainly adsorbed as a negative complex. In HCl of low molarity many separations are possible through differences in selectivity. The alkali metals for example can be separated from each other or by elution as a group from many more highly charged ions (cfr. 6.1.). These separations can also be carried out with chloride salts such as NaCl or NH_4Cl. The highly charged ions such as the rare earths and Th can be separated from most other elements by **preferential adsorption.**

A few ions such as Hg^{2+} can be complexed even at very low molarities of HCl and are then eluted before most other ions. This is also the case for the chloride complexes of the platinum elements. These can be separated even from ions that are adsorbed only at very low HCl concentrations such as Te^{4+} (568).

Ahrens et alii (2) used HCl to separate the ions present in silicate rocks

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(*) A number of figures and tables of D-values are reproduced in the data section.

in two fractions. Each of these was analysed by spectrography. Analogous separation procedures coupled to Ge(Li) γ spectrometry could be useful in activation analysis. With 2 N HCl Ti, Sn, Pb, Zn, Zr, Al, Li, Na, V, Fe, Mg, Mn, Ni, Co, Ga, K, Rb, Cs, Ca were eluted and with 6 N HCl Sc, Y, La, Ce, Nd, Sr and Ba were.

The separation of a large number of radioelements with HCl was described among others by Aubouin et alii (19) and by Fourcy et alii (173). The first authors described the separation P-S (0.1 N), Na (0.2 N), Cs (0.55 N), Mn (0.9 N), Ca (1 N), Sr (1.8 N), Ba (2 N) and the second P (0.1 N), Na (0.2 N), K, Rb (0.55 N), Cs (0.55 N), Mn (0.9 N), Ca (1 N), Sr (0.05 N HF), Sc (1.8 N HCl), R.E. (0.5 M α-IHBA), Ba (4 N) (fig. 17).

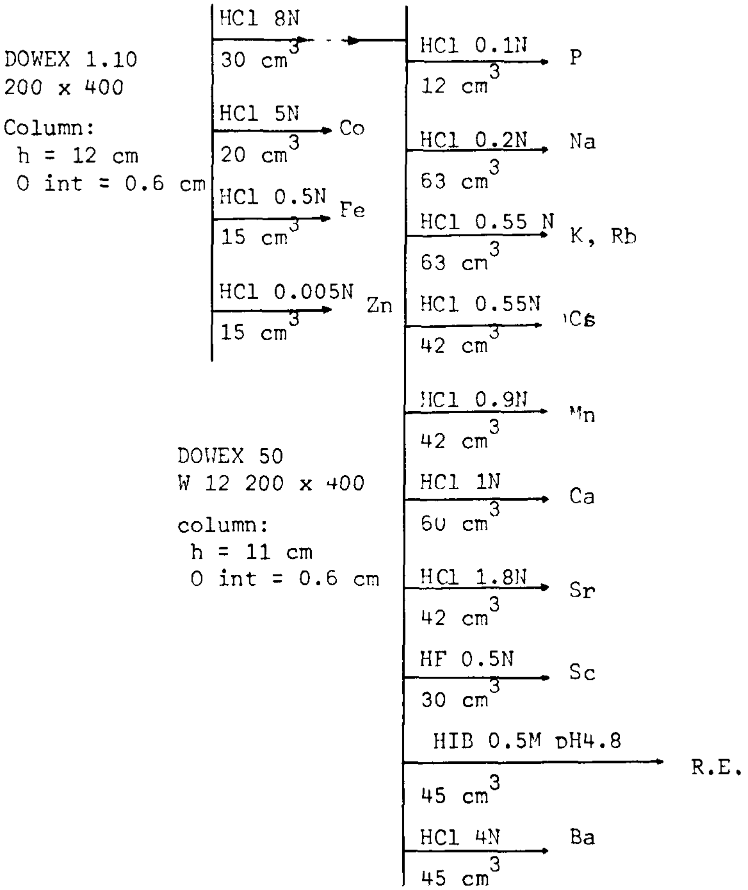


Figure 17

Ion exchange scheme for radioecological studies based on ion exchange in HCl medium (173)

5.2. HBr and HI

Distribution constants of the rare earths in HBr and HI were determined by Choppin (108). The distribution coefficients in HBr are of the same order of magnitude as in HCl and show also a minimum at an intermediary concentration. Those in HI are higher.

Nelson and Michelson (436) have systematically investigated the cation exchange behaviour of the ions in HBr medium. From their results it appears that a large number of ions, i.e., the anions and the platinum elements (strong complexation) are not adsorbed over the complete range of molarities (0.2 M - 12 M). This is also the case for Hg^{2+}, Pb, Ag.

Several other elements are strongly adsorbed in weakly acidic solutions. The distribution coefficients decrease with increasing molarity. Some elements (such as Zn) which are known to form bromide complexes are not adsorbed at high HBr concentrations. Many other elements are however strongly adsorbed. Among these the alkaline earths, the rare earths and Th are probably sorbed as cations while Fe, In, Ga are adsorbed as complex anions.

For all these elements a minimum distribution coefficient value is found at some intermediary HBr concentration. Finally, elements such as Au are adsorbed even from dilute HBr as negative complexes. Their adsorption increases with increasing HBr concentration. Several separations are possible in HBr. Examples are Na-Li, Mg-Ca, Be + Mg-Ra-Ba-Sr + Ca, Cs-Hf, W^{6+}-Mo^{6+}, Al-In-Ga, Al-In-Tl, Ag-Au, Cd-Sn-In, Se-Te, Zn-U^{6+}-U^{4+}-Th, U^{6+}-Np^{4+}, Pu^{3+}-Np^{4+}.

5.3. $HClO_4$

The cation exchange behaviour of the elements in $HClO_4$ media was investigated by Nelson et alii (438). Contrary to what happens in HCl where the distribution coefficient-molarity functions of several metal ions show no minimum but decrease continuously, nearly all the metal ions show a minimum in $HClO_4$. While HCl forms complexes with many ions, $HClO_4$ does not. Therefore the ions are better sorbed in concentrated $HClO_4$ than in concentrated HCl. The extent of adsorption is least in HBr. Many ions are sorbed strongly in 9 M $HClO_4$ ($D_V > 10$) (the rare earths Sc, Y, the actinides, Ca, Sr, Mn, Cd, Pb, Fe^{3+}, Ga, Bi, Ti, Zr, Hf, V^{4+}, V^{5+}, Nb, Ta, Pa, Cr^{6+}, Mo^{6+}, W^{6+}, U^{6+}). The authors describe several separations such as Be+Ba-Sr, K-Ti, Na-Hf, Co-Mn. The author of this review carried out a Ni-La separation (140). Nelson et alii described a Mg-Ca separation. Mg was eluted with 6 M $HClO_4$-2.6 M HCl and Ca with 5 M HCl (435).

5.4. HF

Fritz, Garralda and Karraker (183) report that with 0.1 N HF the following metal ions can be eluted because of the formation of negative fluoride complexes: Al, Cd, Mo, Nb, Sc, Sn, Ta, Ti, U^{6+}, W, Zr. Of the ions that remain adsorbed on the resin the following are eluted with 1 N HF: As^{3+}, Ba, Fe^{3+}, Ga, Hg, Mn, Sb^{3+}, Sr, V^{4+}, Zn. The ions Ag, Be, Co, Fe^{2+}, Cr^{3+}, Cu, In, La, Mg, Ni, Pb, Th and Y remain on the column.
Moiseev et alii (411) separated the radioelements obtained by neutron irradiation of Si in two groups by elution with 0.1 N HF on a KU-2 column. Eluted were: As, P, W, Sb, Mo, Sn, Ta(Cr) and adsorbed: Na, K, Rb, Cs, Ca, Sr, Ba, Mn, Ni, Ag, Cr, Co, Cu, In, Ga, Fe, Zn, Cd, rare earths. A group separation of elements, present in irradiated Ta, Hf, W or U targets with HF as the eluting agent, was elaborated by Nikitin (444). The elements named form anions and are not adsorbed on a KU-2 column from M HF. Cr, Fe, Ca, As, Cd, In are eluted with 5 M HF; Na, Rb, Cs, Mn, Pb, Bi with 10 M HF; Ni, Zn, Ti, Hg with 15 M HF; Co, Cu, Tl with 20 M HF; and R.E.'s and alkaline earth metals with HNO_3 plus H_3BO_3. It seems that some of Nikitin's findings (for As and Mn) are not in agreement with Fritz's and Moiseev's.
The use of HF in combination with strong mineral acids offers several advantages such as the formation of fluoride complexes and the prevention of hydrolytic precipitation. Cation exchange data for 27 metal ions of metallurgical importance in mixtures of 0.1 N and 1 N HNO_3, 0.1 N and 1 N H_2SO_4 and 0.1 N and 1 N HF were given by Danielsson (124). Ag, Cd, Co, Cu, Mg, Mn, Ni, Pb and Zn are strongly adsorbed from all the solutions investigated. Al, As^{3+}, As^{5+}, Mo, Nb, Sb^{3+}, Sb^{5+}, Sn^{4+}, Ta, Ti, W and Zr are not appreciably adsorbed from any of the solutions studied. Bi, Cr^{3+}, Fe^{2+}, Fe^{3+}, V^{4+} and V^{5+} are strongly adsorbed from 0.1 N HF and less from 1 N HF containing mixtures.

5.5. HNO_3

Strelow et alii (583) measured the equilibrium distribution coefficients of

49 cations between BIO-RAD AG 50WX8 and HNO_3 0.1 N to 4 N. The coefficients in HNO_3 are slightly higher than in HCl. However, for some cations which form relatively stable chloride complexes such as Hg^{2+}, Bi^{3+}, Cd^{2+}, In^{3+}, Fe^{3+}, Pd^{3+} very substantial differences are noted. Thus, a separation of Fe^{3+} from Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+} which is very poor in HCl becomes feasible in HNO_3. The following separations were given as illustrations of the possibilities of this eluting agent: **Na-Be-Ba-Y-Zr; Hg^{2+} (0.2 N HCl),** Cd^{2+} (0.5 N HCl), Be (1.2 N HNO_3), Fe^{3+} (1.75 N HCl), Ba^{2+} (2.5 N HNO_3), Zr^{4+} (5 N HCl) (fig. 18). The separation of bivalent metal ions from tervalent metal ions as groups with 1.5 N HNO_3 was described by Fritz and Garralda (181).

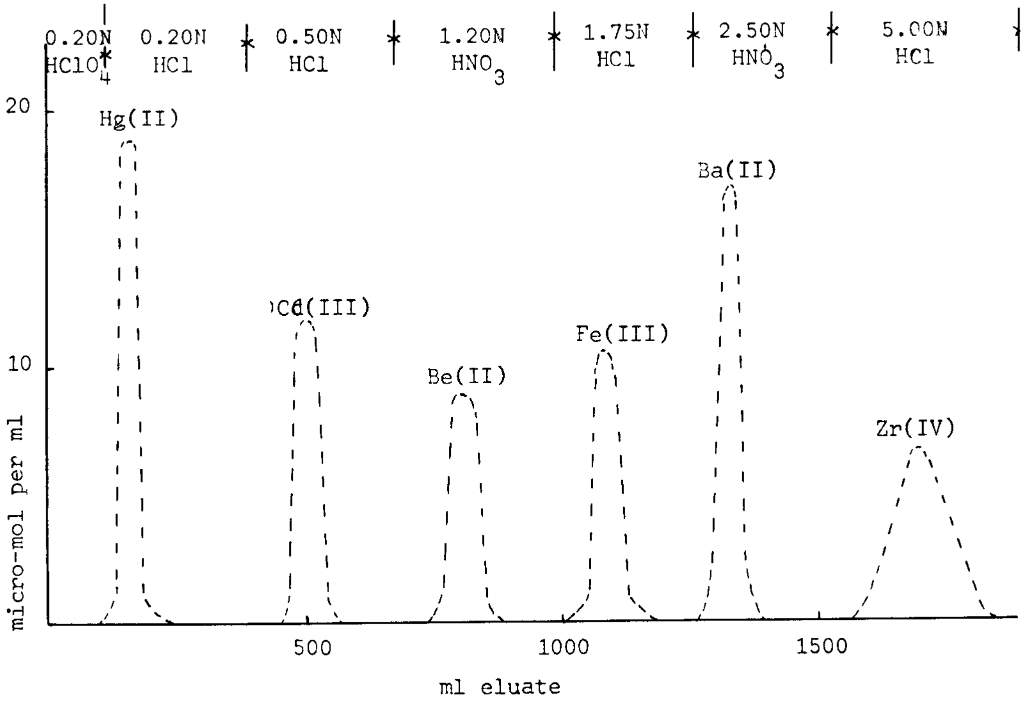


Figure 18

Separation of a mixture of Hg^{2+}, Cd^{2+}, Be^{2+}, Fe^{3+}, Ba^{2+}, Zr^{4+} (583)
Column: 20 grams of dry AG50WX8, 100-200 mesh. Flow rate 3 ml/min.

5.6. H_2SO_4

The distribution coefficients are normally higher in H_2SO_4 than in either HCl or HNO_3 (583) since sulphuric acid, because of its lower degree of dissociation, supplies less hydrogen ions than the two other acids. However, a number of cations form complexes in H_2SO_4 and this causes a marked decrease in distribution coefficient for ions such as Zr^{4+}, Th^{4+}, UO_2^{2+}, Ti^{4+}, Sc^{3+} and in a lesser degree Fe^{3+}, In^{3+}, Cr^{3+}. A separation of V^{5+} (0.5 N H_2SO_4 + H_2O_2), UO_2^{2+} (1 N H_2SO_4), Sc^{3+} (2 N H_2SO_4), Y^{3+} (4 N HCl) is possible. The chromatographic behaviour of 24 metals in $(NH_4)_2SO_4$-H_2SO_4 media was investigated by Kuroda et alii (288, 344). Interesting separations of Sc and of Be from the 23 other metal ions are described.

5.7. H_2O_2

H_2O_2 forms complexes with several elements among which the earth acids and Ti, Mo, V are the more important. Mo, V, W can be eluted from a cation exchanger with dilute H_2O_2 (8). Janousek (274) used H_2O_2 to elute V from a column of Katex FN in the analysis of fuel oil ash. Fritz and Abbink (179) separated vanadium from most other ions by eluting it from a cation exchange column with a 1% solution of H_2O_2 in 0.01 M H_2SO_4. Chan and Riley (102) separated V from Fe, Al, Co, Zn, Ti, U and Ce by elution with 0.3 % H_2O_2 from many other elements occuring in natural waters except Mo and W which accompany the V. The separation of W with H_2O_2 was studied also by Ryabchikov and Bukhtiarov (514) and Strelow (577). Fritz and Dahmer (180) separated Mo, W, Nb, and Ta from other metal ions by elution with 0.25 N H_2SO_4 + 1 % H_2O_2 (Mo, W) or 0.25 M HNO_3 + 1 % H_2O_2 (Ta, W, Nb). Bukhtiarov (662) separated Nb from Zr and Hf with 0.6 - 1 M HCl + 1 % H_2O_2.

5.8. Other inorganic eluting agents

Bhatnagar (48, 663) reported the ion exchange separation of a few ions with $NaNO_2$ on Amberlite Ir-120. Cd was eluted with a 2 % solution, Zn, Mn, Co and Ni with 5 % and Bi with HCl or HNO_3. Distribution coefficients of a number of metal ions in thiosulphate media were determined by Katsura (285). The extent of adsorption increases in the following order: Cu, Cd, Pb, Zn, Mg, Ni, Co, Mn, Ca, Sr, Ba, Al, Fe. Majumdar and Mitra (375) also studied the ion exchange behaviour of a few metal ions in thiosulphate media. The following ions were successively eluted from an Amberlite IR-120 column: Cu^{2+} (eluted with 0.02 N), Cd, Ag, Pb partially (0.05 M), Pb, Ag partially (0.1 M), Ag, Th, Zn, Fe^{2+}, Cr^{3+} partially (0.25 M), Cr^{3+}, Ni, Co, Mn partially (0.4 M), Mn^{2+} (0.5 M), Ba^{2+} (1.5 M). The same authors investigated the ion exchange behaviour of 21 ions in thiocyanate media (376). Fritz and Karraker (185) eluted 24 metal ions with 0.1 M and 0.5 M ethylenediammonium perchlorate solutions. Separations of 33 pairs of cations are given. Other inorganic eluting agents include: $NH_4Cl + NH_3$ (664), **hydroxylamine (665), ammoniacal pyrophosphate media (666).**

5.9. Mixed organic-inorganic solvents

Mixed organic-inorganic solvents have come into use rather recently and have only been applied infrequently in radiochemistry. However the method seems promising and therefore we will briefly discuss, in this section, the literature pertinent to these eluting agents. A review was published by Moody and Thomas (414).

In these media three reactions seem to determine the distribution coefficients i.e. first the ion exchange reaction, then the complexing in the mobile phase, and finally the solvation reactions with the solvent (where the word solvation should be used in a very broad sense).

Because of the lesser hydration of the cations, they leave the mobile phase with less reluctance and thus enter more easily into the resin phase. Furthermore ion pair formation with the fixed groupings of the resin is enhanced and the distribution coefficients are higher in mixed than in **pure inorganic media. Thus an increase of selectivity is often noted. Gable** and Strobel (192) for example found that K_H^{Na} increases from 1.5 in water to 17.2 in 75 % methanol.

For the same reason interaction with the anions in solution is also larger, thereby leading to an enhanced neutral or negatively charged complex or neutral ion pair formation. This causes a decrease of the distribution constant for the cation in question and explains the maxima which are sometimes found in the graphs of log D against organic solvent concentration. Indeed, at higher organic solvent concentrations the complex form may become predominant so that sorption by the resin is no longer possible.

According to Korkisch (320) a solvent effect can be noted with tetrahydrofuran (THF) and acetone. This is shown by the fact that the D-values in solvents with the same dielectric constant are not the same. It is this author's opinion that the effect is due to the Lewis basicity of the solvent, which should be high for a solvent such as THF. THF is thought to accept a proton from the inorganic acid present. It is supposed that the resulting cation forms an ion pair with the nitrate ion and acts as a liquid anion exchanger by the exchange of the nitrate anion against a negative complex or else by combination with a neutral species such as uranylnitrate. Because of the similarity of this process with extractive processes, ion exchange in such circumstances has been termed by Korkisch CIESE (combined ion exchange and solvent extraction).

From all this it is clear that ion exchange in mixed media can be very selective. This is demonstrated for example by the fact that Fritz (187) was able to separate 11 cations (Bi, Cd, Co, Cu, Mn, Ni, Zn, VO^{2+}, Al, Y) on a single cation exchanger column in acetone-HCl-H_2O media.

A systematic study of the behaviour in many mixed media was carried out by Korkisch and coauthors. The effect of the following distribution constants of UO_2^{2+}, Th, Zr, Ce, Mo, V^{5+}, Fe, Al, Ga, In, Bi, Mg, Ca, Pb, Zn, Cd, Cu, Mn, Co, Ni, was investigated: first an increase in the concentration of organic solvent from 0 to 90 % in solutions with a constant overall acidity of 0.6 M HNO_3, and second, a change in the acidity from 0.15 to 1.2 M while keeping the concentration of organic solvent constant at 90 %. The organic solvents were methanol, ethanol, n-propanol, isopropanol, methylglycol, acetic acid, tetrahydrofuran, acetone and the inorganic acids HCl (324) and HNO_3 (326). Korkisch and Huber (328) also determined in the same solvents and at the same concentrations the distribution coefficients of UO_2^{2+}, Ti, Zr, V^{5+}, Nb, Ta, Pa, Mo, Fe, Zn, Cd, Cu, Mn, Co, Ni in the presence of HF. Korkisch and Klakl (329) reported on the cation exchange behaviour of several elements in HBr-organic solvent media. Another systematic investigation was conducted by Fritz (187) for some 15 elements in acetone-HCl-H_2O media (fig. 19).

Several other separations with HCl-acetone-H_2O as eluting agent were described. As examples one can mention the separation of Li, Na and K)130, 217), Ca from Cu, Zn, Hg^{2+}, Cd, Fe^{3+} (373), Sc from Mn (35), Co from 29 other elements (327), Cu from Zn (94, 268), Cu from Ni (290), In from Ga

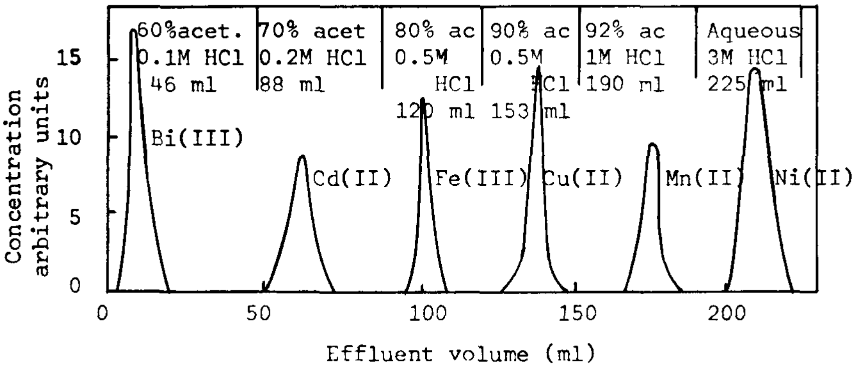


Figure 19

Separation of Bi^{3+}, Cd^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+} with mixed organic-mineral eluting agents (187)

(672), large amounts of Cd, Fe and Zn from small quantities of impurities (178). The concentration of trace elements from biological ashes by separations into groups Mo, Mg, SO_4, PO_4-Fe, Cu, Zn, Pb-Co, **Mn-alkali metals,** Ca, Sr, Ba with an analogous solvent was studied by Van Erkelens (627). The adsorption of Pr from acetone media (513) and from methanol, ethanol, isopropanol, methylethylketone and glycol (222) was investigated. The sorption behaviour of Sc (223) from the same solvent mixtures and of Cs, Ba and Zn (226) from methanol, isopropanol and acetone was also examined. A Cu-Fe separation with ethylmethylketone-HCl was reported (290).
Much research was devoted also to the use of alcoholic eluting agents and more particularly to the separation of alkali metals and alkaline earths with such **eluents.** The behaviour of the alkali metals in these (and a few other) systems was studied by Gable and Strobel (192), Fessler (667) and Pauley et alii (668). The use of methanol-HCl (72, 105, 217, 437, 441, 446, 447, 451, 501, 592, 646, 648), ethanol-HCl (440, 592), phenol-methanol-HCl (629, 630) for the separation of the alkali metals and of metha-

nol-HCl (501, 521, 602, 646) and ethanol-HCl (569, 586) for alkaline earths was reported. A systematic investigation of distribution coefficients in ethanol-HCl was carried out by Strelow et alii (587). The following separations are cited as examples: Fe-U-Ca-La, Cd-Zn-Fe-Ca-Ba, In-Ga-Be-Al-Y and in another article of the same research team (579), Al+Fe+Ti-rare earths. Other applications include the sorption of In from ethanol-HCl (619), the separation of La from other rare earths in methanol-HCl (673), the separation of large quantities of Bi from U in isopropanol-HCl (322), the separation of Zn from Cd, U from Th and several other applications with NH_4SCN-methanol (468). The sorption behaviour of Th and U in HNO_3-aliphatic alcohols was described (332).
Separations in tetrahydrofuran were studied by Korkisch and coworkers. These authors report the separation of U from many other metals (319, 320, 325) with HNO_3 as the mineral acid and of large amounts of Fe from Co, Ni and Al with HCl as the mineral constituent. These separations are based on the CIESE principle as in the separation of Cs from fission products in a thenoyltrifluoroacetone-pyridine solvent (331). To study the same effect Cummings and Korkisch (121) and Orlandini and Korkisch (669) investigated systems which contain amines and/or organic complexing agents in addition to organic solvents and mineral acids. The use of a few other media such as dimethylsulphoxide (53, 670, 671, 674), ethanolamines (248) and liquid ammonia (467) was also reported.

5.10. Organic complexing agents.

From paragraphs 5.1. to 5.8. it is clear that the selectivity obtained with inorganic eluting agents is enhanced by their ability to form complexes. Much time was also devoted to organic ligands. The two most important classes of compounds that were investigated are the aminopolyacetic acids and the hydroxycarboxylic or aminoacids. The sequences of elution of many di- and tervalent ions with EDTA, HEDTA and citric acid were determined by James et alii (273). Blaedel, Olsen and Buchanan (56) used the same three complexing agents to achieve a sequential separation scheme for the identification of 36 metallic radioelements. A procedure was described by which the elements are separated into 6 groups. Each of the elements falls mainly into its own group, with less than 1 % into any other group. Recoveries for most elements are higher than 90 %. Fritz and Umbreit (188) investigated the general usefulness of EDTA for the separation of binary mixtures. The method depends on selective complexing of the metal ions by control of the pH. The solution is buffered so that the chelate of one metal ion is formed quantitatively while the other is largely present as a cation. The technique was used for several mixtures containing two of the following ions: rare earths, Bi, Fe, Cu, Th, Hg, Zn or uranyl.

Many other applications of EDTA were reported by several authors. A very important one is the separation of series of closely related elements with the same ionic charge. The differences in distribution coefficients of these elements are often insufficient in the usual inorganic eluents. The separations of the alkaline earths and of the rare earths are discussed in paragraphs 6.2. and 6.3.

The same remark can be made about the hydroxycarboxylic acids. Lactate, α-hydroxyisobutyrate (α-HIBA), citrate and others were used to separate the alkaline earths (cfr. 6.2.) and the rare earths (cfr. 6.3.) or the two groups from each other. Divalent transition metals can also be separated with α-HIBA or lactate. For both ligands the observed sequence of increasing stability is the same: $Mg^{++} < Mn^{++} < Cd^{++} < Co^{++} < Ni^{++} < Zn^{++} < Pb^{++} < Cu^{++} < UO_2^{++}$ (610). The separation factor is largest for α-HIBA. A Zn-Co separation was reported (679). Several separations with α-HIBA were described by Perdue et alii (461): Ba+Ca/Ra, Ba+Ca/Sr, Y/Sr, Ba/rare earths, Zr/all fission products and actinides, Nb/Zr. The aminoacid glycocol was used to effect a separation of Co, Cu, Zn and Ni (494). The adsorption of Pb, Cu, Bi, Cd, Mn, Ga, Y, Zr and Th from aqueous solution of formic acid on the cation exchanger Dowex 50 WX8 was studied by Qureshi et alii (493). Separations of Zr from Th and Ga were described. The elution of 19 metal cations by oxalate solutions from Amberlite IR-120 was studied (676). Oxalic acid was used for the selective elution of Zr and Nb from fission product mixtures (115, 614) and for the separation of ^{95}Zr from ^{95}Nb (524). Th can be stripped from cation exchange columns with this acid (10, 32, 45, 160, 211 and others). Other applications: ref. 677, 678.

Inczedy, Gabor-Klatsmanyi and Erdey (265, 266) report on the use of sulphosalicylic acid for the separation of a number of transition metal ions. The following separations were obtained: Fe-Cu-Ni, Fe-Cu-Co, Fe-Cu-Mn, Cu-Ni-Mn, Cd-Zn, Fe-Cu-Co-Mn. Fritz and Palmer (186) eluted with sulphosalicylate of pH 6-7 Al, Fe, Ti, U, V^{4+}, Zr and partly Th and Cu. Other bivalent metal ions and rare earths are quantitatively retained. Sulphosalicylate was also used by a few other workers (12, 129, 452, 534, 656). Suranova (675) used 4-aminosalicylic acid to separate Ga from Cd and Zn.

Chapter 6 Cation - exchange separations of the elements

6.1. Alkali metals

6.1.1. Introduction

Alkali metals rarely form complex compounds, and therefore the separation of alkali metals from each other has to be based on differences in selectivity. For the same reason negative or neutral complexes of other metals can be used to separate these metals from the alkalis. Such separations can also be carried out by speculating on selectivity differences since the alkalis are monovalent and therefore possess a lower selectivity towards a cation exchange resin than the higher charged cations.

6.1.2. Separations based on a difference in selectivity

6.1.2.1. Separations of alkali metals from other alkali metals

A large number of separations of alkali metals from each other that are based on differences in selectivity has been described in the literature. The elements are eluted in the order Li, Na, K, Rb, Cs. Table II lists some examples of **nonradiochemical separations.**

Table II

Nonradiochemical separations of alkali metals based on selectivity differences

Li, K+Rb+Cs	HCl	(685)
Li, Na, K, Mg, Ca, Sr, Ba	HCl	(397)
K, Rb, Cs	HCl	(527, 528)
Li, Na, K	HCl	(598)
Na, K, Rb, Cs	HCl	(289)
Alkali metals	formate buffer	(624)
Li, Na, NH_4, K	Ca acetate	(117)
Alkali metals	HCl-methanol and HCl	(103)
Li, K, Na	HCl-methanol and HCl	(448)
Na, K, Ca, Mg	HCl-methanol and HCl	(646)
Li, Na, K	HCl-ethanol	(440)

Li, Na	Methanolic or ethanolic HCl	(592)
Li, Na	Methanolic-HCl	(501)
Li, Na, K	Phenol-methanol-HCl	(629, 630)
Na, K	HCl-ethanol	(441)
Na, Rb, Cs	NaOH	(508)
Li, Na, K, Rb, Cs	HNO_3	(684)

It will be seen that the eluting agents used can be classified more or less as belonging to one of three categories, namely, mineral acids (mostly HCl), salts and mixtures of mineral acids and organic solvents. The best results are obtained by using the last class of eluants.
Nelson et alii (437) compared the separation factors in HCl-methanol-water on a polystyrene-divinyl benzene-sulphonic acid resin (Dowex 50 WX 8) and on a phenol-formaldehyde-sulphonic acid resin (Duolite C3). The latter yielded by far the best results (fig. 20). The addition of methanol had a beneficial effect on the separation coefficients of Li/Na and Na/K but not on those of Rb/Cs and Cs/Fr for which a slight decrease was noted. Several examples of radiochemical separations are described such as Li (2,4 M HCl - 80 % CH_3OH)-Na(idem)-Cs + Rb + K (6 M Cl - 50 % methanol); Rb (2.5 M HCl) - Cs (9 M HCl); Cs from Fr (with 4.5 M HCl) and a separation of all the alkali metals from Li through Cs. Li and Na are eluted with the agent described above, K + Rb with 1.5 M HCl and Cs with 6 M HCl. About 20 column volumes (column bed dimensions: 4 cm x 0.28 cm^2) are needed. The K-Rb fraction is separated on a larger column (15 cm) with 1.5 M HCl from which Rb is eluted with 6 M HCl.
A non-radiochemical separation using a phenolformaldehyde resin was reported later by Strelow et alii (582). They separated Li-Na-K-Rb-Cs with HCl-ethanol and HCl as eluting agents.
The preparation of Fr tracer is also described by Nelson (437). ^{223}Fr, a daughter of ^{227}Ac was separated from Ac and ^{223}Ra, ^{227}Th, ^{211}Pb, ^{211}Bi on a Dowex 50 WX 4, -400 mesh resin (1 cm x 0.20 cm^2). The last two elements are not adsorbed at all from 1 M HCl. Fr is eluted with the same eluting agent while Ra, Th and Ac are not desorbed. The separation of Fr from Cs and Rb with HCl as the eluting agent was described by Lavrukhina and coauthors (658).

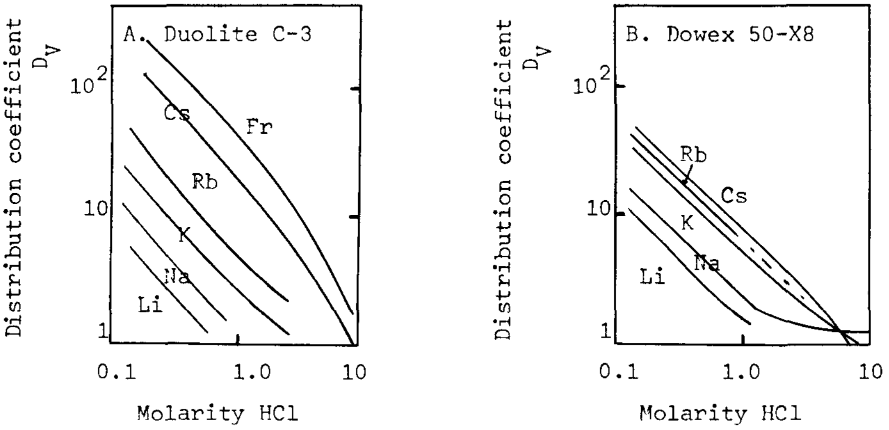


Figure 20

Adsorption of the alkali metals on a phenolformaldehyde resin (Duolite C-3) and on a polystyrenedivinylbenzene resin (Dowex 50-X8) (437)

The separation of K, Rb and Cs from irradiated rocks was described by Cabell (97). The elements were eluted in the order listed from Zeokarb 315 with successively 0.1 N HCl, 0.5 N HCl and 1 N HCl.

Brooksbank (77) described a separation of ^{22}Na, ^{42}K, ^{86}Rb and ^{137}Cs with 0.1 N HCl. More than 7 liters of solution were necessary to complete the elution of Cs (fig. 21).

Kurchatova and Levin (342) described a Na-K separation in the course of an experiment for the evaluation of the cross-sections of (n,α) and (n,p) reactions on Sc and Ca, resulting in the formation of K-activities. ^{24}Na was eluted with 0.2 N HCl from a KU-2 column and $^{42+43}$K with 0.5 N HCl.

