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CHAPTER 8

ACTIVATION ANALYSIS WITH POST-IRRADIATION RADIOCHEMICAL SEPARATIONS

The most simple way of performing an activation analysis is by means of an instrumental method, without any chemical treatment. A number of analyses can be performed in this way by gamma spectrometry, particularly with selective detectors such as Ge(Li) and/or using coincidence set-ups, computer calculation of photopeak areas, etc.; in other cases, decay curve analysis is required. Examples can be found in Chapter 9. Such procedures can easily be applied if the matrix activity is low or short-lived, e.g. in the case of lead, silicon, iron.

It is often possible to determine a number of impurities in a sample without further chemical separations, on condition that the bulk of the matrix activity is eliminated, i.e. a single radiochemical separation may be sufficient.

I. Removal of Matrix Activity

(A) Pure Elements

After distillation of the selenium matrix as the bromide, one can detect the following impurities (1): sodium, potassium, scandium, chromium, iron, cobalt, copper, zinc, gallium, silver, cadmium, lanthanum, tungsten and gold as appears from Figure 8.1. One gram of tin can be distilled for more than 99.999(9)% as tetrabromide (2). The gamma spectrum of the residue of 1 g of irradiated tin is shown in Figure 8.2. Note the interference from the radioactive indium daughters of tin with the detection of some impurities. If irradiated titanium is brought on a Dowex 1–X8 column in 1M HF–9M HCl, most of the impurities remain on the resin (As, Sb, W, Cu, Ta, Zn, Co, Fe, Au, Sn, Mo) whereas the matrix activity, mainly ^{46}Sc, ^{47}Sc and ^{48}Sc from (n, p) reactions, is eluted (>99.5%) together with Cr, Na, Ag(3). If the eluate is passed through a column in 1M HF, Ti and Sc are retained

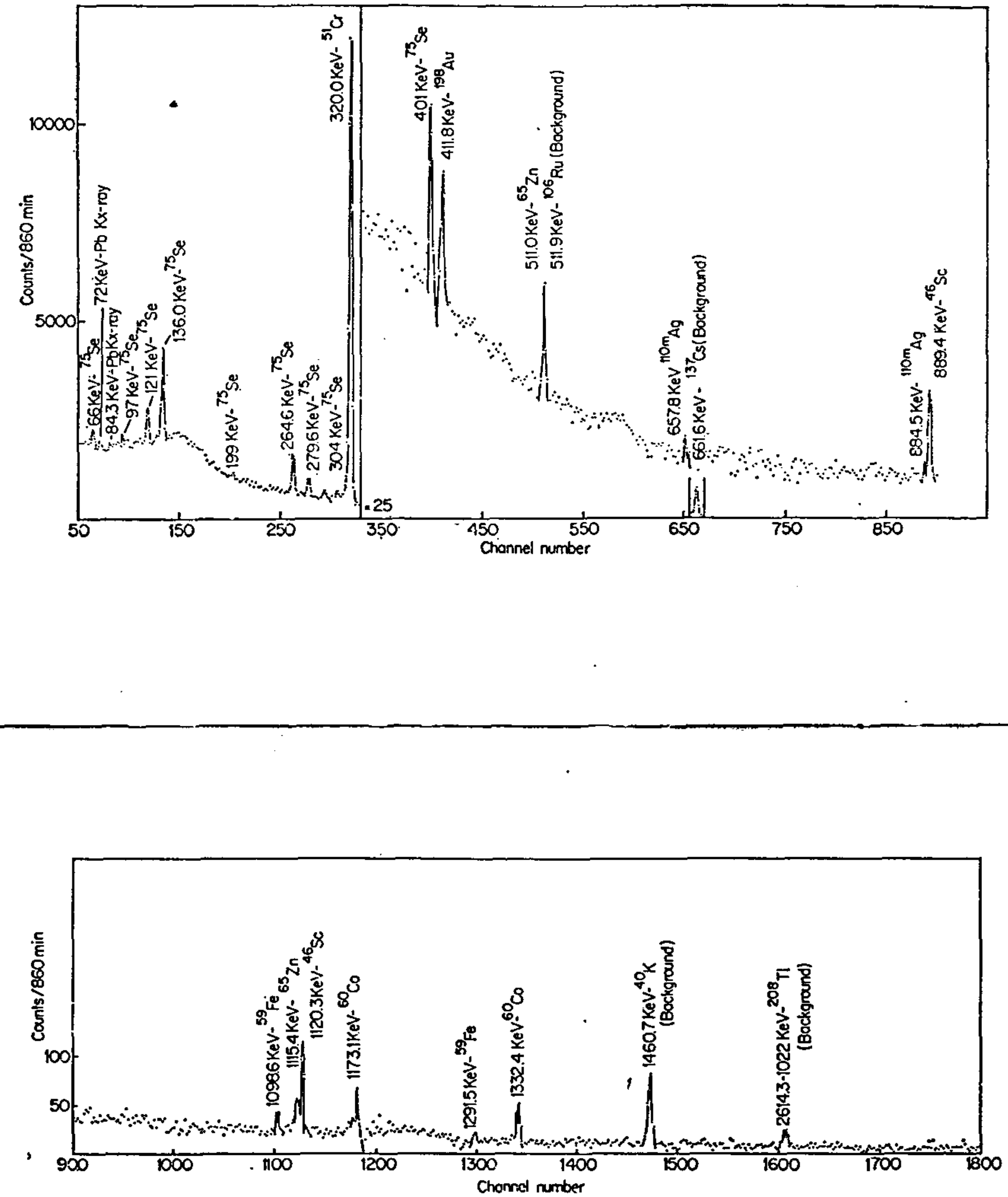

Fig. 8.1. Gamma-ray spectrum of the residue of irradiated selenium, after matrix distillation (1).

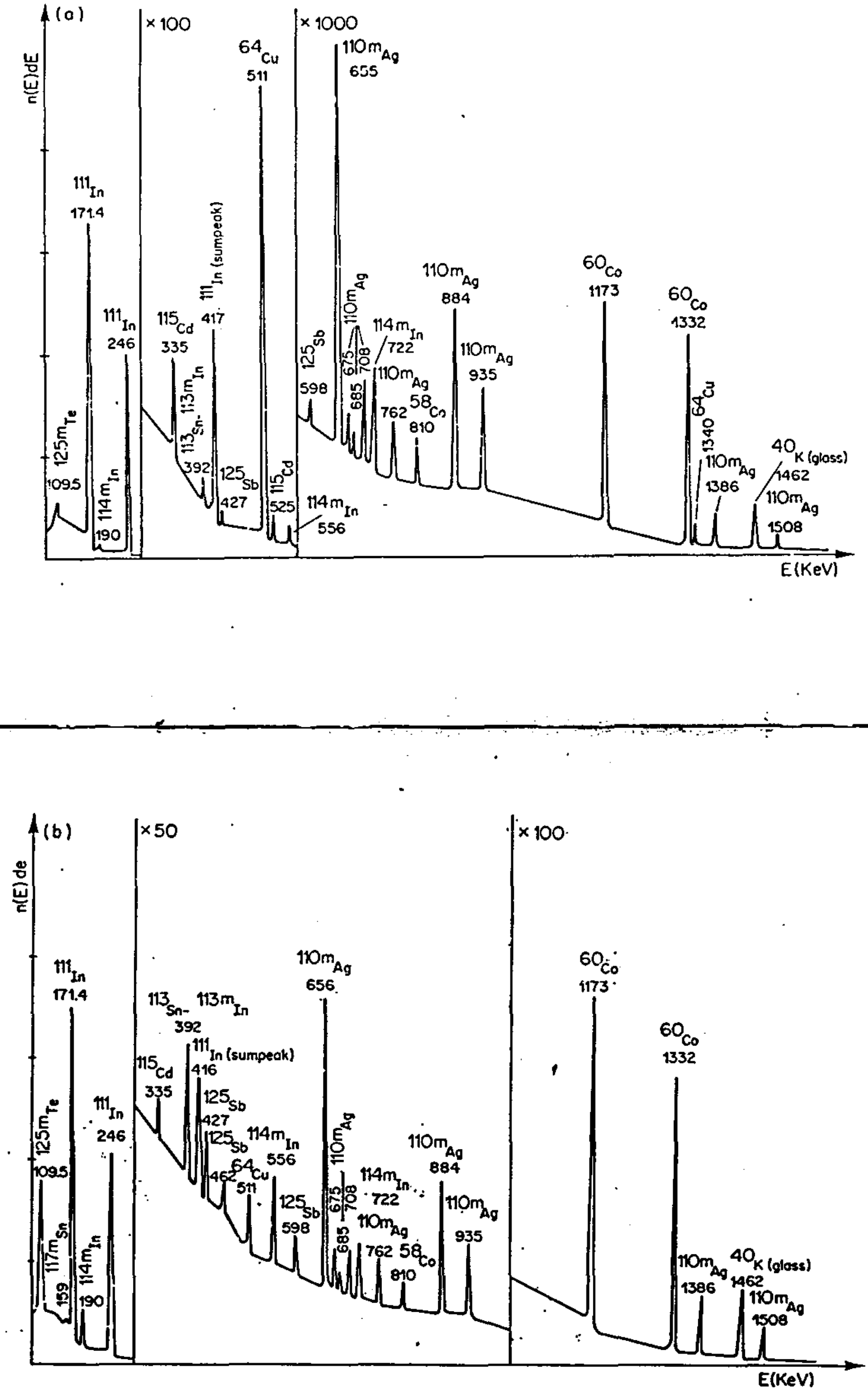

Fig. 8.2. Gamma-ray spectrum of the residue of irradiated tin after matrix distillation (2).

Curve a: after 5 d decay Curve b: after 16 d decay.

on the resin and Ag, Cr and Na are eluted. The two fractions containing the trace impurities can be measured by Ge(Li) spectrometry.

In Table 8.1 some methods are indicated for the elimination of matrices.

TABLE 8.1
Elimination of matrix activities after irradiation (4,5)

Matrix	Separation method
Antimony	distillation as $SbCl_3$ or as $SbBr_3$ (99.99%) (2)
Arsenic	distillation as $AsCl_3$ or as $AsBr_3$ (99.999%) (1)
Chromium	distillation or extraction as CrO_2Cl_2
Gallium	extraction as $GaCl_3$ in ether
Germanium	distillation or extraction as $GeCl_4$
Graphite	volatilization as CO_2
Indium	extraction as $InBr_3$ in isopropylether
Iron	extraction as $FeCl_3$
Manganese	distillation as permanganic acid (6)
Mercury	steam distillation of the element (7)
Osmium	distillation as OsO_4 (from H_2SO_4-H_2O_2) (> 99.999%) (8)
Ruthenium	distillation as RuO_4 (from H_2SO_4-$NaBrO_3$)
Selenium	distillation as $SeBr_4$ (99.9999%) (1) radioactive daughters and (n, p) or (n, α) reaction products of Se are also volatilized (Br, As, Kr, Ge)
Silicon	volatilization as SiF_4
Sodium	selective "sorption" on hydrated antimony oxide powder (9)
Tin	distillation as $SnBr_4$ (99.9999%) radioactive Sb daughters also distill as bromides from H_2SO_4-HBr at 200–220°C (99.99%); indium daughters extracted as $InBr_3$ in isopropylether
Titanium	$^{51}Ti + ^{46}Sc$ eluted with 1M HF + 9M HCl from Dowex 1–X8 (> 99.5%) together with Ag, Cr, alkali and alkaline earth elements (3)

Since the removal of the matrix activity is often done by distillation, it may be worthwhile to remember the volatilization of metallic compounds (chlorides, bromides) from perchloric and sulfuric acid solution at 200–220°C, as described by Hoffman and Lundell (10). Their results are summarized in Table 8.2.

Radioactive matrix removal by isotopic ion-exchange is discussed in section IV, A, of this chapter.

(B) BIOLOGICAL AND GEOLOGICAL MATERIALS

Many materials, including most of the biological ones show, after thermal neutron activation, a gamma spectrum in which ^{24}Na is the prevailing isotope, sometimes to such an extent as to become a radiation hazard. The elimination of sodium (and possibly bromine, chlorine, phosphorus, potassium) without affecting the concentrations of the other elements would in many cases permit the simultaneous determination of many traces without further chemical separations. Several procedures have been proposed in the literature, some of which will be mentioned here. Note that in many cases, the elimination of ^{42}K is a worse problem than the elimination of ^{24}Na.

1 *Precipitation of Sodium as Sodium Chloride from a Solution of the Sample by a n-Butanol-Hydrochloric Acid Mixture* (11).

