

### 6.1.3.3 Reference materials; error sources

#### - Reference materials

Normally primary standards have been irradiated together with the samples if one hundred per cent chemical yield of the separation procedure (if any used) can be assumed. The reference material can then be counted without being processed any further. In this case the analyst should ascertain complete recovery of the carbon (as well as any other component to be determined) prior to the analysis of unknown material. This can be accomplished by separation of radio-carbon-doped samples with appropriate matrix compositions or by analysis of certified reference materials. In the case of incomplete radiocarbon recovery a reference material with a similar gross composition has to pass the same separation procedure as the sample so as to obtain a chemical yield. This problem is discussed further below in the error sources section. Regarding the information given in Tab.6.1-2, sixth column, it is obvious that in the case of carbon analysis mostly graphite been used as primary standard (see e.g.<sup>750</sup>); being stoichiometrically well-defined and available with a high purity level, this material offers itself as ideally suitable. Moreover, it is inexpensive and can be supplied in almost any geometrical shape, does survive excessive radiation doses and heat. Finally, high purity material assumed, it does not produce any matrix-inherent background radiation.

However, pure carbon also bares some disadvantage. First, in many cases it is of advantage to use material as a reference with virtually the same matrix composition as the analysed sample, particularly if an instrumental procedure is applied. Second, the use of a matrix-inherent internal flux monitor is not possible, and finally, if multi-component analyses are to be performed the standardisation procedure is simplified if a multi-component reference material is also used, again particularly in the case of purely instrumental application. Therefore, other material has been used, too. In the analysis of carbon in alkali metals, frequently the appropriate carbonates have served as reference materials so as to provide an internal standard via the induced activity of the alkali cation, e.g.  $^{22}\text{Na}$  or  $^{132}\text{Cs}$ . These carbonates may be processed as the analysed samples in order to enable separation yield assessment or readily be measured whichever is more convenient.

Particularly for instrumental analysis of carbon and oxygen, mylar has often been used as bicomponent reference materials. Besides 4% of hydrogen mylar contains 60% carbon and 36% oxygen. This material can be easily handled (e.g.

cleaned from outer contaminants after bremsstrahlung exposure) and the combined decay curve due to the resulting activities can be easily resolved (see e.g.<sup>49, 726, 728</sup>). Moreover, its composition is reproducible and it is well resistable against heat and radiation attack<sup>17, 49</sup>.

Beard et al.<sup>707</sup>, Pronman et al.<sup>730</sup> and Persiani et al.<sup>768</sup> used polyethylene in non-destructive carbon analysis of high-purity beryllium. However, operating at higher electron beam current, Lutz and Masters<sup>750</sup> found polyethylene unsuitable due to radiation attack effects. The same behaviour was complained by Baker et al.<sup>719, 783</sup> testing a variety of organic polymer materials. They concluded that either graphite or standard steels optimally met their requirements. Also in the authors' laboratory standard steels have frequently been used with satisfactory results.

#### - Chemical interference

Non-destructive carbon analysis are perhaps more problematic than oxygen or fluorine determinations since the threshold energy of the photonuclear reaction is comparably high, namely about 19 MeV. This is higher than that of most other ( $\gamma, n$ ) thresholds encountered throughout the Chart of Nuclides. Moreover, in order to achieve appreciable sensitivity for trace analysis, the electron energy has to be set well above the giant resonance maximum energy, as already noted. In the case of carbon this would require an electron energy of at least 30 MeV which is far beyond any ( $\gamma, n$ )-threshold. Therefore, selectivity of the carbon activation normally cannot be achieved. This also applies to nuclear interference discussed below. Thorough investigations of chemical interference in photon activation analysis of carbon can be found in Ref's. 17, 24, 45, 707, 719, 749, 763, 783 and many others.

A selected number of possible contaminants with half-lives close to that of  $^{11}\text{C}$  is given in Tab. 6.1-3. As already noted, in radiochemical analysis interference by higher Z nuclides normally may be disregarded, but in disadvantageous cases might occur as reported by Schmitt et al.<sup>737</sup>. Therefore a thorough study of the physico-chemical behaviour of the matrix components during chemical separation is particularly recommendable if one or more of those nuclides listed in table 6.1-3 are produced during bremsstrahlung exposure.