The ion exchange separation of Rb and Cs activities was studied by Ishibashi et alii (270). On a column of Dowex 50 X8, 6 mm x 225 mm, 7 mg RbCl can be separated from 9.8 mg Cs with 0.5 N HCl. The separation of Na activities and Cs activities from each other and from divalent metals with HCl was described by Aubouin et alii (19) and that of the alkali activities from each other and di- and tri- valent metals by Fourcy et alii

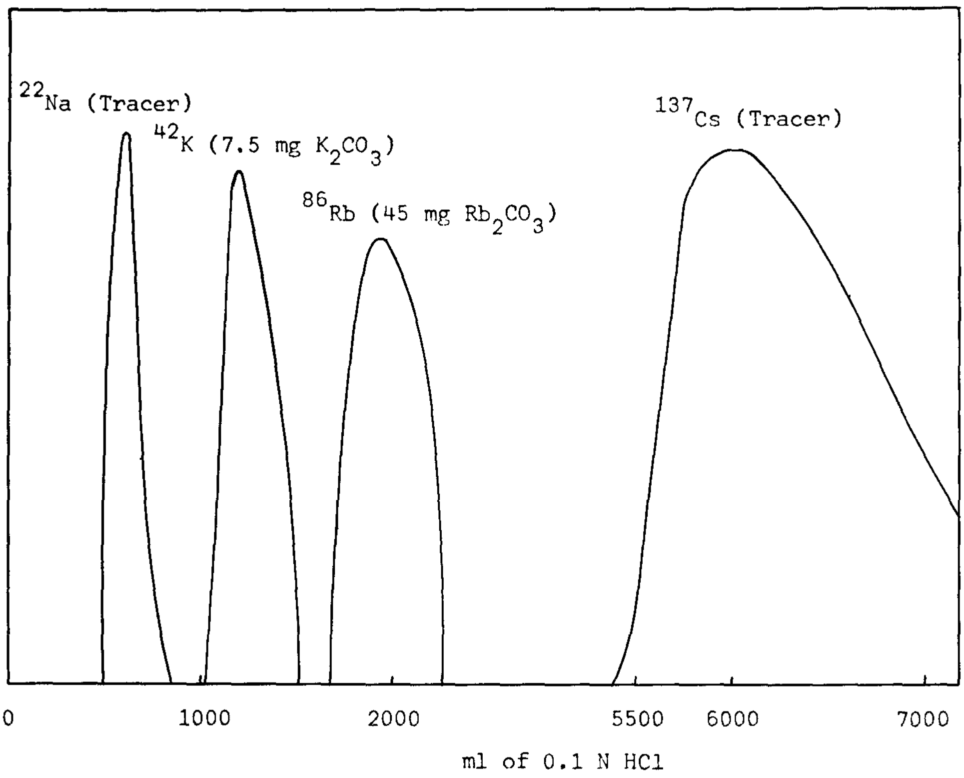


Figure 21

Separation of alkalimetals by elution with HCl (77)

(173). Both separations are described in more detail in paragraph 5.1.1. A separation of Cs, Rb + K, Na on a thin layer of Dowex 50 WX2 was carried out by Berger et alii (41) with 1 N LiCl as the solvent.

6.1.2.2. Separation from other metals

Elution with HCl has been used very often to separate the alkali metals from other metals and more particulary from the alkaline earths. It should be noted that cation exchange from other cations with HCl is a less advantageous method than anion exchange with the same eluting agent. Indeed, while the alkali metals show a certain retention on cation exchange resins they are not at all adsorbed by anion exchangers because they do not form chloride complexes. This explains in part why the metals from which the alkali metals are separated by cation exchange with HCl are usually the other metals that are not adsorbed on anion exchangers from the same **eluting agent.**

This is the case for separations of the alkalis from the alkaline earth metals as a group (105, 502, 598, 685), Cs from Sr (538) (fig. 22), Rb from Sr (194), Li from Ca (245), Cs from the rare earths (409). The last separation was carried out with NH_4Cl + HCl. NH_4Cl was also used for the separation of Li from Ca (62), and Na and K from Mg and Ca (218). A **separation of the alkalis from the alkaline-earth metals with a formic acid-ammonium formate buffer was described by Tsubota and Kitano (624).**

Strelow and collaborators (581, 683, 684) described the use of HNO_3 for the separation of the alkalis from alkaline earths and other elements (Mn, Ti, Fe). According to these authors the separation factor between the last eluted alkali (Cs) and the first eluted important alkaline earth element (Mg) is higher in this eluent (2, 77) than in HCl (1, 75).

A few radiochemical applications have been reported. The carrier-free production of ^{24}Na from MgO was discussed by Parker, Bildstein and Getoff (459). After a separation from the largest part of the matrix by extraction with water, the final purification was carried out on a Dowex 50 X8 column (50-100 mesh, 300 x 20 mm, H^+ form) with 1 N HCl as the eluting agent. The production of ^{22}Na from cyclotron-bombarded Mg by separation on a KU-2 column was described by Bliznyokova and Krotenko (58). Smales and Loveridge (553) described the determination of submicrogram quantities of Na in Li metal by radioactivation. After elimination of the Li by NaCl precipitation Na was separated from the other impurities (Cu, Sr, Y) with HCl as the eluting agent.

The separation of Na and K activities from each other and from Ca and Sc was carried out on Dowex 50 WX8 (15 x 1.5 cm) with 1.14 N HNO_3. The procedure was used by De Regge et alii (139) for the determination of the cross-section of the reactions $^{45}Sc\ (n,p)\ ^{45}Ca$ and $^{45}Sc\ (n,\alpha)\ ^{42}K$.

A systematic scheme for the separation of radioisotopes obtained by radioactivation of Al, Fe or Zr containing a separation of the alkalis from the alkaline earths and the rare earths was described by Albert (3). The alka-

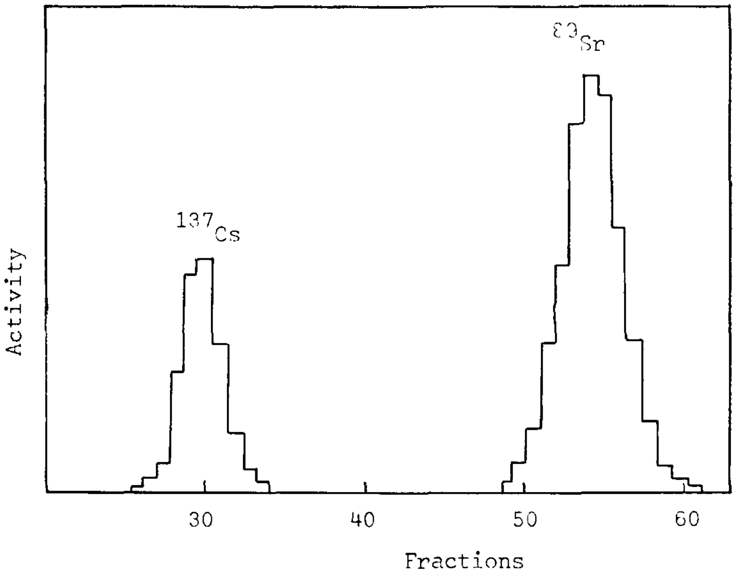


Figure 22
Separation of Cs and Sr present in meteorites with
3 N HCl. Volume of one fraction: 7 ml (538)

lis were preferentially eluted as a group from a Dowex 50 X8 200-400 mesh (600 mm x 9 mm) with NaCl and NH_4Cl and then separated from each other on a smaller column (350 mm) with HCl. The separation of alkali activities from alkaline earth activities with NH_4Cl 2 N was reported by Moiseev et alii (411).

Dybczynski and Sterlinski (159) determined Cs in mineral salts by means of neutron activation. The method consisted of a concentration step before and a separation step after irradiation. The preconcentration was carried out first on a MK-3 (H^+ form, 14.3 cm x 0.49 cm^2) column. Macroamounts of Na, K, Rb were eluted with 0.4 N HCl and Cs, Ba and other ions with 1.5 N HCl. The Cs-fraction was then adsorbed on an Amberlite IR-120 (H^+ form, 1 x 0.04 cm^2) column. Cs was eluted with 0.3 N HCl and Ba with 1.5 N HCl.

After irradiation the first separation was carried out on MK3 (H^+, 2 x 0.033 cm^2). ^{32}P, ^{35}S, ^{24}Na, ^{42}K were eluted with 0.1 N HCl and $^{134m+134}Cs$, ^{54}Mn, ^{64}Cu, ^{65}Ni, ^{153}Sm with 1.5 N HCl. The final purification was carried out by anion exchange.

Lieser and Kluge (356) separated ^{223}Fr from ^{227}Ac and its decay products. The ^{227}Ac is adsorbed onto a column of Dowex 50 (NH_4^+ form) in series with a column of silica gel coated with $BaSO_4$ or $BaCrO_4$ on which the decay **products are retained. The ^{223}Fr is eluted with a NH_4Cl solution containing** CrO_4^{2-} and is obtained in 99,9 % purity and yield.

The sorption of all the cations and the selective elution with a mineral acid or salt was often applied to the separation of ^{137}Cs from precipitation or other environmental samples. Benes (39) collected the cations on a Katex S column (12 x 1 cm) and eluted with dilute HCl. Johnson and coworkers (276) carried out the collection on a Dowex 50 WX12 column and **achieved selective elution with 0.5 N NH_4NO_3. The absolute recovery of** ^{137}Cs in this procedure was complicated by the presence of airborne sediments that fixed ^{137}Cs irreversibly. A few other articles on the same subject have also appeared (59, 640). A determination of ^{22}Na (85) and ^{24}Na (682) in rain water, based on the same principles was also reported. Radioactive Cs was likewise separated from organic matter and interfering ions in fluid milk by collection on a Dowex 50 WX10 or Amberlite-IR120 column (34 x 3.2 cm, 1:1 mixture of 25 and 100 mesh sizes) in the Li^+ form (230). It was eluted from this column with 6 M HCl. The separation on a cation exchange column of ^{137}Cs and ^{90}Sr in ashed milk from ions (such as phosphate) that could interfere in the further chemical processing was studied by Boucquiaux and Barruh (65).Senegalnik and Paljk (680, 681) determine ^{137}Cs from fall-out in water by sorption on a cation exchange **column. ^{144}Ce and ^{137}Cs are eluted with M ammonium lactate while $^{89-90}Sr$ and** ^{140}Ba remain on the column. In this separation, Ce is complexed by lactate while Cs is displaced by the NH_4^+-ions.Alkali metals, unlike many other metal ions, show no appreciable increase of the distribution constant in high molarities of HCl, $HClO_4$ or HBr (436, 438). Therefore, many separations of these metals are possible. A few, such as K/Ti/Sc, Na/Hf, Cs/Hf were described by Nelson and coauthors.

6.1.3. Separations based on complex formation

The alkalis rarely form complexes and therefore few separations have been described in which complexes of the alkalis were used. Exceptions reside in the separation of the alkali metals from each other with uranyldiacetate (91bis) and with EDTA (554). A more frequent application is the formation of neutral or negative complexes of the other metal present. The non-complexed alkali metal ions are then selectively adsorbed. Such a separation of the alkaline earths and Cd from the alkalis was reported by Olsen (453) with EDTA as the complexing agent.

Complexation can also be achieved with the solvent itself as the ligand (see CIESE effect) (331). Alkali metals are strongly retained on cation-exchange resins from organic solvent media containing 2-thenoyltrifluoroacetone (TTA) and pyridine while interfering elements are eluted. ^{137}Cs is taken up from 0.1 M TTA-pyridine solution by a Dowex AG50WX8 100-200 mesh column (0.5 cm x 25 cm) and Sr, Y, Zr, Nb, Yb, Ce, Sc, Ru, Tc, Am, Pu, Np, Hf, Sb, Mn, Ag, Tl, Co, Ir, Cd, Bi and Ti are eluted. Cs is then eluted with 6 N HCl. The whole procedure takes about 4 hours. A separation based on the same principles allows the carrier-free production of ^{22}Na from deuteron irradiated Mg targets. The eluting agent consists of 50 vol % ethanol and 50 vol % pyridine containing enough TTA to complex all the Mg. The recovery for both separations is 99.9 % and the purity virtually 100 %.

6.2. Alkaline earths

6.2.1. Introduction

Cation exchange is without doubt the most important separation technique for alkaline earths from each other and also from alkali metals and rare earths. Among the many applications of cation exchange is the separation of such pairs of elements as ^{90}Sr-^{90}Y, ^{140}Ba-^{140}La, ^{45}Ca-^{45}Sc. These separations are discussed in the chapter on the R.E.'s and will be cited only occasionally in the paragraphs on alkaline earths.

For the separation from other metal ions (such as transition metals, etc.) one uses in most cases anion exchangers with mineral acids as eluting agents thereby taking advantage of the fact that alkaline-earth ions are not readily complexed by inorganic ligands while most other metal ions are.

6.2.2. Separation with inorganic eluting agents

In non-complexing solutions the affinities for a strong cation exchanger of Mg, Ca, Sr, Ba and Ra increase in that order and differ sufficiently to permit separations with mineral acids or salts. These separations have been applied very infrequently in radiochemistry, although they have been frequently used for non-radiochemical applications. Table III summarises some representative non-radiochemical applications (no attempt for completeness was made).

A separation of all the alkaline earths with HCl was described by Milton and Grumitt (406)(fig. 23). It should be noted that the authors preferred elution with lactate (see 6.2.3.1.2.) as the separation method. However, the ease of recovery of the ions from HCl was considered to be a factor in favor of this eluting agent. The method was applied to the determination of ^{90}Sr in milk ash. Aubouin and Laverlochère (19) separated Ca, Sr and Ba from each other and from the alkali metals with HCl. P and S activities were eluted with 0.1 N HCl, Na with 0.2 N, Cs with 0.55 N, Mn with 1 N, Sr with 1.8 N and Ba with 2 N.

An interesting development resides in the use of mineral acids of high concentration. Nelson et alii (435) found large separation factors for Ca and Mg in 9 M $HClO_4$ or $HClO_4$-HCl. They separated radioactive tracers of these elements from each other on a Dowex 50 WX4 (6 cm x 0.25 cm^2) column with 6.4 M $HClO_4$ + 2.6 N HCl. Mg was eluted with 5 M HCl. The **separation of Mg and Ca with 9 M HBr and of Be + Mg/Ra/Ba/Sr + Ca in 12 M** HBr was described by Nelson and Michelson (fig. 24).

Aubouin et alii (19) described a determination of Ca in stainless steel by neutron activation and ion exchange. Two anion-exchange steps were followed by the separation of Ca from Cr, Mn, Ni, S, P activities by **elution of the latter group of elements with 12 N HCl. Ca was desorbed** with 5 N HCl.

A number of radiochemical separations of the alkaline earths from other metal ions were achieved with mineral acids. For the largest part, these concern separations of the type ^{90}Sr-^{90}Y that are discussed elsewhere.

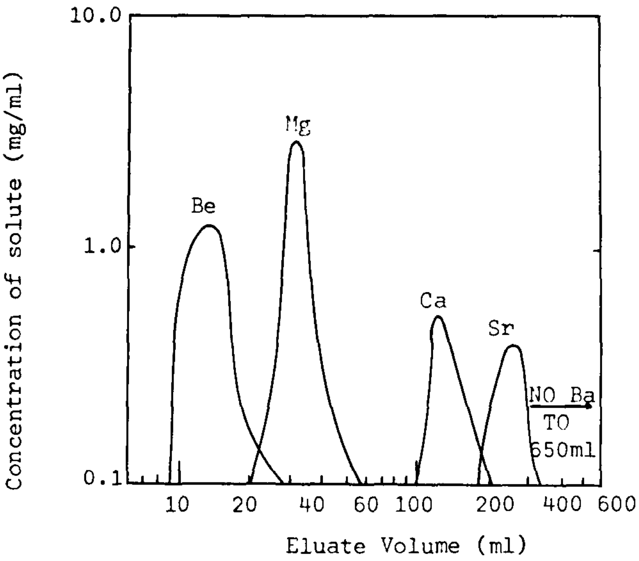


Figure 23

Separation of alkali earths with 1.5 M HCl (406)

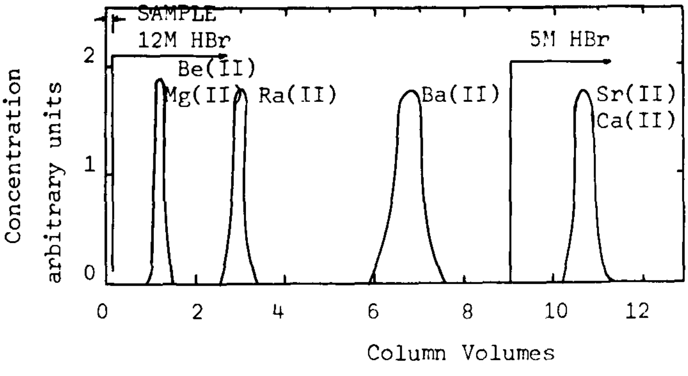


Figure 24

Separation of alkaline earths with HBr (436)

Cabell (95) separated small amounts of Ca from the products of its neutron activation (^{45}Sc and active impurities). The sample solution containing less than 2 mg of Ca was passed through a 4.5 cm high column of Zeo-Karb 225 (50 μ particle size). The elements were eluted in the following order: univalent cations, Ca and some other bi- and trivalent cations as three separate fractions with 1.5 M HCl, ^{45}Sc with 3 M HCl and some other tri- and quadrivalent cations with a second portion of 3 M HCl. Breibert, Lee, McCoord and Forbes (76) used radioactive isotopes to study the separation of Mg from Ca and Na from bone ash. They used a Dowex 50 (50-100 mesh) resin in a 37 cm x 0.5 cm column and 0.7 M HCl for separating quantities of the order of 50-100 mg ash. Bouquiaux and Gillard-Baruh(66) discuss the separation of the alkaline earth group as a whole from anions and alkali metals as a step in a scheme for the determination of ^{90}Sr in environmental samples (the final separation step of this scheme is described under 6.3.2.). In a later revised version (65) they eluted first the anions and the alkali metals with HCl of pH 1-1.5, then Mg and Fe with 12 N and finally Ca, Sr and Ba with 4 N HCl. Huys and Baetsle (260) separated ^{226}Ra, ^{227}Ac and ^{228}Th. The mixture was loaded onto a column in 12 N $HClO_4$. Ra was eluted immediately, but 20 column volumes were necessary for complete elution because of tailing. The other elements remained on the column. Hadzistelios and Papadopoulou (229) described a radiochemical method for the microdetermination of Mn, Sr and Ba in plant tissue. An elution was carried out on Dowex 50 WX8 (6 mm x 90) at a flow rate of 0.4 ml/min. The following separation was obtained: Na (eluted with 1.33 N HCl), Mn (2 N HCl), Sr (1.38 N HNO_3), Ba (1.75 N HNO_3), Sc (1.8 N H_2SO_4), the rare earths (6 N HNO_3). The separation of P (HCl 0.1 N), Na (0.2 N HCl), K + Rb (HCl 0.55 N), Cs (HCl 0.55 N), Mn (HCl 0.9 N), Ca (HCl 1 N), Sr (HCl 1.8 N), Sc (0.5 N HF), rare earths (α-hydroxyisobutyric acid), Ba (HCl 4 N) was described by Fourcy (173).

A few separations of fission products by ion exchange paper chromatography were reported by Getoff and Bildstein (199). Berger et alii (41) described the separation of Ba, Sr and Ca isotope on a thin layer of Dowex 50 WX2 resin (solvent: 1 N LiCl). (see fig. 25).

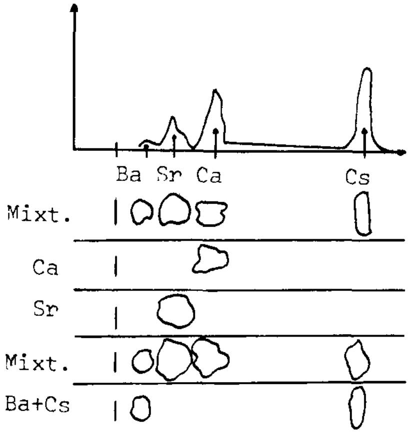


Figure 25
Separation of alkaline earths and Cs on thin layers of Dowex 50WX2 with 1 N LiCl (41)

6.2.3. Separation with organic complexing agents

Many authors have found that larger separation coefficients of the alkaline earths from each other are obtained by the use of complexing agents and more especially organic complexing agents. The largest success has been obtained with hydroxycarboxylic acids and aminopolyacetic acids. Strelow and Weinert (689) determined distribution coefficients of Be, Mg, Ca, Sr, Ba with the following complexing agents: acetate, formate, lactate, citrate, tartrate, α-hydroxyisobutyrate, malonate, malate, acetylacetonate and three different aminopolyacetic acids. The best separations are obtained for Be/Mg with 0.1 N **ammonium malonate of pH 7, for Ca/Mg with** 0.2 M **ammonium acetylacetonate (pH 9), for Sr/Ca with 0.1 M diaminocyclo**hexanetetraacetic acid (pH 4.7) containing 0.3 M **ammonium acetate and for** Ba/Sr with 1.2 M ammonium-α-hydroxyisobutyrate of pH 7.

Some other complexing agents have also been used, but with two exceptions for non-radiochemical applications. Table IV summarises some of these **sep-**

arations. Kapatsinskaya and Syromyatnikov (281) described a few separations of natural radioelements including the separation of Pb and ^{228}Ra. Pb was eluted from a KU-2 column (6 cm x 1.3 cm) with 5 % ammonium acetate and Ra was stripped with 10 % ammonium chloride or 20 % nitric acid. Sugimura and Tsubota (591) isolated Ra from seawater by coprecipitation with Ba. Ra was separated from the Ba-carrier on a cation exchange column (20 cm x 0.6 cm, H^+ form, 100-200 mesh) by sorption in 0.4 N HNO_3 and sequential elution of Ba and Ra with ammonium formate buffer.

Table III

Ca/Mg	HCl	(646)
Mg/Ca/Sr/Ba	HCl	(396,397)
Alkalis/Mg, Ca, Sr/Ba	HCl	(541)
Mg/Ca/Al	HCl	(601)
Ca/Sr	$(NH_4)_2SO_4$	(301)
Mg/Ca/Sr	$(NH_4)_2SO_4$	(302)
Mg/Ca/Sr/Ba	NH_4Cl	(257)
Ca/Mg + other elements	HCl + ethanol	(586)
Sr + many other elements/Ba	HCl + ethanol	(569)
Mg/Ca/Sr/Ba	HCl + methanol and HCl	(602)
Ca, Mg, Sr, Ni/R.E.'s, Y, Al	HNO_3	(181)
Sr/many others	HCl and complexing agents	(374)
Ba/rocks	HCl	(530)
Ca/many others	HCl + acetone	(373)
Sr/Ba	HCl	(687)
Ni + Mg/Ca, Ba, Sr, R.E.	HNO_3	(688)
Na + K/Mn/Mg/Ca	HNO_3 and HCl + acetone	(683)

Table IV

Mg/Ca/Sr	NH_4Cl, NH_4 acetylacetonate	(196)
Be/Mg/Ca/Sr/Ba	malonate	(588)
Ca/Ba	NH_4-acetate	(373)
Mg/Ca/Sr/Ba	NH_4-acetate	(105)
Ba/many others	NH_4-acetate and other eluting agents	(297)

Ca/Sr	NH_4-formate + acetone or NH_4-acetate + methanol	(623)

6.2.3.1. Hydroxycarboxylic acids

6.2.3.1.1. Citric acid

Separations of radioactive tracers of alkaline earth elements with citric acid as a complexing agent were carried out as early as 1947. Tompkins, Khym and Cohn (614) separated fission products on a 40-60 mesh column of Amberlite IR-1. Zr and Nb were eluted first with 0.5 % oxalic acid, followed by Y, Ce and the rare earths with 0.26 M citric acid of pH 3 and by Sr and Ba (as separate fractions) with 0.26 M citric acid of pH 5. A similar method was proposed for the separation of fission products in radioactive dust by Kimura (303). Te, I, Ru, Rh, Zr, Nb were eluted with HCl and oxalic acid, the rare earths with 5 % ammonium citrate of pH 3.5 and Ca, Sr and Ba with citrate of increasing pH's. A short separation of radioactive Sr (20 mg), Ba (20 mg) and Ra (20 g) was carried out by Tompkins (612) on a 15 cm x 1 cm^2 colloidal Dowex 50 column with 0.5 M ammonium citrate of pH 7-8. The separation took less than one hour. **Power and coworkers (485) separated barium and radium on a Dowex 50 column** with 0.32 M citric acid of pH 5-6. Here also very large radium to barium mass ratios were separated (1/1000). An isolation of ^{228}Ra from Harwell effluent by adsorption on a cation exchange resin and elution with citrate was described by Henry et alii (244).

6.2.3.1.2. Lactic acid

Milton and Grumitt (406) compared the suitability of ammonium citrate, ammonium lactate and HCl for the separation of all the alkaline earths. The procedure that was finally adopted by these authors consisted in an elution with ammonium lactate (0.55 M, pH 5 for Be, 1.5 M, pH 7 for Mg, Ca, Sr, Ba, Ra) on a Dowex 50 resin (300-400 mesh size) at 80°C (see fig. 26). A quantitative separation was obtained in 5 hours. The method was applied to the determination of ^{90}Sr in milk ash. Lerner and Rieman (354) also preferred lactate for the separation of Ca, Sr and Ba.

Titze (611) used this eluting agent for the isolation of **carrier free** ^{89}Sr and ^{140}Ba from irradiated uranium after elimination of the latter by anion exchange in HCl medium. The rare earths are more strongly complexed and therefore it is possible to elute the rare earths before the alkaline earths. This was applied to fall-out monitoring of water (680, 681): ^{144}Ce and ^{137}Cs were eluted with M ammonium lactate. $^{89-90}$Sr and ^{140}Ba were stripped from the column with 0.15 M ammonium citrate.Other interesting but **nonradiochemical contributions to the study of lactate** as a complexing eluting agent are due to Pollard and coworkers (477, 478) and Loveridge et alii (363).

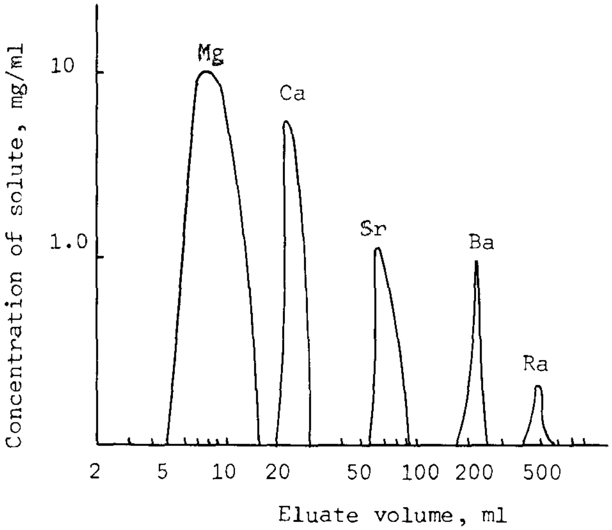


Figure 26

Separation of alkaline earths with 1.5 M ammonium lactate (pH 7) (406)

6.2.3.1.3. α-hydroxyisobutyric acid

Better separations than those obtained with lactate or citrate can be **achieved with α-hydroxyisobutyric acid as the eluant. The use of this** eluting agent for alkaline-earth separations was first reported by Baerg and Bartholomew (27) for the separation of Ba, Sr, Ce and La from ^{235}U fission products. The elution was carried out on Dowex 50X12 at 87°C. Wish (641) compared two procedures for the separation of Ce, Ca, Sr and Ba from fission products (fig. 27). The first made use of 16 % cross-

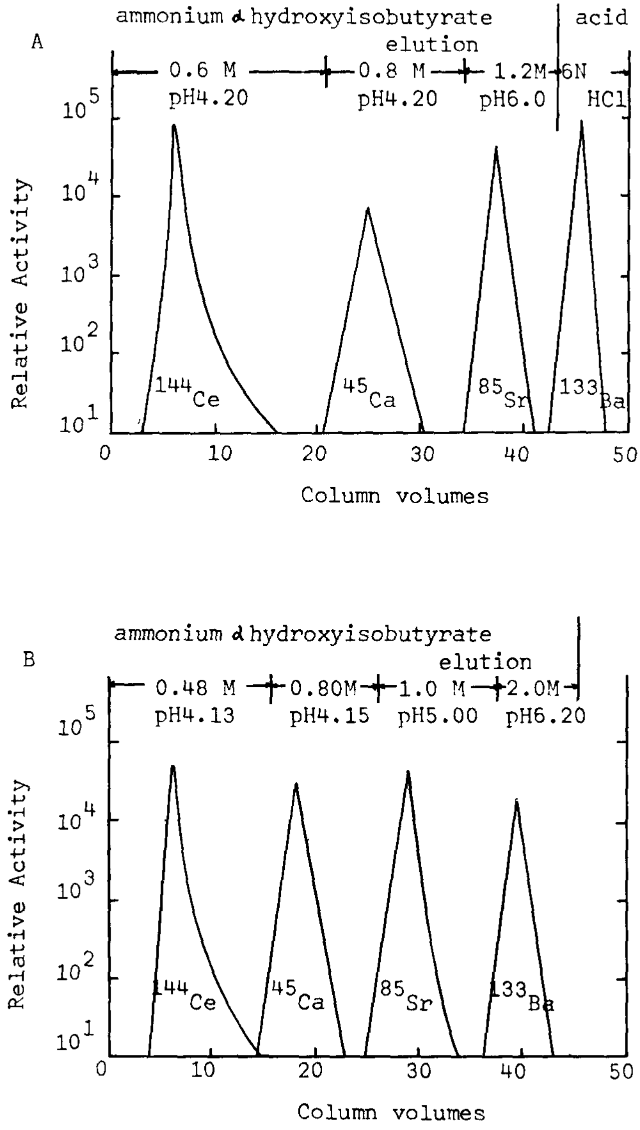


Figure 27

Separations of ^{144}Ce, ^{45}Ca, ^{85}Sr, ^{133}Ba with α-hydroxyisobutyrate (641). A = 87°C, 16 % cross-linking, B = room temperature, 8 % cross-linking.

linked Dowex 50 at 87°C and the second of 8 % cross-linked resin at room temperature. The second procedure is somewhat shorter and the separation of the alkali metals remains complete. The concentrations of the eluting agent were successively 0.48 M (pH 4.13), 0.8 M (pH 4.15), 1.0 M (pH 5.0) and 2.0 M (pH 6.2). Riedel (506) used α-**HIBA** solutions with increasing molarity and pH to fractionate fission products. The following fractions were obtained: Cs, Y + rare earths, Sr, Ba. Albert (3) separated Ca, Sr and Ba activities by elution with increasing molarities. The rare earths were eluted first.

Polak (476) separated Sr and Ba from an uranium target and rare-earth + Y activities through adsorption from α-**HIBA** solution. The adsorbed ^{93}Sr was given time to decay to its daughter ^{93}Y. The latter was then milked from the column with the same eluting agent. Separations of Ra and Ca from Ba, Ba and Ca from Sr, ^{90}Y from ^{90}Sr, Ba from the rare earths were reported by Perdue et alii (461). A **nonradiochemical separation procedure** was described by Pollard, Nickless and Spincer (479).

6.2.3.1.4. Glycolic acid

The elution and the separation of Mg, Ca, Sr and Ba with ammonium glycollate-sodium chloride mixtures was described by Senegacnik et alii (692).

6.2.3.2. Aminopolyacetic acids

Although other polyaminoacetic acids have been used for separating the nonradioactive alkaline-earth elements (for example 1.2 diaminocyclohexane-N.N.N'.N'.-tetraacetic acid (482, 593), ethylenebis(oxyethylenenitrilo)tetraacetic acid (75), ethyleneglycolbis(β-aminoethyl ether)-N.N'.-tetraacetic acid (481, 690), cyclohexane-1,2 dinitrotetraacetic acid (15)) radiochemical procedures are, with one exception, restricted to the use of EDTA as the eluting agent.

The elution of alkaline earth metals with EDTA was studied by Bovy and Duyckaerts (67). They applied the method to the separation of Ba and Sr on a Dowex 50 (250-500 mesh) column (19 cm x 1 **cm^2) in the Na^+ form with** 10^{-2} M complexon III (disodium salt of EDTA) of pH 7.4-9. Several other reports describe work by the same research group. Sr and Ba were **separated from Y and La and from each other on Dowex 50 with 0.01 M EDTA (172).**

The rare earths were eluted at pH 6 and the alkaline earths at pH 8. Similarly Ca, Sr, Ba and Ra were separated from each other with the same eluting agent (pH's resp. 7.4 and 9). The versatility of EDTA as an eluting agent in cation exchange chromatography was demonstrated by carrying out the following separations of carrier free isotopes on Dowex 50: Sr - Y - La, Ca - Sr - Ba - Ra (fig. 28) and the preparation of ^{228}Ra from Th (156). A separation of Ba and Ra with EDTA was also described by Nelson (433) (fig. 29). Moiseev et alii (411) determined many elements in silicium by activation analysis. The alkali metals are separated from alkaline earths with 2 N NH_4Cl and Ca, Sr and Ba from each other with EDTA 0.01 N (pH 7.1 - 8 - 10).

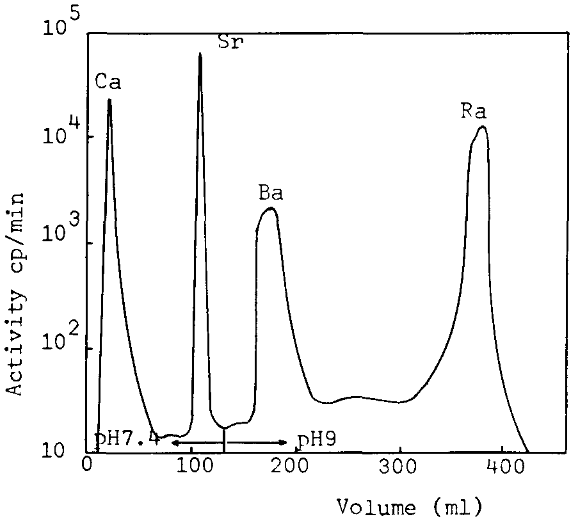


Figure 28

Separation of alkaline earths with EDTA (156)

EDTA was applied frequently to the isolation of ^{90}Sr from environmental materials. Several authors described techniques whereby accompanying elements were preferentially chelated and eluted while Sr remained on the resin. Davis (131) added strontium and calcium to a Zeokarb 225 column in an EDTA solution of pH 5.25. The calcium complex passed through the

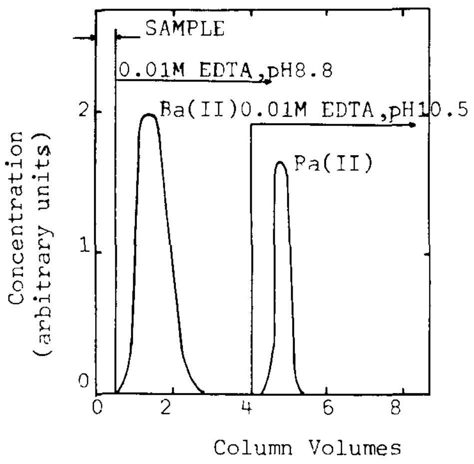


Figure 29
Separation of Ba and Ra with EDTA (433)

column and Sr was subsequently eluted with 3 N HCl.