This procedure not only removes active sodium, but also reduces the chlorine activity to a negligible level. HCl-gas is generated by the action of conc. H_2SO_4 on NaCl and is dried by being bubbled through conc. H_2SO_4 in a wash bottle. The dried gas is passed through ca. 100 ml of *n*-butanol for about 2 h. The resulting mixture is used for the precipitation of NaCl in the following procedure.

Radiochemical procedure: The activated material is brought into solution in the presence of 1 mg of each of the carrier elements. The biological samples are digested by heating with 3–5 ml of conc. HNO_3 and a few drops of conc. HCl. To this solution is added: 1 ml of sodium chloride solution containing 20 mg of inactive sodium and the mixture evaporated to a small volume. This is treated with 2 ml of conc. HCl to expel the excess of HNO_3. The volume of the solution is then reduced by evaporation to about 2 ml and sodium chloride precipitated by the addition of 5 ml of *n*-butanol—HCl mixture. The mixture is then rapidly cooled in an ice bath and centrifuged. The supernatant liquid is transferred to a separating funnel. The sodium chloride residue is washed with 2 ml of the same alcohol—HCl mixture, centrifuged and the washings added to the previous extract. This liquid is then shaken with 5 ml of water for about 1 m. The aqueous phase is separated and the sample prepared for counting.

TABLE 8.2

Approximative percentage of element volatilized from 20–100 mg portions by distillation with: (10)

Element	HCl-$HClO_4$(1)	HBr-$HClO_4$(2)	HCl-H_3PO_4-$HClO_4$(3)	HBr-H_3PO_4-$HClO_4$(4)	HCl-H_2SO_4(5)	HBr-H_2SO_4(6)
As (III)	30	100	30	100	100	100
As (V)	5	100	5	100	5	100
Au	1	0.5	0.5	0.5	0.5	0.5
B	20	20	10	10	50	10
Bi	0.1	1	0	1	0	1
Cr (III)	99.7	40	99.8	40	0	0
Ge (a)	50	70	10	90	90	95
Hg (I)	75	75	75	75	75	90
Hg (II)	75	75	75	75	75	90
Mn	0.1	0.02	0.02	0.02	0.02	0.02
Mo	3	12	0	0	5	4
Os (b)	100	100	100	100	0 (b)	0 (b)
P	1	1	1	1	1	1
Re	100	100	80	100	90	100
Ru	99.5	100	100	100	0	0
Sb (III)	2	99.8	2	99.8	33	99.8
Sb (V)	2	99.8	0	99.8	2	98
Se (IV)	4	2–5	2–5	2–5	30	100
Se (VI)	4	5	5	5	20	100
Sn (II)	99.8	100	0	99.8	1	100
Sn (IV)	100	100	0	100	30	100
Te (IV)	0.5	0.5	0.1	0.5	0.1	10
Te (VI)	0.1	0.5	0.1	1	0.1	10
Tl (c)	1	1	1	1	1	1
V	0.5	2	0	0	0	0

Procedure 1: ($HClO_4$-HCl) 15 ml 60% $HClO_4$ added to metal chloride or perchlorate soln. in a Scherrer distilling flask. Dist. in a stream of CO_2. Temp. raised to 200°C, and HCl added at such a rate that temp. remained at 200–220°C. Distill. stopped after 15 ml HCl had been added over a period of 20–30 minutes.

Procedure 2: ($HClO_4$-HBr): as in (1) except 40% HBr used in place of HCl.

Procedure 3: ($HClO_4$-H_3PO_4-HCl): as in (1) except 5 ml 85% H_3PO_4 added to flask before dist.

Procedure 4: ($HClO_4$-H_3PO_4-HBr): as in (3) except HCl replaced by HBr.

Procedure 5: (H_2SO_4-HCl): as in (1) except H_2SO_4 (sp. gr. 1.84) substituted for $HClO_4$.

Procedure 6: (H_2SO_4-HBr): as in (2) except H_2SO_4 (sp. gr. 1.84) substituted for $HClO_4$.

The following elements are not volatilized in any of the procedures: Ag, alkalis (Li, Na, K, Rb, Cs), Al, Ba, Be, Ca, Cd, Co, Cu, Fe, Ga, Hf, In, Ir, Mg, Nb, Ni, Pb, Pd, Pt, R.E., Rh, Si, Ta, Th, Ti, U, W, Zn, Zr.

Note: (a) H_2SO_4 and $HClO_4$ solns. heated to 200°C before admitting HCl or HBr.

(b) At 200–220°C no Os is volatilized from H_2SO_4, but at 270–300°C it is completely volatilized.

(c) No Tl distills if it is univalent (reduction with SO_2).

used for the determination of trace elements in hair via both short- and long-lived radionuclides.

Radiochemical procedure: The irradiated sample is transferred to the Erlenmeyer flask of a Bethge apparatus (Figure 8.3) together with 5 mg of the following carriers: As_2O_3, Sb_2O_3, CuO, HgO, $MnSO_4.H_2O$, $ZnSO_4.7H_2O$, SeO_2 and $AuCl_3$. The following reagents are then added while stirring: 0.5 ml 14N HNO_3, 0.5 ml 35N H_2SO_4, 1 ml 12N $HClO_4$ and 0.25 ml H_2O_2. After 1 h destruction at 170°C, 1 ml 12N HCl is added to dissolve Sb_2O_3. In order to avoid losses, the reflux condenser is rinsed with the HCl solution, which was placed in the safety funnel, and an additional 20 ml of water. The yields for Hg, Au, Zn, Cu, As, Sb and Se are better than 96%. In order to eliminate the relatively high ^{24}Na, ^{42}K and ^{32}P activities, two precipitations are carried out: one in acid medium with thioacetamide and another in alkaline medium with 8-hydroxyquinoline. The sulfide precipitate is filtered off in a small crucible which fits in that containing the oxinates, thus allowing the simultaneous measurement of all the precipitated activities with a Ge(Li) detector. With thioacetamide the following elements are precipitated or coprecipitated quantitatively: V, Cr, Co, Ni, Cu, Ga, Ge, As, Se, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, W, Re, Os, Ir, Pt, Au, Hg, Tl, Rb, Bi, Po. With 8-hydroxyquinoline, the following elements are (co)precipitated: Be, Mg, Al, Sc, Ti, Mn, Fe, Cu, Zn, Ga, Y, Zr, Nb, Pd, Cd, In, La, Rare earths, Hf, Ta, Hg, Bi, Ac, Th, Pa, U.

Procedure: Via the side funnel of the Bethge apparatus, 3 ml 14N NH_4OH is added to obtain a pH = 1. After cooling, 8 ml of a 5% thioacetamide solution is added while stirring. The solution is heated and boiled for 3 m while stirring and the precipitate filtered off in a porcelain filtering crucible after cooling and washed with water.

The filtrate is transferred to a beaker and 10 ml of a 2% oxine solution in 2N acetic acid added. When increasing the pH to 8, a yellow-green precipitate of Zn and Mn oxinate is formed: it is boiled while stirring, cooled, filtered off and washed with water. When the precipitates are not sufficiently washed, small ^{24}Na and ^{82}Br activities remain adsorbed.

The following short-lived radionuclides can easily be observed with a Ge(Li) detector: ^{197}Hg, ^{198}Au, ^{69m}Zn, ^{64}Cu, ^{76}As, ^{122}Sb, ^{56}Mn (see Figure 8.4a). After a few weeks, ^{75}Se, ^{203}Hg and ^{65}Zn are observed (Figure 8.4b).

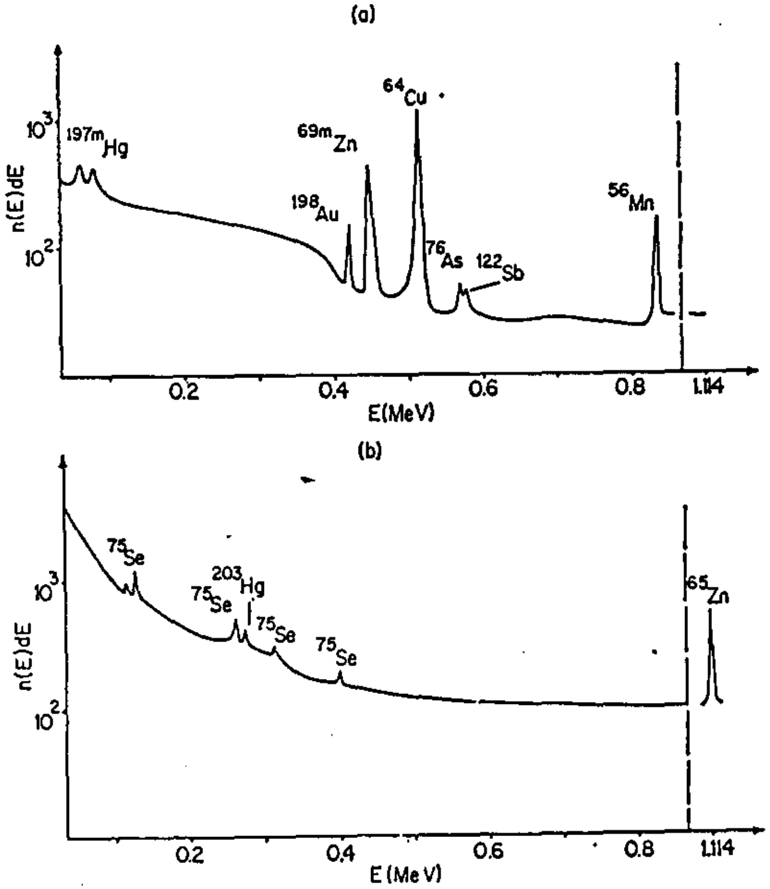

Fig. 8.4. Gamma-ray spectrum of a hair sample, irradiated for 6 h at a flux of 10^{11}n cm^{-2} s^{-1}. Combined sulfide and oxinate precipitates.

Curve a: after 4 h decay
Curve b: after 4 weeks decay.

4. *Removal of Sodium by Anion-exchange*

Several procedures have been described in the literature, using anion-exchange for the removal of sodium (16, 17). The system of Samsahl will be discussed in detail below (section II, G of this chapter). In some cases, ion exchange procedures are not fast enough. For that reason, Spronk (18) developed the following method: the irradiated sample is transferred to a specially designed celluloid centrifuge tube (Figure 8.5), containing ion-exchange resin Dowex 1, through which the sodium ions are eluted with 6N HCl, after wet combustion of the sample, and collected in a glass-wool plug at the bottom of the tube. The other metallic ions are adsorbed on the resin and can be assayed without further chemical separation. The technique gives a sodium removal better than 99.99% and is fast enough for Spronk's investigation involving ^{50}Sc, which has a half-life of only 90 s.

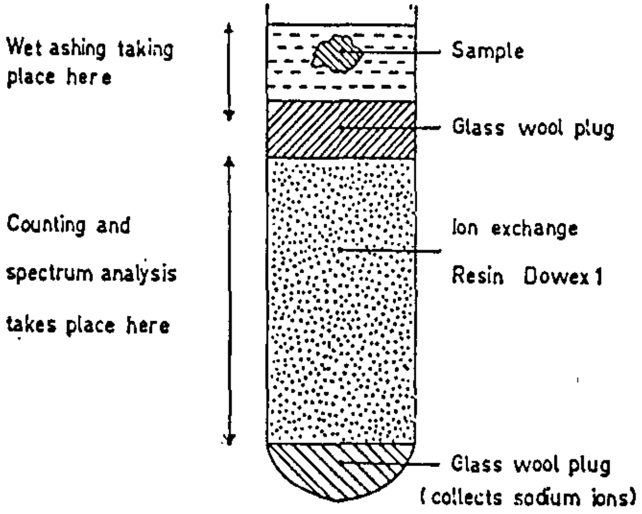

Fig. 8.5. Centrifuge tube described by Spronk (18) for the removal of sodium by ion-exchange.

Van den Winkel *et al.* (19) examined the adsorption of elements on Dowex 1-X8 (100–200 mesh) from acetic acid concentrations varying from 6 to 17.5M. All elements—As(III), Au(III), Br$^-$, Co(II), Cs(I), Cu(II), Fe(III), Hg(II), K(I), Mn(II), Mo(VI), Na(I), Sc(III), Zn(II)—are adsorbed from glacial acetic acid, except the alkali and earth alkali metals. The medium could thus be suitable for the separation of ^{24}Na as well as ^{42}K from the other activities in biological material.

For the determination of Cu, Zn, Cd, Mn and Au in blood, Plantin (20) removed the high ^{24}Na activity (in the beginning ca. 99% of the total activity is due to ^{24}Na) by ion-exchange on Dowex A-1.

Radioactive "matrix" removal by isotopic ion-exchange chromatography, using Dowex 50 W-X8 cation-exchange resin, is discussed in section IV A of this chapter.