Tab.6.1-3: Bremsstrahlung-produced radionuclides with half-lives  
close to 20 minutes

T(m)	Nuclide	Target	T(m)	Nuclide	Target	T(m)	Nuclide	Target
15.5	$^{91}\text{Mo}$	$^{92}\text{Mo}$	18	$^{119\text{m}}\text{In}$	$^{120}\text{Sn}$	21	$^{52\text{m}}\text{Mn}$	$^{54}\text{Fe}$
15.9	$^{120}\text{Sb}$	$^{121}\text{Sb}$	19	$^{94}\text{Y}$	$^{96}\text{Zr}$	21	$^{84\text{m}}\text{Rb}$	$^{85}\text{Rb}$
16.3	$^{45}\text{K}$	$^{46}\text{Ca}$	20	$^{113\text{m}}\text{Sn}$	$^{114}\text{Sn}$	21.1	$^{70}\text{Ga}$	$^{71}\text{Ga}$
17.6	$^{80}\text{Br}$	$^{81}\text{Br}$	20	$^{115}\text{Ag}$	$^{116}\text{Cd}$	22.2	$^{44}\text{K}$	$^{46}\text{Ca}$
18	$^{81}\text{Se}$	$^{82}\text{Se}$	20.8	$^{112\text{m}}\text{In}$	$^{113}\text{Sn},$ $^{114}\text{Sn}$	24	$^{106}\text{Ag}$	$^{107}\text{Ag}$
						25	$^{128}\text{I}^1$	$^{127}\text{I}$

$^1$ photoneutron-produced

- Nuclear interference

In photon activation analysis of carbon, due to the high activation threshold the use of lower activation energy to discard interfering reactions normally is not possible with regard to the required analytical sensitivity. Therefore, one or several competing reactions are unavoidable in the most cases and their contribution to the common resulting  $^{11}\text{C}$  activity has to be taken into account. In Tab.6.1-4, photonuclear reactions are listed which lead to  $^{11}\text{C}$ .

Tab.6.1-4: Nuclear reactions by which  $^{11}\text{C}$  is produced

No.	Reaction	Threshold (MeV) <sup>1</sup>	No.	Reaction	Threshold (MeV) <sup>1</sup>
1	$^{12}\text{C}(\gamma, n)^{11}\text{C}$	18.7	10	$^{24}\text{Mg}(\gamma, ^{13}\text{C})^{11}\text{C}$	27.7
2	$^{14}\text{N}(\gamma, t)^{11}\text{C}$	22.7	11	$^{24}\text{Mg}(\gamma, 3\alpha n)^{11}\text{C}$	40
3	$^{16}\text{O}(\gamma, \alpha n)^{11}\text{C}$	26	12	$^{27}\text{Al}(\gamma, ^{16}\text{N})^{11}\text{C}$	33.5
4	$^{19}\text{F}(\gamma, ^8\text{Li})^{11}\text{C}$	33	13	$^{28}\text{Si}(\gamma, ^{17}\text{O})^{11}\text{C}$	31.1
5	$^{19}\text{F}(\gamma, \alpha t n)^{11}\text{C}$	37.6	14	$^{31}\text{P}(\gamma, ^{20}\text{F})^{11}\text{C}$	35
6	$^{20}\text{Ne}(\gamma, ^9\text{Be})^{11}\text{C}$	29	15	$^{32}\text{S}(\gamma, ^{21}\text{Ne})^{11}\text{C}$	31
7	$^{20}\text{Ne}(\gamma, 2\alpha n)^{11}\text{C}$	30.6	16	$^{14}\text{N}(p, \alpha)^{11}\text{C}$	4.0 <sup>2</sup>
8	$^{23}\text{Na}(\gamma, ^{12}\text{B})^{11}\text{C}$	33.5	17	$^{11}\text{B}(p, n)^{11}\text{C}$	2.5 <sup>2</sup>
9	$^{23}\text{Na}(\gamma, 2\alpha t n)^{11}\text{C}$	48			

<sup>1</sup>taken out of Ref.<sup>754</sup> or calculated

<sup>2</sup>taken out of Ref's. 56, 858

Since, due to  $(\gamma, p)$ -reactions in the matrix, also considerable fluxes of photoprotons might be produced in the sample matrix, also secondary interference by proton reaction is considered in this table.