Talvitie and Demint (600) employed an analogous technique. 2 % NH_4EDTA (pH 4.8) was used in the sorption step. Washing was carried out at pH 5.3. The column consisted of a 26.5 ml bed (i.e. 13.5 mm) of Dowex 50 WX8. On the same column a $^{90}Sr-^{90}Y$ separation was carried out with 0.5 M α-hydroxyisobutyric acid, pH 3.55, as the eluting agent. Y was eluted and Sr stayed on the column. Ibbett (263) preferred a mixture of citric acid (0.5 %) and EDTA (14 %) of pH 5 to selectively complex and elute Ca and Mg. Sr was eluted with HCl 12 N after washing the column with water.

Bouquiaux and Gillard (64, 686) described a modification of a technique used first by Wade and Seim (635) (for the separation of small quantities of Ba and Sr from large quantities of Ca). The already purified alkaline earth group was fixed on a Dowex column in 0.1 M EDTA of pH 4.8. Ca was eluted with EDTA of pH 5.25. When this elution was complete, a sudden increase of pH occured in the eluate (from pH 4.8 to 5.25). At this moment the elution of Sr was started with pH 6.0 and finally Ba was eluted with pH 9.0 (fig. 30).

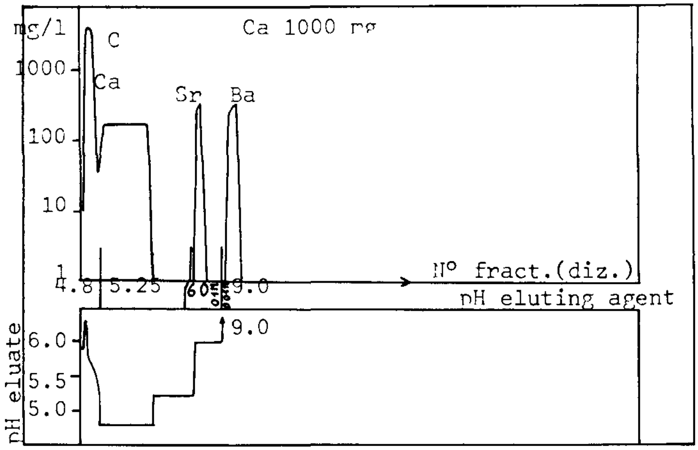


Figure 30
Separation with EDTA of ^{90}Sr from alkaline earths present in environmental materials (64)

EDTA was used by Strong (589) in the determination of Sr in environmental media by flame photometry. The chemical yield was determined with the aid of ^{85}Sr-tracer.

For the determination of ^{90}Sr in milk and bones, Ca was removed from the column with 1,2 diaminocyclohexane-N,N',N'-tetraacetic acid (CyDTA) (691).

6.2.4. Beryllium

Be occupies a special place among the alkaline earth elements and is therefore discussed separately. The preceeding paragraphs should however be consulted for separations where Be behaves as a typical alkaline earth.

A summary of the literature about Be-separations up to 1962 was compiled by Smythe and Florence (558). Beryllium has a low affinity for cation exchangers and can therefore be separated from most other elements by elution with a non-complexing eluting agent. Strelow (574) separated Be from many elements (Fe, Al, the rare earths, the alkaline earths, Zr and Th) by elution with 1 M HCl or 1.2 M HNO_3. Co, Ni, Mn, Cu, Zn, Mg and Ti accompany Be. Nelson et alii (436, 438) separated Be from Ba and Sr with 9 M $HClO_4$ and Be + Mg from the other alkaline earths with 12 M HBr. A separation from 23 other metal ions in acid ammonium sulphate media was reported by Kawabuchi, Ito and Kuroda (288) (fig. 31). Vetejska and Mazacek (631) and Ehman and Kohman (162) separated Be from Al with respectively 0.5 N H_2SO_4 and 1.1 N HCl, and Gordeeva and Prosviryakov (216) from Al and Fe with 0.5 N HCl. Strelow et alii (587) separated Be from the Al-group elements by elution with ethanol-HCl. Indium was eluted first with 0.2 M HCl-90 % ethanol, then followed successively by Ga (0.75 M HCl-90 % ethanol), Be (1 M HCl), Al (3 M HCl-50 % ethanol) and Y (3 M HCl).

Piper (473) described a method for the determination of ^{10}Be in environmental samples, based mainly on the use of a complexing resin described at an earlier date by Kennedy and Wheeler (294). Two anion exchange steps and one cation exchange step were included in the scheme. The latter was used to achieve further decontamination of Be from the rare earths, Zr, and Ra. This was done by preferential elution from a Dowex 50 WX8 column (50-100 mesh, 13 x 1 cm) with 1.2 M HCl.

A separation from Zr is possible by elution of Be with 2 N HCl (36). ^7Be remains adsorbed, however, when Li (irradiated target) is eluted with 0.1 N HCl from a KU-2 column (512). Be is eluted with 1 N HCl.

Be can be adsorbed preferentially after complexing the accompanying ions. In this way it can be separated from Al, Ca, Fe and Ti with EDTA and H_2O_2 (429). An analogous method was elaborated by Merrill, Honda and Arnolds (401) to isolate Be from seawater or sediments. Fe and other ions are eluted as complexes with 0.12 M oxalic acid while Be remains on the column. The method can be applied to the determination of ^{10}Be in environmental samples. Separations of Be from Fe and Al with oxalate (pH 4.4) (515), from Ga with gluconate (656) and from Zr with tartrate (656) or

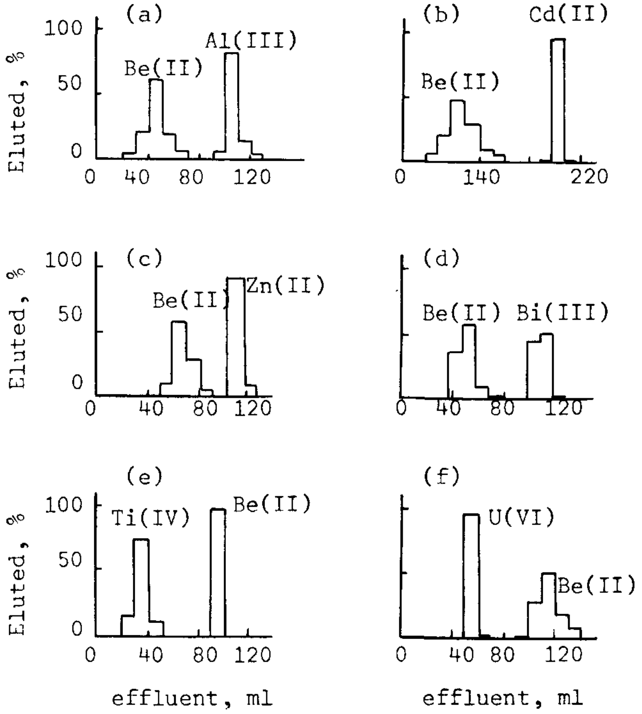


Figure 31

Separation of Be from other metal ions with ammonium-H_2SO_4 eluents (288)

EDTA (36) were reported.

On the contrary sulphosalicylic and gentisic acid form strong complexes with Be. This is used to elute Be (0.02 M complexing agent, pH 3-4.5). Cu^{2+}, UO_2^{2+} and Ca^{2+} (536), Cd (657) and In (656) are not removed from the column.

In order to separate Be by elution from Cu and Ni, Belyavskaya and Fadeeva (37) passed the mixture through an SBS (NH_4^+-form) cation exchanger in 10% ammonium carbonate (pH 8.5 to 9).

6.3. The rare earths, Y and Sc

6.3.1. Introduction

The first chromatographic separations of all rare earths (R.E.) from each other were achieved on cation exchangers. Later on, anion exchange and liquid ion exchange methods were developed, but cation exchange is still the most widely used. Most separations of the R.E. are radiochemical methods. This is due to the importance of some R.E. isotopes as fission products and to the fact that a great deal of the determinations of individual R.E. elements, after separation, have been carried out by neutron activation analysis.

A review on the separation of R.E. elements by ion exchange is contained in Stevenson and Nervik's monograph on the radiochemistry of the rare earths, scandium, yttrium and actinium (563). Although it appeared in 1961, it is still an excellent review and in a certain sense it is even up to date, particularly on the subject of cation exchange separations. Indeed, although many new applications have been described since 1961, there has been no important new basic development. The present day cation exchange methods are thus refinements of the older methods already described in this review. Two other reviews in this field have been published in Flemish by Deelstra (136) and Massart (384). Finally, a list of references up to 1962 is due to Vojtech (633).

6.3.2. Inorganic eluting agents

The study of the common inorganic eluting agents for the separation of the R.E.'s from each other has not yielded many interesting separation procedures. The differences in selectivity for strong acidic cation exchangers are very small as appears, for example, from the work of Surls and Choppin (595), who measured the distribution coefficients in 0.1 M $HClO_4$ solutions. It appears from their data that heavy R.E.'s are held less strongly than light R.E.'s. The distribution coefficients show a gradual decrease from La to Lu with the highest slope between Pr and Tb. The separation factor between the extreme members of the R.E. series is slightly higher than 2. Therefore some separations are possible but certainly no separations between neighbouring R.E. elements. Analogous results were obtained in HCl or $HClO_4$ by Diamond et alii (142), Choppin and Dinius (108) and Nelson (438). According to the data given by the last author, Sc seems to be adsorbed with about the same distribution coefficient as La while Y behaves as a heavy R.E.

Although the usual mineral acids are of no use for separating R.E.'s from each other, they are frequently employed when separating the R.E.'s as a group from other elements. Owing to the high ionic charge of the R.E.'s, they show high distribution constants in mineral acids of low molarity and can be separated from many other ions by adsorption on a cation exchange column. The present author has applied this method in separating the R.E.'s as a group from common ions present in minerals in a preirradiation procedure (387). The separation from minerals of Sc and the R.E.'s has been also investigated by Strelow (575, 576), Chung (113) and Murugaiyan et alii (685).

Ward and Foreman (636) determined ^{143}Nd, ^{149}Sm and ^{155}Gd in irradiated U by elution of most of the fission products while retaining the R.E.'s The anionic complex of ^{103}Rh is first eluted with 0.3 M HCl from Zeokarb 225 (12 cm x 0.5 cm), then ^{95}Zr-^{95}Nb with oxalic acid, the alkaline earths and the alkalis being eluted with 1 M NH_4Cl and 0.3 M HCl. The R.E.'s, U and Pu are eluted as a group with 11 M HCl and separated by anion exchange.

The method is of a more particular importance for the separation of alkali and alkaline earth metals that are less adsorbed and from Th which is much more strongly adsorbed. Indeed the R.E.'s can easily be **separated from most elements by elution with HCl on anion exchange resins.** Unfortunately on tnese resins the group of mentioned elements **accompanies, however, the R.E.'s.**

De Regge (139) separated, for instance, carrierfree ^{45}Ca and alkali activities present as impurities from irradiated Sc. The elution was carried out on a Dowex 50 WX8 column (15 cm x 1.5 cm^2) with 1.14 N HNO_3. K eluted after 110 ml and Ca after 360 ml. A complete decontamination was achieved. An analogous separation was previously described by Rane and Bhatki (498) for ^{90}Sr - ^{90}Y and ^{45}Ca - ^{46}Sc. Channell and Kruger (104) separated Na from the R.E.'s in a postsampling activation analysis procedure for estuary water tracing. The sample was percolated through a 0.7 cm x 10 cm

Dowex 50 X8 column (50-100 mesh) in the Ba^{++} form. The column was washed with 0.08 N NaCl until no ^{24}Na remained. The R.E.'s were retained by the resin. Strelow and Stärk (584) separated alkali metal activities from Sc with HCl in the course of an activation analysis procedure for Ca in KCl. Alimarin et alii (10) separated Ce and Th by elution of the former with 3.6 N - 4 N HCl and desorption of Th with ammonium oxalate.

At higher molarities of HCl and $HClO_4$ the distribution coefficients of the R.E.'s increase again (436). One separation of possible radiochemical interest is mentioned, namely Ti-Sc. Both are adsorbed on the resin from 9 N $HClO_4$. Ti is eluted with 9 N HCl and Sc with 4 N HCl-0.1 N HF. The present author applied this property to separate radioactive Ni and La isotopes (140). Ni was eluted from a Dowex 50 WX8 column with 6 N $HClO_4$ and La with 4 N HCl. Albert and coworkers (4) eliminated Sc from the sample solution in a procedure for the determination of S and P in Al and Mg metals by neutron activation by adsorption of Sc on Dowex 50 X8 from 12 N HCl. ^{122}Sb, ^{232}Pa, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{51}Cr leave the column together with phosphate and sulphate. In concentrated HBr also, the R.E.'s are adsorbed on a cation exchange column (436). A separation in 9 N HBr of Cs and Eu isotopes is given to illustrate the separation possibilities in this system. Cs leaves the column (Dowex 50 WX4 0.28 cm^2 x 3 cm, 60°C) first.

UO_2^{2+} ions form anionic complexes with fluoride (100) and with sulphate (73), while the R.E.'s remain in a cationic form. The latter are thus adsorbed on a cation exchange resin.

Some success has been obtained in separating R.E.'s from each other with inorganic complexing agents. Sodium tripolyphosphate allows reasonably good separations as reported by Subbaraman et alii (590) while, according to Moslova (417), pyrophosphate permits very good separations. The separation on a column of KU-2 (100 cm x 0.65 cm), particle size 0.12 - 0.10 with a flow rate of 1 ml/cm^2 . min and a 0.01 M pyrophosphate pH 5.18 - 8 continuous gradient was equivalent to that obtained with 0.25 M lactic acid (pH 3.52 - 3.80 stepwise gradient) at a flow rate of 0.5 ml/cm^2 . min on a 20 cm x 0.65 KU-2 column (mesh size 0.07 - 0.05). Ce^{4+} forms strong polyphosphate complexes. Therefore, when a mixture of the polyphosphates of Ce^{4+}, Co, Cu and Ni in a medium up to 0.4 N in H_2SO_4 is passed through a Dowex 50 X12 column, the Ce^{4+} remains in the percolate (509).

Surls and Choppin (594) investigated the use of ammonium thiocyanate and concluded that no easy separations in the R.E.group would be possible. The separation of Sc from the R.E.'s and of the lighter R.E. elements from other elements such as Ti, Fe, Zr, Th, Ca with ammonium thiocyanate-HCl solutions has been reported by a group of Japanese workers (233, 234). Sulphate is a good eluting agent to separate Sc from the R.E.'s. Strelow (580) used 2 N H_2SO_4 and Kuroda and coworkers (344) 0.3 M $(NH_4)_2SO_4$ - 0.025 M H_2SO_4. Though no radiochemical application is **mentioned, this last separation is of considerable interest since it** permits a selective Sc separation not only from the R.E.'s but also from many other cations.

A few applications of mixed solvents remain to be discussed. Ionescu et alii (267) investigated the behavior of La and Ce on KU-2 resin with HCl-acetone-water mixtures as eluent. In contrast with the expected sequence, La elutes before Ce and a separation coefficient of about 3 is obtained in a mixture of 65 % acetone, 20 % concentrated HCl and 15 % water. Starobinets et alii (673) separated La from the other rare earth metals by elution with N HCl in 50 % methanol. The ion exchange equilibrium between KU-2 and Pr in solutions containing HCl, organic solvent and H_2O was studied by Grigorescu-Sabau (222). For the same KU-2 resin Belyavskaya (35) described the separation of Mn and Sc by elution of the former with 2 N HCl-acetone (2:3) and desorption of Sc with 4 N HCl. The rare earths and Sc can be separated from Al, Fe^{3+}, Ti^{4+} and other elements by elution of the latter group with 3 M HCl + 50 % ethanol (579). The separation coefficient between Al (last eluted element) ans Sc (least adsorbed lanthanide) is 13.2 and compares favorably with the coefficient 2.3 found in HCl without ethanol. A rather unusual application is an Y-Eu separation with thenoylfluoroacetone (5 g)-dioxane (45 ml)-H_2O (50 ml) at a pH around 6 (272). Here an unusual sequence is also obtained since Eu elutes before Y. Sc tracer can be separated from R.E. tracers by elution with 95 % tetrahydrofuran - 5 % 6 M HCl, 0.1 M in tri(n)octylphosphine oxide. The D for Sc is < 1 and for the R.E.'s > 4000

(455).

6.3.3. With organic complexing agents

Since the ratios between the stability constants of the R.E.'s and some organic complexing agents are much higher than the ratios between their intrinsic distribution coefficients with the resin, much better results have been obtained in the separation of R.E.'s from each other with these complexing agents. The strongest complexes being formed by the heavy R.E.'s, these are eluted first. The two most important categories of complexing agents consists of the hydroxycarboxylic and the aminopolyacetic acids.

6.3.3.1. Hydroxycarboxylic acid

6.3.3.1.1. Citric acid

The earliest hydroxycarboxylic acid to be used was citric acid (in 1947, by Tompkins, Khym and Cohn (614), Tompkins and Mayer (615) and Ketelle and Boyd (295, 296)). The use of this acid as an eluting agent is now superseded by other hydroxycarboxylic acids, but it has proved to be very valuable in developing R.E. separation techniques and has found several uses in radiochemistry. Cornish (118) employed it for the activation analytical determination of individual R.E.'s. He used a Zeo Karb 225 column (115 cm x 0.20 cm^2). The pH of the 5 % ammonium citrate solution was increased in five discrete steps from pH 3.3 to pH 3.9.

Brooksbank and Leddicotte (77) also applied it for activation analysis while Tsong used it in isolating 3 mC of ^{227}Ac from 160 mg of La (622). The elution was achieved under saturated column conditions so that the La band is flat topped and no complete purification is obtained. Petrow and Allen (465) separated Ac from the R.E.'s with citrate in the course of a determination of Ac in uranium mill effluents. Radhakrishna (495) used citric acid of different pH's to separate Sc, La and Y. Shibata et alii (693) separated the Ce-group R.E.'s with citrate-acetate mixtures. Their method is not applicable to the Y-group R.E.'s.

Citric acid has now been replaced for the separation of the R.E.'s from each other by acids such as lactic or α-hydroxyisobutyric acids that show larger separation coefficients and therefore necessitate less time for carrying out the separation. Indeed, Cornish's (118) separation took not less than 90 hours while Ketelle's (295, 296) took more than 100 hours for the separation of either the light or the heavy R.E.'s. Citric acid still finds an application in the separation of ^{90}Y from ^{90}Sr. Since Sr forms less stable complexes it stays on the column and functions as a ^{90}Y generator. Such separations have been carried out by Lepsky (353), Bonnin (61), Niemann and Frühauf (442), Doering et alii (146), Hamaguchi et alii (232) and Marathe (378). In the last case pyridine citrate buffer of pH 4 was used and a decontamination factor exceeding 10^7 was obtained. A special application is the determination of ^{90}Sr in milk as described by Porter and Kahn (480). The milk is passed through a cation exchanger in the Na^+ form. Sr is sorbed but Y, contrary to expectation, is not. This is presumably due to its presence as a negatively charged citrate complex since it is subsequently adsorbed on an anion exchanger. A separation of the rare earths as a group from ^{45}Ca, $^{89-90}$Sr, ^{140}Ba was reported by Kimura (303).

6.3.3.1.2. Lactic acid

It was shown by Mayer and Freiling (395) that lactate allows better separations than citric acid. This discovery was exploited by several authors to achieve the determination of fission product R.E. activities. Freiling and Bunney (177), Petrow (464) and Troianello and Sugihara (617) all separated 10-20 mg quantities of the light R.E.'s and Cunninghame et alii (122) about 1 mg quantities. Cunninghame's method was later applied by Bullock et alii (83) for the preparation of ^{151}Gd for Mössbauer spectrometry. In most of these studies the elution was performed at higher temperatures. This is justified not only because sharper peaks are obtained but also because the separation coefficients are larger (531) (a similar behaviour is not found with α-hydroxyisobutyric acid). Freiling and Bunney (88, 177) employed a stepwise gradient, but Nervik (439) proved very conclusively that a continuous gradient is simpler to operate and that it allows sufficiently good separations. There are two ways to increase the free ligand concentrations: one is increasing the pH at constant total lactate concentration (Nervik (439)); the other is increasing the total concentration while keeping the pH constant (Preobrazhenski et alii (489)). Both authors obtained separations with very small volumes of eluting agent. Nervik separated Y to La in 110 drops (although the Eu-Gd separation was incomplete) and Preobrazhenski separated Lu to Nd in 180 drops (fig. 32) (or three hours including a nearly complete Eu-Gd separation). Nervik's method was used by Lyle et alii (366) to separate Pr from other R.E.'s in a study of the chain yields of ^{232}Th-fission. A very short separation was reported also by Alstad and Pappas (14) who used elution with 0.4 M lactate of constant pH 4.2 to separate fission product R.E.'s from Y to La to which

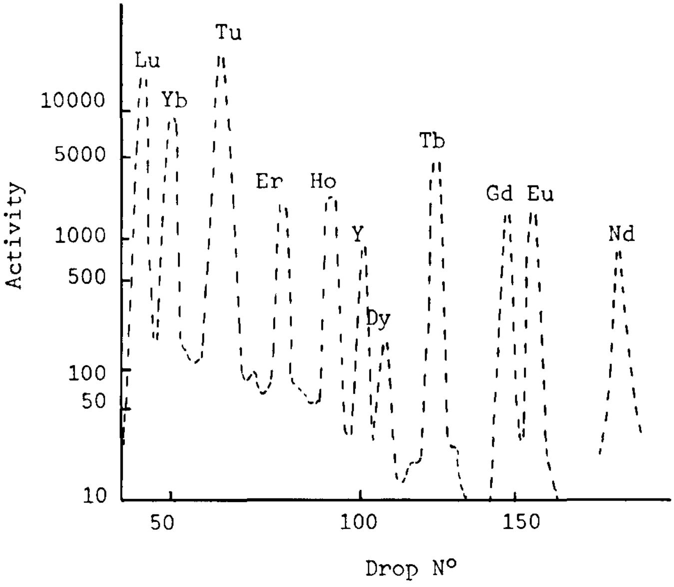


Figure 32

Separation of trace rare earths on KU-2 with a lactate gradient (489) as a common carrier a quantity of 1 mg of La had been added. A column of 2 mm x 5 cm of Dowex 50 X8 (15-30) at 87°C was eluted at the rate of 1 drop a minute. Less than 150 drops were sufficient to carry out the whole separation. This procedure is an exception in that it does not use a gradient. Another very rapid separation procedure was **described by Beranova and Petrzila (40). Mixtures of isotopes such as** ^{91}Y**,** ^{152}Eu, ^{242}Cm and ^{241}Am were separated in 6 minutes. A S-Katex X8 column (3 x 17-20 mm, particle diameter 24.5 μ) was developed at 0.054 ml/cm^2. sec.

Mosen et alii (416) separated about 0.3 mg of each of the R.E.'s from meteorites. Thereafter, the R.E.'s were separated by elution with 1 M lactate using a pH gradient as described by Nervik. Beginning at pH 3.2, the pH varied at a rate of 0.08 pH units/hour. The separation was complete after 10 hours at 80°C on a column of Dowex 50 WX12 minus 400 mesh, 0.5 cm x 60 cm but was of a poor quality since Tm was covered under the trailing edge of the Yb peak and the same occurred with Gd/Eu. **Sc, too, was eluted. It appeared necessary, however, to eliminate the largest part of the Sc activity before the elution since otherwise a Tm** peak contamination took place. A very similar procedure for the determination of the R.E.'s, Sc and Y in stony meteorites was developed by Schmitt and several other authors (529). It also used Dowex 50 WX12 minus 400 mesh (with a specially selected narrow **range of settling rates) at 80°C. The elution began at pH 3 with 1 M lactate and after the** elution of Lu a gradient of 0.06 pH units/hr was started. Gebauhr and Martin (196) used an analogous separation technique for the determination of traces of R.E.'s in graphite. Lesbets (694) determined R.E.'s by activation analysis in high purity Mg. The R.E.'s were separated on Dowex 50 X12 at 90°C with a linear pH gradient (pH 3.2 - 4.5, 1 M lactate).

A concentration gradient was used by Clanet (114) for the separation of a number of light R.E.'s. The elution was carried out on a Dowex 50 200-400 mesh column of unspecified cross-linking on a column of 7 mm x 60 cm at a temperature of 95°C. An apparatus was described permitting variations of temperature, pressure, flow rate and eluting agent concentration during the elution. The separated R.E.'s were present in quantities of 10 mg each. About 400 ml were necessary to elute 5 elements with peak to valley ratios of 1/15 or better. Gradient elution of an Y, Sm, Eu mixture was not possible and the author achieved this separation by eluting at constant pH with 0.24 M lactic acid.

A group separation within the R.E.'s was described by Welford (639) who separated Y from the light R.E.'s as a group in the analysis of long range fallout debris with 4.5 % lactic acid. The first 100 ml contained Y and the second the light R.E.'s.

Preparative radiochemical separations were described by Bhatki, Gopinathan and Rane (47) who used a stepwise gradient for the separation of Tb of high specific activity from Gd. The column (16.4 mm x 18.5 cm) of Dowex 50, 80-120 mesh was eluted with 0.5 M lactic acid + 0.4 % phenol (to avoid bacterial breakdown of the eluting agent). About 100 mg Gd_2O_3 were subjected to the experiment. A good separation was obtained in 33 hours at pH 3.4 augmented to 3.7 after elution of Tb. An analogous separation was applied to ^{148}Pm obtained from successive neutron capture followed by beta decay on ^{146}Nd. Perdue and Hicks (462) also used lactate to separate ^{241}Am from 30 mg of Ce on Dowex 50 WX12.

Dowex 50 X8 with lactate as complex builder was investigated as a milking system for ^{90}Y from ^{90}Sr and ^{140}La from ^{140}Ba by Lieser and Bächmann (355). In both cases decontamination factors of 10^5 were obtained. Y was eluted with 0.2 M lactate of pH 4.6 at a rate of 0.1 ml/min. from a 0.6 x 11 cm column. The separation took 5.6 hours. La was milked with 0.5 M lactic acid at pH 4.6 in 100 minutes. An analogous application was reported by Herrman and Strassmann (246). Senegacnik and Paljk (681) separated ^{144}Ce and ^{137}Cs from $^{89-90}$Sr and ^{140}Ba by elution with M ammonium lactate.

Brücher and Szarvas (80, 81) separated mixtures of fission product R.E.'s on a column (2 mm x 7 mm) of Dowex 50 X8 (H^+form) with 0.002 M EDTA-0.4 M lactic acid as the eluent, the pH being increased from 3.0 to 3.5 during the elution. The separation factors in this mixture were better than with α-HIBA and the widths of the elution peaks the same as with lactate alone.

Two drawbacks of lactate as an eluting agent have to be mentioned. It is easily attacked by bacteria thereby excluding the preparation of large quantities of eluting agent a long time before use. Moreover a dimer can be formed so that the reproducibility of distribution coefficients is poor.

6.3.3.1.3. α-hydroxyisobutyric acid

This eluting agent (α-HIBA) is now generally considered to be superior to the other hydroxyacids for separating the R.E.'s. It has been applied, first by Choppin and Silva (111). A 0.2-0.4 M solution of pH 4.0-4.6 and a temperature of 87°C was used for the separation of radioactive traces of Dy, Tb, Y, Gd, Eu, Sm, Cm, and Pm in that order (fig. 33).
As already mentioned in the preceding section the separation factors do not decrease appreciably (and in fact there is a slight increase for most) when working at room temperature as shown by Smith and Hoffman (556). One of these authors (250) employed α-HIBA to obtain pure R.E. activities for half-life determinations. Initial purification of Tb activities produced by thermal neutron irradiation of Gd_2O_3 was accomplished by two or three lactate elutions to remove the mass of the target. This was followed by a final purification with α-HIBA on a **"very small"** (dimensions unspecified) column of Dowex 50 X4.
Separation coefficients and distribution data have been determined by Deelstra and Verbeek (137) as well for α-HIBA as for lactate. They have established that d(log K_D)/d(pH) falls between -4.5 and -6. By addition of NH_4ClO_4 as an indifferent electrolyte a value of -3 is found. **This addition, however, decreases the practical separation efficiency.**
The addition of organic solvents was investigated by several Czeckoslovak workers. They reported an increase in the separation coefficient of Eu-Pm when pyridine is added (393). A great many other solvents (mostly alcohols were studied) cause a decrease of the distribution coefficients of $^{152-154}Eu$ and ^{90}Y (634) and an increase in the separation coefficient with increasing concentration of the organic solvent (5). The **nonaqueous** component should preferably have a low dielectric constant and a high molecular weight. Mixed organic-water α-HIBA eluting agents were used by the last authors for the separation of Eu, Y and Pm.
Gradient elution is used by most authors when more than a few R.E.'s must be separated. A method predicting the elution maxima of R.E.'s with

α-HIBA for a few generally used types of gradients was developed by the present author (385). It appeared impossible, however, to use this mathematical method to carry out an optimisation of the elution conditions because the sharpness of the peaks which codetermine the separation efficiency depends on the elution time and also on the steepness of the gradient. In one experiment in which all the R.E.'s ($\pm$ 0.1 mg per element) were separated with peak to valley ratios higher than 1/50, apparent HETP's of 0.2 mm for Lu and 0.04 mm for La were obtained (with constant ligand concentration elution 0.5 mm). Because of the relatively sharper peaks of the light R.E.'s, the separation is easier and the gradient may be steeper. In separations of 10 μg-1 mg amounts of the R.E.'s a composite gradient was therefore used. The free ligand concentration changed linearly with volume until the elution of Y, after which the slope of the gradient was increased by substitution of the reservoir eluting agent by another of higher pH. This system was used for the activation analysis determination of R.E.'s in minerals (388). The separation was achieved on Dowex 50 WX8 columns (15 cm x 0.4 cm^2). A communicating vessels gradient with V_t = 500 ml, C_1 = 0.03, C_0 = 0.165 was used at first. After the elution of Y, C_0 was increased to a value between 0.30 and 0.35. The concentrations are expressed as free ligand molarities. The analytical concentration of the eluting agent was 0.5 M. All R.E.'s were separated except the Lu-Yb pair. This was collected in one fraction and determined by mixed γ-spectrometry.

A comparable procedure is advocated by Mastalka (632) who for the separation of traces of R.E.'s obtained by fission of Ta used a continuous concave gradient. Very good separations were obtained in 200 drops on Dowex 50 X8 (1.8 x 100 mm) with 0.075 M and 0.1 M α-HIBA in the two mixing chambers and 1.8 M α-HIBA of pH 4.7 in the reservoir.

A concave gradient was also used by Aubouin and Laverlochère (21). After elution of Pm these authors changed the gradient into a linear one. The elution was carried out on a minus 400 mesh and also on a specially graded resin (10-25 μ fraction). The authors found that to obtain the same result with both resins an elution time of 19 hours was needed for the former, but only 4 for the latter. Höhlein et alii (252) found that the use of a resin with very small and absolutely spherical particles

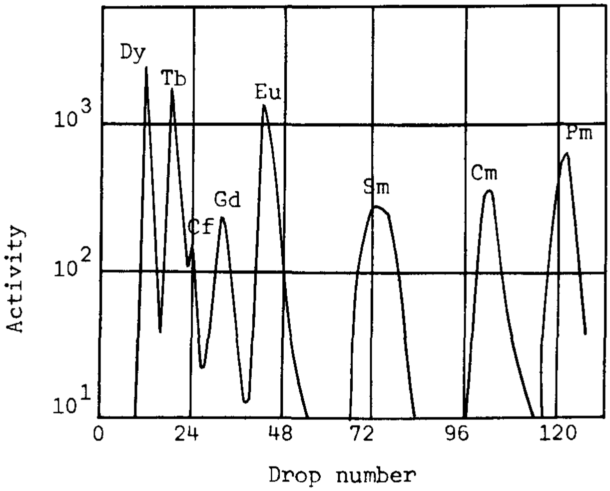


Figure 33

Separation of trace rare earths on Dowex 50 X12 with a α-hydroxyisobutyrate gradient (111)

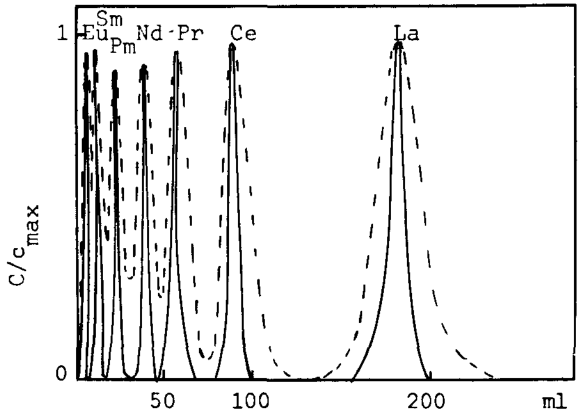


Figure 34

Effect of homogeneity of resin particle size distribution on elution. ----- Dowex 50X8, ——— Aminex A5 (selected particle size). Elution with α-hydroxyisobutyrate (252) with a very homogeneous diameter distribution allowed far better separations (3 or 4 orders of magnitude) (fig. 34).

A graded resin was used also by Haskin, Wildeman and Haskin (239). According to the authors, this procedure was used for the analysis of R.E.'s in nearly 200 natural rock and mineral samples. The cation exchange step is conducted on a column of Dowex 50 WX4 resin with a mesh size of 200-400, graded so that only the largest particles remain, i.e., about 1/4 of the initial quantity. The elution which took about 16 hours was carried out with 0.5 M α-HIBA and an exponential gradient from pH 3.1 to 4.05. The same gradient was used by others (703).

Seyb et alii (542) preferred a stepwise pH gradient. According to these authors such a gradient is superior to molarity gradients where the pH is kept constant. As optimal working conditions they chose Dowex 50 X8 at 83°C with 0.1 M α-HIBA with a pH that was increased in steps from 2.5 to 5. The time needed for elution from Tb to Ce was 8 hours. The separation of fission product R.E.'s has been investigated by several other authors. 5 to 10 mg of each of the following R.E.'s Y, Gd, Eu, Sm, Nd, Pr, Ce and La were separated by Wolfsberg (643) in 30 hours time with peak to valley ratios of 1/1000 (fig. 35). The column consisted of Dowex 50 WX4 (62.5 cm x 8 mm). The initial eluting agent was 0.5 M α-HIBA of pH 3.40 and this was increased with 0.025 pH units/hour. This method was also applied by Lange and Münzel (347) and Thein et alii (606). Zeligman (653) undertook the optimization of the separation of milligram amounts of Y, Tb, Gd, Eu, Sm, Pm, Nd, Pr, Ce and La (8 mg of each with ^{145}Pm as tracer). The author investigated several mesh-sizes and degrees of cross-linking. Eventually, Dowex 50 WX8 100-200 mesh was chosen. This author also made use of what in a certain sense may be called a concave gradient. Indeed, after 5 hours of elution with 0.1 M α-HIBA of pH 5.2 (i.e. at constant free ligand concentration) the molarity was increased at a rate of 0.0085 M/hour until a value of 0.4 M was reached.