5. *Selective Removal of Sodium by Retention on Hydrated Antimony Pentoxide (HAP)*

This method, described by Girardi and Sabbioni (9) has an excellent selectivity towards sodium in strong acid solution.

HAP can be used in the form of a chromatographic column, or in batch equilibration, or in a combination of the two techniques. A retention capacity of ca. 30 mg Na/g HAP has been obtained. The decontamination factor was 10^{10} in column experiments and 10^3 in batch equilibration.

From radioactive tracer studies it appeared that out of 60 ions tested, only sodium and tantalum were quantitatively retained from a 12M HCl solution; fluoride ions were retained partially. The other 58 ions were quantitatively (97–100%) eluted with 15–30 ml of 12M HCl: Ag(I), Al(III), As(?), Ba(II), Br$^-$, Ca(II), Cd(II), Ce (III), Cl$^-$, Co(II), Cr(III), Cs(I), Cu(II), Eu(III), Fe(III), Ga(III), Ge(IV), Hf(IV), Hg(II), I$^-$, In(III), Ir(III), K(I), La(III), Lu(III), Mg(II), Mn(II), Mo(VI), Nb(V), Np(IV), Au(III), Ni(II), Os(IV), Pa(V), Pd(II), Pt(IV), Ra(II), Rb(I), Re(VII), Ru(IV), S(VI), Sb(?), Sc(III), Se(IV), Sn(?), Sr(II), Tc(VII), Tb(III), Te(IV), Ti(IV), U(VI), V(?), Y(III), Yb(III), W(VI), Zn(II), Zr(IV).

At a lower acid concentration (6M HCl) a few per cent of Cs, Sr, Ba, Ra and Pa are also retained. At concentrations lower than 6M, the retention of sodium is still complete, but the selectivity decreases.

Sodium is also retained from the following acid media: 7M HNO_3, 1M HNO_3, 8M $HClO_4$, 6M HF, 28M HF and the acid mixture 6M HCl–3M HNO_3. Other elements have not been investigated, however, in these conditions.

At trace sodium levels, a column of 6 mm dia. and 20 mm length (0.6 g HAP) has been operated successfully at a flow rate of 3 ml/m, allowing the completion of sorption and washing operations in ca. 5 m. Large quantities of radio-sodium are better removed by a batch equilibration with the proper amount of HAP (ca. 35 mg HAP/mg Na$^+$) followed by passage of the supernatant through a small HAP column.

It must be noted, that the concentration of potassium in many biological specimens is sufficiently high to require the removal of ^{42}K as well as that of ^{24}Na prior to gamma spectrometric analysis for other trace elements. Decrease of the acid concentration is sufficient to eliminate both Na and K in one passage on HAP. Their removal is, however, not as selective as that of Na at high acid concentration.

Figure 8.6 shows a Ge(Li) spectrum of irradiated urine. After the removal of sodium, ^{42}K and ^{64}Cu can be detected. If ^{42}K is removed

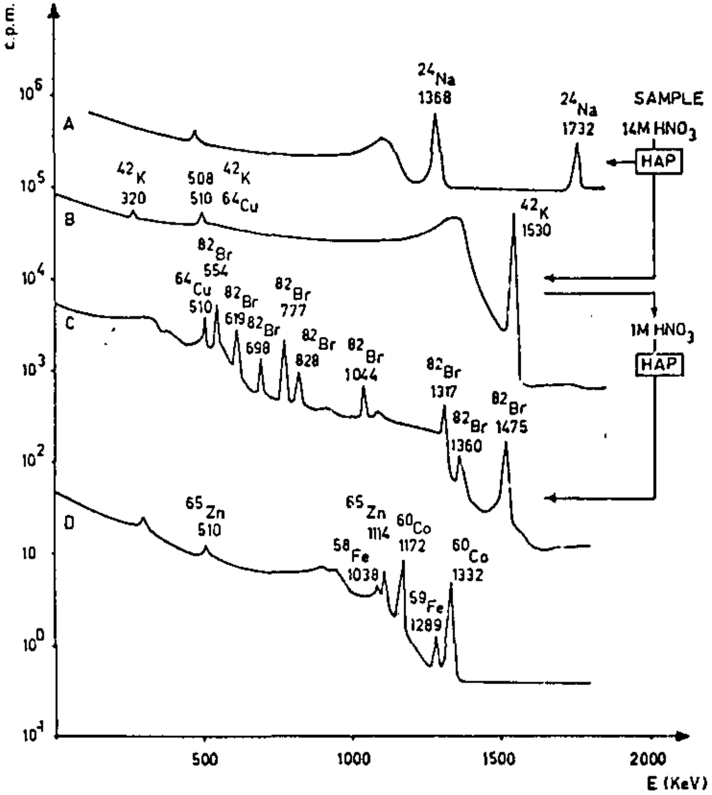

Fig. 8.6. Application of HAP to activation analysis of urine (9).
A. Gamma spectrum of HAP column after passage of the sample solution in 14M HNO$_3$
B. Gamma spectrum of the effluent
C. Gamma spectrum of the effuent after passage of (B) in 1M HNO$_3$ on HAP
D. Gamma spectrum of (C) after decay of ^{82}Br.

by means of a HAP column using 1M HNO$_3$, ^{82}Br is detected. After decay of ^{82}Br, ^{65}Zn, ^{59}Fe and ^{60}Co can be observed. If bromine is removed by volatilization during wet combustion, filtration through HAP should allow a rapid determination of Zn, Co and Fe, without the necessity of waiting for the decay of ^{24}Na.

Adsorption on HAP has also been used for the elimination of ^{24}Na (and ^{182}Ta) from irradiated rock samples (140, 141).

II. Group Separation Systems

Much progress has been made in recent years towards simple and selective procedures for the determination of one or a few trace elements at a time. In the bibliography, numerous examples can be found (21,22). Reference is also made to a review on radiochemical separations for activation analysis (142). Most of the techniques used in such procedures are well known: ion-exchange, chromatography, liquid-liquid extraction, distillation, precipitation,... Excellent textbooks on these subjects exist, so that they will not be discussed here. Some less common techniques, which are typical for radiochemical separations, e.g. isotopic exchange reactions, amalgam exchange, isotopic ion exchange, and some others (electrophoretic focusing of ions, internal electrolysis, fast separations, automatic separations) will, however, be discussed in more detail in section IV of this chapter.

In addition to "single species analysis", there exists also the problem of the simultaneous determination of a large number of trace elements ("multispecies analysis"). For that purpose, several group separation systems have been presented.

From the analytical point of view, a group separation system is mostly easier if the matrix and/or the main component(s) (or activities) can be removed in the very beginning of the procedure. In this way one also avoids working for longer periods with highly active samples. This problem has been discussed already (section I of this chapter).

After removal of the matrix a solution remains, containing most of the impurities, possibly with a small residual fraction of the matrix. The question arises what trace elements should be included in a general separation scheme. In most cases one will not consider those elements which are below the detection limit, this means, in practice, one will not go below 10^{-8}–10^{-10} gram.

The following elements will practically be present in any matrix, since they are abundant in nature: Na, Ca, Mg, Si, Al, Cl, S, P, Fe, Pb, Zn, Cu, Ti and O, N and C. In lower concentrations one finds Ag, Cd, Ge, Sb, Sc, Sn and Co, Cr, Mn, Ni, the rare earth elements (La, Ce), but also Au, Ba, Ga, In, K, Se, Sr, Tl and Zr (4,5). When analyzing highly purified materials and zone-refined samples one will find Ta, W, Pt and Ir as a result of contamination from the crucibles used for their preparation.

Moreover, one will detect in a given matrix, elements having similar chemical properties. Example: in ruthenium one will practically always find some osmium, but also iridium and other noble elements. In high-purity iron, typical residual impurities will be Cr, Mn, Co, Ni and Mo. In cerium one can expect La and Sm, for instance.

Anyway, a good group separation should include the elements listed above. For that purpose, classical methods such as the H_2S system can be used. If isotopic carriers are added, it is possible to determine the chemical yields in the case of non-quantitative separations.

Since the techniques of ion-exchange chromatography are relatively simple they are very suitable for radiochemical purposes. They can easily be used for routine analyses by nonspecialized personnel. Some radiochemical group separation systems by ion-exchange will be discussed in section II, D, I of this chapter; these methods should have a high chemical yield, a good selectivity and a sufficient speed (depending on the half lives of the radionuclides of interest). Ion-exchange separation systems can easily be automated, as will be discussed in section IV of this chapter.

(A) GROUP SEPARATION SYSTEM OF ALBERT AND GAITTET

The following separation scheme (Figure 8.7) was used by Albert and Gaittet (23) for the determination of impurities in high purity aluminium after thermal neutron activation. With minor modifications, it could also be applied for trace analysis of high purity iron.

The irradiated (aluminium) sample is etched and dissolved. After addition of carriers of Cu and As, H_2S is passed through the acid solution. The resulting precipitate of Cu-As-sulfide, which also contains Se, Hg, Sb, Te, Au, Ag, Mo, Bi and W, is dissolved in conc. sulfuric acid, and HBr added. The volatile compounds of the elements Se, Hg, As and Sb are distilled (*cf.* Table 8.2) and Se separated by reduction with hydrazine in HCl medium, after addition of Se carrier. Hg is

then reduced in ammoniacal medium, and As precipitated as $MgNH_4AsO_4$. After addition of Sb carrier, Sb is precipitated as sulfide.

To the residue of the distillation, Cu and Te carriers are added and precipitated as sulfides, together with Au, Pd, Ag, Mo and Bi. To the filtrate, Mo carrier is added and radioactive W traces are coprecipitated with Mo-α-benzoinoximate.

The sulfide precipitate of Cu, Te, Au, . . . Bi is redissolved in HCl-HNO_3 and Te precipitated by reduction with hydrazine in 3N HCl; Au, Pd . . . are also reduced. Ag carrier is added and AgCl precipitated. Cu is precipitated with salicylaldoxime at pH 3–4. After destruction of the excess of organic reagent, Mo is precipitated with

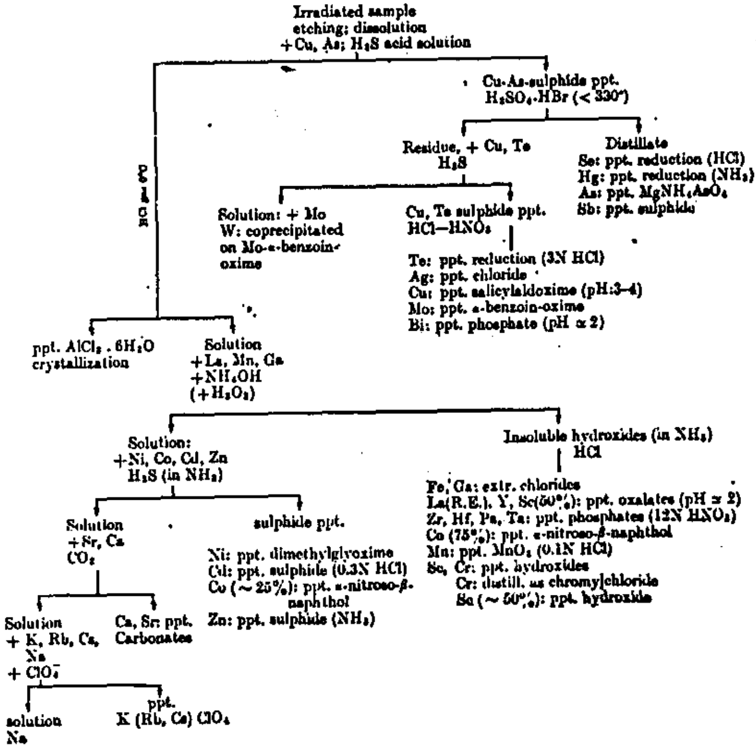

Fig. 8.7. Chemical separation scheme after Albert *et al.* (23). Carriers of the underlined elements are added. Starting at * the scheme represented in Fig. 8.8 can be applied.

α-benzoinoxime. Finally, Bi is precipitated as phosphate at pH ≃ 2, after destruction of the excess of α-benzoinoxime.

In the filtrate of the sulfide precipitation in acid medium, the bulk of the aluminium matrix can be removed by crystallization of $AlCl_3.6H_2O$ at 0°C, by passing HCl gas; the solution volume must be 100 ml per gram of aluminium. At this stage, the procedure can be continued by means of the "classical" analytical chemistry (Figure 8.7) or using liquid–liquid extraction and ion-exchange chromatography (Figure 8.8).