Out of these reactions, besides the analytically evaluated No. 1, the No's 2 and 3 and eventually No's 16 and 17 might interfere, if irradiations are conducted at electron energies around 30 MeV. The other ones have too high threshold energies and low activation cross sections and therefore might be disregarded unless the concerned target elements are main matrix components (see 6.1.2.5). Quantitative interference yields are given in the literature cited in 6.1.2.5. As an example: Engelmann<sup>23</sup> found that by 30 MeV bremsstrahlung activation 1 microgram carbon yields the same  $^{11}\text{C}$  activity as 56 micrograms nitrogen through  $^{14}\text{N}(\gamma, t)$  and 1000 micrograms oxygen through  $^{16}\text{O}(\gamma, an)$ , respectively.

- Other error sources

Besides the error sources discussed in 6.1.2.5 and above in this paragraph, others might appear in the separation step during radiochemical carbon analysis. These show up as a chemical yield other than 100%, be it due to poor radiochemical purity of the counted fraction or uncomplete radiocarbon recovery after separation. This might have the following reasons:

- a) The sample was not completely burned (during the combustion process) or was not completely dissolved (during fusion in an oxidising bath or any other approach). To avoid incomplete radiocarbon extraction high-level carbon-bearing fluxes have been used to support fusion of the samples (see Tab. 6.1-2). A thorough study of this problem has been carried out by Fedoroff and co-workers<sup>781,784</sup>. They found that in some cases the classical fusion method using lead borate was not applicable. Other bath compositions were proposed (see also Tab.6.1-2).
- b) Any  $^{11}\text{C}$ -compound was adsorbed during transport and processing prior to sorption in the  $^{11}\text{CO}_2$  collector; under normal conditions, however, the transport gas and the added inactive carrier enable loss-free recovery of the radiocarbon.
- c) Radiocarbon was not completely oxidised; to avoid losses of  $^{11}\text{C}$  as  $^{11}\text{CO}$  the gas has been made pass multiple oxidation steps, viz. heated  $\text{CuO}$ , Schütze-reagent or other oxidants, e.g. Hopcalite<sup>776</sup>.



- d)  $^{11}\text{CO}_2$  has not been completely absorbed by the collecting agent; normally this malfunction does not occur. If alkaline solution is used a gas distributor is recommended to form small bubbles and thus create a large chemical exchange area. If solid collecting media, e.g. ascarite, is applied one has to select a suitable grain-size, for the same reason<sup>751</sup>. By proper adjustment of the flow-rate the analyst has to ascertain a sufficient residence period of the  $^{11}\text{CO}_2$  in the collecting vessel. This is of particular importance if a liquid nitrogen-cooled trap is used (see e.g.<sup>719,783</sup>).
- e) The radiocarbon in the counting vessel is contaminated with other activities, particularly  $\beta^+$ -emitters; normally activities other than radiocarbon dioxide are removed by the different purification steps within the radiochemical analysis procedure (see also Figs. 6.1.3 and 6.1.4). However, in critical cases, radioactive contamination of the counted fraction was reported<sup>737</sup>. If these contaminants are non-positron emitters their influence is ruled out by coincidence counting, if the contamination level is not excessively high. If the contamination is positron-emitting it can be accounted for by decay-function analysis as already noted in 6.1.2.5. However, if the positron-emitting contamination decays with a half-life close to 20 minutes it cannot be accounted for; in this case the purification procedure has to be reconsidered<sup>737</sup>. A particular problem in this instance is the contamination of the radiocarbon fraction with radiofluorine in the case of sodium analysis. Although having greatly different half-life (109.7 minutes)  $^{18}\text{F}$  might be troublesome since at high bremsstrahlung energies, say more than 30 MeV, it is produced in significant amounts through  $^{23}\text{Na}(\gamma, \alpha n)$  from the matrix (see 6.1.6.3) and high-level contamination of the  $^{11}\text{C}$ -fraction with  $^{18}\text{F}$  might result in severe loss of significance of the carbon signal. Therefore,  $^{18}\text{F}$  has been separated by different agents, namely boric acid (Lutz and DeSoete<sup>722</sup>), zirconium oxychloride (Nordmann et al.<sup>743,744</sup>) and silver wool (Bock et al.<sup>756</sup>, Marschal et al.<sup>775</sup>).