The carrier free separation of R.E. radionuclides from fission product mixtures was achieved by Wish and Foti (642) with 1 M α-HIBA and a pH gradient. Later, the same authors (171) published a method allowing more rapid separation by using 0.1 M α-HIBA with higher pH's. This

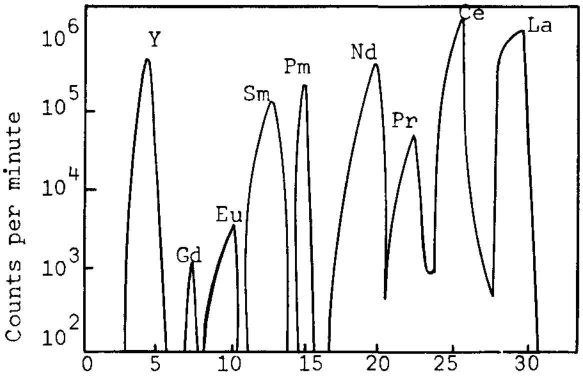


Figure 35

Separation of 5 to 10 mg quantities of individual rare earths with an α-hydroxyisobutyrate gradient (643)

separation took 14 hours.

Bächmann (25) separated Y-TB-Gd-Eu-Sm-Pm-Nd on a Dowex 50 X12 column with α-HIBA of unknown molarity and of pH 4.35. To determine the burn-up in fuel reactors the ^{148}Nd was determined by isotope dilution analysis with ^{150}Nd and the Nd separated by a constant pH elution with α-HIBA. The Nd fraction is identified by the emergence from the column of ^{241}Am which is eluted immediately before Nd (315). Marsh (382) separated lanthanide fission products by elution with 0.5 M α-HIBA, first at pH 3.5, then at pH 3.9. The fractions were collected on an automatic collector that incorporated a γ-ray monitor. To eliminate the α-HIBA, 6 M HCl is added to each R.E. fraction to diminish the free ligand concentration. The R.E.'s are then adsorbed on a Dowex 50 WX8 column and recovered with 6 N HCl.

Another domain of application for α-HIBA is the separation of a few

R.E.'s in which one is often present in large quantities and the other as traces. When eluting, trace quantities approximate the normal distribution, whereas a characteristic asymmetry is obtained at higher loading. The peak rises slowly and after reaching the maximum falls abruptly (386) (the same effect was noted also by Nervik (439) in lactate solutions). (see also 2.2.4.6.) The asymmetry is accompanied by a shift in distribution coefficient. According to Seyb (543) quantities larger than 1 mg/cm^2 lead to serious distortions of the elution peaks.

To optimize the separation of Eu traces from milligram quantities of Gd, the effect of flow rate, cross-linkage and molarity of the eluting agent was investigated by Massart (unpublished results). It appeared that the width of peaks for milligram quantities increased much more rapidly for increasing flow rates than for tracer peaks. Dowex 50 WX12 gave better separation factors but more diffuse peaks than Dowex 50 WX4 and 0.5 M α-HIBA gave slightly better results than 0.1 M. Therefore for this category of separations Dowex 50 WX8 was preferred as stationary phase with 0.5 M α-HIBA as the eluting agent and with the lowest flow rate compatible with the time in which separation is necessary.

For the determination of Sm and Eu in 2 mg specpure Gd_2O_3, the following elution conditions were used (388): column 16 cm x 0.36 cm^2, Dowex 50 WX8 200-400 mesh with an exponentially changing ligand concentration, 50 ml of initial free ligand concentration 0.119 M in a constant volume mixing chamber and 0.156 M in the reservoir. Incidentally it should be remarked that Co (present as flux monitor) is separated on the same column. It is adsorbed more strongly than the R.E.'s mentioned and desorbed with 0.4 M free ligand concentration. ^{160}Tb + ^{161}Tb were separated from 2 mg irradiated Gd on a Dowex 50 WX8 (14 cm x 0.38 cm^2) column with a stepwise pH gradient so that the 0.5 M α-HIBA solution is successively 0.073 M in free ligand for the elution of heavy R.E.'s and Np + Pa, 0.102 M for Tb and 0.143 M for Gd (390).

A table containing a list of conditions for the separation of R.E. radioisotopes from salts of adjacent R.E.'s was given by Martin (383) (see procedures). These separations were carried out on Dowex 50 WX12 (200-400 mesh) at elevated temperatures. It was found that 12, 25 and 30 mg of the major component R.E. could be accomodated on columns of

13.2, 17.6 and 19.1 mm diameter without adverse effects.

Orth and Dropesky (457) used 0.5 M α-HIBA of constant pH 3.1 for the separation of 18 mg Er and traces of other R.E.'s on a 56 cm x 12 mm column. Orth (456) separated in the same manner 32 mg Ho from R.E. traces. Butement and Glentworth (92) used 0.4 M α-HIBA pH 3.3 - 3.85 to separate daughter activities from 1 mg quantities of irradiated Yb, Tm, Er, Tb and Dy.

The purification of 285 mg $PmCl_3$ with respect to Sm and Nd was described by Ritzman et alii (510). The separation was achieved on Dowex 50 WX4 with 0.48 M α-HIBA of pH 3.35. The preparation of ^{145}Pm from neutron irradiated ^{144}Sm (232 mg Sm_2O_3) was carried out in two steps (472). The first separation was achieved with 0.4 M α-HIBA on a 70 x 12.5 mm column of BIO-RAD 50 WX12 200-400 mesh column at 80°C. The Pm fraction was still contaminated with ^{145}Sm. Therefore it was diluted with 50 mg ^{152}Sm and subjected to another separation run, this time on a 340 mm x 5 mm column. In this manner ^{145}Pm virtually free of ^{145}Sm was obtained. The purification of a 5 C (5.5 mg) sample of ^{147}Pm was reported by Fenner and Large (169). The α-HIBA eluent yielded sufficient separation from other R.E.'s but not from ^{241}Am.

A few other separations still need to be mentioned, such as the separation of Pm from Sm and Nd in the course of its determination in pitchblende (20) and the separation of ^{141}Pr for the determination of its fast fission yield (471). Rengan and Meinke (504) separated in very short times a few pairs of R.E.'s on very small columns (2.8 x 2 mm). Good separations of Tb and Nd and of Tm were obtained. A complete Tb-Gd separation was, however, not possible.

Deschuyter et alii (140) determined the cross-section of the reaction $^{140}Ce(n,p)^{140}La$ by extracting away the largest quantity of Ce and then carrying out an elution on Dowex 50 WX8 200-400 mesh (column 7 cm x 0.5 cm^2). First 25 ml of α-HIBA (0.5 M, free ligand concentration 0.16 M) were sent through the column and then an exponential gradient was applied (50 ml 0.16 M ligand concentration in a constant volume mixing chamber, 0.380 M ligand concentration in the reservoir). Lu was separated from Yb and other R.E. elements present in gadolinite by Massart and Hoste (389). A complete separation was obtained on a 14 cm x 0.4

cm^2 column with 0.05 M free ligand concentration and a less complete one (where Lu was determined by γ-spectrometry) with 0.07 M. Lu was separated not only from other R.E.'s but also from Np and Pa activities present. These eluted before the R.E. group.

Alimarin et alii (13) separated traces of Y, Dy, Eu, Sm and Gd from each other on a KU-2 column with 0.17 M α-HIBA in 120 drops. Y was initially present as the matrix and the bulk of it was separated beforehand by an anion exchange step.

Sc elutes before the R.E.'s. This was used in an activation analysis procedure to determine La in Ti (391). The Sc activity generated by (n,p) reaction on the matrix is eluted (together with ^{122}Sb and ^{82}Ta) with 0.06 M ligand concentration, Gd (present as chemical yield monitor) with 0.12 M and La with 0.4 M from a 15 cm x 0.4 cm^2 Dowex 50 WX8 200-400 mesh column.

Y elutes usually between Ho and Tb. It is, however, a troublesome element in that it changes place relative to the other R.E.'s depending on the pH of elution. This can cause difficulties especially if one keeps in mind that the distribution coefficient is also influenced by the quantity present and that in some minerals Y is present in much larger quantities than the other R.E.'s. A trial and error method is then necessary to find conditions under which the Y peak is in a location that does not cause interference (387). A variation of the elution temperature causes a shift of the position of Y with HEDTA (see 6.3.3.3.). This was used as the basis of the separation method by Morton and James (415).

The R.E.'s form stronger complexes than the alkaline earth metals. This was used for example by Polak (476) for the preparation of a ^{93}Y source by separating it from ^{93}Sr. A separation of ^{90}Sr, ^{90}Y and ^{137}Cs on cation-exchange paper pretreated with NH_4Cl with M α-HIBA of pH 5 was carried out by Getoff and Bildstein (199).

6.3.3.2. Other hydroxycarboxylic acids

Stewart (564, 565) used glycolic acid for the separation of carrier free R.E.'s. A high speed separation of light R.E.'s on centrifugally accelerated ion exchange paper with glycolic acid was described by Heininger and Lanzafame (241).

Several research teams have investigated the possibility of developing a hydroxycarboxylic acid with still better separating power and two of them claim to have found a better eluting agent. Thun (609) described a Tb-Gd-Eu-Sm separation with phenylmethylglycolate. The Eu-Sm separation coefficient was better than with α-HIBA. This was not the case for the other R.E. pairs. Also, a larger HETP was obtained. Finally, it must be noted that 0.2 M NH_4ClO_4 was added to this eluting agent. The following sequence of separating power (as determined by the stability constants) was given: glycolate $<$ lactate, diethylglycolate $<$ isopropylmethylglycolate $<$ dipropylisobutylmethyl-, phenyl-, propylmethyl, ethylmethylglycolate, α-hydroxyisobutyrate $<$ phenylmethylglycolate. 1,3,4,5-tetrahydroxycyclohexanecarboxylate is inferior to α-HIBA for column separation (454).

In contrast with this series, Nishi and Fujiwara (446) stated that ethylmethylglycolate is a better eluting agent than α-HIBA. Their elutions were carried out on Dowex 50 X8 columns (32 cm x 2 cm) at 87°C with 0.2 M solutions of the eluting agent of appropriate pH. Some excellent separations illustrate the possibility of this ligand. Fig. 36 (446) shows the separation of Sm (carrier free?), Pm and 200 mg Nd. Table V gives a summary of the separation coefficient obtained with glycolate, lactate, α-HIBA, phenylmethylglycolate, ethylmethylglycolate. In this context the work of Rowlands (511) who compared separation factors obtained with fifteen complexing agents of different types should be mentioned. An important conclusion is that there are few regularities to be observed in the R.E. series concerning the place of maxima and minima in separation factors. Furthermore, Rowland remarks quite rightly that definite conclusions can be reached only, if researchers standardize their techniques and the variables in the system they investigate, such as the supporting electrolyte used and the ionic strength of the medium and, we may add, in the case or elution column parameters, loading and temperature.

Keeping this in mind, it may be concluded that it is still doubtful whether any of the three ligands, α-HIBA, phenylmethyl- or ethylmethylglycolate is better than the other in all cases. It seems however certain that they are all better than either lactate or glycolate.

Table V

Separation Coefficients with Hydroxycarboxylic Acids (561)

	Citric	Lactic	Glycolate	α-HIBA	α-HIBA	Phenylmethyl-glycolate(*)
	87°C	90°C	20°C	87°C	20°C	25°C
La						
		1.83	1.64	2.20		
Ce						
	1.69	1.73	2.20	1.60		
Pr						
	1.18	1.36	1.37	1.57		
Nd						
	1.09	1.33	1.83	1.61	2.0	
Pm						
	1.38	1.32	1.33	1.82	1.57	
Sm						
	1.19	1.28	1.08	1.60	2.06	2.03
Eu						
	1.12	1.22	1.00	1.40	1.54	1.51
Gd						
	1.37	1.73	1.08	2.20	1.57	2.00
Tb						
	1.40	1.56	1.04	1.88	1.84	
Dy						
	1.37	1.38	1.23	1.62	1.95	
Ho						
	1.58	1.52	1.28	1.23		1.79
Er						
	1.60	1.47	1.40	1.30		1.38
Tm						
	1.53	1.43	1.37	1.33	1.37	1.41
Yb						
	1.31	1.31	1.33	1.36	1.45	1.30
Lu						

(*) ref. 709

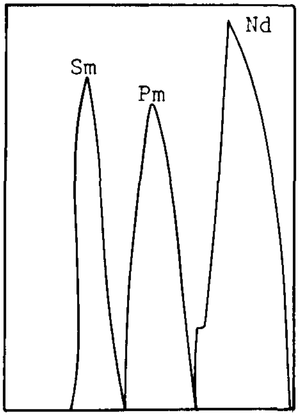


Figure 36

Separation of Sm and Pm from 200 mg Nd with α-hydroxy, α-methylbutyric acid (385)

6.3.3.3. Aminopolyacetic acids

Several aminopolyacetic acids have been investigated for the separation of R.E.'s. Among them the most important are ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylenediaminetetraacetic acid (HEDTA) and nitrilotriacetic acid (NTA).

EDTA, according to Mayer and Freiling (395), shows larger separation constants between neighbouring elements than lactate or citrate. This was confirmed by Cornish (119) who proved however that the elution characteristics were poorer than with citrate.

Therefore few applications to radiochemistry have been published. These acids are however often applied in large scale separations. Duyckaerts and Fuger (155) described a separation procedure for Y, Eu, Pm and Ce activities with 0.025 M EDTA and Macasek and Ceck (367) employed 0.01 M EDTA of pH 5.11 to effect a ^{90}Y-^{90}Sr separation on Dowex 50 WX2 resin (NH_4^+-form, 200-230 mesh). A sub-stoichiometric determination of heavy

R.E. metals by isotopic dilution analysis was described by Prasilova (487). A sub-stoichiometric amount of EDTA is added to a sample solution labelled with ^{166}Ho or ^{175}Yb. Anionic complexes are formed by heating at 50°C for 30 min. at pH 5.5. The solution is then passed through a column of Dowex 50 X8 resin in the Na$^+$form and the activity of the eluate is measured.

The use of HEDTA for the separation of R.E.'s and actinides was investigated by Merciny and Duyckaerts (399). They studied more particularly the influence of pH on the separation factors and the column efficiency for the pair Gd-Eu (and Am-Cm). Holleck and Hartinger (238, 253, 254) reported on the separation of R.E. fission products with NTA.

Finally a separation cited by Stevenson and Nervik (page 149 of reference 563) of 5 mg Y from 5 mg Dy with diethylenetriaminepentaacetic acid should be mentioned.

6.3.3.4. Other organic eluting agents

Yosimura, Takashima and Waki (647) separated Sc and Er by elution of the former from Dowex 50 columns with a solution of 0.5 M ammonium acetate + 0.5 M acetic acid. Mikler (404) investigated the sequence of elution of Y and Eu with an analogous eluting agent. With ammonium acetate-acetic acid (47:3), 0.73 M in acetate, Y and Eu elute together. At lower concentration Eu elutes before Y and at higher concentrations, Y before Eu. A shift of the position of Y relative to other R.E.'s was discussed earlier for α-HIBA. Acetate was used in the separation of ^{90}Sr and ^{90}Y by Minami et alii (409).

The same separation was achieved by Suzuki (597) with ammonium oxalate. This eluting agent can also be employed for the separation of ^{140}Ba and ^{140}La or for the separation of R.E.'s from alkaline earths in fission products (303). Orlandini (677) eluted Sc with 0.1 M oxalic acid. The R.E.'s remain on the column. After washing with 0.2 M HNO_3, they are eluted with 5 M HNO_3.

Sulfosalicylate solutions elute many elements while the R.E.'s remain adsorbed. A separation of microquantities of R.E.'s from macro amounts of Th and U was reported (129). The application of thenoyltrifluoroacetone and of tri(n)octylphosphineoxide was discussed already in section

6.3.2.

6.4. Actinium and the transplutonium elements

6.4.1. Introduction

The chemistry of actinium and the trivalent transplutonium elements (the whole group will be called actinides) is in many aspects similar to that of the rare earths.This has several consequences:

1. One of the major separation problems **is the separation of the** actinides from the lanthanides (or from La itself, since La is often used as a carrier for the coprecipitation of the actinides).
2. As is the case for the R.E.'s, ion exchange is the most important tool in the separation of the actinides from each other.
3. The same eluting agents were studied and in most cases **analogous results were obtained for both groups.**

Reviews were published by Vojtech (633) and by Stary (561).

6.4.2. Inorganic eluting agents

The adsorption behaviour of the actinides in HCl was studied **extensively by Diamond, Steet and Seaborg (143) and by Choppin and Chetham-**Strode (107). Their results were confirmed by Nelson et alii (438). At low molarity the adsorption is similar to that of the R.E.'s. At high molarity however there is no increase of the distribution coefficients of the actinides. Therefore a group separation of the actinides from the rare earths is possible. Diamond, Street and Seaborg (143; 567) performed this separation on a Dowex 50 column with 13 N HCl. Many **other methods inspired by this procedure were published. Milham (405),** Hall and Herniman (231), Naito (430) and Campbell (98) used it to purify milligram (or even gram amounts) of Am. A still better separation of the group and also a slightly better separation **within the actinide group was obtained by Thompson et alii (608) on Dowex 50 AG with 20% ethyl alcohol saturated ($\sim$12.5 N) with HCl (fig. 37). Ethanol saturated with HCl was also used by de Wet and Crouch (141) for the sepa**ration of Am + Cm from the rare earths in a sequential scheme for the carrier free separation of microgram quantities of individual fission product and actinide elements from highly burnt-up fuels. The R.E./actinide group separation can also be carried out with 1.8 N thiocyanate

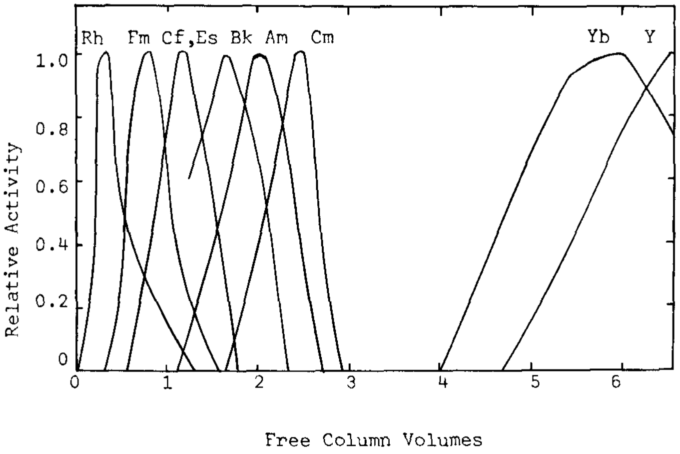


Figure 37

Relative elution positions of transplutonium actinides, Y, Yb and Rh from Dowex 50 AG with 20% ethanol saturated (≈12.5 M) with HCl (608)

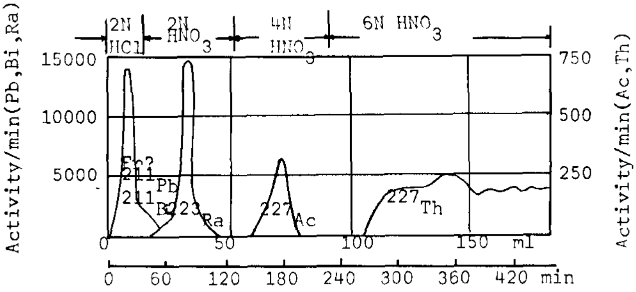


Figure 38

Separation of ^{227}Ac and daughter activities with HCl and HNO_3 (418)

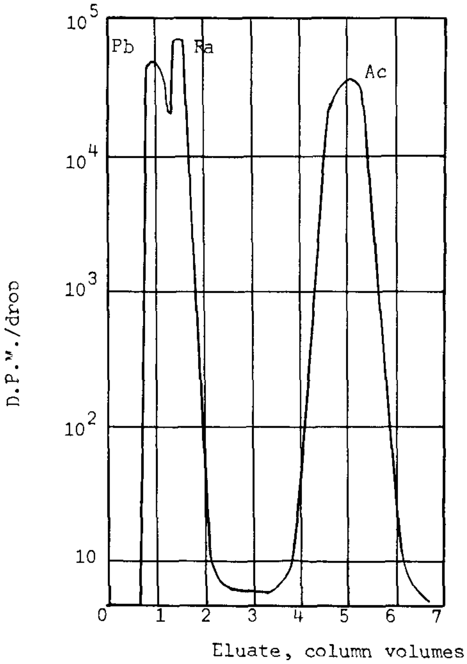


Figure 39

Separation of ^{227}Ac from daughter activities with HNO_3 (57)

(143, 595) but the separation is less effective than with HCl.

Low molarity HCl cannot be used to separate the actinides from the rare earths but it can be employed to separate the actinides from many other elements, since the actinides have a higher affinity for strongly acid cation exchangers than most other ions. Phillips et alii (466) eluted Cr, Ni, Ca, Fe, Al with 2 N NH_4Cl from a 4 cm x 20 cm Dowex 50 X12 column at 87°C. The actinides were then eluted with α-hydroxyisobutyric acid. Surls and Choppin (594) removed macro impurities (Au, Pd, Pt, Bi, Cd, Li, Mo, Cu, Fe, Na, Be, Mg, Rb, Ni, Ca, Al, Sr, Ba) from tracer transcurium elements by elution with 2 M HCl at 87°C on a Dowex AGX4 column. The impurities were eluted with less than 70 drops. The actinides and lanthanides emerged from the column after 75 drops. The elution was complete in 10 drops. During the preparation of ^{241}Am from plutonium, Am is freed from macro impurities of mono- and divalent cations by elution of the latter with 6 M HNO_3 (161).

Th is more strongly adsorbed from HCl and HNO_3 than the actinides. Kapatsinskaya and Syromyatnikov (281) developed a few separation methods of natural radioelements. Among the separations reported by these authors there is a selective elution of Ac from KU-2 (6 cm x 1.3 cm) with 20 % HNO_3. Th is retained and eluted later with 5 % oxalic acid. Müller (418) separated ^{227}Ac from its daughter products. One microcurie of ^{227}Ac in equilibrium with its daughter activities was brought on a Dowex 50 WX8 column (100-200 mesh, 6 mm x 120 mm) in 2 N HCl. ^{211}Pb and ^{211}Bi were eluted with 2 N HCl, ^{223}Ra with 2 N HNO_3, ^{227}Ac with 4 N HNO_3, and ^{227}Th with 6 N HNO_3. The elution of Th is not satisfactory (fig. 38). Blair et alii (57) undertook the same separation on BIO-RAD AG50WX4 (20-26 μ). First lead and radium and then actinium are eluted with 2.5 N HNO_3 at 60°C (Fig. 39). Th is recovered with 2 N H_2SO_4.

In $HClO_4$ (438) and also in HBr (436), the actinides show a minimum in adsorption at an intermediate acid concentration and are strongly adsorbed from concentrated acid. Huys and Baetsle (260) used 12 N $HClO_4$ to separate ^{226}Ra from ^{227}Ac and ^{228}Th (see alkaline earth metals) and Nelson (434) isolated ^{227}Ac from ^{231}Pa and its daughters (Fr, Pb, Bi, Ra) by elution of the latter group elements with 8.5 M $HClO_4$-0.5 M HCl-0.1 M HF. Ac was removed from the column with 8.5 M $HClO_4$-0.5 M HCl and Th with 6 M HCl-1 M HF. Actinide tracers (^{241}Am and ^{244}Cm) were sepa-

rated from nonadsorbable elements such as ^{134}Cs in 9 M HBr (436). **Naka**shini and Sakanoue (431) described the separation of the daughters of ^{231}Pa with anion- and cation exchange separations. The cation exchange step was used to separate some isotopes that were eluted together with 0.5 M oxalic acid from the anion exchanger. ^{223}Fr was eluted with 0.5 M $HClO_4$, ^{211}Pb with 1.5 M HCl + 15 % methanol, ^{223}Ra with 9 M $HClO_4$ and Ac with 6 M HNO_3.

6.4.3. Organic eluting agents

Many separations of actinides from each other have been described with the use of hydroxycarboxylic acids and aminopolyacetic acids as complexing agents. The history of the use of the hydroxycarboxylic acids is much the same as for the rare earths. The use of citric acid (74, 539, 607, 608, 622), glycolic acid (565), tartaric acid (212) for **separations of the trivalent actinides from each other is of historical** interest. So are the separations with lactic acid (74, 109, 112, 395, 488) (in contrast with the R.E.'s where lactic acid is still used). However, a few relatively recent separations of R.E.'s from actinides (40, 462, 465) (description, see R.E.'s) were carried out with lactic acid.

All recently published separations make use of α-hydroxyisobutyric acid (α-HIBA). A comparison of the elution positions obtained with this eluant with the other acids can be found in table VI, taken from Stary's review (561). The use of citric acid and lactic acid was discussed at length in the paragraph on the R.E.'s. Therefore, the **description of the elution with hydroxycarboxylic acids will be limited** to the more important α-HIBA. One of the advantages of this eluting agent is that it leads to sharp separations and that thin, almost weightless samples (408) can be prepared on Pt by evaporating and **igniting the eluate, preferably with the addition of a spreading agent such** as tetraethylene glycol. On other backing materials the same results are obtained by vacuum evaporation.

Choppin et alii (109), Smith and Hoffman (556) and Milsted and Beadle (407) reported in 1956 on the separation of actinides with α-HIBA. Dowex 50X12 and α-HIBA of pH 4.2 were used by Choppin at 87°C (fig. 40). Smith and Hofmann used Dowex 50WX4 at room temperature and proved that results equivalent to those of Choppin are obtained at this temperature (see also R.E.'s). Milsted and Beadle used Zeokarb at 77°C. Later, Seaborg (540) described a separation at 87°C. None of these articles includes information about Ac and none uses gradient elution. Furthermore it should be noted that these eluting agents cannot be used for actinide-lanthanide separations.

A few separations for the isolation of specific elements were described. Gatti et alii (195) discussed the ion exchange behaviour of Md with α-HIBA and Ghiorso et alii (200) purified Md produced from ^{253}Es. The separation of Md-Fm-Es-Cf was carried out with α-HIBA 0.4 M at pH 4 on a Dowex 50 WX12 column (2 mm x 5 mm) at 87°C in 50 drops. Auer-Welsbach et alii (22) separated ^{242}Cm from ^{241}Am on Dowex 50 WX8. The elution positions are marked by the use of Sm and Pm (figure 41). The purification of ^{242}Cm was described by Dedov et alii (135) and by Höhlein and coworkers (251). The Russian group separated 2 mg Cm from 20 mg ^{241}Am on a Dowex 50 34.5 cm x 5 cm^2 column with α-HIBA of pH 3.7. Höhlein et alii adsorbed first the lanthanides and the actinides on a cation-exchange column. Ru, Zr, Nd and Pu^{4+} impurities were then eluted as oxalate or sulphate complexes and the trivalent metals stripped from the column with α-HIBA 0.5 N of pH 6. The latter fraction was put on a larger column on which the separation of Y-Cm-Am-Ce and Pu^{3+} was performed with a continuous α-HIBA gradient (see fig. 42). Eventually the Cm fraction was concentrated by adsorption on a third column and eluted with HCl. The purity of the Cm was 98.5 % and its yield 91.6 %. The same group of authors found that much better separations are obtained on Aminex-resin (very small and absolutely spherical particles, homogeneous diameter distribution) (252). ^{249}Cf and ^{249}Bk were separated from other actinides with α-HIBA by Milsted et alii (408).

Bhatki and Adloff (46) described a rapid method for the milking of ^{228}Ac from ^{228}Ra. ^{228}Ra was adsorbed on a Dowex 50 X8 column and ^{228}Ac was removed daily with 0.5 M ammonium glycolate or α-hydroxyisobutyrate of pH about 4. Farrar, Cooper and Moore (167) described a combined chromatographic-solvent extraction procedure for the isolation of ^{249}Bk from highly radioactive solutions containing transuranium and fission product activities. The ion exchange step is in fact a modification of

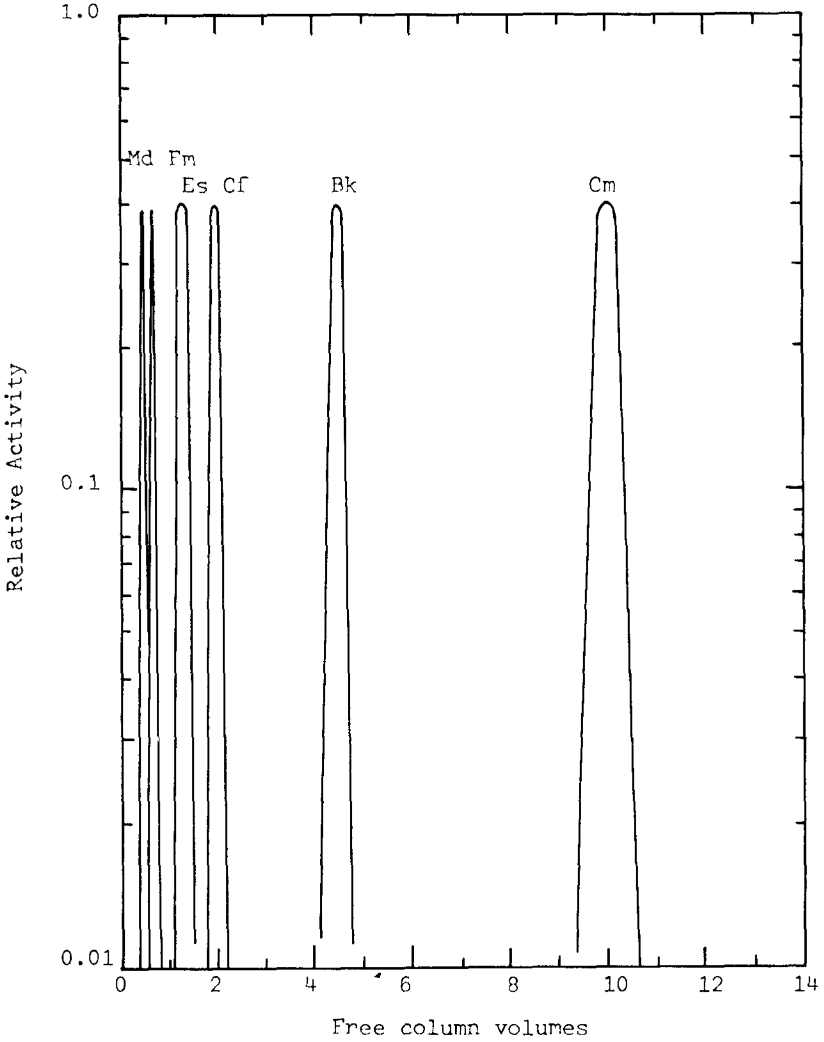


Figure 40

Relative elution positions of Cm and the transcurium actinides from Dowex 50 12 % cross-linked resin with pH 4.2 NH_4- -hydroxyisobutyrate at 87°C (109)

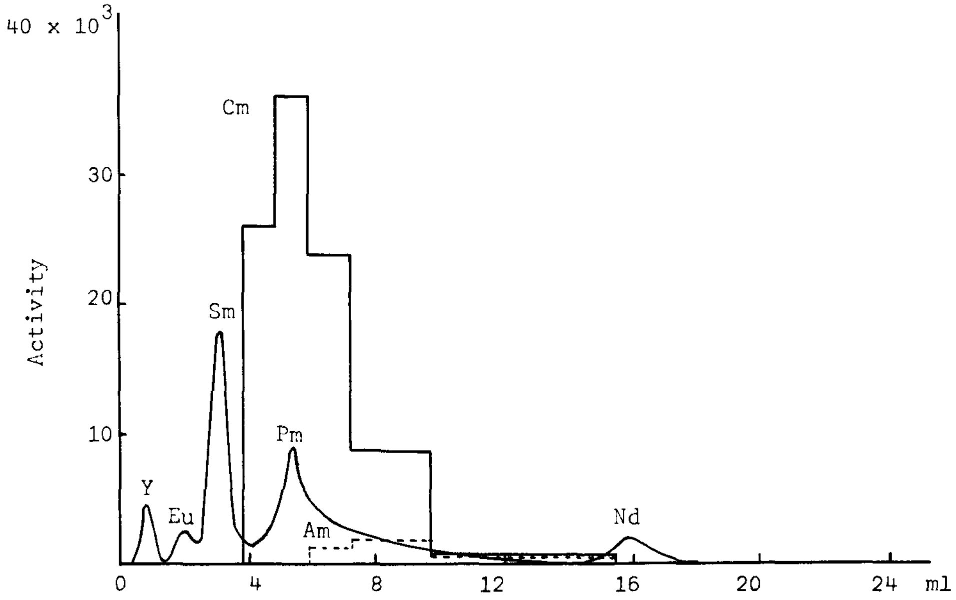


Figure 41
Elution curve of Sm - Cm - Pm - Am - Nd with 0.25 M ammonium α-hydroxy-isobutyrate (22)

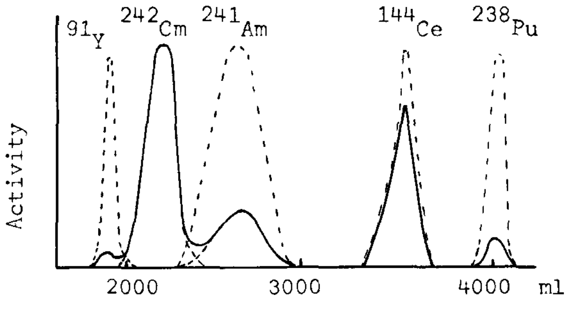


Figure 42
Separation of ^{242}Cm from ^{91}Y, ^{241}Am, ^{144}Ce and ^{238}Pu with α-hydroxyisobutyrate (251)

the procedure of Choppin. A very rapid separation was possible by the use of very fine particles (20 to 40 μ, Dowex 50 WX12) and elution with a high pressure pump (1800 to 2500 psi). Another separation of the actinides at high pressure and on very fine particles was **described by Buxton and Campbell (93).**

EDTA shows even higher separation coefficients than α-HIBA (198, 190). Nevertheless, α-HIBA still seems to be preferred (see also R.E.'s). Fuger separated Am, Cm, Bk and Cf from each other on a **Dowex 50 (NH_4^+ form) column with 0.001 M EDTA, pH = 2.35. Actinides** with $Z \geq 98$ are eluted ahead of all the R.E. fission products and can be purified in this way. Preliminary experiments of the same author showed that hydroxyethylenediaminetetraacetic acid (HEDTA) is a still better eluting agent for the separation of the trivalent actinides from the lanthanide fission products. The separation of the actinides from each other and more particularly of the pair Am-Cm with HEDTA was investigated in detail by Merciny and Duyckaerts (399, 400, 532). The effect of pH, reagent and salt concentration on the separation factors and on the efficiency of the column was investigated.