In the former system, La, Mn and Ga carriers are added and precipitated together with the elements which form insoluble hydroxides in ammoniacal solution (Fe, rare earth elements, Zr, Hf, Pa, Ta, Mn, Sc). When performing the precipitation in a reducing medium, Cr is coprecipitated. The precipitation is carried out in the presence of H_2O_2 in order to precipitate MnO_2. It must be noted that Co is partly coprecipitated and that P precipitates as phosphate. After filtration, the hydroxide precipitate is dissolved in HCl and Fe and Ga extracted as their chlorides. The rare earth elements, Y and Sc (≃50%) are coprecipitated with La-oxalate at pH ≃ 2 and can further be separated by ion-exchange chromatography. Zr, Hf, Pa and Ta are precipitated as phosphate in 12N HNO_3, after addition of Zr carrier. Co (≃75%) is separated as α-nitroso-β-naphthol complex, Mn as dioxide and Sc + Cr as hydroxides.

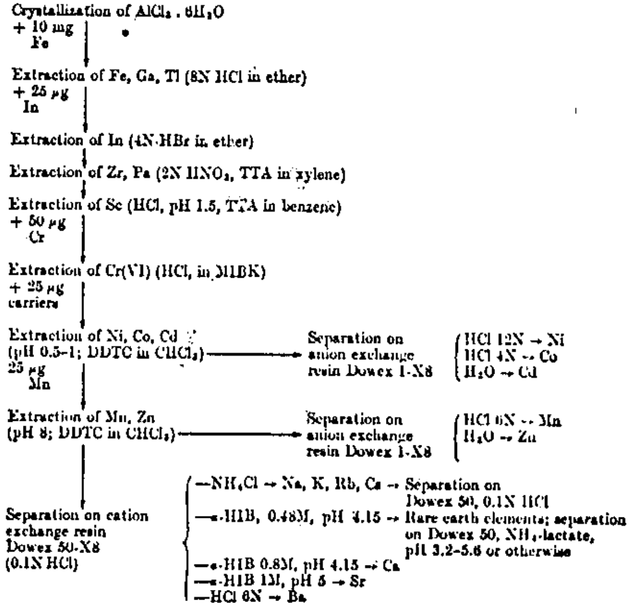

Fig. 8.8. Alternative separation scheme after Albert *et al.* (24). This scheme follows after the precipitation of the acid insoluble sulfides (see Fig. 8.7).

To the filtrate of the hydroxide precipitation in ammoniacal solution, Ni, Co, Cd and Zn carriers are added. These elements are separated from the alkali metals and the alkaline earth elements by passing H_2S. Further separation in this group is possible, e.g. as indicated in Figure 8.7: Ni is precipitated as dimethylglyoximate, Cd as sulfide in 0.3N HCl, Co (≃25%) as α-nitroso-β-naphtholate, and Zn as sulfide in ammoniacal solution.

In the filtrate, the alkaline earth elements are precipitated as carbonates, after addition of Ca and Sr carriers. In the residual solution the alkali metals Na, K, Rb and Cs remain.

In the above procedure, the carriers are added just before a precipitation is carried out; this could possibly give rise to incomplete isotopic exchange between radioactive tracer and carrier.

An alternative separation scheme for the elements which are not precipitated as sulfides in acid solution is shown in Figure 8.8.

(B) GROUP SEPARATION SYSTEM OF ROSS

Ross (25) has described the neutron activation analysis of high purity samples of beryllium, aluminium and iron for trace amounts of 62 possible impurities by measuring the gamma activities. Non-destructive and chemical procedures have been combined to achieve this goal.

Ten elements are determined by non-destructive techniques after bombarding a portion of the sample (1–100 mg, sealed in high-purity polyethylene tubing) for 10 seconds at a flux of 6.10^{13} n cm^{-2} s^{-1} and making a rapid measurement of the short-lived radionuclides (^{27}Mg, ^{28}Al, ^{41}Ar, ^{51}Ti, ^{52}V, ^{56}Mn, ^{104}Rh, ^{165m}Dy, ^{152}Eu, ^{116}In).

A second portion of the sample (1 g) is activated for 20 minutes at a flux of 8.10^{11} n cm^{-2} s^{-1} and analyzed for chlorine, bromine and iodine, after dissolving in H_2SO_4 + 1 ml of each HCl, HBr and HI and distilling to fumes of SO_3. The volatile acids are collected in cold NaOH solution and the activities measured by gamma spectrometry.

passed through a Dowex 1X8 column. The effluent and wash (8N HCl) are extracted with TBP: Sc, Zr, Hf and Pa appear in the organic phase whereas the aqueous phase contains the rare earths, Cr, Ca, Ba, Sr, K, Rb and Cs.

The anion exchange column is eluted with 0.5N HCl. The eluate contains Fe, Co, Cu, Ni, Ga, In, W, Mo and Np whereas Zn, Cd, Sb, Re, In, Hg and Au are counted on the resin.

(N) Group Separation System of Laul *et al.*

Another group separation system for geological samples is described by Laul *et al.* (146). The elements Au, Ga, Ge, Mo, Sb, Fe and Tl are extracted from 6N HCl with diethylether and further separated by a number of precipitations. From the aqueous phase the elements As, Hg, Re, Sb and Se are distilled at 200°C as the bromides. Excess bromine, which would seriously interfere with the chemical yield determinations by reactivation (^{82}Br) is removed by precipitating the desired elements as sulfides.

After distilling the bromides, all elements which form insoluble sulfides in acid medium (e.g. Bi) are precipitated. In the supernate, Co, Sc and Zn are precipitated and further purified. This treatment leaves the alkali metals in solution.

(O) Group Separation System of Allen *et al.*

Allen *et al.* (147) have described a procedure for neutron activation analysis of 39 elements in geologic samples. The elements are separated into 12 chemical groups (4 of which are single elements), the order of separation being dictated by the short half-lives of some of the radionuclides of interest: group 1 (Ag, Cl, Br); group 3 (Mn); group 2 (Au, Ba, Pt, Ta); group 4 (In); group 5 (Cu, As, Se, Sb, Pd); group 6 (Fe); group 7 (lanthanides); group 8 (Cr, Hf, Sc); group 9 (Ni); group 10 (Co, Ga, Zn), group 11 (Ca, Sr), and group 12 (K, Rb, Cs). The twelfth group is separated and ready for radioassay within seven hours after the end of irradiation, when work is done by 3 persons. Chemical yields are typically between 50 and 90% and are determined by reactivation, except for Fe and Ni.

In several papers (140, 147, 148, 149) the lanthanides are separated from the irradiated sample as a group and the individual activities measured by Ge(Li) spectrometry. Higuchi *et al.* (151) separated the lanthanides into a light and a heavy fraction by cation exchange.

III. The Design of a Radiochemical Procedure

There are innumerable radiochemical procedures published in the literature. They have been designed for several purposes (39)

—speed of operation where short-lived nuclides are to be determined;
—multi- or single-species analysis;
—extreme radiochemical purity;
—high chemical yield;
—carrier-free product.

They range from "excellent" to "of little value" and in many cases must be used for the specific purpose for which they were designed.

The usual methods of analytical chemistry suitable for the separation of the elements can also be used in radiochemical analysis. These include:

—dissolution of the sample;
—separation by precipitation, extraction, chromatography, distillation, electrolysis, etc.

Hence reference can be made to textbooks on these subjects.

However, radiochemical analysis also has particular aspects.

For the determination and identification of short-lived radioisotopes, fast separation methods are required, excluding a number of standard methods of analytical chemistry. In this case it is often more important to obtain a satisfactory radiochemical purity than a quantitative separation.

To some extent, this is an advantage of radiochemical analysis, since the range of methods and reagents is broadened as compared with analytical chemistry. Indeed, to allow for the loss of radioisotopes during their isolation, one can add isotopic (or chemically analogous) carriers before dissolving the irradiated sample and determine afterwards the chemical yield. Sometimes it is even possible to use a radioactive isotope of the same element with a known activity but possessing a widely differing half-life or a different radiation energy. Example: neutron activation analysis for rhodium via 4.4 m ^{104m}Rh, using 210 d ^{101}Rh for the determination of the chemical yield.

It is very important that the radioisotope of interest and the carrier (or radiotracer) added, have the same chemical and physical form in solution; this means, for instance, that they must have the same valency. In Chapter 10, section II, F, 4, it is mentioned that the radioactive isotopes, formed in nuclear reactions, are sometimes present in many different valency states. Moreover, the state and valency of the radioisotopes and carriers in solution may vary with time during the analytical process, for instance due to the action of the radiation. An excellent review of the state and behavior of radioelements in solutions is given by Lavrukhina *et al.* (43).

(A) THE BEHAVIOR OF AN ELEMENT AT AN EXTREMELY LOW CONCENTRATION

The behavior of an element at an extremely low concentration can be completely different from that at a "normal" concentration. This is well known for adsorption processes, e.g. on glass or container walls and on chromatography paper. The separation of carrier-free fission products by electrophoretic focusing of ions in the presence of uranium yielded very sharp focuses only, if ca. 10 μg carrier was added for each element (40). The behavior of iridium in boiling perchloric acid (ca. 200°C) also depends on the amount of the element present: small amounts (<30 μg) can be distilled quantitatively in a stream of chlorine gas, probably as a chloride (41). When dealing with mg amounts, however, iridium is not distilled but converted to a deep blue violet Ir(IV) solution (42).

A loss of the individual properties of micro components in the colloidal state has been observed in many cases: the element present in excess (e.g. target material) can determine the properties and the behavior of the whole solution. If gelatin is added to a colloidal solution of gold, the gold ceases to undergo coagulation when NaCl is added, but can be precipitated by tannin (43).

(B) THE CHEMICAL STATE OF ATOMS DURING NUCLEAR REACTIONS—RECOIL

Radioactive atoms formed in nuclear reactions acquire a recoil energy E_x, given by:

$$E_x = \epsilon_x \frac{m_x}{A} \tag{8.1}$$

where A is the mass of the atom expelling a particle of mass m_x and ϵ_x is the excitation energy of the nucleus (in MeV). E_x can reach several MeV, thus greatly exceeding the binding energy of atoms in molecules and crystal lattices so that rupture of these bonds occurs. The exact state of the recoiling atom at the moment of its formation is not exactly known. In general, however it has a comparatively large positive charge and is chemically very active. Due to the interaction with the target material, new chemical compounds are formed: ^{32}P, formed by the reactions ^{35}Cl(n, α)^{32}P and ^{32}S(n, p)^{32}P in chlorides and sulfates, for instance, is present in various forms (44). The most probable form of the "hot" atoms is practically independent of the energy and nature of the bombarding particles, but depends on the chemical composition of the target substance.

When the irradiated target is dissolved, change in valency of the radionuclide of interest is possible due to interactions with the solvent.

(C) ISOTOPIC EXCHANGE

As already stated above, it is very important that the radioelement of interest and the carrier (or radiotracer) added have the same chemical and physical form in the solution. Whereas the carrier added is present in the form of a definite compound, the state of the radionuclide is mostly unknown. The rate of isotopic exchange can be expressed in terms of $t_{1/2}$, the time necessary for achieving half the equilibrium distribution; it depends on the medium and on the ion under investigation: the half-exchange time between Cr^{2+}/Cr^{3+} is 2 m in hydrochloric acid medium, but 14 h in perchloric acid; in perchloric acid, $t_{1/2}$ (Mn^{2+}/Mn^{3+}) is, however, 10–20 s only. Whereas the exchange time of Co^{2+}/Co^{3+} is very small, it may be more than 80 days for Co(NH$_3$)$_6^{2+}$/Co(NH$_3$)$_6^{3+}$ (43). Low exchange rates are also typical for the pseudocolloidal state, as mentioned already; improvement is possible by the creation of an acid medium, or by the presence of a complexing agent.

In the course of electrophoretic focusing experiments with a mixture of carrier-free ^{54}Mn tracer and Mn-carrier, the two species were found to be in a different state, as the positions of maximum activity and the visual focus did not coincide (45). No improvement was obtained after repeated evaporation of tracer and carrier in hydrochloric acid. Better results were obtained if the mixture was first taken to dryness in perchloric acid, then evaporated with hydrochloric acid, and the residue taken up in a mixture of EDTA and NaOH (pH = 7.9).

In orde avoid errors due to incomplete isotopic exchange, it is customary to add a carrier in a given valency state and to carry out a cycle of reducing and oxidizing reactions whenever possible.

(D) THE STATE OF RADIOELEMENTS IN SOLUTION

According to Lavrukhina *et al.* (43), ultramicro amounts of radioelements in solution may be present in the ionically disperse, molecular, true colloidal and pseudocolloidal states, or in a combination of them.

The ionic state is characteristic for radioisotopes of the alkali and alkaline-earth elements, but complex ions can also be formed with a number of other elements, particularly if complex forming substances are present in the solution.