All in all, the radiocarbon recovery has mostly been reported to be around 100%, except in a few cases, e.g. in the analysis of sodium as reported by Bock et al.<sup>756</sup> or in the carbon determination in molybdenum reported by Schmitt and Fusban<sup>737</sup>. Many workers have investigated the radiochemical behaviour of  $^{11}\text{C}$  during separation and collection (see e.g. Hislop and Williams<sup>776</sup> and various publications of Engelmann and co-workers) and many have carried out radioactive tracer studies of the different mechanisms. However, the application of tracers bears the danger of non-representativeness; in several cases they might not show the same behaviour as the determined element in the sample matrix (see

e.g. <sup>682</sup>). However, normally they have been applied successfully as far as it could be verified by analysis of certified reference materials.

#### 6.1.3.4 Sensitivity

The intrinsic sensitivity of the carbon determination primarily depends, as was stated in 6.1.2.6, on the integrated cross section of the reaction used for analysis, the actual electron energy and the mean electron beam current of the bremsstrahlung source. In Tab.6.1-5 intrinsic sensitivities at different incident bremsstrahlung energies are given. The actual sensitivity is influenced by many other parameters, as also was explained in 6.1.2.6. Therefore, one would expect reported detection limits of carbon analysis to vary greatly. However, according to the literature inspected by the authors, there is a remarkable agreement of the achievable sensitivities between many of the different working groups. In comparing laboratory sensitivities in photon activation analysis of carbon one has to bear in mind that at electron energies around 30 MeV photon activation is performed in the close vicinity of the giant resonance energy region and thus small electron energy shifts might result in huge differences in the induced activity.

Reviewing the literature, it is sometimes difficult to compare sensitivity information since values either are given in terms of absolute minimum detectable masses or concentration limits. Some authors, giving minimum detectable concentrations, do not mention the total sample mass, and others, publishing detection limits in terms of absolute mass units, have calculated them using different criteria, be it a pulse number limit or, more informatively, Currie's criterion<sup>785,786</sup>, or do not give any calculation basis at all.

Anyhow, it appears that the detection limit for photon activation analysis of carbon performed instrumentally varies from 40 nanograms to five micrograms. If one can quote a value of maximum agreement, it is one microgram (20 min exposure to 30 MeV bremsstrahlung, mean electron beam current of 100 microamperes, and measurement after a total decay period of 20 minutes). The individual detection limit is, of course, contingent upon the chemical interference activities of the sample components other than carbon, particularly the main constituents.

In the radiochemical approach reported sensitivities (in terms of detection limits) range from one to 500 nanograms quasi-peaking at 20 nanograms. Normalised to the above described experimental conditions, the reported data are more

consistent than those given for instrumental analysis since in radiochemical analysis sensitivities suffer from chemical interference to a much lesser extent.

Table 6.1-5: Sensitivity of carbon detection by photon activation, normalised to 100 microamperes mean electron beam current and 20 minutes irradiation period as a function of the electron energy (Nordmann<sup>744</sup>).

$E_e$ -(MeV)	sensitivity ( $\mu\text{g C}$ )
25	0.48
30	0.13
35	0.048
40	0.024
45	0.017
50	0.012
55	0.010
60	0.008

#### 6.1.4. Nitrogen

The analytically exploited nitrogen reaction



has a threshold energy of 10.55 MeV<sup>753,754</sup>. Although having, like the carbon reaction, a comparatively small integrated cross section, nitrogen can be analysed very sensitively if high-efficiency fast separation steps are included in the analysis procedure.

At comparable sensitivity requirements, the chemical separation of nitrogen from the matrix must be considerably shorter than in radiochemical carbon determination. However, since mostly the same separation method, namely oxidising fusion, is applied for both elements, detection limits for nitrogen analysis usually have been reported to be higher, typically about 50 nanograms.

##### 6.1.4.1 Non-destructive analysis

The instrumental analysis of nitrogen is more problematic than that of carbon since it underlies multiple interference (see 6.1.4.3) and in the most cases the decay function cannot be resolved, particularly if trace determinations are to be carried out<sup>708</sup>. Therefore, nitrogen can be analysed instrumentally in exceptionally favourable cases only, e.g. in very high purity beryllium<sup>45</sup>.

If nitrogen has been analysed instrumentally in organic or other carbon-rich material, irradiations frequently were carried out at electron energies less than 19 MeV to exclude the carbon reaction (see e.g.<sup>714,715</sup>).