A separation of Am from the R.E.'s was described by Bubernak et alii (82). These elements were chromatographed with 5 % NH_4NO_3 saturated with EDTA (pH 2.3). Am leaves the column between Y and Eu. An ORNL-developed separation of gram amounts of Pm from Am with diethylenetriaminepentaacetic acid was cited by Stary (561).

Table VI

Gadolinium numbers (D_V normalised to $D_V(Gd) = 1$) and separation factors of Transplutonium elements on Dowex 50 in the presence of some complexing agents (561)

	H_3Cit		HLact		HGlyc		α-HIBA			
	87°		90°		20°		87°		20°	
Element	Gd.No.	β	Gd.No.	β	Gd.No.	β	Gd.No.		Gd.No.	β
Am	1.80		2.27		1.45		5.0		6.3	
		1.20		1.21		1.25		1.45		1.4

Cm	1.50		1.87		1.16		3.45		4.55	
		1.63		1.54				2.22		2.7
Bk	0.92		1.21				1.63		1.68	
		1.42		1.58				2.25		2.0
Cf	0.65		0.77		0.543		0.76		0.86	
		1.2		1.24		1.20		1.54		1.46
Es	0.54		0.62		0.457		0.49		0.59	
		1.2		1.77				1.84		
Fm	0.45		0.35				0.264			
		1.18		1.3				1.4		
Md	0.38		0.27				0.189			

6.5. Th - Pa - U - Np - Pu

6.5.1. Thorium

The highly charged nature of the Th^{4+}-ion in solution causes it to be more strongly adsorbed than almost all other ions. Therefore most **separations of Th are based on the sorption of Th on a cation exchanger** from mineral acids and elution of the accompanying elements. Th itself cannot be eluted with mineral acids because the distribution coefficient shows a minimum value at 6 N HCl of ± 80 and at 3 N $HClO_4$ of 1000 (438). Therefore it has to be eluted with complexing agents. **Hyde (261) cities, as suitable ligands, citrate, lactate, sulphate, car**bonate, oxalate and fluoride.

Diamond, Street and Seaborg (143) showed that Th^{4+} is held very **strongly on the resin from all molarities of HCl and that Sr^{2+}, La^{3+}, Ce^{3+},** Ac^{3+} are readily eluted. Ions such as Np^{4+}, Pu^{4+} and U^{6+} form complexes at a concentration of more than 6 M and are also eluted. A non-radiochemical separation of U from Th on AG X12 was described by Strelow (570) who eluted U with 4 M HCl and determined Th after ashing the **column. Gleu et alii (213) described a generator for the production of** carrierfree ^{212}Bi and ^{212}Pb. A Nalcite HCR column loaded with ^{228}Th was eluted with 0.5 N HCl for the former and with 2 N HCl for the latter. Bane (31) fixed Th on an Amberlite IR-1 resin from a 0.15 M uranyl nitrate + 0.1 M HNO_3 medium. After washing the column with 0.25 M H_2SO_4 to remove completely the uranium, Th was eluted with 1.25 M $NaHSO_4$. Nabinavets and Kudritskaya (428) also used bisulphate in the preparation of Th concentrates. Cr, Fe, Co, Ni and Mn were eluted from a KU-2 column with 5 N $HClO_4$ + 0.1 N H_2SO_4, the rare earths with NH_4Cl, Th with bisulphate (and Nb with sulphuric acid + hydrogen peroxide). In another non-radiochemical procedure (applied to the analysis of monazites), Chung and Riley (113) eluted Al, Ca, Mg, Fe, Pb, Ti, U, Mn, K, Na and the rare earths with HCl and stripped Th from the column with 3.6 N H_2SO_4. Nietzel et alii (443) eluted many ions with 2 M HCl from Amberlite IR-120. Th was stripped with 3 M H_2SO_4. Blair et alii (57) separated ^{227}Ac and its daughter products by elution with 2.5 M HNO_3. Th was stripped from the column with 2 N H_2SO_4.

Two publications by Russian authors describe the separation of ionium (^{230}Th) from other elements. Palei et alii (458) eluted U, Fe, Mn, Eu and part of the Pa present with 2 N HNO_3. The rest of the Pa was **eluted with 1 N H_2SO_4 and after washing the column with aqueous ammonia** (1:1), ^{230}Th was eluted with saturated ammonium carbonate solution. Karalova et alii (282) reported on the rapid separation of ^{230}Th from U. U, Pa, Zr, Po and part of the Th were adsorbed on an anion **exchanger from 1 M H_2SO_4. The Th present in the eluate was sorbed on a** 20 cm x 1 cm KU-2 column together with Eu, Fe and Mn. The latter elements were eluted with 2 N HNO_3 and after an alkaline wash as **described above, Th was stripped with saturated ammonium carbonate solution.** The anion-exchanger was eluted with 1 N H_2SO_4 to remove the Th, which was again adsorbed on and then recovered from a KU-2 column as **described before. In a later publication, Karalova (695) eluted U with N** H_2SO_4 from KU-2X15 and ^{230}Th with 3 N H_2SO_4.

Dyrssen (160) separated ^{234}Th from U by the adsorption of Th on **Wolfatit KS from 2 M HCl. ^{234}Th was eluted with 0.5 M oxalic acid. By evaporation and sublimation of the oxalic acid a carrier free preparation** was obtained. Gizon; Lagrange and Pelletier (211) also used oxalic acid to **extract** Th from the column. In their procedure which permits the **separation of carrierfree ^{231}Th from ^{235}U the elements were separated** from each other on an anion exchange column in HCl medium. To eliminate

HCl, Th was adsorbed on a cation exchanger and eluted with oxalic **acid. A cation exchange application along the same general lines was** described by Barnes (32) who used oxalic acid for the concentration by elution of the purified Th. The same author discussed the separation of Th from fission products. The method requires among other chemical steps a sorption of Th from dilute HCl on a 0.6 cm x 7 cm column of AG 50X4 and (after washing out of the other activities) a desorption with oxalic acid 0.5 M. Another cation exchange column was used for the final concentration by elution with oxalic acid. The production of ^{234}Th tracer was studied by Bhatki (45) who eluted U with a dilute acid or NH_4Cl and recovered the ^{234}Th with oxalic acid or ammonium carbonate. Alimarin et alii (10) reported a separation of Ce from Th on KU-2 in which Ce was eluted with 3.6 N to 4 N HCl and Th was desorbed with ammonium oxalate. The final purification step in a method for the measurement of thorium isotopes in sea water consisted in the sorption on an Amberlite IR-120 column (15 cm x 2 cm) and elution of the contaminating elements with H_2O and HCl 2.5 to 7 N (316). Th was stripped from the column with 0.5 N oxalic acid.

The separation of ^{234}Th from uranyl nitrate solutions was carried out by Murase, Lind and Nelson (419). Two successive separations were **necessary of which the first served to concentrate the Th. U was eluted** from a large column (1.75 cm^2 x 5.7 cm) with 6 M HCl and Th with 6 M HCl + 1 M HF. A purification was then carried out on a smaller (0.28 cm^2 x 3 cm) column from which U was eluted with 4 M HCl and Th again with 6 M HCl - 1 M HF. The isolation of ^{227}Ac from ^{231}Pa and the ^{227}Ac daughters was dsecribed by Nelson (433). Fr, Pb, Bi, Pa, Ra were eluted with 8.5 M $HClO_4$ - 0.5 M HCl - 0.1 M HF, Ac with 8.5 M $HClO_4$ - 0.5 M HCl, Th with 6 M HCl - 1 M HF.

Asaro (16) separated ^{228}Th from a mixture with its daughter products by the adsorption of Th from dilute nitric acid on a 3 mm x 3 cm Dowex 50 column thermostatised at 87°C. Bi, Pb and Ra were eluted with 4 M HNO_3 and Th with 50 % lactic acid solution of pH 3. This eluting agent **proved to be very efficient and allowed the elution of the Th activity in** one ml.

An analytical method for the determination of ^{230}Th and ^{232}Th was **de-**

scribed by Meyer et alii (402). The Th is adsorbed on a 20 ml bed of Dowex 50 WX8, 100-200 mesh. The interfering elements are eliminated by elution with 2.5 N HCl and Th is stripped from the column with EDTA solution (1 % of the di-Na-salt).

Two non-radiochemical applications of mixed aqueous-organic solvents should be noted. Korkisch and Tera (332) separated U and Th from each other on Dowex 50 with aliphatic alcohol-nitric acid solutions while Pietrzyk and Kiser (468) achieved a Mn^{2+}-Mg^{2+}-$UO_2{}^{2+}$-Th^{4+} separation with an NH_4SCN-organic solvent-water eluting agent. A combined ion-exchange solvent extraction method for the separation of Th from the R.E.'s was reported by Korkisch and Orlandini (331bis). Tracer or milligram amounts of Th are eluted ahead of the R.E.'s and many other elements with a solution of 0.1 M tri(n)octylphosphine oxide (TOPO) in methanol containing 5 vol % of 12 M HNO_3.

To separate La from Th the preferential chelation of the former with 10 % citrate of pH 3 was used. Th was eluted with 6 N H_2SO_4 (497). The same author separated Th from Ac and from Ra by preferential elution with 7 % oxalic acid (496).

6.5.2. Protactinium

Nelson and coworkers (436, 438) determined the distribution coefficients of Pa^{5+} in concentrated $HClO_4$, HCl and HBr to which small quantities of HF were added. In the pure acids hydrolytic difficulties were encountered. Muxart and coworkers (421) investigated the adsorption behaviour of Pa^{5+} over the range 1-10 HCl and 1-9 M $HClO_4$. Adsorption minima were found at 2.5 N $HClO_4$ ($K_D \approx 7$) and at 9 N HCl ($K_D \approx 2$). The results were characterised by good reproducibility. The same authors determined the distribution coefficients of Pa^{4+} in HCl. Two minima were found (at 5 and 9.5 N). Hardy and coworkers (236) determined the distribution coefficient of Pa^{5+} as a function of the molarity of HNO_3 on Zeokarb 225. A **minimum value was found at 4 N. Equilibrium was reached in about 15 minutes.**

In most applications a complexing substance is added to elute Pa. Kirby (307) found that ^{231}Pa is not adsorbed on a Dowex 50 column from 0.05 N HF - 1 N HNO_3 or from 0.004 N HF - 0.04 N HNO_3. The decay products

^{227}Ac, ^{227}Th and ^{223}Ra remain quantitatively on the column. A yield of more than 99.5 % was obtained for the elution of ^{231}Pa. The separation by elution of Pa from Ac and Th with a $HClO_4$-HCl-HF eluent is described in the preceding paragraph (433).
Kuroda and Ishida (343) achieved the separation of ^{233}Pa from irradiated Th on a Dowex 50 WX8 (4 cm x 1 cm) column by elution of the protactinium with N NH_4SCN-0.5 N HCl. Th was stripped with 2 N NH_4SCN-0.5 N HCl. Recoveries of 93 % for the former and 100 % for the latter were obtained.
Pillai (470) reported on the estimation of trace amounts of Pa in Th-nitrate. An anion and a cation exchange procedure were developed. In the latter U was eluted first with 1 N HNO_3, then Th with 0.2 M $(NH_4)_2SO_4$ (pH 3.4) and finally Pa with 0.05 M oxalic acid at a pH of 3.5. Oxalic acid was also used by Kimura et alii (306) in a rapid separation procedure for the production of ^{234}Pa from ^{234}Th. Pa was quantitatively **eluted with 0.05 to 0.7 % oxalic acid or 0.8 to 2.0 N HNO_3 from a Dowex 50** X12 column (1.5 cm x 1 cm^2 ; flow rate 5 ml/min.).

6.5.3. Uranium

A review of the ion exchange methods for the separation of U was **published by Korkisch (321).**
U^{6+} is strongly adsorbed from dilute HCl and the distribution coefficient decreases with increasing molarity (142, 438). In 9 N HCl the distribution coefficient is less than 1. This is not the case for HBr, $HClO_4$ and HNO_3. According to Hardy (236), the distribution constant between Zeokarb 225 and HNO_3 decreases rapidly with increasing **molarity from 0 to 2 N HNO_3. After that the distribution constant remains** virtually constant at a value of about 7 over the whole range of investigated molarities (up to 10 N HNO_3). Nelson et alii (438) have shown that a minimum in distribution coefficient occurs in $HClO_4$ at ≈ 3 N after which there is a rapid increase. The distribution coefficient in 9 N $HClO_4$ is of the order of 10^4. Nelson and Michelson (436) found a very shallow minimum in the curve for HBr. In 12 N HBr a distribution coefficient of 2.6 was determined.
Other data were obtained by Ishimori and Okuno (271). They studied the adsorption on cation exchange resins in the presence of Na_2SO_4, **carbon-**

ate, oxalic acid and sodium acetate. No adsorption is found in carbonate media. In the other media there is an adsorption at low concentrations and a rapid decrease with increasing concentration. The authors particularly recommend acetate for the elution of adsorbed U. Khopkar and De (298) investigated the behaviour of U in various eluting agents such as HCl, HNO_3, $HClO_4$, acetic acid, citric acid. UO_2^{2+} forms a stable complex with phosphate and can be eluted with 1 M H_3PO_4, while Fe, Mn, Cu, Ca, Al, Ni, Co, Mg remain on the column (341). A few other media (iodide, EDTA, fluoride) were studied occasionally. Quite a few separations of U on cation exchange resins have been described. The rather low affinity of U for strongly acidic ion exchangers in HCl or HNO_3 media compared to higher charged ions was used by several authors for the separation of U from ions such as the rare earths or Th. This is the case in separations of natural radioelements described by Kapatsinskaya and Syromyatnikov (281). The metal ions are sorbed from a neutral or slightly acidic medium on a KU-2 column (6 cm x 1.3 cm). For the separation of U and Th, U is eluted with 20 % HNO_3 after which Th is extracted from the column with 5 % oxalic acid. The same separation is carried out by Khopkar and De (298) with 1 N HCl and by Pillai (470) with 1 N HNO_3. A more complete (non radiochemical) scheme for the selective separation of U on a AG50X8 resin was described by Strelow and Van Zijl (585). W, Mo, Nb, V^{5+}, In, Bi, Sn^{4+}, Pb are eluted with 0.5 N HCl + 1 % H_2O_2, followed by 0.6 N HBr; U^{6+} is eluted with 1.75 N HCl. Sr, Ba, the rare earths, Zr, Hf and Th are retained by the column. An anion exchange step is necessary for the removal of a few other elements such as Fe. Other U/Th separations based on the same principle are reported (30, 596). The same method is used for the separation of U from a few other elements. This is for example the case for the separation U/Np^{4+} (275), U/Fe^{3+} (310) and U/Al (616). Ions that form strong chloride complexes can be eluted before UO_2^{2+}. Cd can be separated in this way by elution with 0.5 N HCl, while UO_2^{2+} remains on the column (572). Alkali metals have a lower affinity for the resins than UO_2^{2+}. This was applied for example by Athavale and Krishnan (18) who eluted the alkalis with N NH_4Cl.

The affinity of U^{6+} for the resin is much higher after addition of organic solvents. This was shown by Ishimori (271) for methanol-HNO_3 mixtures, Ionescu et alii (267) for HCl-acetone, Korkisch and Ahluwalia (322) for isopropanol-HCl, Korkisch and Tera (332) for HNO_3-alcohols. At very high percentages of organic solvents, the distribution coefficients usually decrease again. A separation procedure for U in a mixed solvent was published by Korkisch and Ahluwalia (322). U^{6+} is **completely adsorbed on a small column of Dowex 50 with 90 % isopropanol-10 %** 6 N HCl while Bi passes into the eluate. The affinity of Th remains higher so that U can be eluted while Th remains on the column. Korkisch and Tera (332) adsorbed both ions in 90 % ethanol - 10 % HNO_3 and **eluted U with 10 % ethanol - 90 % N HNO_3 and Th with 3 N HNO_3. In the same** way, Ionescu et alii (267) separated UO_2^{2+} from Th^{4+} with 90 % acetone-5 % HCl on a 20 cm x 0.8 cm KU-2 column.

The intermediate value of the distribution coefficient of UO_2^{2+} in 9 N HBr permits two modes of separation with this eluting agent (436). U can be separated by adsorption from non-sorbable elements such as Zn or by elution from more strongly sorbed elements such as Np^{4+} or Th^{4+}. The adsorption function for U^{4+} shows a minimum near 4 N HBr. At 9 N HBr a distribution coefficient of 100 is attained so that U^{4+} can be separated from UO_2^{2+}. This is illustrated by the separation of radioactive isotopes of Zn^{2+}, UO_2^{2+}, U^{4+} and Th^{4+} on a Dowex 50X4 column ($0.28\ cm^2$ x 4 cm). Zn and UO_2^{2+} were eluted consecutively with 9 N HBr, U^{4+} with 12 N HCl and Th with 6 N HCl + 1 N HF. It should, however, be noted that in HBr and at tracer concentrations U^{4+} is oxidised partially to U^{6+}.

UO_2^{2+} forms complexes with many ions and can therefore be eluted more or less selectively with several complexing agents. Oxalic acid is used for example by Kapatsinskaya (281) in the already mentioned study on the separation of natural radioelements. U, Th, Bi and Ac isotopes are eluted as a group with 5 % oxalic acid, after which Pb and Ra are successively stripped from the column. Draganic et alii (151) and Dolar and Draganic (147) employ 0.5 N or N oxalic acid to elute U. The elements from which the separation of U was studied are in the first case Cd, Ni, Co, Mn and the rare earths and in the second case ^{152}Eu. Zr forms **stronger oxalate complexes than UO_2^{2+} so that it can be eluted while U remains** adsorbed (298).

Anionic complexes are also formed with sulphate. With N H_2SO_4 U can be eluted while Sc, Y, La, the rare earths, Th, Al, Ga, Fe^{3+}, Fe^{2+}, Be, Mg, Mn, Cu, Co, Ni, Zn, Cd are retained (578). This was applied by Karalova (695) to the separation of U from ^{230}Th with 1 N H_2SO_4. Braier (73) separated U from Eu by bringing the ions on the column in a H_2SO_4 medium. UO_2^{2+} is not adsorbed and passes into the eluate. Boyd (68) separated U by elution from a sulphonated phenolformaldehyde resin with 0.2 M to 0.3 M H_2SO_4 from fission products (eluted with phosphoric acid and 1 N HNO_3) and Pu (eluted with 0.8 N H_3PO_4 and 1 N HNO_3).

Carter and Dean (100) described a method on the same principle with fluoride as the ligand. U was eluted as an anionic complex from a Dowex 50 X8 resin while R.E. traces (Dy, Eu, Gd, Sm) remained adsorbed. U can also be eluted with a 0.64 M **hydroxylammonium chloride solution of pH 6,** while Fe remains on the column (665).

A few separations based on selective complexation of the other ion were also reported. Khopkar and De (298) separated U from Hg by complexation of the latter with KI and from Ce^{3+}, Cu, Ni by elution of these three ions with EDTA. Ryabchikov (518) separated U from most other elements by adsorption of U from EDTA medium.

U can be separated by selective solvent effects (CIESE). It is eluted almost selectively with 90 % tetrahydrofuran - 10 % 6 N HNO_3. Elements which remain adsorbed, are Fe^{3+}, Ga, In, Pb, Cu, Zn, Cd, Co, Ti, Ni, Al, the rare earths, the alkaline earths, Zr, Th, Cr (325). U is separated from Mo according to the following method (168): percolate the test solution in tetrahydrofuran (THF) - 6 N HNO_3 (9:1) through a column of 10 g of Dowex 50 X8 (100-200 mesh, H^+ form) at a flow rate of 1 ml/3 min. U and some of the Mo are adsorbed, but V, H_3PO_4, Au and the platinum **metals are not. Elute Mo with THF - 6 N HNO_3 (9:1), then elute U with THF-** 3 N HCl (4:1).

Ion exchangers with P in their functional groups show a high selectivity for U. The affinity series on a diallylphosphate polymer is $UO_2^{2+} > Fe^{3+} > La^{3+} > Cu^{2+}, Co^{2+}, Ca^{2+} > Na^+$. A separation of UO_2^{2+} from Fe^{3+}, Cu^{2+}, Co^{2+} and La^{2+} was described. The four latter ions were eluted with EDTA and UO_2^{2+} with carbonate (293). A separation from fission products was also described. According to Marhol (381) only UO_2^{2+} is adsorbed on the resins VAP-1 ($-OPO(OH)_2$ functional group) and KF-2 ($-PO(OH)_2$) in 0.3 M to 0.5 M HNO_3 from a mixture with the other bivalent ions Cd, Zn, Cu, Ni, Co, Fe, Ca, Sr and Mg.

6.5.4. Neptunium

A review of the ion exchange properties of Np has been published by Burney et alii (86). Np is adsorbed from acids of low molarity in all its oxidation states by a strongly acidic cation exchange resin such as **Dowex 50. The affinity towards the resin is determined by the ionic charge** so that the following series is obtained: $Np^{4+} > Np^{6+}$ (as NpO_2^{++}) > Np^{5+} (as NpO_2^{+}). Np^{4+} is adsorbed more strongly than for example Na^+, K^+ or UO_2^{++} and can thus be separated from these elements.

At high ionic strength Np^{4+} and Np^{6+} are only slightly or not at all adsorbed from HCl (143, 438). From 9 N $HClO_4$ however, Np^{4+} is strongly adsorbed (438). In HBr (436) the distribution coefficient decreases to a minimum of 15 near 4.5 N HBr, increases to a maximum value of 160 at 9 N HBr and then slightly decreases. It was not possible to hold Np in the 5+ or 6+ states in this medium. The high adsorption of Np^{4+} in 5 N HBr was used to effect a separation of a few mg U^{6+} from tracer Np. U^{6+} was eluted from a 2 cm x 0.2 cm^2 column of Dowex 50 X4 and Np was stripped with 5 N HCl. Separations of Np from Pu with HNO_3, HF or HBr are discussed in the next paragraph.

One of the difficulties in working with higher oxidation states of Np is that Np^{6+} and Np^{5+} are reduced to Np^{4+} by the resin. In very carefully controlled conditions it was however possible to separate Np^{5+} from Th (87).

6.5.5. Plutonium

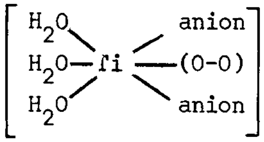
The adsorbability of the different Pu-ions decreases with decreasing ionic charge. Therefore the affinity series is $Pu^{4+} > Pu^{3+} > Pu^{6+}$ (PuO_2^{2+}). Specht and Höhlein (560) showed that it is possible to separate Pu in four fractions (colloidal, Pu^{6+}, Pu^{3+}, Pu^{4+} in that order of elution) by elution with 5.25 N HCl. The sorption in HCl was studied by Diamond et alii (143) and later also by Nelson (438). The distribution constants for the three ion species decrease with increasing HCl

molarity. In 9 N HCl Pu^{6+} is not adsorbed (438).
In HBr the predominant oxidation state is Pu^{3+}. Adsorption measurements of this ion were carried out by Nelson (436) with 3 to 12 N HBr solutions. The distribution coefficient of Pu^{3+} decreases with increasing molarity of HBr to a minimum of 3 at 6 N HBr, then increases to a value of 15 near 12 N HBr. In HNO_3 both Pu^{3+} and Pu^{4+} are strongly adsorbed at low molarities on C-50 (a French resin comparable to Dowex 50) (491). At molarities higher than 4 both show distribution constants lower than 1. In 9 N $HClO_4$ (438) Pu^{6+} is strongly adsorbed. Distribution coefficients in a few molarities of H_2SO_4 on several resins were determined for Pu^{3+} and Pu^{4+} by Neill and Higgins (432). Pu^{3+} is the normal oxidation state in dilute sulphuric acid. At 0.5 N a distribution coefficient was found on Dowex 50 X8 and at 3.6 N a value of 3.6.
Pu^{3+} can be separated from UO_2^{2+} in 1.5 N HNO_3. The uranyl ions are eluted (145). An analogous procedure was described by Lingjaerde (358) for the separation of Pu from irradiated U. U and fission products are eluted with 2 M HCl from Dowex 50 (140-160 mesh) while Pu is retained as Pu^{4+}. Later, Pu is stripped with 8 M HCl. A further purification by anion exchange is necessary.
Several separations of Np from Pu were reported. In one procedure, Np, initially present as Np^{6+} is reduced to Np^{5+} by the resin and eluted with 1 N HNO_3; Pu is stripped with 3 N HNO_3 (655). Zagrai and Sel'chenkov (652) carried out the same separation with 0.02 N HF after a reduction to Pu^{3+} and Np^{4+} with SO_2. Nelson (436) separated ^{237}Pu from ^{238}Np on a Dowex 50 X4 column (0.28 cm^2 x 3 cm at 60°C). Pu^{3+} was eluted with 6 N HBr and Np^{4+} with 9 N HBr - 0.2 N HF. A method for the isolation of 10 p.p.m. ^{237}Np from $\pm$ 10 mg ^{238}Pu starts with the separation of Np^{5+} from the bulk of the Pu by cation exchange in HBr medium (696).
A cation exchange step for the separation of Pu from Fe was incorporated by De Bortoli (134) in a procedure for the radiochemical determination of Pu in soil and other environmental samples. Fe is eluted as a negatively charged or neutral EDTA complex while Pu remains on the column. An analogous application resides in the selective complexation and elution of Ni with potassium cyanide. Again, Pu remains on the column (170).

6.6. Transition metals

6.6.1. Ti - Zr - Hf

The distribution coefficient of Ti^{4+} in HCl decreases with increasing molarity to a shallow minimum ($D < 1$ at 6 M HCl), then increases to a value of 10 in 12 N HCl (438). In $HClO_4$ a minimum of D = 6 is reached near 3 M. At higher molarities high distribution coefficients are found ($D > 10^4$). These properties were used to separate ^{42}K, ^{44}Ti and ^{44}Sc. K is not retained in 9 M $HClO_4$. Ti is eluted with 9 M HCl and Sc with 4 M HCl - 0.1 M HF. The occurence of a minimum in adsorption at a concentration of 3 N $HClO_4$ was used by Dosch and Conrad (150) to separate Ti and Zr. Ti was eluted with 25 % $HClO_4$ and Zr with 1 % $HClO_4$ - 0.1 N NH_4F.
At low acidities, hydrolytic reactions can cause difficulties. Therefore complexing agents were often used for the chromatography of Ti. H_2O_2 was used by Massart and Hoste (391) in a procedure for the determination of La in TiO_2 by activation analysis. The matrix (100 mg of Ti) was eluted with 3 N HCl + 2 % H_2O_2 and separated from ^{140}La traces on a Dowex 50 WX8 column (20 cm x 2 cm^2). A speedier elution was obtained with this eluting agent than with 3 M HCl alone in which tailing occured.
The adsorption of Ti from acid + H_2O_2 was studied more exhaustively by Alimarin and Medvedeva (9). The general formula of the **titanium peroxide** complex is



It is therefore not surprising to find that the adsorption depends on the nature of the anion. The adsorption decreases when the stability of the complex increases i.e. in the order $ClO_4^- > Cl^- > SO_4^{2-}$. The adsorption of Ti is high at acidities under 0.6 N and decreases from there on. These properties were put to advantage in several non-radiochemical procedures. Mo and V were eluted at pH 1 with 1 % H_2O_2 while Ti remained adsorbed (9) and Ti was eluted with 3 N HCl + 0.5 % H_2O_2 while Th was not desorbed (11). V can be eluted with 0.02 N H_2SO_4 - H_2O_2 from Ti (2 N H_2SO_4 - H_2O_2) and from Ni, Mn and Al (not eluted) (138). V^{5+} can be separated by elution with 0.01 M HNO_3 + H_2O_2 (683). Ti is subsequently eluted with 1.25 M HNO_3. At this stage of the separation Al and Zr remain on the column. The separation of Ti from the R.E.'s, Be, Nb, Fe, Al, Th, Mg, Mn and a few other elements with 1 N H_2SO_4 - 1 % H_2O_2 was also reported (577).

A few other complexing agents were used. Ti was separated from Mn by elution with 0.1 N oxalic acid (621), from Cr by elution with 0.5 % EDTA solution (6) and from La by elution with 2 % oxalic acid (645). Brown and Rieman (79) separated Ti from Zr and Th by elution with EDTA. Kenna and Dosch (292) eluted Ti selectively with H_2SO_4 + NH_4F.

The cation exchange behaviour of Zr and Hf and the cation exchange separations of these elements from each other and from other elements was studied extensively in the period before 1960. Thereafter the attention of most authors was shifted to anion exchange techniques. Two factors determine the application of cation exchange to the chromatography of Zr and Hf, namely the relatively strong affinity towards the resin from dilute and concentrated acids and the strong complexing properties of these cations.

The cation exchange behaviour of Zr and Hf in HCl and/or $HClO_4$ was studied by Lister and Mc Donald (361), Larsen and Wang (348), Benedict and alii (38) and more recently by Nelson et alii (436, 438). Both elements are rather strongly adsorbed from dilute HCl. This property was used in some separations. Kozlycka (333) for example, eluted Ti, Fe, Al with 2 N HCl and Zr with 2 % citric acid while Belyavskaya et alii (36) eluted Be with 2 N HCl and Zr with 4 N HCl. Zr and Hf display the usual dependence on acidity: a minimum (of $D \approx 2$ at 6 M HCl) and a rise from then on ($D = 40$ at 12 N HCl).

Hf is less strongly adsorbed in HCl medium than Zr and this was used by Street and Seaborg (566) who first adsorbed the elements on a Dowex 50 column from 2 N $HClO_4$ and then separated them by elution with 6 N HCl. In $HClO_4$, a strong adsorption of both elements is obtained with a minimum at 6 N of $D \approx 20$. This strong affinity towards the resin was used by Nelson et alii (438) to retain ^{181}Hf on a 4 cm x 0.25 cm^2 Dowex 50 X4 column while eluting non adsorbable elements such as Na^+ with 9 N $HClO_4$. Hf was eluted with 9 N HCl - 0.2 N HF. An analogous (non radiochemical) separation of Ti and Zr was reported by Dosch and Conrad (150). Ti was eluted with 25 % $HClO_4$ and Zr with 1 % $HClO_4$ - 0.1 N NH_4F. In HBr a minimum is found at 6 N. In 9 N HBr both elements are strongly adsorbed so that a separation of Hf from a typical non adsorbed element such as Cs could be achieved on a 0.28 cm^2 x 4 cm column (436). Hf was desorbed with 6 N HBr - 0.1 N HF.

Belyavskaya and Dobrushina (698, 699) made a study of the sorption of Zr from mixed aqueous organic solutions of H_2SO_4. The sorption is decreased by increasing the organic solvent content owing to the formation of SO_4^{2-}-complexes. H_2SO_4 was used by several authors to separate Zr and Hf (258, 317, 359, 360). Lister (359, 360) eluted Zr with 1 N H_2SO_4 from Dowex 50 and Hf with 0.05 N oxalic acid - 0.2 N H_2SO_4 or with 3 N H_2SO_4. Grover (226) carried out the separation with 0.5 N H_2SO_4. Zr was also separated from Al by elution of the former with 2.5 N H_2SO_4 (88).

In most separations of Zr and Hf complexing is used. Sometimes this is done only to speed up the elution of an element retained in the first elution step. This is the case for the various HBr and HCl - HF eluting agents, used to elute Hf, that were cited in the preceding paragraphs.

One of the earliest applications of cation exchange to radiochemistry was the selective elution of Zr (and Nb) with oxalic acid. This was used by Tompkins, Khym and Cohn (115, 614) to separate Zr - Nb from a fission product mixture. Zr and Nb were eluted with 0.5 % oxalic acid, while the alkaline earth metals and the rare earths remained on the column. Subsequently the rare earths were eluted with a 5 % citrate buffer of pH 3 and the alkaline earths at pH 5. Kimura (303) separated Zr and Nb from other fission products present in radioactive dust with 0.5 % oxalic acid. ^{95}Zr and ^{95}Nb can be separated, for example, according to the method of Sano and Shiomi (524). The elements are adsorbed from dilute HCl medium and Nb is eluted with 1 N HCl + 0.3 - 3 % H_2O_2. ^{95}Zr is recovered as the oxalate complex with 0.5 % oxalic acid (figure 43). After bombardment of a Hf target with protons of high energy, the Hf-activity was separated from R.E.'s by dissolution in 0.5 N HCl + 5 % oxalic acid. Hf was not adsorbed on a cation exchanger (486). Culkin and Riley (120) determined Zr and Hf in silicate rocks. Mn, Fe, Ti were eluted with 1.5 M HNO_3, Zr and Hf with 0.025 M oxalic acid, Th with 0.5 M

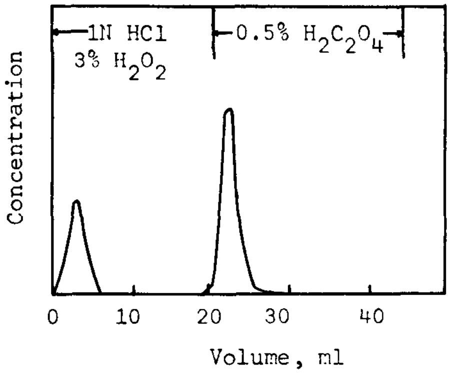


Figure 43

Separation of ^{95}Nb and ^{95}Zr (254)

oxalic acid and Ce with 6 N HCl. The separation of Zr from U can also be carried out with oxalic acid (298).

Citric acid was used by Benedict et alii (38) for the separation of Zr from Hf. Zr is eluted first from a Dowex 50 column with 0.45 N HNO_3 + 0.09 M citric acid. Extremely large volumes are however necessary. Ryabchikov and Bukthiarov (516) carried out the same separation on KU-2 (H^+ form). Zr was eluted with 0.24 M citric acid in N HCl. Hf was recovered by elution with 0.3 M oxalic acid in N HCl.In a later article, Bukthiarov (697) describes a Zr-Hf separation, by elution of Zr with 0.057 M citric acid in M HCl. Hf is recovered with 0.33 M oxalic acid in 1.5 M HCl. Another hydrocarboxylic acid, α-hydroxyisobutyric acid, allows the selective elution of Zr from all the other fission products and actinides (461). A ^{95}Nb - ^{95}Zr separation is described in the same article.