In the presence of suitable organic and/or inorganic ligands, conditions may be created in which the radioelement exists predominantly in the molecular state. Example: rare earth + lactic acid gives a neutral complex of the type ML_3. In the presence of large amounts of nitrates, ^{95}Zr and ^{95}Nb form neutral complexes of the type $M(OH)_x(NO_3)_y$.

The existence of true colloids has been observed in solutions in which insoluble hydrolysis products can be formed. Of more practical importance are, however, pseudocolloidal solutions, i.e. adsorption on foreign colloidal particles present in the solution. The pseudocolloidal state is possible for all radioelements and depends on the nature (sorption capacity and sign) and the amount of impurities in the solution. This effect can cause important losses and an anomalous behaviour of radioelements, for instance anomalies in

—adsorption properties, e.g. on ion exchange resins;
—extraction with organic solvents;
—cocrystallization with various precipitates;
—isotopic exchange capacity.

Colloid formation can be reduced by the creation of an acid medium or by the presence of complexing agents.

Losses of radioelements by adsorption phenomena (on glass walls, filter paper, etc.) are also decreased in acid medium and by the presence of complex-forming reagents and of an isotopic carrier.

Inversely, if one wants to isolate an element by $Fe(OH)_3$ scavenging, it is sometimes necessary to destroy possible complexes. Example: if coprecipitation of Rh on $Fe(OH)_3$ is incomplete, one should first take the solution to fumes of perchloric acid.

(E) SEPARATION AND DECONTAMINATION FACTORS (46)

If a quantity w_A of an element A has been isolated from a quantity $(w_A)_0$, originally present,

$$R_A = w_A/(w_A)_0 \tag{8.2}$$

is called the recovery factor. In a similar way, $R_B = w_B/(w_B)_0$ is called the recovery factor for element B.

The ratio

$$S_{B/A} = \frac{w_B/w_A}{(w_B)_0/(w_A)_0} = \frac{(w_A)_0}{(w_B)_0}\frac{w_B}{w_A} = \frac{R_B}{R_A} \tag{8.3}$$

is called the separation factor. If the element of interest A is quantitatively recovered, $R_A = 1$, so that $S_{B/A} = R_B$. The factor $1/S_{B/A}$ is called decontamination factor.

The factor $S_{B/A}$ is sometimes called enrichment factor (for A) or, perhaps better, depletion factor (for B) since A remains essentially constant in a quantitative separation.

In separations based on distribution equilibria, e.g. in immiscible solvent extraction, $S_{B/A}$ can be calculated if the distribution coefficients D_A and D_B and experimental variables such as phase volumes and the number of equilibrium stages are known. If A and B are extracted to a different extent, and if $V_{org}/V_{aq} = r$, then

$$S_{B/A} = \frac{R_B}{R_A} = \frac{(rD_B + 1)^n - 1}{(rD_B + 1)^n}\,\frac{(rD_A + 1)^n}{(rD_A + 1)^n - 1} \tag{8.4}$$

The ratio $\alpha = D_A/D_B (D_A > D_B)$ should not be called separation factor but, for instance, the quotient of the distribution coefficients.

(F) DISSOLUTION OF IRRADIATED SAMPLES

The dissolution of inorganic samples (metals, oxides, minerals, etc.) by the action of acids and alkalis, by fusion with potassium bisulfate, peroxide or alkalis and nitrates, or by the action of acids at higher temperatures and pressures in sealed tubes is described in great detail in general handbooks of analytical chemistry and will not be discussed here. The sealed-tube technique has been mentioned in Chapter 7, section I, 7.

If carriers are added, in order to determine the chemical yield of the separation, the necessary steps must be taken in order to ensure a good isotopic exchange between carrier and radioactive trace element (see section III, C of this chapter and section II, F, 4 of Chapter 10).

For the dissolution (destruction) of organic samples, reference is also made to general handbooks. Dry ashing is often used before activation, in order to enrich the trace elements in the ashes. This technique can also be applied to irradiated samples (Chapter 7, section I, I). A modification is low-temperature ashing, which has been discussed already in Chapter 7, section I, I.

Wet combustion is widely used for the mineralization of irradiated organic samples. This can, for instance, be done using the apparatus shown in Figure 8.3 (Bethge apparatus).

Another method of destroying organic matter is the Schöniger combustion. This technique was recommended by Schöniger (47,48) for the determination of sulfur and halogens in organic compounds and its usefulness in trace analysis of metals demonstrated by several authors (27,49,50).

The apparatus used by Van den Winkel *et al.* (29) consists of a thickwalled 500 ml Pyrex flask with an elongated type of glass stopper and fused-in platinum wire, supporting a platinum spiral (Figure 8.20). The weighed samples are wrapped in pieces of ashless filter paper so that a narrow tail extends to the ignition unit. The top of the extending strip is dipped into a 20% solution of potassium nitrate and dried before ignition. A few milliliters of water are added before ignition to absorb the residue. The flask is filled with pure oxygen, the platinum spiral wound around the sample and fastened to the wire to hold the sample in the center of the flask. The electrical ignition, used by Van den Winkel *et al.* provides an easier and safer method for burning the samples without losses of volatile elements during the combustion. Combustion is started by heating the top of the paper strip with a 3-ohm Kanthal wire resistor placed inside the stopper and heated by a 6.3 V power supply. The authors describe an electronic timer for interrupting the heating current after a preselected time.

After ashing, the flask is cooled in ice water for 15 m. The stopper is removed after pipetting a few drops of water on it. The water is sucked into the flask and the stopper is easily removed. The platinum

wire is rinsed with 10 ml of concentrated nitric acid to which a few drops of hydrogen peroxide were added. The resulting solution is heated for several minutes and is then subjected to chemical separations.

No explosions or other hazards were observed by the authors after several hundred combustions. Up to 100 mg of plant powder can be

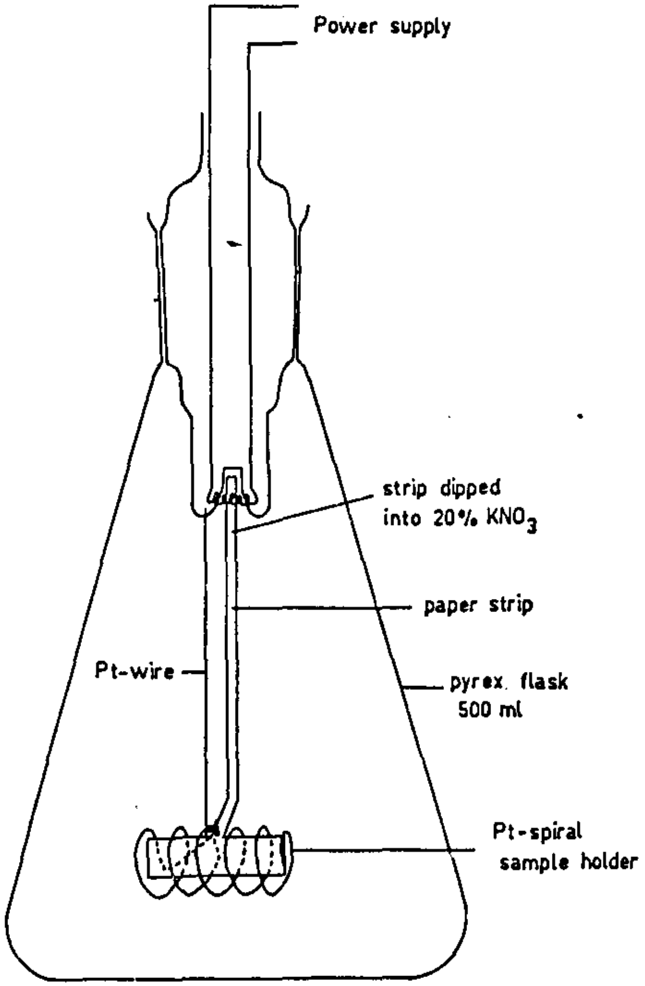

Fig. 8.20. Apparatus for Schöniger combustion (29).

completely ashed in a 500 ml combustion flask. Radioactive tracer studies showed that yields of at least 98% were obtained for Mo, Hg, Se, Co, Zn and Fe, whereas Au and Ag apparently form an Au–Pt and Ag–Pt alloy at the high combustion temperature. A quantitative recovery of these elements is, however, possible by boiling the platinum spiral three times for several minutes with 5 ml of aqua regia. This treatment gradually attacks the wire so that it must be replaced after about 50 combustions.

An interesting advantage of the Schöniger combustion is the fact that a dilute solution of volatile acids is obtained. The classical wet combustion requires the use of sulfuric acid, resulting in poor separations by ion exchange and thin-layer chromatography.

(G) RADIOCHEMISTRY OF THE ELEMENTS

A number of monographs on the radiochemistry of the elements have been edited by the National Academy of Sciences, dealing with the properties of the elements and their compounds of analytical interest. The main radionuclides are listed, and a number of selected procedures for activation analysis, for the preparation of carrier-free tracers and for the preparation and standardization of carrier solutions is given. For detailed analytical information, reference is also made to the text books of analytical chemistry.

Decay schemes of radioisotopes are given by Dzhelepov, Kunz and Schintlmeister, Lederer–Hollander–Perlman, and the "Nuclear Data Sheets" (see Chapter 6, section I, B).

The radionuclides, formed by (n, γ), (n, p), (n, α), (n, 2n) and (n, n′) reactions after bombardment with thermal, fission or 14 MeV neutrons are listed in the Appendices of this book. In the appendix, reference is also made to catalogues of gamma-ray spectra, recorded with NaI(Tl) or Ge(Li) detectors.

IV. Special Radiochemical Separations

In this section, some less common analytical techniques will be briefly discussed, such as electrophoretic focusing of ions and internal electrolysis. For common techniques, such as ion-exchange chromatography and liquid–liquid extraction, excellent handbooks are available, so that these subjects will not be discussed here.

Attention will also be paid to techniques which are typical for radiochemical separations and activation analyses such as isotopic exchange reactions, isotopic ion exchange chromatography, amalgam exchange, fast separations and automatic separations.

(A) RADIOCHEMICAL SEPARATIONS BY ISOTOPIC ION EXCHANGE

In conventional cation exchange the elements can be arranged in a selectivity scale according to their distribution coefficients, see for instance, Table 8.3 (51,52). Although good separation factors may exist between several elements in a given system, the general tendency toward tailing at moderate and high distribution coefficients (≥ 5) precludes a rapid separation in many cases because of the large elution volumes required. When isotopic exchange is combined with ion exchange, this limitation is overcome (53). The former is independent of the chemical ion exchange selectivity of the element and can be adjusted to optimum conditions by changing the concentration of the element in the liquid phase. Indeed, the matrix solution adjusted to an appropriate matrix concentration is used as the eluent. This extra degree of freedom, which is obviously characteristic for radiochemical work, offers versatility in adopting the approach to rapid radiochemical separations of a large amount of a given radioactive element from trace amounts of many other radioelements.

Two approaches are suggested by Tera and Morrison (53) for radioactive matrix removal, depending upon its relative position in a given selectivity scale, e.g. Table 8.3.

TABLE 8.3
Ion exchange selectivity scale for cations in 0.1N HCl using Dowex 50W–X8 resin

Distribution coefficient	
$> 4 \times 10^4$	ZrO(II) $\simeq$ Th(IV) $\simeq$ La(III) $\simeq$ Ce(III) $\simeq$ Y(III)
$> 4 \times 10^3$	Ba(II) $\simeq$ Ga(III) $\simeq$ Ti(IV) $\simeq$ Sn(IV)
4×10^3–1.5×10^3	Fe(III) > Al(III) > UO_2(II) > Sr(II) > Ca(II)
1×10^3–5×10^2	Mn(II) > Zn(II) > Fe(II) > Mg(II) > Co(II) > Ni(II) > Cu(II)
2×10^2–15	Cd(II) > Be(II) > Cs(I) > Rb(I) > K(I) > Na(I) > Li(I)
> 10–< 1	V(V) > Mo(VI) > Hg(II) > As(III) > Se(IV) > Au (III)

platinum ga[illegible] electrode (G) (height 4.5 cm, radius 2.5 cm) can pass through it. The electrode itself is concentric with the stirrer and the lead anodes. The stem of the platinum cathode is clamped in the bush with a small screw (H). Good electrical contact is made between the two lead anodes and the copper bush with the aid of soldered heavy gauge copper wire (I). The average distance between cathode and anodes is 0.7 cm. The electrolysis vessel is a glass beaker 7 cm high and 7 cm in diameter.

More practical details are given by Op de Beeck and Hoste (86).