Instrumental analyses of nitrogen were reported by Engelmann<sup>764</sup> (general), 45,761 (beryllium), <sup>764</sup> (several high purity elements), Rocco et al.<sup>714</sup> (diamonds), Schmitt et al.<sup>715</sup> (air dust filters). A very interesting application of instrumental nitrogen analysis by photon activation is described by Meijers<sup>787</sup>. Relative age determinations of fossile bones were performed on grounds of the nitrogen/fluorine weight ratio.

#### 6.1.4.2 Radiochemical analysis

In metals, nitrogen normally is present elementally; during heat extraction mostly no chemical reaction of nitrogen takes place. It is evolved as  $N_2$  or  $^{13}N_2$  from the melted matrix. It can be analysed simultaneously with carbon by oxidising fusion under oxygen or inert gas atmosphere<sup>777,778</sup> or simultaneously with oxygen by reductive fusion under vacuum<sup>772,788,789</sup> or inert gas atmosphere<sup>776,790,791</sup>. Generally the setups as described in the preceding paragraph have been used, but different collecting agents for the active gas fractions.

Sometimes also the Kjeldahl method has been applied (Hashitani et al.<sup>792</sup>). However, as is explained below, this entails experimental difficulties in some cases.

For better understanding of the mechanisms of the various nitrogen extraction methods generally applied, a thorough review article by Goward<sup>793</sup> is recommended.

##### - Separation by the Kjeldahl method

This method was first applied for radiochemical photon activation analysis of nitrogen<sup>763</sup>. The irradiated samples are dissolved in reducing environment and nitrogen is thus converted to ammonia, eventually with the help of catalysts, e.g. mercury compounds<sup>763</sup>. The resulting ammonia containing  $^{13}N$  is then evolved, separated with help of a carrier gas, e.g. argon, purified and collected by any means, and then counted using the spectrometer described in 6.1.2.3. This method has been modified frequently. E.g. Pronman et al.<sup>730</sup> fused the samples in sodium, collected the ammonia in dilute acid solution and precipitated it with sodium tetraphenyle borate which was then counted (see also Kohler<sup>794</sup>).

Carrier substances evolving inactive ammonia, e.g. ammonium chloride<sup>17</sup> are added to the irradiated sample to ensure quantitative distillation of the active gas fraction. Frequently the formation of different reaction products, viz. ammonia, hydrazine, elemental nitrogen have been observed. This is surely dependent upon the chemical form of the nitrogen originally present in the sample, but the experimental conditions obviously have much more influence upon the composition of the extracted nitrogen-containing gas fraction<sup>795</sup>. However, to ensure quantitative collection on a unique sorbent, only one  $^{13}N$ -bearing compound has to be present. The easiest way is to convert all radionitrogen to elemental nitrogen gas<sup>795</sup>. This can then be collected in molecular sieve cooled

with liquid nitrogen<sup>796</sup>.

Marschal et al.<sup>775</sup> carried out a thorough study about the sorption mechanism of  $^{13}\text{N}_2$  in molecular sieve. Nitrogen can be collected as well on heated metal wool or granulate, e.g. titanium or calcium where it is bound as nitride<sup>797-799,876</sup>. The oxidation of nitrogen-hydrogen compounds ( $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ ) can be performed by heated cuprous oxide. Thereby its function is frequently double, namely to oxidise  $^{11}\text{CO}$  to  $^{11}\text{CO}_2$  and  $^{13}\text{NH}_3$  or  $^{13}\text{N}_2\text{H}_4$ , respectively, to  $^{13}\text{N}_2$  in the case of simultaneous analysis of carbon and nitrogen (see e.g. Fedoroff et al.<sup>795</sup>).

The chemical yield is not always 100%. Depending upon many experimental parameters, matrix material, chemical state of the nitrogen etc., it can be as low as 70% (see e.g.<sup>17</sup>).

Frequently poor reactivity of several matrix materials with the solvent has been complained<sup>56,716,763</sup>. In these cases, the separation procedure consumes too much time and thus the Kjeldahl method is not applicable because of severe loss of sensitivity.

#### - Heat extraction

As was mentioned in the introductory paragraph, oxidising or reductive fusion has been applied for radionitrogen extraction after bremsstrahlung activation. The oxidising fusion method is described in 6.1.3.2. Carbon and nitrogen can be analysed simultaneously using one extraction and collecting the gas fractions to be counted ( $^{11}\text{CO}_2$  and  $^{13}\text{N}_2$ , respectively) stepwise selectively in suitable sorbents (see above). Molecular sieve cooled by liquid nitrogen has frequently been used for radionitrogen collection. It can also be caught by sorption with heated calcium or titanium so as to form the corresponding radionitrides (see Fig. 6.1.4, 11).