Qureshi et alii (493) made use of the complexation of Zr with formic acid to separate this element by elution with a 0.05 M solution from Th and from Ga. Zr is eluted before Be with 0.1 M Na-tartrate (656). Korkisch and Orlandini (330) developed a method for the separation of Zr and Hf from many accompanying ions. Hf and Zr were not retained on Dowex 50 from a mixture consisting of methanol and 12 N HNO_3 (19:1), 0.1 N in tri(n)octylphosphine oxide (a reagent often used in extractions). Ti, R.E.'s, alkalis, alkaline earths, Fe, Co, Mn, Zn are retained. Tracers are used to follow the elution.

A special application of cation exchange is the separation of trace constituents from zirconium colloids. In water polymerised zirconium cations are formed that are not retained by the column while impurities such as Be^{2+} or La^{3+} are (23). Of special importance in radiochemistry is the behaviour of "radiocolloids". The uptake by cation exchangers of Zr and Nb from their radiocolloidal solutions was studied by Schubert (533, 534, 537).

6.6.2. V - Nb - Ta

The adsorbability of V^{4+} in HCl (438) and in HBr (436) decreases continuously and the adsorption is negligible at high concentrations. A separation of V^{4+} (and Mn^{2+}, Co^{2+}, Cr^{3+}) from Fe^{3+} is possible by elution of the former with 9 M HBr (Dowex 50 X4, 0.28 cm^2 x 3 cm, 25°). In $HClO_4$ (438), the adsorption shows a minimum at 3 M ($D \approx 5$). In 10 M $HClO_4$, D = 100 and therefore V^{4+} is separated by retention while Ni and Cr^{3+} are eluted with 9 M $HClO_4$. The former is removed with 6 M HCl. V^{5+} is strongly adsorbed from 9 M $HClO_4$ and weakly from 9 M HCl. In both media V^{5+} reduces to V^{4+}. De and Majumdar (133) were however able to elute V^{5+} with 0.5 N HCl and to separate it quantitatively from Cu, Zn, Ni, Co, Fe, Mn, Zr, Al, Ce^{4+}, V^{6+}, Th and Ti.

Solutions containing vanadate are not adsorbed on cation exchange resins in the ammonium form. According to Kraus et alii (338) part of the vanadate is adsorbed by precipitation or by reduction on resins in the H^+ form. Nevertheless, Shiskov and Shiskova (549) were able to elute V as the vanadate from a KY-3 (H^+ form) column with 10 % NaOH, while Ti remained on the column.

Vanadium is easily eluted with eluting agents containing H_2O_2, even at low acidities. Chan and Riley (102) describe a V - Fe separation with 0.3 % H_2O_2, de Gelis (138) a separation from Ti, Ni, Mn and Al with 0.02 N H_2SO_4 - H_2O_2 and Strelow et alii (683) a separation from Ti, Al, Zr with 0.01 N HNO_3 + H_2O_2. A separation from at least 25 other metal ions by elution with 0.01 M H_2SO_4 or $HClO_4$ containing 1 % H_2O_2 was reported by Fritz and Abbink (179).

Linstedt and Kruger (700, 701) concentrated quinquevalent vanadium (the form expected in natural waters) form water samples prior to activation by passage of the sample through a Dowex 50 WX8 column. The elution of V was achieved with 2 N HNO_3.

In 9 N $HClO_4$, in the presence of a small amount of HF, Nb and Ta are strongly adsorbed. In 9 N $HClO_4$ without HF hydrolysis occurs. In 9 M HCl Ta and Nb are weakly absorbed and in 9 - 12 M HBr with 0.2 M HF they are not adsorbed. In 9 M HBr - 0.05 M HF, Nb is eluted in 4 - 5 column volumes. Nelson describes (436) a purification of ^{95}Nb in this medium. Non-identified non-adsorbed elements eluted ahead of the Nb band.

Nb and Ta are best eluted with complexing agents. As just described, HF can be used for this purpose. HF solutions were also used by Nikitin (444) to separate a bombarded Ta-target from trace activities (see also chapter 5). Tompkins et alii (115, 614) and Kimura (303) described the use of oxalic acid for the isolation of Zr and Nb from fission product mixtures (cfr. 6.6.1.). With α-hydroxyisobutyric acid ^{95}Nb is eluted before ^{95}Zr which is itself eluted before all the other fission products (461). With tartrate Nb and Ta are not adsorbed on a cation exchange column, while Ti and Fe are (7). Complexing with H_2O_2 was used by Nabinavets and Kudritskaya (428). After the elution of Cr, Fe, Co, Ni and Mn from a KU-2 column with 5 N $HClO_4$ - 0.1 N H_2SO_4, of the rare earths with 1 M NH_4Cl of pH 5 and of Th with bisulphate, Nb is eluted with 1 M H_2SO_4 - H_2O_2. Bukhtiarov (697) separated Nb from Zr and Hf by elution of the former with M HCl - 1 % H_2O_2. A procedure for the separation of ^{95}Nb and ^{95}Zr (524) was described earlier (cfr. 6.6.1. and fig. 43). This is also the case for the use of colloids (23) and the study of radiocolloids (533, 534, 537).

6.6.3. Cr - Mo - W

The cation exchange chromatography of Cr is based to a large extent on the formation of non adsorbable chromate anions. Reduction of this anion by the eluent or the resin can lead to erratic results. Cr^{3+} is adsorbed and Cr^{6+} is not adsorbed on Dowex 50 in the H^+ form from less than 1 M H_2SO_4. Cr^{6+} can be separated from U, Cu, Fe, Sn, Co, Zr, Al, Ni, Ti and Mn (26). Babachev (24) described the separation of chromate from iron and aluminium by elution of the former with 0.01 N H_2SO_4. De Gelis (138) described an analogous separation from V, Ti, Ni, Mn and Al with 0.2 N H_2SO_4. A rather surprising fact is the strong adsorption of Cr^{6+} from 9 M $HClO_4$ (438). Reduction by the resin makes separations in this medium however impossible.

Cr^{3+} is not adsorbed from concentrated HBr (436) and weakly from concentrated $HClO_4$ (438). Separations by elution with 9 M HBr from Fe and with 9 M $HClO_4$ from V^{4+} were described.

Cr forms a stable complex anion with thiocyanate. Fe^{3+} remains a cation and is retained by a cation exchange resin (517).

At low molarities investigations into the behaviour of W^{6+} and Mo^{6+} in HCl, $HClO_4$, HBr are difficult because of hydrolytic interferences. According to Ginzburg and Shkrobot (205) at pH 3 to 5 a cationic species of Mo is formed. This is not the case for Re so that both metals can be separated by passage through a cation exchange at this pH (see also (128)). W^{6+} and Mo^{6+} are slightly adsorbed in high molar HBr and a separation of these elements from each other was described (436). W is eluted first from a 0.2 cm^2 x 6 cm column of Dowex 50 X4 (60°) with 9 M HBr.

The non-adsorbance of molybdate and tungstate has given rise to several methods of separation. Bottei and Trusk (63) for example found that in 1 M NaOH, tungstate is not adsorbed by the column.

Mo is separated from solutions containing Pb, Cu, Ni, Fe, Cr and V^{4+} in a procedure devised by Klement (311). Molybdic acid leaves the column as the citrate complex. The others are adsorbed. Watkinson (637) adopted a very similar procedure to separate tungstate and molybdate from Fe, Cu, Sn and V.

According to Darbinyan and Garbakyan (127), Mo is poorly adsorbed from oxalic, citric, tartaric and phosphoric acid medium because of the formation of an anionic complex. From acetic acid it is however adsorbed (presumably as MoO_2^{2+}). Therefore a separation is possible in this medium from non adsorbed elements such as Re. The best separation is obtained in 2 N acetic acid on a 20 cm x 1 cm KU-2 column. Mo is desorbed with 0.1 N oxalic acid.

H_2O_2 can be used to complex W (102, 180, 514, 577). Chan and Riley (103) describe such a technique for the determination of W in silicates and natural waters. Ryabchikov and Buktiarov (514) separated Ti and W by **elution of the latter from a column of SBS with solutions containing sulphate and 10 % hydrogen peroxide at pH 5. Pavlenko (460) separated Mo** and W from Fe with 0.45 N sulphuric acid containing H_2O_2.

In HF solutions W is present as an anion and therefore W target activities can be separated easily from other activities present (see also section 5.) (444). Feik and Korkisch (168) separated U from Mo on a **Dowex 50 X8 column with tetrahydrofuran - 6 N HNO_3 (9:1). Mo is only slightly adsorbed and leaves the column while U is retained.**

6.6.4. Mn - Tc - Re

Permanganate is reduced by the resin and is thus unsuitable for separation purposes. This is not the case for rhenium. Perrhenate is not **taken up by the resin and this can be used to carry out separations from** other metals (128, 205, 550). Mo - Re separations are described in the preceding paragraph.

Several cation exchange separations of Mn from the alkaline earths were reported. Hadzistelios and Papadopoulou (229) determined Mn, Sr and Ba by activation analysis in plant tissue. The separation is carried out with inorganic acids (fig. 44). Fourcy et alii (173) included Mn in a scheme for the determination of metal ions by radioactivation. A separation from the alkali metals, the alkaline earths and the rare earths is obtained (for more details concerning Hadzistelios' and Fourcy's work cfr. 6.2.).

Povondra and Sulcek (482) studied the separation of Mn from alkaline earths with complexing agents such as 1.2 diaminocyclohexane-N.N.N'.N'.-tetraacetic acid. These same authors (483) described a separation with

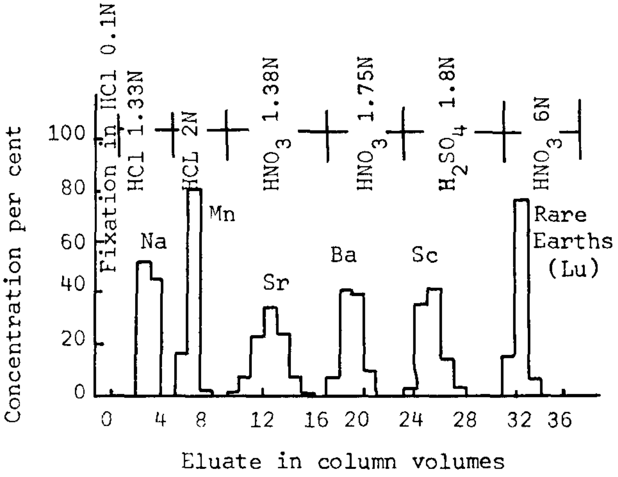


Figure 44

Separation of Na, Mn, Sr, Ba, Sc, rare earths with mineral acids (229)

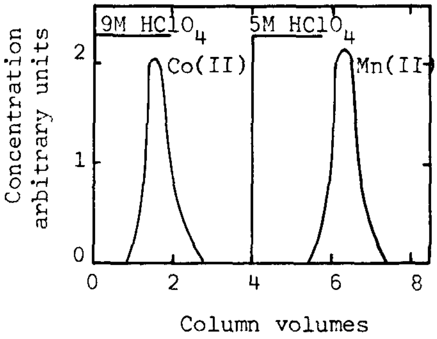


Figure 45

Separation of ^{60}Co from ^{54}Mn by elution with $HClO_4$ (438)

citrate. At pH 3.5 - 4, Fe and Al pass into the effluent and at pH 4.5 Mn does while Ca and Mg remain on the column.

Belyavskaya et alii (35) separated Sc from Mn by preferential elution of the latter with 2 N HCl - acetone (2:3). The separation of Mn from Cd, VO^{2+}, Ni, Mg, UO_2^{2+} and Th with NH_4SCN - organic solvent - water eluants was described by Pietrzyk and Kiser (468). In $HClO_4$, Mn has a minimum in adsorption near 5 M $HClO_4$ (438). This can be exploited to effect several separations such as ^{60}Co from ^{54}Mn by elution with 9 M $HClO_4$. Mn is eluted with 5 M $HClO_4$ (fig. 45).

Dowex 50 WX1 is used in the last step in a procedure for the separation and determination of ^{99}Tc in fission products. The solvent is ethanol and Tc is not adsorbed (702).

6.6.5. Fe - Co - Ni

Very few methods for the specific separation of Co or Ni have been described. Many methods however exist in which Co or Ni are one of a group of elements separated from another element. In any case very few radiochemical cation exchange separations for the determination of these elements seem to have been published. Mathers and Hoelke (394) included Co in a study on the automated separation of fission products. The following sequential elution procedure was proposed Ru + Sb (0.1 N HCl + 0.02 N HOx), Cs (0.5 N HNO_3), Co (0.45 N HCNS), Sr (1.0 N HNO_3), Y (2.0 N HNO_3) (fig. 46).

A selective separation method for Co was proposed by Korkisch and Gross (327). With 80 % acetone - 20 % 3 N HCl Fe, Ga, In, Cu, Au, Zn, Cd, Hg, Pb, UO_2^{2+}, Bi, Sn^{2+}, Sn^{4+}, V^{5+}, Mo, Ge and the platinum metals are eluted. Co, Ni, Al, Mg, Ca, Pr, Ce^{3+}, Sr^{3+}, Ti, Zr, Th, V^{4+} remain on the column at this stage. Mn and Co are then selectively eluted with 90 % acetone - 10 % 6 N HCl. Separations of Co from Ag and from Zn can be achieved by eluting Co respectively with EDTA (89) or α-hydroxyisobutyric acid (387). Co and Ni can be separated from each other with oxalate as the eluent (678).

Ni and Co are not adsorbed from 9 M $HClO_4$ and can thus be separated from many metal ions that are strongly adsorbed. Nelson (438) cites as an example the separation of Ni + Cr^{3+} from V^{4+} and Co from Mn (fig. 45).

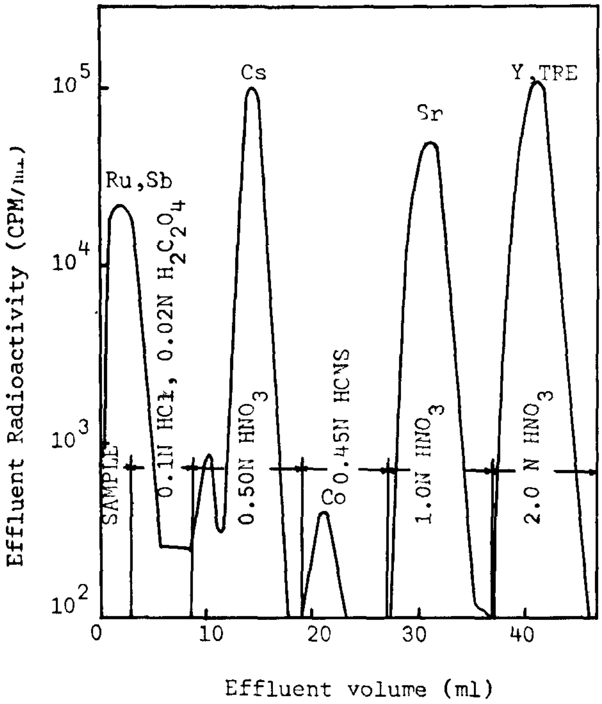


Figure 46

Separation of a fission product sample containing Ru, Sb, Cs, Co, Sr, Y, and rare earth activities (394)

Deschuyter et alii (140) purified Ni-activity by adsorbing ^{140}La (present as a contaminating activity) from concentrated $HClO_4$.A very efficient method for the separation of Ni^{2+} from other metals is achieved through sorption from 90 % acetone and 10 % 6 M HCl and desorption with 0.25 M dimethylglyoxime in 90 % acetone - 10 % 6 M HCl (712).

In low molarity HCl, Fe^{3+} does not show the affinity expected from a trivalent metal ion. This is due to complex formation. Separations from divalent metals are poor in this medium. Separation of Fe from Ru, Zr, Nb fission products present in bomb debris is however possible (364). The latter group of elements is eluted with 0.2 - 0.5 N HCl. Fe is then eluted with oxalic acid and separated from Cs, Ce, Pr, Zn, Co, Mn and Sr - isotopes. In HNO_3, much better separations are obtained and **according to Strelow et alii (583), the separation of Fe from Cu, Ni, Co, Zn,** Mn is possible with HNO_3 as the eluting agent. According to Blaedel and Olsen (55) some reduction of Fe^{3+} and Fe^{2+} can occur during its passage through the resin. This can be prevented by treating the resin with chlorine. At high molarities of HCl, Fe is very strongly adsorbed on cation exchangers. This was taken advantage of by Giovannetti et alii (206) for the neutron activation analysis of plant tissues (for more details cfr. 6.6.11.). The same behaviour is found in HBr. V^{4+}, Cr^{3+}, Mn^{2+} and Co are eluted with 9 M HBr, while Fe is retained. It is eluted later with 3 N HBr (438). The separation of Ag, Co, Cu, Mg, Mn, Ni, Pb and Zn from large amounts of Fe in HF medium on Dowex 50 WX8 was **studied by Danielsson and Ekström (125).**

Fe can be selectively eluted by complexation with SCN^- and EDTA (215) (separated from Mn, Zn, Be, Mg, Ba, Ca, Li and K), with 80 % tetrahydrofuran - 20 % M HCl (323) (separated from Co, Ni, Al), by complexation with sulphosalicylate (265) (separated from Cu, Co, Mn, Ni) in ammoniacal pyrophosphate medium (666). De Bortoli (134) described a Fe - Pu separation performed in the course of a procedure for the **radiochemical determination of Pu in soil and other environmental samples.** Fe forms stronger complexes with EDTA and is therefore eluted while Pu remains on the column.

Fe was determined in antimony by activation analysis. After a preliminary separation by precipitation, a final purification was performed by eluting the residual Sb with 20 % tartaric acid solution and Fe with 6 N HCl (551).

6.6.6. The platinum elements

The separation of the platinum elements from each other and from other metals by cation exchange is a very difficult problem. The pretreatment of the sample solution is of extreme importance and in many instances it is not exactly known what species is present in the solution. Therefore it is often difficult to predict whether or not adsorption on a cation exchanger will occur. It cannot be the purpose of this review to discuss this aspect of the problem. Beamish (34) has published a critical review on the separation of the noble metals in which many references to work concerned with the determination of the exact species responsible for elution or absorption can be found. Investigations on the mechanism of the sorption of nitrosoruthenium nitrate complexes on ion exchangers were summarised by Nikol'skii (445).

Most separations of the platinum elements from other elements use anionic complexes (mostly chloride) to elute the platinum elements selectively. Separations of Pt, Pd, Rh, Ir from Te (568); Pt and Pd (475), Ir (605) and Rh (525) from Fe, Cu, Ni; Pt and Pd (28), Ir (1) and Rh (29) from Cu; Pd, Rh, Ir (650), Os (628) and Ru (650) from base metals; Pd from Fe and Cu (552); Pd and Pt from Fe, Cu, Zn, Pb and Cd (345); Pt and Rh from Cu, Al, Fe, Bi, Cd, Zn, Co, Ni, Pb, Mn (704); Pd from Ni (671) were reported.

Several radiochemical applications have been developed. Ward and Foreman (636) determined ^{103}Rh in irradiated U. Rh as the anionic complex was eluted with 0.3 M HCl from Zeokarb 225 (12 cm x 0.5 cm), Zr, Nb and rare earth activities remain on the column. A further anion exchange separation from U is necessary. Kimura (303) carried out a radiochemical analysis of radioactive dust. Te, I, Rh and Ru activities were recovered from a cation exchange column in a first fraction with 0.2 N HCl. Zr, Nb, ^{237}U, the rare earths and the alkaline earths remained on the column at this stage. Guillon et alii (227) described the separation of Ru from 50 day old fission products also by elution as the anionic chloride complex. This was achieved by elution from a Dowex 50 X8, 100-200 mesh, 70 mm x 5 mm column with 0.2 N HCl. The formation of the chloride complex presented no difficulties when the fuel was dissolved directly in HCl. When the solution was dissolved in HNO_3 the transformation into the chloride complex upon the addition of HCl and NaCl was not instantaneous.

Only a few separations by cation exchange of platinum elements from each other have been described. McNevin and Crummett (370) separated Pd from

Ir in ammoniacal chloride solution. Pd is adsorbed as the $Pd(NH_3)_4^{2+}$ complex while Ir passes through as $IrCl_6^{3-}$. McNevin and McKay (368, 372) also described separations of Rh from Pt, Pd and Ir.

In perchlorate media sorption of the platinum elements can occur. Stevenson et alii (562) percolated a perchlorate solution of a mixture of Pt, Pd, Rh and Ir through a Dowex 50 column. Only Pt passed through. The three other elements were separated from each other by elution with various molarities of HCl. Karttunen and Evans (283) described a method for the isolation of Rh from uranium-based fission alloys. After extraction of the U and volatilisation of Ru, a perchlorate solution was transferred to the resin column. Pd was removed with 0.3 M HCl and Rh with 6 M.

6.6.7. Cu - Ag - Au

Cu is adsorbed from dilute HCl but above 6 N the distribution coefficient falls to zero. Koch (314) was able to separate Cu from the less adsorbed elements Hg, Cd, Zn with 0.4 M HCl. Kemula and coworkers (291) developed a procedure for the separation of Ag from Cu based on the adsorption of both ions on the cation exchanger, Wofatit KPS-200. When HCl was passed through the column, Cu was eluted while Ag was precipitated on the column. Cu and Pb can be separated by adsorption of Cu as $Cu(NH_3)_4^{2+}$ from ammoniacal tartaric medium. Pb is eluted as the tartaric anionic complex (340). Marczenko (379) developed an analogous method for the separation of Cu from Sn and Sb.

Cu is eluted first from Amberlite IR-120 column with $Na_2S_2O_3$ and can thus be separated from Cd, Ag, Pb, Tl, Zn, Fe^{2+}, Cr^{3+}, Ni, Co, Mn and Ba (375). With 2 % $NaNO_2$ Cu is eluted before Co and Ni (49). Cu is eluted before Zn, Ni and Pb with 0.5 M ammonium acetate (705).

Cu^{2+} forms a much more stable EDTA chelate than Mg, Sr and Ba and could therefore be separated from these ions by elution with EDTA on a Zerolit-225 column (91).

From 0.2 M to 9 M HCl the adsorbability of Ag is negligible. In HNO_3, however, adsorption occurs. This adsorption is relatively strong: in the course of a separation of Ag from many other metal ions Rangnekar and

Khopkar (500), eluted Cu, U, Al, Zn with 0.5 N HNO_3. Ba and Ag **remained on the column from which Ag was eluted first with 2 N ammonium ace**tate. Sr is more strongly adsorbed from HNO_3 than Ag since Majumdar and De (374) were able to elute Ag with 4 N HNO_3 while Sr was retained. Ammonium acetate was also used by De and Majumdar (132) to separate Ag, Pb and Hg^{2+} from each other. Pb is eluted with 0.25 M NH_4Ac, Ag with 0.5 M NH_4Ac and Hg^{2+} with 4 M NH_4Ac. Several other procedures for the separation of Ag based on the use of organic complexing agents were reported in the article by Rangnekar and Khopkar. Sb^{3+} is eluted with tartaric acid (5 % at pH 1), Sr with citric acid (5 % at pH 2), Ce and Zr also with citric acid (5 % at pH 2.7), Bi, Fe and Th with EDTA (0.01 M at pH 2). A separation of Co from Ag by elution of the former with EDTA was described by Burriel-Marti and Alvarez-Herrero (89).

Among the fission products Ag is the only element apart from the alkalis to remain as a positive ion in an ammoniacal solution of ammonium triacetic acid. Kjelberg et alii (309) used this property to milk ^{115}Cd from ^{115}Ag adsorbed on a Dowex 50 WX4 100-200 mesh column (0.4 cm high). The elution was carried out with 0.0125 M ammonium triacetic acid in 3 N ammonia.

At high molarities of HCl, Au is strongly retained by Dowex 50 resin (438). This was put to advantage in a neutron activation procedure for the determination of trace elements in plasma. Au and Sb^{5+} were held on a Dowex 50 WX4 100-200 mesh (10 cm x 5 mm) column from 8 N HCl - 0.1 N Na^+. Zn and Cu activities were not retained (206). Platinum shows negligible adsorption and this was used by Fu-Tszyun et alii (191) for the separation of ^{199}Au from an irradiated platinum target.

Nelson et alii (438) did not investigate the behaviour of gold in low molarities of HCl. Three other publications describe the non-absorption of Au from low-molarity HCl. Kutil and Cuta (345) determined metal impurities in gold by adsorbing the impurities from a chloride medium onto a column packed with Lewatit-S-100. Cd, Fe, Cu, Zn and Pb are retained, Au, Pd and Pt are eluted. Macnevin and Lee (371) adsorbed Hg^{2+} from 2 N HCl while Au was eluted. Pitts and Beamish (474) separated Au from base metals by elution with HCl of pH 1 - 1.5. Au is also strongly adsorbed from concentrated HBr. Nelson (436) eluted first Ag with 9 M

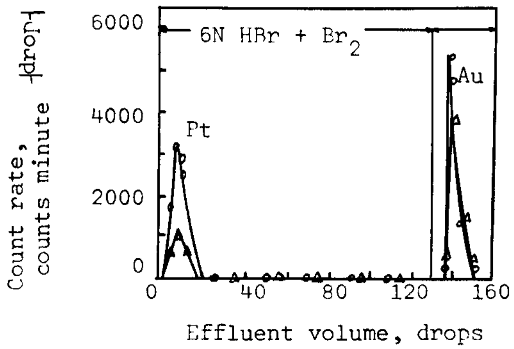


Figure 47a

Separation of 1 mg (0-0-0) and 10 mg (Δ-Δ-Δ) Pt from Au (carrierfree) (377)

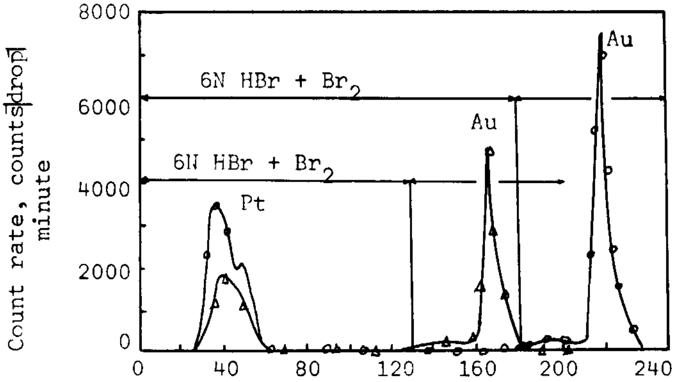


Figure 47b

Separation of Pt from Au (0-0-0): 5 mg of each, (Δ-Δ-Δ): 10 mg of each

$HBr-Br_2$ and then Au with 0.5 M HBr. The behaviour of Au in the $HBr-Br_2$ system was also investigated thoroughly by Dybczynski and Maleszewska (158). Au is adsorbed strongly from concentrated HBr, while Pr, Ir, Pd and Rh show negligible adsorption. They showed that Au can be separated both in milligram quantities and carrierfree from these metals. Au is stripped from the column with acetylacetone. A separation of ^{199}Au (carrierfree) from Pt was described by the same workers (377) (fig. 47 a) and 47 b)).

6.6.8. Zn - Cd - Hg

Hg, Cd and Zn form complexes with chloride even at low concentration and can therefore be separated by elution from many metals. Such a separation was described for Cd by Strelow (572). After the elution of Au^{3+}, Pt^{4+}, Se, V^{5+} and Mo with less than 0.2 N HCl, Cd is eluted together with Be, Sn^{4+}, Li and Na with 0.5 N HCl. U, Co, Ni, Zn, Mn, Cu, Ti, Fe, Al, Y, Zr, Th, Cs, the alkaline earths and the rare earths remain on the column. Meyer separated Cd from Zn by elution with 0.5 M HCl (706). Ionescu et alii described the separation of Zn from Cu by elution with acetone-HCl-H_2O (267). Constantinescu et alii described a radiochemical Cd - In separation with t-butanol-HCl and isoamylalcohol-HCl (707). McNevin and Lee (371) reported, however, sorption of Hg from 2 N HCl, which allowed a separation from the not adsorbed Au.
From other acids, the three elements are not as easily removed by the column. Hg can be separated from Tl by elution of the latter with 12.5 % $HClO_4$ (149). Hg is also retained in 1.5 N H_2SO_4 while Cu is eluted (625). These elements also form strong complexes with other halogenides and pseudohalogenides. Cd can be eluted as the CdI_4^{2-} complex with 0.05 M H_2SO_4 - 0.001 M HI (247). The separation of U and Hg with KI solution was also reported (298). Zn is not adsorbed in the presence of CN^- and can be separated from Mg (78). The separation of Zn from Cd, Zn from Ni and Cd from Mn^{2+} with ammonium rhodanide - organic solvent - water eluants was described by Pietrzyk and Kiser (468). The separation of Zn from Cd with HBr - organic solvent media was reported by Korkisch and Klakl (286). Separations of Cd and Zn from each other and from Fe, Ca, Ba in HCl - ethanol (587) and of Zn and Cd from Pb, Bi, Cu in dimethyl-

sulphoxide - HCl (53) are also possible.

Cd and Hg form also strong complexes with sodium nitrite. Bhatnagar and Arora (48) eluted Cd with 2 % $NaNO_2$ while Zn, Mn, Co, Ni and Bi remained adsorbed. Bhatnagar and Pandse (50) separated Hg from Co and Ni in the same manner.

Al forms stronger complexes with EDTA than Zn (210). Therefore Al can be eluted with 0.1 M EDTA pH 3.5 while Zn remains on the column. According to Tsintsevich (618) the most suitable complexing agents for the separation of Al and Zn are tartaric, sulphosalicylic and oxalic acids. Gierst and Dubru (203) separated Zn and Cd with 0.25 M ammonium citrate at pH 4.0. A separation of Pb, Ag and Hg can be achieved by elution of the elements in the order given, with successively 0.25 M, 0.5 M and 4 M ammonium acetate (132). Be is complexed more strongly than Cd by many hydroxyacids and can therefore be eluted preferentially with solutions of these acids (657).

6.6.9. Al - Ga - In - Tl

Al, Ga, In and Tl^{3+} show very different behaviour in HCl solution. The adsorbability of Al decreases continuously and rather slowly over the whole range of molarities (335, 438). Ga shows a very pronounced minimum at 3.5 N HCl (D = 1.5) and a very high adsorption from 6 to 12 N HCl; In is adsorbed only in dilute HCl ($<$ 1 N) and Tl^{3+} is not adsorbed at low concentrations but D increases with increasing molarity. In HCl a few non-radiochemical separations were carried out. Klement and Sandman (312) reported the following separations on Dowex 50: Sb, Cu, Pb, Zn (eluted with 0.8 N HCl) from Ga (1.5 N HCl), In (0.4 N HCl) from Ga (1.3 N HCl), Sb (0.2 N HCl) from In (0.4 N HCl) and Pb, Cu, Zn, Fe (2 N HCl). Strelow (573) utilized the cation exchange technique to separate Al from Ti and Fe^{3+}. The latter elements were preferentially eluted with 2 N HCl. Gordeeva and Prosviryakov (216) and Ehman and Kohman (162) separated Be and Al by elution of Be with 0.5 N HCl and 1.1 N HCl respectively. The same separation was carried out by Vetejska and Mazacek (631) with 0.5 to 0.7 M H_2SO_4.

A very rapid method for the separation of ^{68}Ga (produced with 14 MeV neutrons) was developed by Aubouin et alii (19). Ga is adsorbed from

10 N HCl, while Cu, Ag, Sb^{3+}, Fe^{2+}, Cr are eluted. Ga is removed from the column with 4 N HCl.

The distribution coefficients of In^{3+}, Zn^{2+}, Cd^{2+} and Hg^{2+} in concentrated alkali and Mg halides were measured by Irving and Woods (269). They developed a method for the separation of active In from Cd targets with 2.5 - 4.4 M LiCl eluants. Several separations with organic solvents-HCl as eluting agents were reported. A radiochemical Cd-In separation on resins and ion-exchange papers was carried out with t.butanol-HCl and isoamylalcohol-HCl (707). Non radiochemical methods were reported by Strelow et alii (587) (HCl-ethanol for In-Ga-Be-Al-Y), Janauer et alii (671) (HCl-dimethylsulphoxide for In-Ga-Al) and Tsintsevich et alii (672) (HCl-acetone for In-Ga).

In $HClO_4$ the form of the curves is the same for the four ions. Ga and In show minima of $D \approx 10$, Al of $D \approx 5$ and Tl of $D \approx 1$.

The adsorption of Al, In, Ga and Tl^{3+} in HBr solution was studied by Nelson and Michelson (436). Two separations are reported (figures 48 and 49). In the first, 0.1 M Al and trace concentrations of In and Ga were separated at room temperature on a 0.25 cm^2 x 4 cm Dowex 50 WX4 column by successive elution with 9 N HBr, 9 N HCl and 4 N HBr. In the second, a column of the same characteristics operated at 60°C was used to separate Al, In and Tl^{3+} by successive elution with 9 M HBr-Br_2 (Br_2 is added to keep Tl in the Tl^{3+} state), 9 M HCl - Cl_2 and 1 M HCl.

Several separations make use of the formation of oxygenated anions such as gallate or of complex formation. Separations of Ga from Zn, Co, Ni and Cu (12) and from Pb and Cd (620) in the presence of EDTA, sulphosalicylic acid, oxalic acid or tartaric acid, of Zn from Al and Ti in EDTA medium (210), of Ga from Be with gluconate (656) and of Ga from Cd and Zn with 4-aminosalicylic acid (675) can be cited as examples. The most suitable complexing agents for the separation of Zn and Al are tartaric, sulphosalicylic and oxalic acid (618).

A substoichiometric method for the determination of traces of In in GeO_2 was reported (654). In is extracted from the sample solution with dithizone and reextracted into H_2SO_4 whereupon a substoichiometric amount of EDTA is added. The In - EDTA complex is separated from non-complexed In by cation exchange.