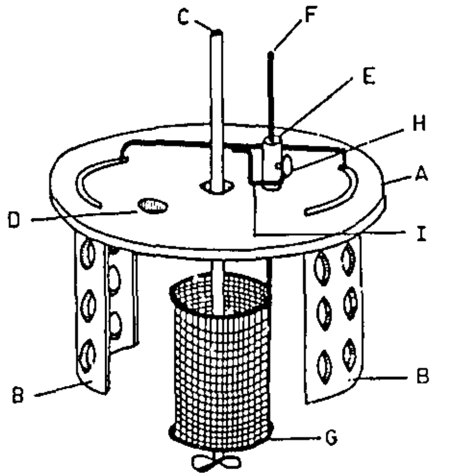

Fig. 8.24. Apparatus for internal electrolysis (86). A = insulating disk; B = perforated anodes; C = glass stirrer; D = thermometer hole; E = copper bush; F = stem of Fisher platina electrode (G); H = cathode clamp screw; I = cathode-anode short circuit.

(E) Fast Radiochemical Separations

One of the main advantages of activation analysis consists in the fact that the chemical separations don't need to be quantitative, as yield determinations are always possible (see section VI of this chapter). Owing to this, fast separation techniques can be achieved, which not only allow the application of short-lived isotopes, but also can shorten very lengthy classical procedures. Meinke and Kusaka (88) surveyed the rapid radiochemical separation methods reported in the literature for isotopes with half-lives shorter than 20 m. As Meinke (89,95) points out, practically all classical techniques can be speeded up to fast separations. To get an idea about the quality of separation that one can obtain with classical rapid techniques, the decontamination of several silver and cadmium separations are shown in Figure 8.25.

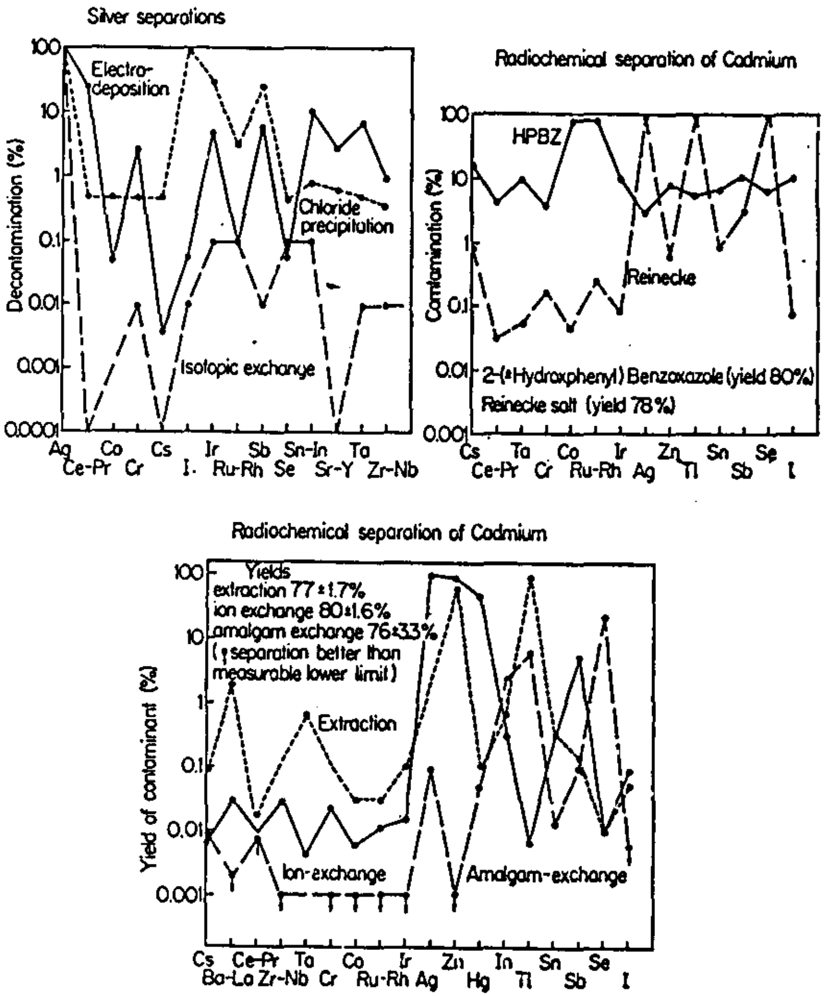

Fig. 8.25. Contamination yield in %, for various elements, using a one-step separation with different techniques for silver and cadmium (89).

However, some special techniques are particularly suited for this purpose. Apart from the techniques already discussed in this section, isotopic exchange (90,91,92) and selective reduction at a dropping mercury electrode (93,94) should retain the attention. In the isotopic exchange procedure an inactive compound is kept in contact with the active isotope and allowed to exchange according to reactions such as:

$$\begin{gathered} {}^*\mathrm{Ag}^+ + \mathrm{AgCl}\downarrow \rightleftarrows {}^*\mathrm{AgCl}\downarrow + \mathrm{Ag}^+ \\ 2{}^*\mathrm{J}^- + \mathrm{J}_2 \rightleftarrows {}^*\mathrm{J}_2 + 2\mathrm{J}^- \end{gathered} \qquad (8.10)$$

Depending on the contact time allowed, the exchange can be quantitative or not. Coryell (89) made use of this technique for the separation of the very short-lived isotopes within a few seconds.

Love (93,94) developed a selective reduction method for the separation of ^{99}Tc from fission products as a fission monitor, instead of using the ^{99}Mo method. For this purpose a polarograph was used in order to obtain the correct voltage required for the reduction. The mercury of the dropping electrode is collected after passing through the 1 ml fission product solution, and drained after 3 m operation. The total yield in these conditions is however only 0.1%, but the method allows 48 separations per day, whereas only 8 could be performed by means of the ^{99}Mo method.

A number of quick separation techniques, for the determination of various elements, is summarized in Table 8.4.

Bowen and Gibbons (106) discuss the times which are necessary to perform an individual separation step. These data, which can be very helpful in planning quick separation techniques, are summarized in Table 8.5.

TABLE 8.4

Quick separation methods for various elements

Element determined	Isotope used	Half-life	Matrix	Separation technique	Ref.
Aluminium	^{28}Al	2.3m	Ores	Fuse with Na_2O_2, dissolve in H_2O and filter, boil the filtrate with NH_4Cl and filter the $Al(OH)_3$ precipitate (yield 50–80%)	103

TABLE 8.4—*cont.*

Quick separation methods for various elements

Element determined	Isotope used	Half-life	Matrix	Separation technique	Ref.
Cobalt	^{60m}Co	10.5m	Rat tissue	Fuse with Na_2O_2, extract with 8-hydroxyquinoline from acetate buffered soln., back extract into strong HCl, precipitate as metal-oxide by Na_2O_2 (yield 40%)	101
Copper	^{66}Cu	5.2m	Rat tissue	Fuse with Na_2O_2, extract with cupferron from acid soln., back extract into base, precipitate as CuS (yield 80%)	96
Magnesium	^{27}Mg	9.5m	Ores	Fuse with $K_2S_2O_7$ or NaOH, acidify with HCl, make pH = 3 with NH_4OH, extract interferences with acetylacetone in ethylacetate, and with sodium diethyldithiocarbamate in ethylacetate. Extract Mg from the aqueous phase at pH = 10 with 8-quinolinol in $CHCl_3$, in the presence of an aqueous soln. of ethylene-glycol-monobutylether (yield 75%)	103
Niobium	^{94m}Nb	6.6m	Ores	Fuse with $K_2S_2O_7$–NaF mixture, extract Nb from a HF–H_2SO_4 soln. with 2,6-dimethyl 4-heptanol (yield 70–90%)	103
			Steel	Dissolve in HF–HNO_3 mixture, extract into hexone, back extract into oxalic acid soln., precipitate from NH_4OH soln. with EDTA (yield 80%)	104
Rhodium	^{104m}Rh	4.4m	Meteorites	Fuse with Na_2O_2, and form rhodium nitrite complex. After iron scavenging, precipitate K–Rh–nitrite complex, dissolve in hot 8N HCl and precipitate with Zn as metallic Rh (yield 50–70%)	100
Silver	^{108}Ag	2.4m	Meteorites	Fuse with Na_2O_2, precipitate as AgCl, dissolve and precipitate as metallic silver with Zn (yield 80%)	100

TABLE 8.4—*cont.*

Quick separation methods for various elements

Element determined	Isotope used	Half-life	Matrix	Separation technique	Ref.
Thallium	^{206}Tl	4.2m	—	Extract as thallium bromide with diethylether, precipitate with thionalide (yield 80–100%).	97
^{232}Th	^{233}Th	22.4m	Ores Rock	Fuse with Na_2CO_3–Na_2O_2 mixture, sorb on Dowex-1 in HNO_3 medium, filter off the resin and elute Th with HCl, precipitate as $Th(OH)_4$ (yield 30%)	105
Titanium	^{51}Ti	5.8m	Ores	Fuse with $K_2S_2O_7$, acidify with H_2SO_4, add NH_4SCN and extract the Ti-complex with tri-*n*-octylphosphine oxide in cyclohexane, back extract into H_2SO_4 (yield 90%)	103
			Rocks Minerals Meteorites	Fuse with Na_2O_2, coprecipitate with $Fe(OH)_3$, extract with cupferron from H_2SO_4 soln., wash with cold NaOH and H_2SO_4 (yield 70%)	102
			Biological samples	Leach with HNO_3, fume with $HClO_4$, dissolve in HCl, coprecipitate with $Fe(OH)_3$, dissolve and extract with cupferron as above	102
Vanadium	^{52}V	3.7m	Ores	Fuse with $K_2S_2O_7$, dissolve and oxidize with $KMnO_4$, extract from HCl soln. with *n*-benzoylphenylhydroxylamine in $CHCl_3$ (yield 85–90%)	103
			Cracking catalysts	Fuse with Na_2O_2, precipitate Al with 8-hydroxyquinoline, extract V with cupferron (yield 50–70%)	96–97
			Marine biological ashes	Leach with NaOH, extract V with cupferron	98–99

TABLE 8.5

Time required for individual separation steps after Bowen and Gibbons (106)

Technique	Time (min)
Fusion of sample with Na_2O_2 and solution of melt	3
Wet ashing biological material	1
Distillation	4
Solvent extraction	1
Ion exchange (10 ml)	10
Precipitation	1
Centrifugation	2
Filtration (100 ml)	2
Electrodeposition	30
Evaporation of 10 ml H_2O	3
Evaporation of volatile solvent	3
Plating and drying final precipitate	2

(F) AUTOMATED RADIOCHEMICAL SEPARATIONS

In recent years, automated radiochemical separations have been introduced with the aim of diminishing the operator's time and the absolute time required for performing radiochemical separations, eliminating the necessity of having trained radiochemists to do the separations, and increasing the reproducibility and the reliability.

In most cases automatic separations by chromatography have been proposed, not only because a great deal of literature is available on chromatographic systems, but particularly because they can be automated rather simply.

1. *Automatic Separation System of Girardi*

Girardi *et al.* (37) described a machine which is composed of a repetition of two fundamental units, which can be connected in different ways: the pump and programming unit; the fraction collector and series-parallel deviator.

A schematic drawing of the pump and programming unit is shown in Figure 8.26. The pump is composed of a 30 ml glass syringe (2), whose piston is driven back and forth by a synchronous motor (1).

Each eluting agent is injected into the column by a different pump. By changing the motor and adjusting a screw, different flow rates and eluent volumes can be obtained. Each pump is connected to a reservoir (4) for refilling. The pumps are connected to the columns by means of 1 mm I.D. teflon tubing. The operation of the pump is programmed on a printed circuit cardboard (5) placed in the upper part of the pumping unit.

The fraction collector shown in Figure 8.26 consists of a collector for eight fractions (7), a column (6), provided with a motor driven three-way stopcock (8) allowing the effluent to be directed to the collecting bottle or to another column according to the program request. The sample solution is introduced into a reservoir, which is connected to the first column by means of a coil of teflon tubing, containing the wash solution. It has to be remarked that the sample and the different eluting solutions are not separated by any stopcock, the mixing being negligible due to the small diameter of the connecting tubes.

By combining a set of pumps and fraction collectors, an apparatus is obtained, which allows sequential elution with several eluents through a single column, or elution through a series of columns, which can be changed at any time to a sequential elution through a selected column. A schematic drawing of this automatic system is shown in Figure 8.27. The three-way stopcocks regulate parallel or serial use of the columns.