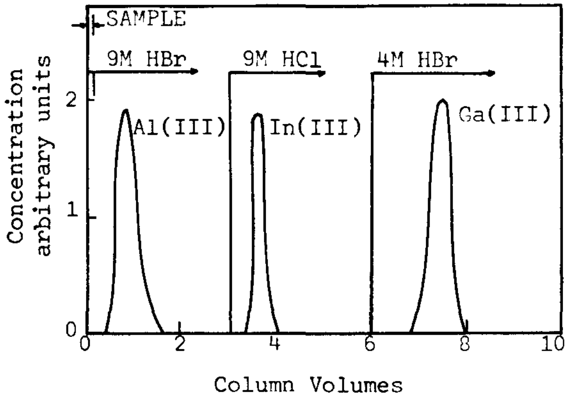


Figure 48
Separation of Al, In and Ga with HBr and HCl (436)

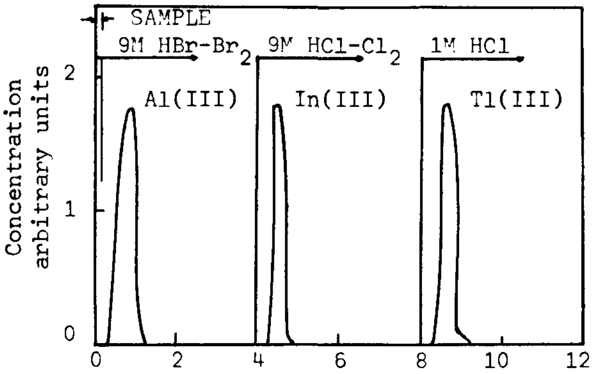


Figure 49
Separation of Al, In and Tl with HBr and HCl (436)

The adsorption of Tl^{3+} from highly concentrated solutions of metal halides has been examined by Pfrepper (708). The cation exchange behaviour of Tl^{+} and its separation from mixtures was investigated by Rangnekar and Khopkar (499). Tl is best eluted with 3 to 6 M H_2SO_4. It is **separated from Cu, Cd, Al, Zn, Mn, Co, Ni, U^{6+} and Ag by eluting these metals** with M H_2SO_4 and from V^{5+} with 0.5 M H_2SO_4. Zr, Ce^{4+}, Ba, Th, Bi, Fe^{3+}, Sr, Sb are not retained in the presence of citrate and EDTA. Pb and Tl^{+} are separated from each other with ammonium acetate. This last separation is also possible by the elution of Pb as the glycerol lead complex in strongly alkaline solution (99). Tl can be separated by adsorption in the presence of pyrophosphate and tartaric acid from Sb (228) and Fe, Cu, Zn, Cd, Pb (550). Hg^{2+}, Ag and Cu can be eluted with $NaNO_3$ while Tl remains on the column (51).

6.6.10. Ge - Sn - Pb

Germanium is not retained on a cation exchange resin at any HCl concentration and can therefore be separated from all the elements that can be adsorbed from this acid. This fact has been taken advantage of by Klement and Sandmann (312) who separated Ge from Ga, In and Sb by retention of the latter group of elements from 0.2 N HCl. Machiroux and Mousty (713) determined Ge in Zn by activation analysis. After dissolution in HCl, the acidity was adjusted to pH 1.42 with NaOH and the resulting solution was percolated through a Dowex 50 column. The Ge was not adsorbed and could be recovered by washing the column with a HCl solution of the same pH while Zn remained on the top of the column. Sn^{4+} is adsorbed **only from very dilute HCl media (571). Burriel-Marti and Alvarez-Herrero** (90) were therefore able to separate Sn from Mn, Fe, Co, Ni, Cu, Zn, Mg and Ca by elution of Sn^{4+} with 0.5 N HCl. In 12 N HCl Sn-tracer is **eluted while Sb^{5+}-tracer remains strongly adsorbed (335) (fig. 50). A separation** by elution as the complex oxalate was described by Kataev and Slezko (284). At pH 1 Sn passes into the effluent from a KU-2 column, while Cu, Zn and Pb are retained. By elution with 0.33 M tartaric acid, Sn^{4+} passes through an Amberlite IR-120 resin together with Sb^{3+}, while Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Rb, Cs, Mg, Ba, Ce, Ag, Al, Tl and Pb are retained (547).

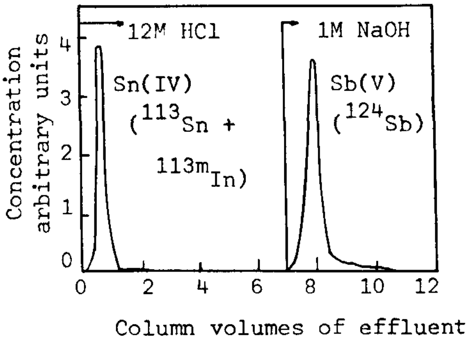


Figure 50

Separation of ^{113}Sn and ^{124}Sb tracers (335)

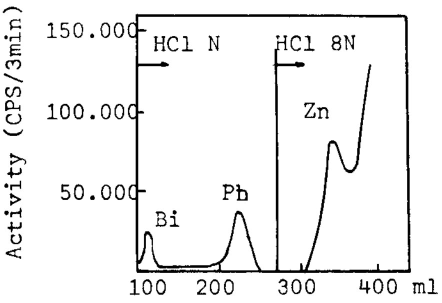


Figure 51

Separation of Pb and Bi traces from Zn-matrix (351)

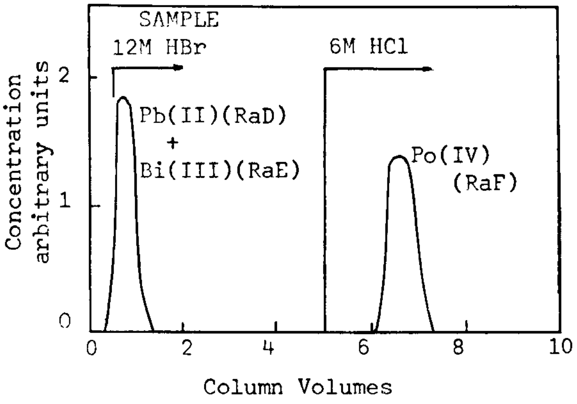


Figure 52

Separation of Pb, Bi and Po (436)

Pb forms strong chloride complexes and is therefore easily eluted with 1-2 N HCl. Leclerq and Duyckaerts (351) separated Pb from $ZnSO_4$ by adsorption on a cation exchanger from a neutral medium, then by elimination of SO_4^{2-} by washing with water and finally by elution of Pb with 1 N HCl. ^{212}Bi is eluted even faster than lead. Zn is removed with 8 N HCl (figure 51). A few separations of ^{211}Pb from Ac were described in section 6.4. Müller (418) for example elutes ^{211}Pb and ^{211}Bi together with 2 N HCl. ^{223}Ra, ^{227}Ac and ^{227}Th remain on the column at this stage of the separation. A cation exchange column (such as Nalcite HCR) loaded with ^{228}Th can be used as a generator for ^{212}Pb. 0.5 N HCl elutes the ^{212}Bi and 1 % ^{212}Pb, 2 N HCl elutes ^{212}Pb and 1 % ^{224}Ra (213).

Pb also forms strong bromide complexes. Fritz and Greene (184) were able to separate it from Al, Co, Cu, Dy, Fe, Ga, Mn, Ni, Sr, Y, Zn and Zr by elution with 0.6 M HBr. Bi and Cd are eluted before Pb with 0.5 N HCl.

Bi forms stronger bromide complexes than Pb and is therefore eluted first. This was put to advantage for the separation of both elements from each other (182). A separation of Bi and Pb tracers with 12 M HBr from Po was described by Nelson and Michelson (436) (fig. 52). Pb forms weak fluoride complexes in 1 M HF. It can therefore be retained from this medium together with Co, Mn, Cu, Ni, Cr^{3+} (partly) while As^{5+}, Sb^{5+}, Al, Fe, Sn, Ti, Zr, V^{5+}, Nb, Ta, Mo, W and most of the Cr^{3+} are eluted (235).

Several other separations of Pb make use of the complexing properties of this element. Bhatnagar and Trivedi (52) describe several separations of Pb with $NaNO_2$. Pb is eluted before Tl and Bi with a 5 % solution. Cd however forms stronger complexes and can be separated from Pb by elution with a 2 % solution. Pb is eluted with 0.1 M $Na_2S_2O_3$ from Amberlite IR-120 while Pb, Ba, Ca, Sr, Mg, Fe^{3+}, Fe^{2+} are not (286).

Several authors describe the use of acetate solutions. Khopkar and De (299) separated Pb by elution with 1 M ammonium acetate as Sr, Ba and Al remain on the column. De and Majumdar (132) eluted Pb with 0.25 M ammonium acetate while Ag and Hg^{2+} were retained. A separation from Ba was also reported by Minami (410).

Pb can be separated from Cu by elution as the tartaric acid complex. Cu is retained as the $Cu(NH_3)_4^{2+}$ ion (340). Elution as the glycerol complex serves to separate Pb from Tl (99). Pb elutes before Ba (638) with EDTA

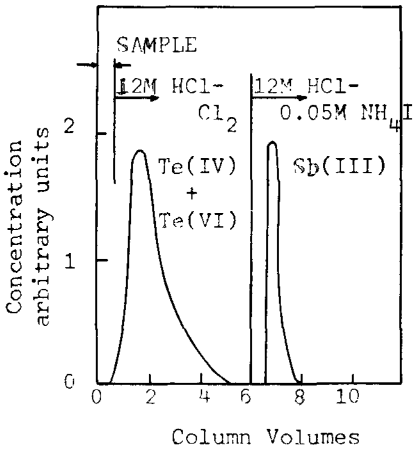


Figure 53
Separation of Te^{4+} and Te^{6+} from Sb^{3+} with HCl (438)

of pH 4 - 4.5 and Ca (362). With a 0.01 M solution of pH 2.2 Pb **is, however, adsorbed while Bi, Fe and Th elute (299). With 5 % citric acid** of pH 2.7 Ce and Zr are eluted while Pb is retained.
A special procedure for the isolation of ^{212}Pb from Th was described by Kahn (277). Thorium was distilled from a $Th(NO_3)_4$ solution into the upper part of a Soxhlet extractor, where Pb, its decay product, was collected on a small cation exchange column from which it was removed later with 1 N HCl.

6.6.11. As - Sb - Bi

Arsenic is not taken up by cation exchange resins and this has been used as the basis for some separation methods such as As from Cu, Co and Ni (449) and from Sb and Sn (365). In the presence of Fe^{3+}, As^{5+} is not completely recovered (154). Reduction to Fe^{2+} eliminates this interference. As and Sb can be eluted together with 0.5 N HCl, while Cu remains on the resin. This separation was included in a scheme for the analysis of purified Zr by neutron activation analysis (403).

Sb^{3+} is weakly adsorbed from HCl and HBr and from low molarity $HClO_4$ but relatively strongly from high molarity $HClO_4$ (436, 438). Sb^{5+} is very strongly adsorbed from the three concentrated acids (see also: 335). Sb^{3+} and Sb^{5+} can be separated by elution with 9 M HBr. Sorption in 12 M HCl - Cl_2 permits the elution of Te^{4+} and Te^{6+} but causes the adsorption of Sb^{5+}. Sb is eluted as Sb^{3+} with 12 M HCl - 0.05 M NH_4I (fig. 53). Giovannetti et alii (206) use the same principle in a neutron activation analysis technique for the determination of trace elements in plasma. Au and Sb^{5+} or Fe and Sb^{5+} are adsorbed selectively from 8 N HCl-0.1 N Na^+ on a Dowex 50WX4 column (100-200 mesh, 10 cm x 5MM), ^{122}Sb is then removed by elution with 12 N HCl - 0.05 N NH_4I or alternatively Fe can be eluted with 5 N HCl while Sb is retained. The separation of Sb^{3+} by elution as an anionic tartrate complex was described by Khorasani and Khundar (300) by Kimura et alii (305) and by Sulcek et alii (714). The method was used to eliminate Sb-matrix activity from Fe activity in a neutron activation procedure described by Simkova et alii (551) (see 6.6.5.). Sb^{3+} can be separated from Rb, Cs, Mg, Ba, Ce, Ag, Tl and Pb by elution with 0.33 M tartaric acid (547). Dilute oxalic acid was used for the separation of Sb^{3+} and Sb^{5+} (520).

Bi is not adsorbed from HBr and HCl $>$ 0.5 M and can thus be separated by elution from many elements. Bi (^{212}Bi) was separated from Pb and Zn with 1 N HCl (351) (fig. 51), together with ^{211}Pb (^{211}Bi) with 2 N HCl from ^{223}Ra, ^{227}Ac and ^{227}Th (418) and together with ^{210}Pb (^{210}Bi) from ^{210}Po with 12 M HBr (436). A separation from U was carried out with 90 % isopropanol - 10 % 6 N HCl as the eluting agent (322). Its adsorbability from very dilute HCl was used by Zagorchew et alii (651) for a separation of Te (eluted with 0.1 N HCl) from Bi (2 N HCl). ^{210}Bi can be separated from Po by elution with 2 N HNO_3 (496). Lu're and Filipova (365) separated Bi from Cu and Pb as the iodide complex and from Sb as the thiocyanide complex. Bi forms also stable anionic complexes with EDTA and can be separated in this way from Zn, Cd and Pb (599). The separation of Bi from many other ions by elution with 0.01 M dithizone in tetrahydrofuran - 1 M HNO_3 was described by Orlandini (669).

6.6.12. Se - Te - Po

Se^{4+} is not adsorbed on cation exchangers even from media with low HCl molarity (0.1 N HCl) (568, 571). Te^{4+} (568, 304) and Po (126) however, are adsorbed from such media. The adsorption decreases rapidly with increasing molarity of the acid and according to Nelson (438), Te^{4+} and Po^{4+} are not adsorbed at all from HCl of a molarity higher than 0.5 M. This was put to advantage by Nelson (438) for the separation of Te and Sb (fig. 53). Te^{4+} and Te^{6+} are eluted with 12 M HCl - Cl_2 while Sb as Sb^{5+} remains adsorbed. Sb is recovered by reduction to Sb^{3+} (elution with 12 M HCl + 0.05 M NH_4I). Kimura (303) separated Te together with I, Ru, Rh from other radioisotopes present in radioactive dust (Zr, Nb, U, the rare earths, the alkaline earths) by elution with 0.2 N HCl. An interesting non-radiochemical procedure for Te was described by Russian authors (568). Te^{4+} is separated from the chloride complexes of the **platinum group metals by sorption on a cation exchange column from 0.1 N** HCl. Te is then eluted with an ammoniacal solution. Se and Te were **separated (193) by adsorption of the latter from 0.00001 N to 0.01 N HCl** on KU-2. Te can be separated from Bi by elution with 0.1 N HCl. Bi is recovered with 2 N HCl (651). Te^{6+} is not adsorbed on cation exchange resins. Therefore Te can be separated from Cu, Fe, Ni, Co, Bi after oxidation with dichromate and elution with 0.3 N HCl (626).

Few cation exchange separations of Po have been published. Indeed, the author of a review about the analytical chemistry of polonium, Lange (346), states that ion exchange resins at both tracer and milligram levels are not reliable tools for the separation or the purification of Po. A procedure for the partial purification of ^{210}Bi (RaE) from Po is described by Radhakrishna (496). Bi and Po are eluted from a Dowex 50 column with successively 2 N HNO_3 and 2 N HCl.

A promising elution medium for these elements seems to be HBr. The adsorbabilities of Se^{4+}, Te^{4+} and Po^{4+} in low molarity HBr are low but they increase with increasing molarities (436). This allows for example a separation of Se and Te in 12 M HBr and a separation of Pb and Bi from Po by elution of the former two ions with 12 M HBr. Po is desorbed with 6 N HCl.

Organic complexing agents were studied in a few instances. Smith and

Reynolds (555) found that Te is not adsorbed from 0.1 N oxalic acid. EDTA can be used to desorb Po (304).

Procedures

The series "radiochemistry of the elements" contains several detailed cation-exchange procedures. Therefore this section starts with a short summary of these procedures.

NAS-NS3001 (Cd): contains no cation-exchange procedure

NAS-NS3002 (As): contains no cation-exchange procedures

NAS-NS3003 (Fr): procedure 1 (262) describes the carrierfree isolation of Fr from thorium cyclotron targets involving a cation exchange separation of Fr from silicotungstic acid.

NAS-NS3004 (Th):

Procedure 7 (32): determination of ^{230}Th in coral samples. Th is **adsorbed from mineral acid while other elements are eluted. The desorption** is carried out with oxalic acid.

Procedure 8 (32): determination of ^{230}Th in old fission product material. See procedure 7.

Procedure 9 (32): tracer method for the analysis of Th isotopes. See procedure 7.

Procedure 19 (Choppin and Sikkeland, no further literature reference): a separation of the elements Fr through U. Contains a Ra-Ac separation with HNO_3 as the eluting agent.

NAS-NS3005 (F, Cl, Br, I): contains no cation-exchange procedure

NAS-NS3006 (Am, Cm):

Procedures 5-6: (K. Street in 398) Am and Cm are separated from other activities with the concentrated HCl procedure.

Procedure 9: (Hoof et alii, no further literature reference). Purification of Am and Cm. Contains two elutions with 13 M HCl.

Procedure 11: Separation of Am and Cm from a neutron-irradiated Pu-Al alloy. The concentrated HCl-technique and a lactate separation are **described.**

Procedure 12: (Hoffman et alii, no literature reference). Separation of trace amounts of fission products. The eluting agents used are ethanol-HCl and α-hydroxyisobutyrate solution.

NAS-NS3007 (Cr): contains no cation-exchange procedure

NAS-NS3008 (Rh):

Procedure 7 describes a separation of ^{103m}Rh from ^{103}Rh with HCl.

Procedure 16: describes the separation of Rh as $Rh(CN)_6^{-3}$ from Cu as $Cu(NH_3)_4^{2+}$.

NAS-NS3009 (Mo): contains no cation-exchange procedure

NAS-NS3010 (Ba, Ca, Sr):

Procedure 29: ion exchange procedure for ^{90}Sr in water. ^{90}Sr and ^{90}Y are separated from each other with citrate.

Procedure 34 (166): determination of Sr and Ba in urine. Sr and Ba are separated with EDTA and citrate.

NAS-NS3011 (Zr, Hf):

Procedure 11 (226): separation of Zr and Hf from Ta bombarded with 5.7 BeV Protons. Zr and Hf are separated by successive elution with 0.5 M and 3 M H_2SO_4.

NAS-NS3013 (Be):

Procedure 1 (162): separation of Be from stone meteorite material. Be is separated from Al by elution with 1.1 N HCl.

Procedure 6 (Merrill et alii, no ref. given): separation of Be from clay. Al and Mn are eluted with EDTA, while Be remains adsorbed.

NAS-NS3014 (In): contains no cation-exchange procedures.

NAS-NS3015 (Zn):

Procedure 1 (Hicks et alii, no further literature reference): separation from fission product. Purpose of ion-exchange separation not specified.

NAS-NS3016 (Pa): contains no cation-exchange procedures.

NAS-NS3017 (Fe):

Procedure 4 (364): separation of radioisotopes from bomb debris. Fe is retained while Ru, Zr, Nb are eluted with low molarity HCl and eluted with oxalic acid, while a few other elements are retained.

NAS-NS3020 (rare earths Sc, Y, Ac):

Procedure RE-1, W. Nervik (coauthor of the review): Separation of R.E.'s with lactate (gradient elution)

Procedure RE-2 Bunney et alii (84): Separation of R.E.'s with lactate

Procedure RE-3 Cushing (123): Separation of Nd from other R.E.'s with lactate

Procedure RE-4 Monk (413): Separation of R.E.'s with α-HIBA (gradient elution)

Procedure Ac-2 Cabell (96): **separation** of Ac from its daughters with mineral acids

Procedure Ac-3 Hyde as cited by Meinke (coauthor of the review): **separation of Ac from the rare-earth activities originated by the bom**bardment of thorium metal with protons. Eluting agent: citric acid.

NAS-NS3021 (Tc):

Procedure 1 (694): separation from Cu

Procedure 7 (Anders, author of the review): separation from Cu.

NAS-NS3022 (V): contains no cation-exchange procedures

NAS-NS3023 (Sn): contains no cation-exchange procedures

NAS-NS3024 (Mg):

Procedure 1 and 5: elimination of anionic activities

NAS-NS3025 (rare gases): contains no cation-exchange procedures

NAS-NS3026 (Hg): contains no cation-exchange procedures

NAS-NS3028 (Re): contains no cation-exchange procedures

NAS-NS3029 (Ru): contains no cation-exchange procedures

NAS-NS3030 (Se): contains no cation-exchange procedures

NAS-NS3031 (transcurium elements):

Procedure 2 (no reference): separation from day-old fission product samples. Actinides and lanthanides are separated with ethanol-HCl.

Procedure 3 (no reference): separation of the elements from each other with α-HIBA.

Procedure 5 (200): purification of Mv produced from ^{253}Es. Separation of Mv/Fm/Es/Cf with α-HIBA.

Procedure 7 (594): Removal of macroimpurities from tracer transcurium elements. Elution with HCl.

NAS-NS3032 (Al, Ga):

Procedure 7 (507): preparation of carrierfree ^{26}Al from Mg. The purpose of the cation-exchange step is not described.

Procedure 14 (162): see procedures for Be (NAS-NS13)

NAS-NS3033 (Sb): contains no cation-exchange separations

NAS-NS3034 (Ti): contains no cation-exchange separations

NAS-NS3035 (Cs): contains no cation-exchange separations

NAS-NS3036 (Au): contains no cation-exchange separations

NAS-NS3038 (Te): contains no cation-exchange separations

NAS-NS3040 (Pb): contains no cation-exchange separations

NAS-NS3041 (Co): contains no cation exchange separations

NAS-NS3042 (W): contains no cation-exchange separations

NAS-NS3043 (Ge): contains no cation-exchange separations

NAS-NS3044 (Pt): contains no cation-exchange separations

NAS-NS3045 (Ir): contains no cation-exchange separations

NAS-NS3046 (Os): contains no cation-exchange separations

NAS-NS3047 (Ag): contains no cation-exchange procedures

NAS-NS3048 (K):

Procedure 3 (77): carrierfree separation of ^{42}K from Na, Rb and Cs. Elution with HCl.

NAS-NS3049 (Si): contains no **cation-exchange procedures**

NAS-NS3051 (Ni): contains no cation-exchange procedures

NAS-NS3053 (Rb):

Procedure 7 (97): activation analysis in minerals, rocks, meteorites. Separation from other alkalis by elution with HCl.

Procedure 1 (77): activation analysis in **alkali carbonates, chlorides,** vegetation, water. Separation from other **alkali metals with HCl.**

NAS-NS3054 (S): contains no cation-exchange procedures

NAS-NS3055 (Na):

Procedure 4 (77): see procedure 1, NAS-NS3053

NAS-NS3056 (S): contains no cation-exchange procedures

NAS-NS3058 (Pu):

Procedure 9a (358): separation of Pu from irradiated U. Pu^{4+} remains adsorbed from low molarity HNO_3 and 2 M HCl, while most other metal ions are eluted.

Procedure 18 (652): separation of Np^{4+} from Pu^{3+}. Np^{4+} is eluted with 0.02 N HF.

The reports NAS-NS3012, 3018, 3019, 3027 (Cu), 3037 (Po), 3039 (Nb, Ta), 3050, 3052, 3057 (Ra) and 3092 (U) were not available.

Procedure 1

Separation of carrierfree ^{137}Cs from U-fission products

Source: J. Korkisch, K.A. Orlandini Anal. Chem. 40, 1127 (1968)

Apparatus:

Quartz columns, diameter 5 mm, height of column 250 mm. The column is supported on a pad of quartz wool.

Eluting solution: 0.1 M 2-thenoyltrifluoroacetone (TTA) in pyridine. The solution should be prepared at most 3 days before use.

Preparation of column: soak 1 gram Dowex AG50WX8, 100-200 mesh, H^+ form, in the eluting solution during 30 minutes. Transfer the resin slurry to the column and wash with 10-15 ml eluting agent.

Procedure:

1. To a 50 µl aliquot of the uranium fission product solution add 2-3 ml concentrated HCl.
2. Evaporate to about 0.5 ml
3. Cool down the solution to room temperature.
4. Add 9-10 ml of eluent solution
5. Pass the resulting solution through the column at a flow rate determined by the back pressure of the resin bed.
6. Remove the last traces of U and fission products by rinsing the resin bed with 30-40 ml of eluent at a flow rate of 1.5 ml/min.
7. Remove the residual TTA by washing the bed with 5 ml pyridine.
8. Remove the residual pyridine by washing the resin bed with 5 ml H_2O.
9. Elute ^{137}Cs with 10-20 ml 6 M HCl.

Remark: the authors also describe a procedure allowing the regeneration of the column.

Procedure 2

Separation of ^{223}Fr from ^{227}Ac

Source: K.H. Lieser, E. Kluge Radiochim. Acta 7, 3 (1967)

Principle:
^{227}Ac is adsorbed by Dowex 50 while ^{223}Fr is eluted with a chromate containing eluant. The eluate is sent through a column of **silica gel** loaded with $BaSO_4$. ^{223}Fr is not adsorbed, but ^{223}Ra, ^{211}Pb and ^{209}Tl remain on the column, the former as sulfates, the latter as chromate.

Characteristics of the columns:
Column I: Dowex 50, diameter 4.5 mm, height of bed 60 mm, 100-200 mesh, NH_4^+ form.
Column II: **Silica gel containing 30 % $BaSO_4$, diameter 5 mm, height of** bed 60 mm, particle dimensions 0.2 - 0.5 mm.

Procedure:
1. Load the first column with 0.1 m Ci of ^{227}Ac
2. Elute with 0.5 M NH_4Cl containing 500 mg/l CrO_3. A pH of 9.5 - 10 is obtained by the addition of concentrated NH_4OH. To obtain a flow rate of 3.3 ml/min the application of external pressure is required.
3. Collect the eluate in fractions of 5 ml.

Results:
The largest quantity of ^{223}Fr is present in fractions 2-6 (elution time 9 min.). No other activities can be detected. CrO_3 leaves the column after 100 ml. A yield of 90 ± 2 % with 99.98 % purity is obtained.

Procedure 3

Separation of alkali metals

Source: F. Nelson, D.C. Michelson, H.O. Phillips, K.A. Kraus J. Chromat. 20, 107 (1965).

1. Evaporate a suitable aliquot of the chloride containing solution of the **alkali metals to dryness. Redissolve the residue in 250 μl of water.**
2. Apply the sample to a column of Duolite C-3 (0.28 cm^2 x 4 cm, **pre-treated with distilled water). Let the sample solution pass into the bed.**
3. Elute Li with 3.3 ml 2.4 M HCl-80 % (vol.) methanol at a flow rate of 1 cm/min.

4. Elute Na with 6.6 ml 2.4 M HCl-80 % (vol.) methanol.

5. Elute K and Rb together with 5 ml 1.5 M HCl.

6. Elute Cs with 4.4 ml 6 M HCl.

7. Evaporate the K-Rb fraction to near dryness and take up the residue in 2 M HCl.

8. Apply the solution to a column of Duolite C-3 (0.28 cm^2 x 15 cm, pretreated with 1.5 M HCl).

9. Elute K with 10.5 ml 1.5 M HCl at a flow rate of 0.5 cm/min.

10. Elute Rb with 2.5 ml 6 M HCl.

Note: the whole procedure takes about 31/2 hours.

Procedure 4

Separation and production of carrierfree Sodium-24

Source: W. Parker, H. Bildstein, N. Getoff Radiochim. Acta <u>3</u>, 74 (1964)

1. Irradiate an amount of MgO or $Mg(OH)_2$ paste corresponding to 500 mg Mg in aluminium cans (with a fast flux of 10^{12} n/cm^2/sec and an irradiation time of 7 hours one obtains 100 mC of ^{24}Na).

2. Transfer the irradiated sample to a polyethylene centrifuge tube containing about 10 times as much hot water as the volume of the sample.

3. Heat on a water steam bath for about 15 minutes under vigourous stirring.

4. Centrifuge and repeat steps 2 and 3 on the residue.

5. Transfer the combined water extracts to a Dowex 50X8, H^+ (50-100 mesh) column (dimensions of the bed 300 mm high, 20 mm diameter).

6. Adsorb the ^{24}Na by letting the water run through the column.

7. Wash the resin with 500 ml distilled water.

8. Elute with about 250 ml HCl 1 N and check the elution with a G.M. detector/rate meter combination.

Procedure 5

Separation of Ba and Ra

Source: F. Nelson J. Chromat. 16, 403 (1964)

Apparatus:

Plastic material is used throughout the entire procedure. The chromatographic column consists of a section of plastic tubing, pulled out to a tip at one end. A porous teflon plug is inserted to retain the resin.

Preparation of the eluting agent:

The eluting agent is $(NH_4)_2H_2EDTA$. The pH is adjusted to the required value with conc. NH_3. If no $(NH_4)_2H_2EDTA$ is available it can be prepared from the sodium salt as follows: pass a 10 ml aliquot of 0.1 M Na_2H_2EDTA through a 2.0 cm^2 x 5 cm column of Dowex 50X8 in the H^+ form. Wash the column with distilled water: the effluent contains $(NH_4)_2H_2EDTA$. Adjust the concentration with H_2O and the pH with conc. NH_3.

Procedure:

1. Evaporate the nitric acid solution containing Ba and Ra to near dryness in a teflon beaker. Take up the residue in 0.4 ml of 0.01 M $(NH_4)_2H_2EDTA$ of pH 8.8.
2. Pass the sample through a column of Dowex 50X8 (400 mesh), 0.28 cm^2 x 3 cm, flow-rate 0.6 cm/min.
3. Wash the column with 0.4 ml of 0.01 M EDTA solution at pH 8.8.
4. Elute Ba with 3 column volumes of the same solution.
5. Elute Ra with 2 column volumes of 0.01 M EDTA solution at pH 10.5.

Procedure 6

Separation of trace amounts of ^7Be from Li

Source: N.P. Rudenko, A.S. Zhukovskaya Radiokhimiya 9, 483 (1967)

The sample is a solution of deuteron irradiated $Li_2SO_4.H_2O$ containing 0.05 % ^7Be. The matrix is removed by precipitation as lithium sulphate from water-ethanol. The final purification is carried out by cation exchange.

1. Evaporate the initial solution to a weight ratio of $Li_2SO_4.H_2O$ in solution to water of 1:2, the point at which the first lithium sulphate crystals precipitate.
2. Add an amount of ethanol equal to four times the weight of lithium sulphate in solution and mix thoroughly until the lithium sulphate has precipitated completely.
3. Filter off the precipitate.
4. Wash the precipitate several times with ethanol containing 20 % water.
5. Combine the filtrate and wash waters (4 % of the initial Li-quantity are still present at this moment).
6. Pass the solution through a column of KU-2 (4 mm x 120 mm for an initial quantity of 2-3 g lithium sulphate) in the H^+ form.
7. Elute Li with 50 ml HCl 0.1 N.
8. Elute Be with 50 ml HCl 1 N.

Procedure 7

Determination of Mn, Sr and Ba by activation analysis in biological samples.

Source: I. Hadzistelios, C. Papadopoulou Talanta 16, 337 (1969)

The irradiation is performed on dry ashed plant or animal tissue.

Analytical procedure:

1. Transfer the sample (30-100 mg ash) to a 100 ml beaker.
2. Add one or two drops of a carrier solution containing 200 μg/ml of each of the elements Ba, Sr, Sc, Mn and La.
3. Add 2 ml 8 M HCl and 0.3 ml H_2O_2.
4. Evaporate to almost dryness on a hot plate.
5. Add 2 ml 8 M HCl.
6. Heat until a clear solution is obtained.
7. Apply the solution to the top of a 6 mm X 60 mm Dowex 1X8, Cl^- form column. Rinse the beaker twice with 8 M HCl.

8. Elute with 9 ml 8 M HCl and collect the effluent in a 100 ml beaker.

9. Evaporate to 0.5 ml on a hot plate.

10. Add 1.5 ml H_2O and 0.5 ml H_2O_2 and evaporate again to 0.5 ml.

11. Add 2 ml H_2O and evaporate again.

12. Repeat twice step 11.

13. Add 2 ml H_2O.

14. Apply the solution to the top of a Dowex 50WX8 (100-200 mesh) column, H^+ form.

Dimensions of the water swollen resin bed: 6 mm x 90 mm for animal tissues, 12 mm x 120 mm for plant tissues.

15. Wash the beaker several times with 0.1 N HCl and transfer these washings to the column.

16. Elute Na with 11.5 ml (50 ml for plant tissues) of 1.33 M HCl and discard the effluent.

17. Elute Mn with 9 ml (35 ml) 2 N HCl and collect the effluent for counting.

18. Elute Sr with 19 ml (100 ml) of 1.38 N HNO_3, collect and mount for counting.

19. Elute Ba with 14 ml (55 ml) of 1.75 M HNO_3, collect and mount for counting.

20. Elute Sc with 18 ml 0.9 M H_2SO_4.

21. Elute the rare earths with 6 M HNO_3.

Remarks: - the recovery of the elements is better than 99.8 %

- the main purpose of the method was the determination of Sr, Ba and Mn. It seems that Sc can also be determined by this method.

Procedure 8

Separation of trace rare earth radioisotopes from salts of adjacent rare earths.

Source: G.C. Martin Jr J. Inorg. Nucl. Chem. 26, 1621 (1964)

The elutions are carried out on Dowex 50WX12 (200-400 mesh) at elevated temperatures (60°-90° C). Columns of 13.2, 17.6 and 19.1 mm internal

diameter are used for quantities of resp. 12, 25 or 30 mg target material. Experimental details are listed in the table.