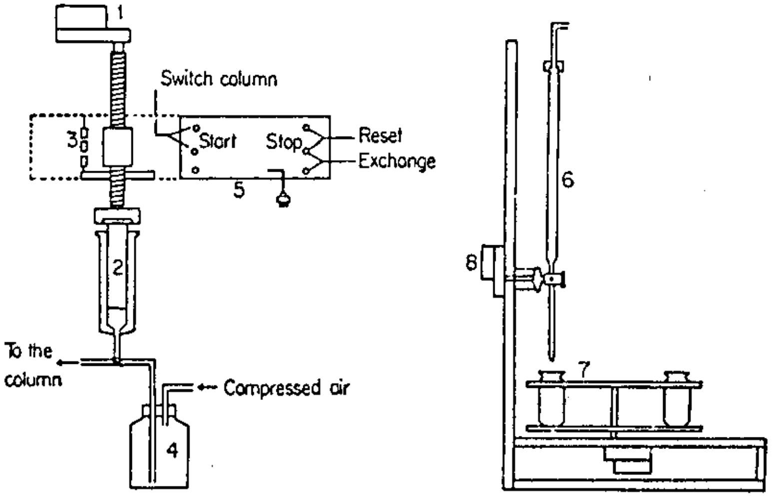

Fig. 8.26. Schematic drawing of the pumping unit with program and the fraction collector for automated ion exchange separation after Girardi *et al.* (36). 1 = synchronous motor; 2 = glass syringe; 3 = micro switches; 4 = reservoir; 5 = programming card board; 6 = column; 7 = fraction bottle; 8 = motor driven stopcock.

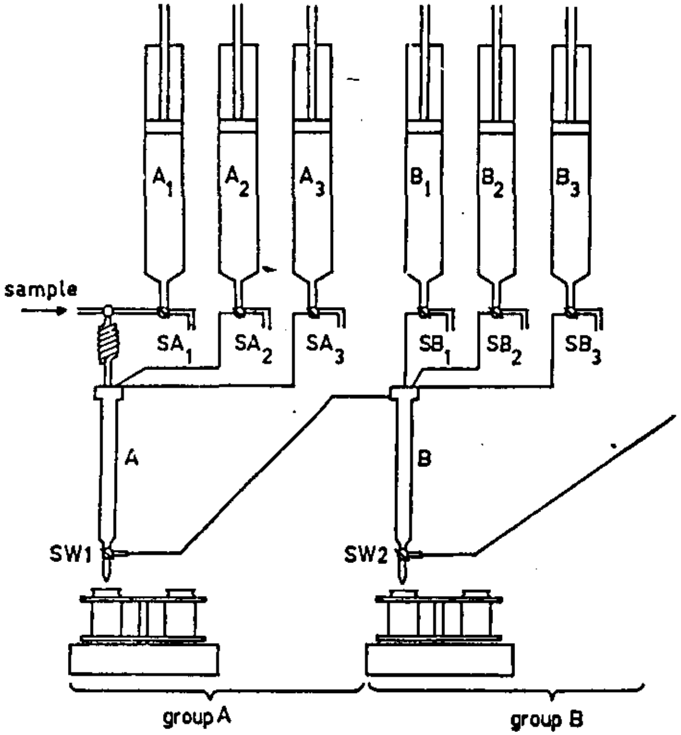

Fig. 8.27. Schematic drawing of two separation groups after Girardi *et al.* (36). A, B, ... = columns; A_1, A_2, ... B_1, B_2, ... = pumps; SA_1, SA_2, ... SB_1, SB_2, ... = connection to the reservoirs, SW_1, SW_2 = motor driven stopcocks.

2. *Automatic Separation System of Samsahl*

The group separation system of Samsahl, represented in Figure 8.15 and in Figure 8.17 can be performed fully automatically (34,35,36). The working principle and the constructional details of this machine have been described (32).

The automatic separation of Hg, Sb, As, and Se (36) is performed as shown in Figure 8.15. Columns D, E and F are respectively brought in the sulfate, chloride and chloride–bromide form (Figure 8.28). The piston barrel A is filled with 48% HBr, and B with 9N HCl. Barrel C contains the sample solution (~3.5N H_2SO_4 and 0.1N HCl) in the upper part and 10 ml 0.1N HCl washing solution in the lower part. Plate I is now forced upwards at constant speed, delivering the sample solution to column D at a rate of ca. 1 ml/m. This column adsorbs Hg. The amounts of acid between the columns, injected simultaneously via A and B, make the influent solution ca. 4.5N HCl for column E and 2.3N HCl–4.5N HBr for F respectively. When the sample solution has been forced out of C, a small glass rod R automatically pushes out the rubber stop in piston H, thus giving free passage for the subsequent washing solution. After ca. 30 m, the sample and the washing solution have been passed through the system of ion-exchange columns and the machine stops. After draining of the columns (D: Hg; E: Sb; F: As, Se), the resin phases are transferred to polyethylene tubes, homogenized by means of the corresponding influent solutions and counted by gamma-ray spectrometry.

The separation is thus performed simultaneously and automatically

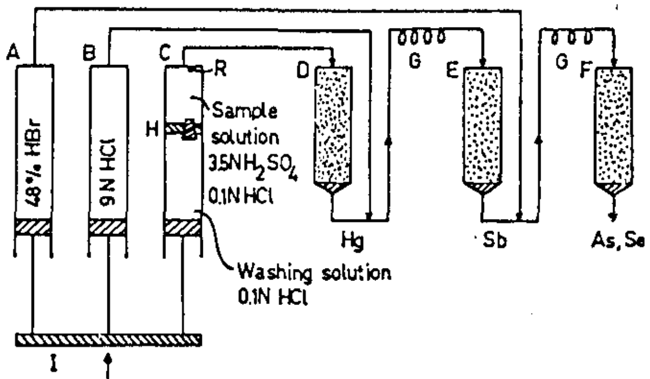

Fig. 8.28. Scheme of automated anion-exchange separation of Hg, Sb, As and Se (32). A = Piston barrel 2.8 × 15 cm; B, C = Piston barrels 2 × 1.5 cm; D = column 0.5 × 5 cm; Dowex −2 (HSO_4^-, 200–400 mesh); E = column 0.7 × 5 cm; Dowex −2 (Cl^-, 200–400 mesh); F = column 1.8 × 5 cm; Dowex −2 (Cl^-, Br^-, 200–400 mesh); G = mixing coils; H = Piston with rubber stopper; I = perspex plate; R = glass rod.

with a piston-driven proportioning pump. A peristaltic pump may also be used, although the latter is more sensitive to differences in flow resistance of the column, which may lead to slightly inexact volumes of liquid being supplied to the series. The same effect may also be caused by differences in the swelling of the plastic tubes transferring the strongly acid or alkaline solutions.

Samsahl (35) describes also the automatic separation of a great number of non volatile trace elements in biological material, which was discussed earlier (section II, G of this chapter, Figure 8.17). A peristaltic pump was used and the working principles shown in Figure 8.29. The pump is equipped with 12 Tygon plastic tubes (I.D. 1.6 mm). Teflon tubes with 1 mm I.D. are used to connect the columns in the series, B, C, D, E, F, G and H. The various influent solutions are thoroughly mixed by pumping them through the mixing coils J. The coils, with a diameter of 15 mm, consist of 8 turns of teflon tubing. As shown in Figure 8.29, the effluent solution from column B is fed back to the suction side of the pump, before entering the remaining columns in series. This is done to decrease the flow rate resistance in the system and to make the proportioning control easier (*cf.* also Figure 8.17).

The working principle is easily understood by comparing Figure 8.17 and Figure 8.29. Note that column B can be subdivided into three smaller, coupled columns, the first being 10 cm high and the remaining two each 5 cm high. This arrangement is made to allow for a further sub-grouping into five different groups of the many trace elements adsorbed on this column (group 5 to 9 in Figure 8.17), nl. Mo, Pa, W, (Ir); Cd; Zn; Fe, Ga, In; Co, Cu, Np.

3. *Other Automated Separations*

It is evident that a complete survey of automated separations falls beyond the scope of this book. Comar and Le Poec describe a system for automatic separation and determination of iodine in biological samples (see Chapter 9, refs. 63, 64). The automated apparatus developed by Vallis at Aldermaston (107) should be mentioned. This system facilitates chemical separations by precipitation, ion-exchange and solvent extraction, in times of the order of 20 s. It also claims to allow quite sophisticated separation schemes to be elaborated for radionuclides with half-lives of about one minute.

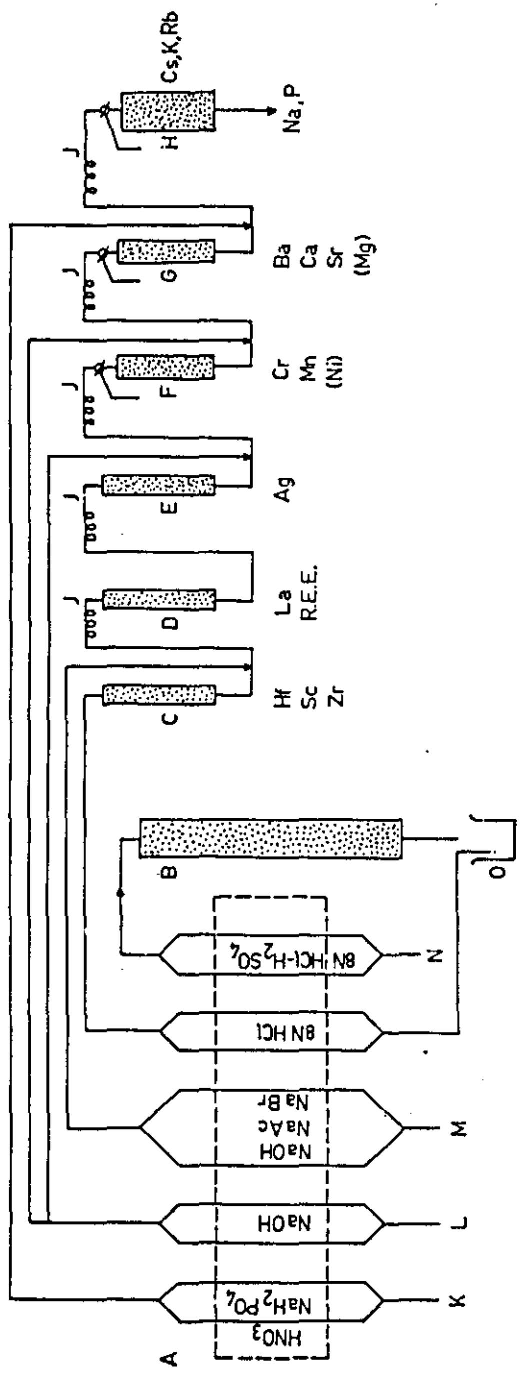

Fig. 8.29. Scheme of automated separation system after Sumsahl *et al.* (35). A = peristaltic pump; B = 0.5 × 20 cm Dowex-2 (Cl^-, 200–400 mesh); C = 0.5 × 5 cm, HDEHP-treated Kieselguhr; D = 0.7 × 5 cm, HDEHP-treated Kieselguhr; E = 0.7 × 5 cm Dowex-2 (Cl^-, 200–400 mesh); F, G = 1.0 × 5 cm chelox-100 (Na^+, 100–200 mesh); H = 2.2 × 9 cm Bio-Rad ZP-1 (100–200 mesh); J = mixing coils; K = point at which 10N nitric acid + M sodium dihydrogenic phosphate (1:1) is introduced; L = point at which 8N sodium hydroxide is introduced; M = point at which 4M sodium acetate—10N sodium hydroxide—5N sodium bromide (15:3:2) is introduced; N = point at which 8N hydrochloric acid-conc. sulfuric acid sample is introduced; O = test tube.

(G) SUBSTOICHIOMETRY IN ACTIVATION ANALYSIS

The principle of reversed isotope dilution making use of changes in specific activity is generally applied in activation analysis, allowing non quantitative separation techniques, as yield determinations can be performed in a simple way. Indeed if a sample contains an element giving rise to an activity A and an amount w_c of carrier is added, the activity a of the recovered amount m, allows the calculation of A according to

$$A = a\frac{w_c}{m} \tag{8.11}$$

provided the added amount is large in comparison to the amount originally present. A very interesting technique, called substoichiometric separation (108,109,110,111,112), allows an activation analysis to be performed without any yield determination. Assume that a sample and a standard are irradiated under identical conditions and subjected to chemical separations after carrier addition. Taking into account the proportionality between the weight and the induced activity, one can write, according to equation (8.11):

$$\frac{w}{w_s} = \frac{A}{A_s} = \frac{a\dfrac{w_c}{m}}{a_s\dfrac{w_{cs}}{m_s}} \tag{8.12}$$

where w is the weight of the element to be determined and the subscript s indicates the standard. When equal amounts of carrier are added to standard and sample ($w_{cs} = w_c$), and equal quantities are separated ($m_s = m$), then equation (8.12) simplifies to

$$w = w_s\frac{a}{a_s} \tag{8.13}$$

To obtain equal amounts of isolated element, a smaller amount of reagent can be added than is required by the stoichiometry of the separation reaction under consideration (substoichiometric separation). The only condition that has to be fulfilled, is that equal amounts of reagent are used for the sample and the standard. Under these conditions equation (8.13) is valid provided the amount X of carrier added is much larger than the weight w of the element present in the sample and the standard. Thus the weight of the element in the sample can be determined by a relative activity measurement without any yield determination. Several authors (111,112,114) point out that all techniques ensuring easy separation of the required (substoichiometric) quantity from the excess of the element: e.g. precipitation, complexing followed by solvent extraction or ion exchange, electrolysis, ... etc. can be used for this purpose.

When the weight of the element is not negligible in comparison to the amount of carrier added, equations (8.11) and (8.13) can be corrected, and the substoichiometric activation analysis still remains possible. Indeed, in this condition, the following relations are valid for sample and standard

$$A = a\frac{(w_c + w)}{m}; \quad A_s = a_s\frac{(w_{cs} + w_s)}{m_s} \tag{8.14}$$

and equation (8.12) becomes

$$\frac{w}{w_s} = \frac{a\dfrac{(w_c + w)}{m}}{a_s\dfrac{(w_{cs} + w_s)}{m_s}} \tag{8·15}$$

or, according to the substoichiometric principle $X_s = X\,(w_{cs} = w_c)$ and $m_s = m$

$$\frac{w}{w_s} = \frac{a\,(w_c + w)}{a_s\,(w_c + w_s)} \tag{8.16}$$

Solving (8.16) for w yields:

$$w = w_s\frac{a}{a_s}\left[\frac{1}{1 + \dfrac{w_s}{w_c}\left(1 - \dfrac{a}{a_s}\right)}\right] \tag{8.17}$$

As is clearly shown in equation (8.17) the weight of the element in the sample can be calculated from a simple activity ratio measurement, provided a substoichiometric separation technique is applied.

Suzuki *et. al.* (108) describe, how for the determination of minor constituents, activation analysis can be performed with the substoichiometric technique, avoiding not only yield determination, but also the need of a standard. In fact when a sample, containing a weight w of the element to be determined is activated and after irradiation is divided for instance into two equal parts, the specific activity [illegible] the first part will be given by:

$$S_1 = \frac{A}{w} \tag{8.18}$$

To the second part an amount w_c of carrier is added, and the specific activity of this part becomes:

$$S_2 = \frac{A}{w + w_c} \tag{8.19}$$

If one separates from both portions a substoichiometric amount m of the element ($m < w$), giving rise to activities respectively a_1 and a_2, combination of equations (8.18) and (8.19) yields:

$$\frac{S_1}{S_2} - 1 = \frac{w_c}{w} \quad \text{or} \quad \frac{a_1}{a_2} - 1 = \frac{w_c}{w} \tag{8.20}$$

From (8.20) it appears that the weight of the element to be determined w, can be obtained from simple activity ratios, without the need for a standard or a yield determination. Moreover, when the isotope used in the determination can also be formed from the matrix by a threshold reaction or by a second order interference; the results obtained by this method are not affected, which is not true for the previous one. A serious disadvantage of this method however, is the impossibility of removing substoichiometric quantities when dealing with trace analysis and the possibility of introducing the element to be determined in the fraction where no carrier is added, as an impurity of the chemical reagents. Therefore, the first technique is superior, and has been applied by numerous authors, as can be seen from Table 8.6, where a survey is given of substoichiometric activation analyses of different elements in various matrices.

Ruzicka *et al.* (112, 113b) discuss the applicability and the optimum conditions for substoichiometry in isotope dilution and activation analysis for a number of elements: As, Sb, Bi, Cd, Cl, Cr, Co, Cu, F, Ga, Au, In, I, Fe, Pb, Mn. Hg, Mo, Ni, Pd, Pt, R.E.E., Re, Sc, Ag, Tl, Th, V, Y, Zn, Zr.

When dealing with substiochoimetric analysis one should always remember that the substoichiometric ratio of unknown and reference are unequal. This can cause in some cases a shift of the equilibrium which is not taken into account by this technique.

TABLE 8.6

Substoichiometric activation analyses of different elements in various matrixes

Element determined	Matrix	Ref.
Ag	GeO_2, Pb	115
As	semicond. Si	116
Bi	granite, Si	117
Ca, Zn	Ga	118
Cu	high purity Al, Si, Fe, Ga, Zn, Sn	119
Cu, Zn	GeO_2	120
Ga	Al, semicond. Si	121
Mn	biological material, KF, Zr	122
Mo	GeO_2	123
Pt, Tl	biological material	124
Re	meteorites, molybdenites	125
So	meteorites	126
Sb	semicond. Si	127

V. Radiochemical Separations of Low-Level Radioactivity

Low-level methods have been mainly applied in environmental studies of naturally occurring or artificial radioactivity, research in cosmic-ray induced radioactivity in meteorites and atmospheric nuclei, determination of nuclear reaction cross sections in the submicrobarn region and studies of nuclear reactions in which the available beam intensities are very low although cross sections are large. Such methods can also be applied to trace-element determination by activation analysis. It is obvious that many separation methods used at ordinary levels may be converted to low-level procedures with only minor modifications, so that there exists potentially an infinite number of low-level separation schemes. Some special precautions must, however, be taken, since for low-level radioactivities, the net signal/noise ratio is, per definition, much smaller than 1.

The background of the counter should be as low as possible in order to obtain the best signal/noise ratio (*cf.* Chapter 11, section III, B). The lower the background of a given counter, the better its "figure of merit". One should also use a counter with the highest detection efficiency for the radionuclide of interest. In Chapter 6, Table 6.7, a number of naturally occurring radionuclides are listed, which are often found in the background. The type of counter used and the methods devised to reduce background are outside the scope of this book. Reference is made to review articles on this subject (128,129,130) and to the book by Ramsden and Watt (131).

One of the most important criteria for evaluating a low-level procedure is the blank. A blank of 1 cpm can be neglected in the case of a counter having a background of 25 cpm, but it becomes the limiting factor when the background is reduced to 0.2 cpm for instance. Hence it is obvious that the design of procedures of minimum blank is as important as engineering low backgrounds. According to Sugihara (132,133) certain requirements must be met for a low-level procedure:

—zero or small and constant blank;
—high chemical yield;
—high radiochemical purity;
—ease of preparing the sample in suitable chemical form for counting.

(A) Reducing the Blank Correction

One of the advantages of activation analysis over other analytical techniques is its practical freedom of a blank, when etching the samples and performing the separation after irradiation. There are, however, obvious complications in attempting to do low-level work in a laboratory devoted otherwise to ordinary levels of activity, particularly if others work with the same radionuclide as that being measured at a low level; a person who wants to determine traces of selenium in biological material should be completely separated from another determining traces in a selenium matrix. A very strict segregation of laboratory glassware, hardware, and other equipment, such as counters, absorbers, ovens, balances, centrifuges, etc. is highly important (132).

To obtain a negligible blank, contaminating activities present in the sample or in the reagents must be completely removed by good chemical separations and by proper choice of reagents. Potassium salts and reagents of other elements which have naturally occurring activities (Rb, Th, . . .) should be excluded from a procedure if the counting method is sensitive to the natural radioactivity. But even then, unexpected radioactive contaminants can be introduced, originating from reagents (Table 8.7); many reagents contain >0.1 cpm per 10 mg. (133b).

If the isotopic carrier, used for the isolation of the radionuclide of interest, is difficult to obtain free of active contaminants, it is often better to use a non-isotopic carrier, e.g. coprecipitation of the carrier-free isotope on ferric hydroxide.

Even ordinary distilled water contains some activity (e.g. ^{7}Be, if prepared from rain water; ^{7}Be is formed as a spallation product due to the interaction of high energy cosmic rays with nuclei in the atmosphere).

TABLE 8.7

Radioactive contaminants in reagents

Reagent	Contaminant
La_2O_3 99.99%	^{227}Ac
Y_2O_3, CeO_2	Th
Ba-salts	Ra-isotopes
Cs-salts (reagent grade)	^{40}K, ^{87}Rb
Reagents containing Cl or S	^{32}P (by cosmic-ray interaction) (0.22 cpm per kg Cl 0.46 cpm per kg sulfur)
Ru	^{106}Ru ($\leqslant$1000 dpm/g Ru)

Many radiochemical procedures require suction filtration in the final step to deposit a precipitate on a filter paper. By drawing a few liters of air through a filter, several cpm of a 30–40 m beta activity can be collected, probably a complex mixture of the daughters of ^{222}Rn (132). This airborne contamination can be excluded by avoiding suction filtration, by prefiltering the air (*cf.* also Figure 7.1) or by purifying the air by a series of traps designed specifically to remove radon and its decay products.

(B) IDENTIFICATION OF VERY LOW ACTIVITIES

The identification of a radionuclide is, obviously, more difficult than its detection. Sometimes one can determine the energy of the gamma radiation by pulse height analysis. Another possibility is the estimation of the energy of the β-rays by the use of absorbers (checking the half-thickness); as aluminium and other metals frequently have an "appreciable" blank correction, plastic absorbers (polyethylene, Mylar) have been recommended; they should be placed over the sample several hours before counting in order to avoid gradual leak off during the counting of the electrostatic charge built up on them by handling (132).

When dealing with relatively short-lived radioisotopes, one can try to follow the decay.

Recent publications concerning low-level methods can be found in ref. (134).

VI. Determination of Chemical Yield

(A) CLASSICAL ANALYTICAL TECHNIQUES

One of the advantages of activation analysis consists in the fact that after irradiation, a known amount of carrier of the element to be determined can be added. In this way, radiochemical separations don't need to be quantitative, since a yield determination can be performed, provided the weight of the element of interest in the sample is negligible in comparison to the amount of carrier added. It is evident that separations obtaining a 100% yield are preferable, but in most cases this cannot be achieved because of multiple separation steps or the need for quick separations. The two most commonly used counting forms are a solution of the element in a counting vial or a precipitate on a counting disk. For yield determinations, weighing of a precipitate is a rather difficult task, because of the uncertainty in composition of the precipitate and sometimes insufficient washing due to the speed of preparing the precipitate for counting purposes. Furthermore, weighing milligram amounts of material, which is in most cases mounted on a filter disk, is very difficult to perform accurately.

On the other hand, any classical analytical technique can be used for yield determination purposes, and the choice of the technique will depend on the matrix, the foregoing separation steps, the equipment available and the chemist. Norton (135) describes in detail the procedures applied for yield determination at the analytical laboratory of the chemistry department of BNL. These techniques are selected in such a way that practically all of them can be performed by a it can be shown that a precise result is only obtained when no interfering elements are present.

If interfering elements are present, precise results can, however, be obtained on condition that carriers are added for all elements in the ratio in which they occur in the sample.

Obviously, the relative trace element composition in a particular sample would not normally be known and the addition of carriers must be based on a probable sample composition, derived from the knowledge of the general composition of sample material. The result will be a statistical improvement of precision, depending on the distribution of trace element ratios around the most probable values.

Heydorn has investigated the degree of improvement when determining arsenic in hair samples, utilizing available information on the trace element composition, namely the correlation between arsenic and antimony.

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CHAPTER 9

ANALYSIS WITHOUT CHEMICAL SEPARATION

I. General Principles

Activation analyses without chemical separations can be applied in special conditions only. In the most simple case the ratio of the activities induced in the matrix and in the element to be determined is low or even zero. If the matrix activity is low, chemical separations can be avoided for the analysis of minor constituents, but generally not down to the trace element level. Determinations even down to this level can be achieved when the matrix does not become radioactive. When the matrix activity is shorter lived than the activity induced in the element to be determined, the former can be allowed to die out before the latter is measured.

Even when a long-lived matrix activity is obtained, an attempt can be made to count the isotope to be determined in a selective way. This can be achieved either by discriminative counting, when the energy of the matrix activity is lower than the isotope of interest, or by the use of an instrumental technique, such as described in Chapter 6, section III, E, which can turn a detection method into a more or less selective one for a given isotope. Anyhow, with this last technique the difficulties generally increase rapidly when reaching the ppm level, due to the fact that the matrix/element activity ratio becomes quite high. This high matrix activity can give rise to saturation and pile-up in the detector and in the electronic measuring circuits. If one minor or trace element gives rise to an intense and high energy radiation, masking of low intensities at lower energies also becomes unavoidable.

Practically every measuring technique can be coupled to an analysis of a decay curve. This provides not only a purity check of the measured activity by half-life, but when interferences of the matrix or of impurities occur, an analysis of this curve can allow the determination of the activity of the isotope of interest. Here again, at the trace impurity level, activities are not normally large enough to allow a precise analysis of the curve, due to the large statistical fluctuation in count rate. The