A = rare earth activity
B = rare earth target
C = concentration of hydroxyisobutyric acid (M)
D = pH of the eluant
E = flow rate in ml/min/cm^2
F = resin height in cm
G = temperature in °C
H = approximate time to beginning of first rare earth (in hours)
I = approximate time to end of first rare earth
J = approximate time to beginning of second rare earth
K = approximate time to end of second rare earth

TABLE

A	B	C	D	E	F	G	H	I	J	K
Lu	Yb	0.125	4.2	0.15	20	60	4	5 1/2	6	
Lu Yb	Tm	0.125	4.2	0.13	20	60	5	7	8	11
Lu	Tm	0.15	4.2	0.12	15	60	2 1/2	4	6 1/2	
Yb	Tm	0.175	4.0	0.16	20	60	2 1/2	4 1/2	4 3/4	7
Yb Tm	Er	0.20	3.8	0.17	20	60	4 1/2	6 1/4	7	9
Yb	Er	0.20	4.0	0.512	15	60	1 3/4	3 1/4	4 1/4	
Tm	Er	0.175	4.2	0.11	20	60	3	4 1/2	5	
Tm	Ho	0.175	4.2	0.16	15	60	2	3 1/4	5	
Er	Ho	0.20	4.2	0.13	20	60	2 1/2	4 1/4	4 1/2	
Er Ho	Dy	0.20	4.2	0.13	20	60	2 1/2	4 1/4	4 1/2	6 1/2
Er	Dy	0.20	4.2	0.13	15	60	2	3		
Ho	Dy	0.275	4.0	0.14	20	80	3 3/4	5 1/4	5 3/4	

A	B	C	D	E	F	G	H	I	J	K
Ho Dy	Tb	0.275	4.0	0.14	20	80	3 3/4	5 1/4	5 3/4	7
Ho	Tb	0.30	4.2	0.12	20	80	1 3/4	3	3 3/4	
Dy	Tb	0.275	4.2	0.14	20	85	2 1/2	4	4 1/2	
Dy Tb	Gd	0.275	4.2	0.13	20	85	3	4 1/2	5	6 1/2
Dy	Gd	0.30	4.4	0.11	20	85	1 1/2	3	4 1/2	
Tb	Gd	0.30	4.4	0.09	20	85	3	4 1/4	4 1/2	
Tb Gd	Eu	0.30	4.4	0.09	20	85	3	4 1/4	4 1/2	6
Tb	Eu	0.35	4.6	0.09	17	85	1 3/4	4		
Gd	Eu	0.30	4.4	0.07	16	85	6			
Gd Eu	Sm	0.325	4.4	0.09	20	85	3 3/4	5	5 1/4	
Gd	Sm	0.325	4.4	0.12	15	85	2 1/4	3 1/4		
Eu	Sm	0.30	4.6	0.14	15	80	2 3/4	4 1/4	4 1/2	
Eu Sm Pm		0.30	4.6	0.14	20	80	3 1/4	4 3/4	5 1/4	7
Sm Pm		0.45	4.2	0.15	20	90	3	5 1/2	5 1/2	
Sm Pm	Nd	0.45	4.2	0.14	20	90	3 1/2	5 3/4	6 1/4	8
Sm	Nd	0.40	4.6	0.12	20	70	1 3/4	3 1/2	4 1/4	
Pm	Nd	0.425	4.4	0.13	20	85	3 3/4	5	5 1/2	
Pm	Pr	0.425	4.4	0.17	15	85	2	3 1/4		
Nd	Pr	0.475	4.2	0.18	20	80	4	5 1/2		
Nd Pr	Ce	0.475	4.2	0.18	20	80	4	5 1/2	5 1/2	7
Nd	Ce	0.475	4.5	0.16	15	80	2	3	4	
Pr	Ce	0.45	4.6	0.17	20	80	3 1/4	4 3/4		
Pr Ce	La	0.45	4.6	0.17	20	80	3 1/4	4 3/4	5 1/4	7 3/4

A	B	C	D	E	F	G	H	I	J	K
Pr	La	0.525	4.8	0.17	15	80	2	3	5	
Ce	La	0.525	4.8	0.17	20	80	2 3/4	4	5 1/4	

Procedure 9

Separation of R.E.'s from neutron irradiated titania.
Source: D.L. Massart, J. Hoste Anal. Chim. Acta 41, 378 (1968)

1. Heat the titania (100-300 mg) with a mixture of 15 ml concentrated H_2SO_4 + 10 g $(NH_4)_2SO_4$.
2. Upon cooling, dilute with water to 100 ml.
3. To eliminate the **alkali metal activities, coprecipitate the R.E.'s** with titania by addition of 14 N NH_4OH.
4. Centrifuge the precipitate, discard the supernatant, wash with water to which a drop of NH_4OH was added and redissolve in 3 N HCl + a few drops of H_2O_2.
5. Dilute with water to 0.5 M HCl and add H_2O_2 until the colour **intensity of the orange peroxide complex remains constant.**
6. Apply the solution to a column of Dowex 50WX8 100-200 mesh(20 cm x 2 cm^2) and adsorb the mixture in the narrowest band possible.
7. Elute Ti with 3 N HCl + 2 % H_2O_2.
8. Elute the R.E. group with 6 N HCl.

Note: The same article describes the separation of ^{140}La from other R.E.'s present and from impurities that accompany the R.E. group during the **separation from Ti (^{51}Cr, ^{181}Ir, residual ^{76}As, ^{24}Na, ^{42}K, ^{122}Sb).**

Procedure 10

Isolation of ^{227}Ac from ^{231}Pa and ^{227}Ac daughters
Source: F. Nelson J. Chromat. 16, 538 (1964)

1. Dissolve 3 mg of ^{231}Pa (present as the hydroxide) in 1 ml of concentrated HF in a Teflon evaporating dish. Reduce the volume to ca. 0.5 ml by evaporation.
2. Take up the solution in 1 ml of 0.5 M HCl - 0.5 M HF, warm up and apply to a column of Dowex 50X4 (-400 mesh, 0.28 cm^2 x 5 cm) which has been pretreated with 0.5 M HCl - 0.5 M HF.
3. Elute Pa with 3 column volumes of the same solvent.
4. Elute Ra, Ac and Th with 10 column volumes of 6 M HCl - 1 M HF.
5. Place the Ac-fraction in a Teflon evaporating dish, add 1 ml of concentrated $HClO_4$, evaporate to a volume of ca. 0.1 ml.
6. Take up the residue in 0.5 ml of warm 8.5 M $HClO_4$ - 0.5 M HCl - 0.1 M HF and apply to a column of Dowex 50X4 (-400 mesh, 0.28 cm^2 x 4 cm, thermostatised at 50°C).
7. Elute with 5 column volumes of 8.5 M $HClO_4$ - 0.5 M HCl - 0.1 M HF and 2 column volumes of 8.5 M $HClO_4$ - 0.5 M HCl. ^{223}Fr, ^{211}Pb, ^{211}Bi, ^{223}Ra and residual ^{231}Pa leave the column.
8. Elute ^{227}Ac with 4 column volumes of 6 M HNO_3.
9. Elute ^{227}Th with 6 M HCl - 1 M HF.

Procedure 11

Separation of the daughter products from ^{232}Th

Source: G. Duyckaerts, A. Lejeune J. Chromat. 3, 58 (1960)

1. To a solution of a few ml containing 3 g of $Th(NO_3)_4$, add HCl and 0.05 g $BaCl_2$.
2. Precipitate $BaCl_2$ with 5 or 6 volumes of 12 N HCl. The precipitation carries a large part of the Ra and its daughter products.
3. Filter off the precipitate on a fritted glass filter.
4. Dissolve the precipitate in the minimum volume of water and apply the solution to a column of Dowex 50.
5. Elute with 0.01 M EDTA (pH adjusted at pH = 9 by addition of concentrated NH_3) at a flow rate of 0.1 ml/cm^2/min.

Result: completely separated peaks of ^{228}Ac, ^{212}Bi, ^{212}Pb and ^{228}Ra are obtained.

Procedure 12

Separation of Hf and Zr tracers from accompanying ions.
Source: J. Korkisch, K.A. Orlandini Talanta 16, 45 (1969)

Ion Exchange resin: air-dried Dowex 50WX8 (100-200 mesh, H^+ form)
Pretreatment of resin bed: soak 1 g of resin for about 5 ml in a few ml of the eluting agent. Transfer the slurry to the column (250 mm x 5 mm). The resulting bed is supported by a pad of glass or quartz wool and washed with 5-10 ml of the eluent.
Eluent: 0.1 M tri(n)octylphosphineoxide (TOPO) in methanol - 12 M HNO_3 (19:1)
Sorption and elution:
A mixture of 0.5 ml of 12 M HNO_3, containing up to 5 mg of Hf and/or Zr (plus ^{181}Hf and ^{95}Zr tracers) and other metal ions, and 9.5 ml of methanol containing 386 mg of TOPO, is cooled to room temperature and passed through the pretreated resin bed at a flow-rate corresponding to the back-pressure of the resin column (about 0.3 ml/min). Under these conditions many elements (the rare earths, alkaline earths, **alkali metals,** Fe, Co, Ti) are strongly retained by the resin while Hf and Zr pass into the effluent. Elution of Hf and Zr is completed by passage of 10 ml of the eluent at the same flow rate.

Procedure 13

Separation of ruthenium from fission product solutions
Source: A. Guillon, M. Colonomos, R. Sauvagnac Radiochim. Acta 1, 89 (1963)

Carriers:
Nb-carrier solution: add 36 N H_2SO_4 to 100 mg Nb_2O_5. Heat until complete

dissolution is obtained and dilute to obtain 12 N to 15 N H_2SO_4 and 200 μg Nb/ml.

Ru-carrier solution (6 μg/ml): dissolve $(NH_4)_2Ru(H_2O)\ Cl_5$ in 6 N HCl.

Zr-carrier solution (200 μg/ml): dissolve $ZrCl_4$ in HCl 6 N. The solution is stable during 1 week.

Procedure:

1. To a beaker of 30 ml, add successively 0.5 ml of the Nb, the Zr and the Ru-carrier.
2. Add 0.1 ml to 1 ml of the fission product mixture (the article **describes the procedure for the dissolution of the irradiated combustible in** HCl 6 N).
4. Add 1-2 ml of a 1 mg/ml solution of NaCl in HCl 6 N.
5. Evaporate to dryness and redissolve the residue in 0.5 ml N HCl.
6. Wash the cation exchange column (height of bed 70 mm, diameter 5 mm, Dowex 50WX8 100-200 mesh, H^+ form) with 0.2 N HCl.
7. Adsorb the fission solution on the top of the column. Wash the beaker twice with 0.5 ml portions of 1 N HCl and apply those washings to the top of the column.
8. Apply successively 1.5 ml, 2 ml, 5 ml of 0.2 N HCl to the column. Wait for the complete passage through the column of each fraction to introduce the next. These fractions contain the Ru-activity.

Yield: 99 %

Purity: 1 ‰ of contamination for 50-day old fission mixtures.

Distribution Coefficients in HCl solutions (583)

Cation	0.1	0.2	0.5	1.0	2.0	3.0	4.0
ZrO^{2+}	10^5	10^5	10^5	7250	489	61	14.5
Th^{4+}	10^5	10^5	10^5	2049	239	114	67
La^{3+}	10^5	10^5	2480	265.1	48	18.8	10.4
Ce^{3+}	10^5	10^5	2460	264.8	48	18.8	10.5
Y^{3+}	10^5	10^4	1460	144.6	29.7	13.6	8.6
Ba^{2+}	10^4	2930	590	126.9	36	18.5	11.9
Hg^{+}[a]	10^4	7600	640	94.2	33	19.2	13.6
Al^{3+}	8200	1900	318	60.8	12.5	4.7	2.8
Sr^{2+}	4700	1070	217	60.2	17.8	10.0	7.5
Ga^{3+}	10^4	3036	260	42.58	7.75	3.2	0.36
Ca^{2+}	3200	790	151	42.29	12.2	7.3	5.0
Pb^{2+}[a]	10^4	1420	183	35.66	9.8	6.8	4.5
Fe^{3+}	9000	3400	225	35.45	5.2	3.6	2.0
Cr^{3+}	1130	262	73	26.69[b]	7.9	4.8	2.7
Tl^{+}[a]	173	91	41	22.32	9.9	5.8	3.3
Ni^{2+}	1600	450	70	21.85	7.2	4.7	3.1
Co^{2+}	1650	460	72	21.29	6.7	4.2	3.0
Mg^{2+}	1720	530	88	20.99	6.2	3.5	3.5
Mn^{2+}	2230	610	84	20.17	6.0	3.9	2.5
Fe^{2+}	1820	370	66	19.77	4.1	2.7	1.8
Cs^{+}	182	99	44	19.41	10.4	...	...
UO_2^{2+}	5460	860	102	19.20	7.3	4.9	3.3
Ag^{+}[a]	156	83	35	18.08	7.9	5.4	4.0
Cu^{2+}	1510	420	65	17.50	4.3	2.8	1.8
Hg^{2+}[a]	4700	1090	121	16.85	5.9	3.9	2.8
Zn^{2+}	1850	510	64	16.03	3.7	2.4	1.6
Rb^{+}	120	72	33	15.43	8.1	...	...
K^{+}	106	64	29	13.87	7.4	...	...
Be^{2+}	255	117	42	13.33	5.2	3.3	2.4
Ti^{4+}	10^4	297	39	11.86	3.7	2.4	1.7

V^{4+}		230	44	7.20	...	...	...
Na^+	52	28.3	12	5.59	3.6	...	...
Li^+	33	18.9	8.1	3.83	2.5	...	...
Sn^{4+}	10^4	45	6.2	1.60	1.2	...	...
Cd^{2+}	510	84	6.5	1.54	1.0	0.6	...
V^{5+}	13.9	7.0	5.0	1.10	0.7	0.2	0.3
Mo^{5+}	10.9	4.5	0.3	0.81	0.2	0.4	0.3
Se^{4+}	1.1	0.6	0.8	0.63	1.0	...	0.7
Bi^{3+}	Ppt.	Ppt.	1.0	1.0	1.0	1.0	1.0
As^{3+}	1.4	1.6	2.2	3.81	2.2	...	...
Sb^{3+}	Ppt.	Ppt.	Ppt.	Ppt.	2.8	...	...
Pt^{4+}	...	...	...	1.4	...	...	...
Au^{3+}	0.5	0.1	0.4	0.84	1.0	0.7	0.2
Hg^{2+}	1.6	0.9	0.5	0.28	0.3	0.2	0.2

[a] Done in nitric acid.

[b] More than one cationic species present.

Distribution Coefficients in HNO_3 (583)

Cation	0.1 N	0.2 N	0.5 N	1.0 N	2.0 N	3.0 N	4.0 N
Zr(IV)	10^4	10^4	10^4	6500	652	112	30.7
Hf(IV)	10^4	10^4	10^4	2400	166	61	20.8
Th(IV)	10^4	10^4	10^4	1180	123	43.0	24.8
La(III)	10^4	10^4	1870	267	47.3	17.1	9.1
Ce(III)	10^4	10^4	1840	246	44.2	15.4	8.2
Yb(III)	10^4	10^4	1150	193	41.3	16.0	9.0
Er(III)	10^4	10^4	1100	182	38.2	14.9	8.0
Y(III)	10^4	10^4	1020	174	35.8	13.9	10.0
Sm(III)	10^4	10^4	1000	168	29.8	10.9	7.2
Gd(III)	10^4	10^4	1000	167	29.2	10.8	6.9
In(III)	10^4	10^4	680	118	23.0	10.1	5.8
Se(III)	10^4	3300	500	116	23.3	11.6	7.6
Cr(III)	5100	1620	418	112	27.8	19.2	10.9

Hg(I)	10^4	7600	640	94	33.5	19.2	13.6
Ga(III)	10^4	4200	445	94	20.0	9.0	5.6
Al(III)	10^4	3900	392	79	16.5	8.0	5.4
Fe(III)	10^4	4100	362	74	14.3	6.2	3.1
Ba(II)	5000	1560	271	68	13.0	6.0	3.6
Sr(II)	3100	775	146	39.2	8.8	6.1	4.7
Pb(II)	10^4	1420	183	35.7	8.5	5.5	4.5
Ca(II)	1450	480	113	35.3	9.7	4.3	1.8
Cd(II)	1500	392	91	32.8	10.8	6.8	3.4
Co(II)	1260	392	91	28.8	10.1	6.1	4.7
Mn(II)	1240	389	89	28.4	11.4	7.1	3.0
Ni(II)	1140	384	91	28.1	10.3	8.6	7.3
Cu(II)	1080	356	84	26.8	8.6	4.8	3.1
Zn(II)	1020	352	83	25.2	7.5	4.6	3.6
Bi(III)	893	305	79	25.0	7.9	3.7	3.0
U(VI)	659	262	69	24.4	10.7	7.4	6.6
Mg(II)	794	295	71	22.9	9.1	5.8	4.1
Tl(I)	173	91	41.0	22.3	9.9	5.8	3.3
Ag(I)	156	86	36.0	18.1	7.9	5.4	4.0
Hg(II)	4700	1090	121	16.9	5.9	3.9	2.8
Cs(I)	148	81	34.8	16.8	7.6	4.7	3.4
Be(II)	553	183	52	14.8	6.6	4.5	3.1
Ti(IV)	1410	461	71	14.6	6.5	4.5	3.4
V(IV)	495	157	35.6	14.0	4.7	3.0	2.5
Rb(I)	118	68	29.1	13.4	6.6	4.1	2.9
K(I)	99	59	26.2	11.4	5.7	3.5	2.6
Te(IV)	40.3	19.7	8.5	5.0	2.4	0.6	0.2
Pd(II)	97	62	23.5	9.1	3.4	2.7	2.5
Rh(III)	78	44.7	19.5	7.8	4.1	2.1	1.0
Na(I)	54	29.4	12.7	6.3	3.4	2.0	1.3
Li(I)	33.1	18.6	8.0	3.9	2.6	1.7	1.1
V(V)	20.0	10.9	4.9	2.0	1.2	0.8	0.5
Mo(VI)	Ppt.	5.2	2.9	1.6	1.0	0.8	0.6
Nb(V)	11.6	6.3	0.9	0.2	0.1	0.1	0.1
Se(IV)	0.5	0.5	0.5	0.5	0.5	0.5	0.5

As(III)	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Distribution coefficients in HF of varied molarity (328)

Ion	Final HF concn., M				
	0.15	0.3	0.6	0.9	1.2
UO_2(II), Ti(IV) Zr(IV)	1	1	1	1	1
V(V)	2	2	2	1	1
Nb(V), Ta(V), Pa(V)	1	1	1	1	1
Mo(VI)	3.5	1.2	1	1	1
Fe(III)	25	5.4	1	1	1
Zn(II), Cd(II), Cu(II), Mn(II), Co(II), Ni(II)	10^3	10^3	10^3	10^3	10^3

Distribution Coefficients in H_2SO_4 (583)

Cation	0.1 N	0.2 N	0.5 N	1.0 N	2.0 N	3.0 N	4.0 N
La(III)	10^4	10^4	1860	329	68	24.3	12.1
Ce(III)	10^4	10^4	1800	318	66	23.8	11.8
Sm(III)	10^4	10^4	1460	269	56	20.1	10.0
Y(III)	10^4	10^4	1380	253	49.9	18.0	9.4
Yb(III)	10^4	10^4	1330	249	48.1	17.3	8.8
Gd(III)	10^4	10^4	1390	246	46.6	17.9	8.9
Er(III)	10^4	10^4	1300	242	48.6	16.7	8.5
Bi(III)	10^4	10^4	6800	235	32.3	11.3	6.4
Ga(III)	10^4	3500	618	137	26.7	10.0	4.9
Al(III)	10^4	8300	540	126	27.9	10.6	4.7
Hg(II)	7900	1790	321	103	34.7	16.8	12.2
In(III)	10^4	3190	376	87	17.2	6.5	3.8

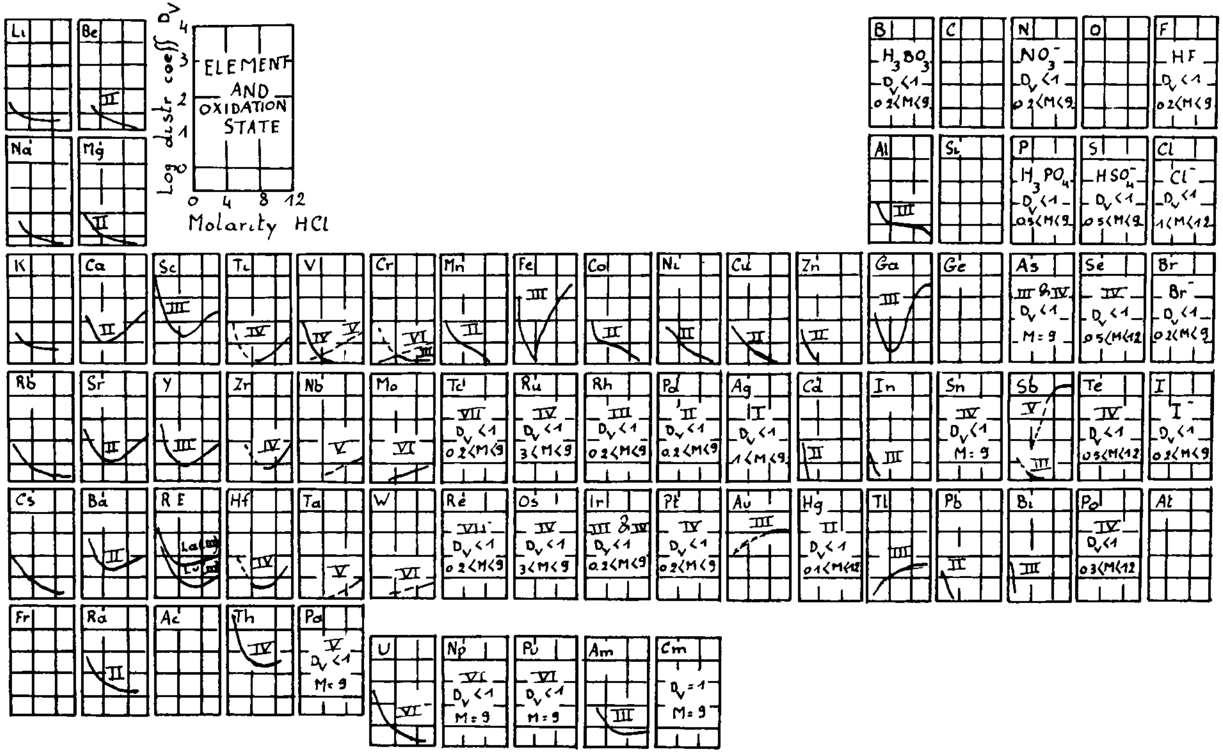
Mn(II)	1590	610	165	59	17.4	8.9	5.5
Fe(III)	10^4	2050	255	58	13.5	4.6	1.8
Cr(III)	198	176	126	55	18.7	0.9	0.2
Th(IV)	10^4	3900	263	52	9.0	3.0	1.8
Tl(I)	452	236	97	49.7	20.6	11.6	8.7
Tl(III)	6500	1490	205	47.4	12.0	7.2	5.2
V(IV)	1230	490	140	46.6	11.5	2.4	0.4
Ni(II)	1390	590	140	46.0	16.5	6.1	2.8
Fe(II)	1600	560	139	46.0	15.3	9.8	6.6
Cd(II)	1420	540	144	45.6	14.8	6.6	4.3
Zn(II)	1570	550	135	43.2	12.2	4.9	4.0
Co(II)	1170	433	126	42.9	14.2	6.2	5.4
Cu(II)	1310	505	128	41.5	13.2	5.7	3.7
Mg(II)	1300	484	124	41.5	13.0	5.6	3.4
Sc(III)	5600	1050	141	34.9	8.5	4.4	3.4
Be(II)	840	305	79	27.0	8.2	3.9	2.6
Cs(I)	175	108	52	24.7	9.1	4.8	3.5
Rb(I)	148	91	43.8	21.3	8.3	4.4	3.1
K(I)	138	86	41.1	19.4	7.4	3.7	2.9
Rh(III)	80	49.3	28.5	16.2	4.5	2.2	1.3
Pd(II)	109	71	32.5	13.9	6.0	3.8	2.7
Hf(IV)	2690	1240	160	12.1	1.7	1.0	0.7
U(VI)	596	118	29.2	9.6	3.2	2.3	1.8
Ti(IV)	395	225	45.8	9.0	2.5	1.0	0.4
Na(I)	81	47.7	20.1	8.9	3.7	2.6	1.7
Li(I)	48.0	28.2	11.7	5.8	3.0	1.6	1.1
Te(IV)	Ppt.	30.8	9.8	5.2	2.6	0.6	0.3
Zr(IV)	546	474	98	4.6	1.4	1.2	1.0
V(V)	27.1	15.2	6.7	2.8	1.2	0.7	0.4
Nb(V)	14.2	7.4	4.0	1.9	0.7	0.5	0.3
Mo(VI)	Ppt.	5.3	2.8	1.2	0.5	0.3	0.2
Se(IV)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
As(III)	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Distribution Coefficients of metal ions in $(NH_4)_2SO_4$ media (288)

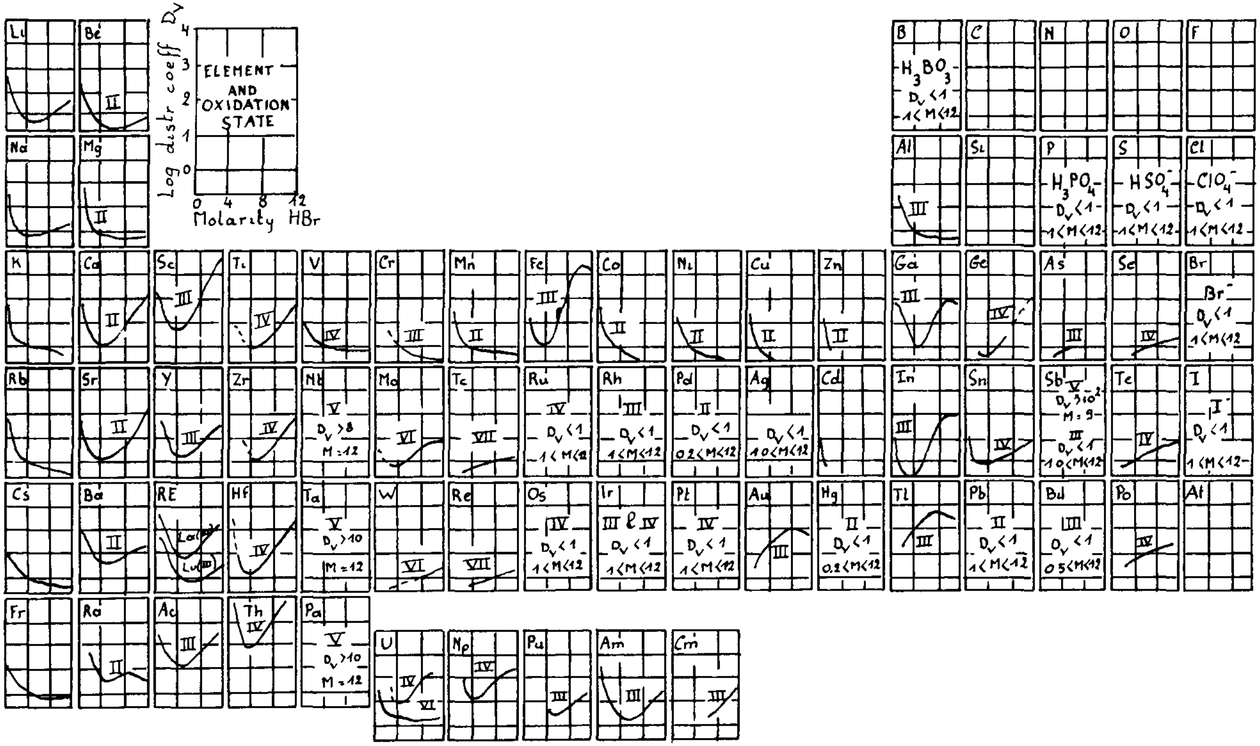
Ion	Concentration of $(NH_4)_2SO_4$ in 0.025 M H_2SO_4 (M)					
	0.10	0.15	0.20	0.30	0.50	1.0
Be	91	34	20	9.3	4.3	2.2
Be[a]	9.8		6.0	4.6		1.8
Mg			47		6.7	2.5
Ca			75	31	12	2.6
Ni			34	17	5.7	2.4
Zn			35	18	6.0	2.7
Co(II)			47	16	5.5	2.3
Cu(II)			47		6.0	2.5
Cd			31	14	4.5	1.7
Al			85	35	8.0	2.5
Cr(III)			2.7×10^2	77	11	0.2
Ga			64	12	5.3	2.5
In			31	10	4.0	2.5
Fe(III)			23	7.7	3.8	1.8
Bi(III)[a]	32		13	6.3	3.3	1.5
Sc	54	20	9.5		4.5	2.5
av.RE	1×10^3		2×10^2	70	12(for 0.60 M)	3.2
Ti[a]	5.4		4.5	3.5	2.5	1.5
Zr			1	1	1	1
Th	1.1×10^2	26	9.2		4.2	2.2
Mo			2.5	1.5	1.0	1
U(VI)	24	13	8.3		4.0	1.8
V(IV)			18	8.2	4.0	1.9

[a] Obtained keeping the concentration of free acid constant at 0.50 M

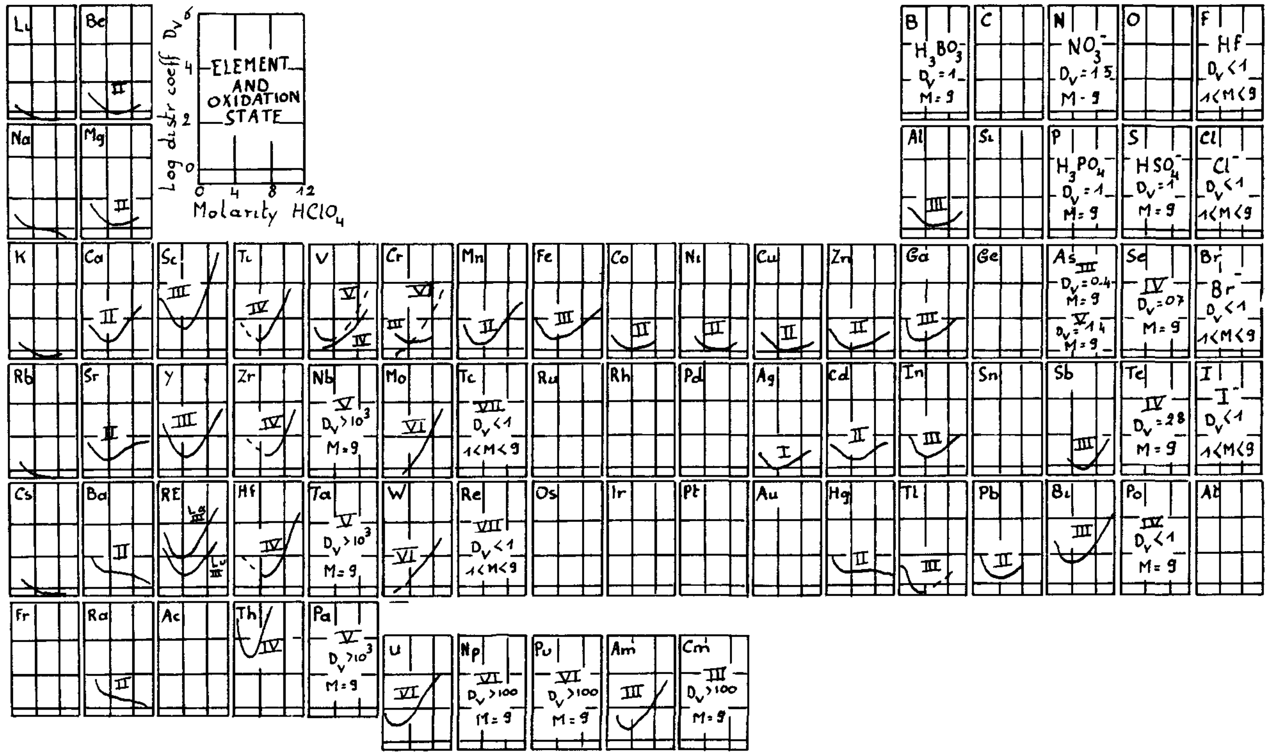
Adsorption of the elements from HCl solutions by a cation exchange resin (Dowex 50 X4) (438)



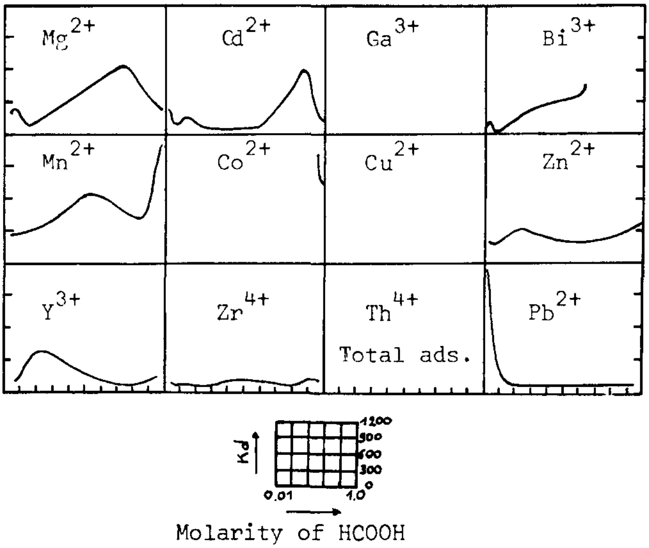
Adsorption of the elements from HBr solutions by a cation exchange resin (Dowex 50 WX4) (436)



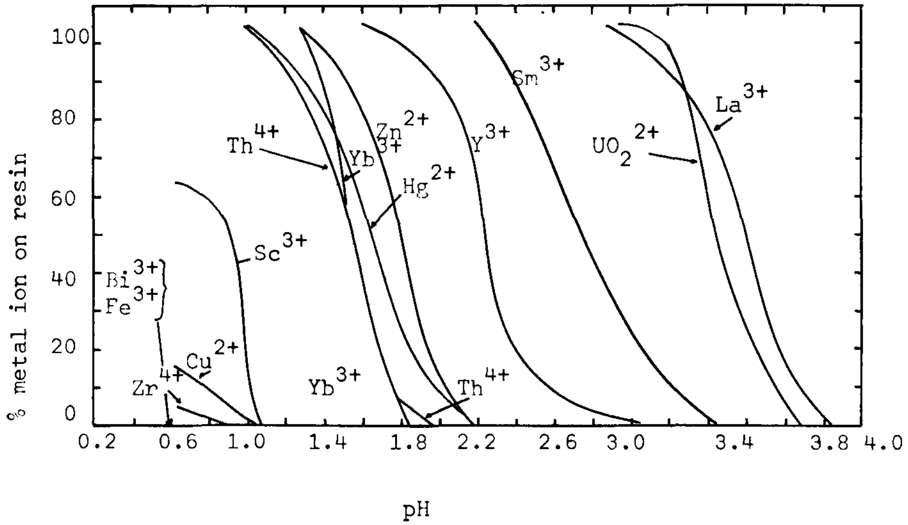
Adsorption of the elements from $HClO_4$ solutions by a cation exchange resin (Dowex 50 X4) (438)



Adsorption of cations from HCOOH solutions (493)



Retention from EDTA solutions of metal ions as a function of pH (188)



A large number of data can also be found in references 124 (HNO_3-HF and H_2SO_4-HF mixtures), 324 (HCl-organic solvent mixtures), 329 (HBr-organic solvent mixtures), 326 (HNO_3-organic solvent mixtures), 328 (HF-organic solvent mixtures), 187 (HCl-acetone), 53 (DMSO-HCl), 587 (ethanol-HCl), 327 (acetone-HCl).

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