Unlike in reductive fusion, nitrogen oxides might be produced during oxidising fusion<sup>24,737,756,800</sup>. These are reduced by heated elemental copper (see Fig. 6.1.4, 7a). The reducing fusion procedure is basically the same as the oxidising but usually is performed in graphite crucibles (so as to provide large excess of reductant for oxygen extraction) under vacuum or inert gas atmosphere. This method is discussed further in the next section about oxygen analysis.

The heat extraction method offers the following advantages as compared to Kjeldahl separation:

- Normally heat extraction can be performed more rapidly; about 10-15 min. of total separation period have been reported; see Tab.6.1-6.
- Heat extraction is quasi-universally applicable whilst in the Kjeldahl procedure the dissolution step sometimes is too time-consuming to allow trace nitrogen analyses; there are very few reports about non-applicability of heat extraction.

Engelmann<sup>742</sup> found incomplete combustion of zirconium during heat extraction of nitrogen and therefore used the Kjeldahl separation procedure described above, dissolving the sample in hydrofluoric acid.

#### 6.1.4.3 Reference materials; error sources

##### - Reference materials

As also described in 6.1.3.3 (carbon analysis) the nitrogen reference standards usually do not pass the separation procedure but are counted after separation of the analysed sample. It can be taken out of Tab.6.1-6 that mostly boron nitride has been used as a reference; this material meets all requirements initially mentioned (stoichiometrical purity, resistance against heat and radiation attack, no interfering background produced, inexpensive; see 6.1.2.4 and 6.1.3.3).

In several cases aluminium nitride was also used. On using this compound, if measured unseparated, one has to take into account considerable background activity by  $^{27}\text{Mg}$  and  $^{24}\text{Na}$  due to reaction with photoneutrons (see Ch.5), whereas no considerable background activity is produced in boron nitride.

However, the internal standard method cannot be applied if AlN is used, since the background activities mentioned above are due to neutron reactions and thus cannot represent any photon activation (see also 6.2.2 and 6.2.3.4).

Also the application of  $^7\text{Be}$  induced by  $^{10}\text{B}(\gamma, p2n)$  into BN eventually utilised as internal reference is risky since  $^7\text{Be}$  and  $^{13}\text{N}$  have largely different half-lives (53.4 days and 9.96 minutes respectively) and no parallel excitation functions (see also above 6.1.2.2).



Beryllium nitride can also be used as a reference material as proposed by Engelman and Albert<sup>24</sup>. However, the use of beryllium compounds is somewhat problematic because of their toxicity.

Multielement reference materials, as far as the authors know, like e.g. Mylar in the analysis of carbon and oxygen, have not hitherto been utilised for nitrogen analysis.

For further discussion about the reference material the reader might refer to 6.1.3.3 above.

Tab.6.1-6: Examples of radiochemical photon activation analysis procedures for nitrogen determination

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Li	Kjeldahl	H <sub>2</sub> O/NH <sub>4</sub> Cl	Ar/not given		H <sub>2</sub> SO <sub>4</sub> , 0.5M	AIN/0.2 µg/g	about 1h/determination; rad.chem. yield 95-97%	851
Be	Kjeldahl	H <sub>2</sub> SO <sub>4</sub> / NH <sub>4</sub> Cl			acid, not specified	not specified/ 0.2 µg/g	20 m/separation	763
Na	a) Kjeldahl	ethanol/ NH <sub>4</sub> Cl	Ar/not given		H <sub>2</sub> SO <sub>4</sub> , 0.5M	AIN/0.2 µg/g	see above, Li	851
	b) vacuum oxid.fus.	Pb <sub>3</sub> O <sub>4</sub> -B <sub>2</sub> O <sub>3</sub> - Fe-NaCl-KCl/ N in Fe	He/400	1000/HF	molecular sieve	AIN/0.01 µg/g	refractory crucible; rad.chem. yield ab.100%; 2 <sup>2</sup> Na as intern. stand.;	756
Al	a) Kjeldahl	HCl/NH <sub>4</sub> Cl			acid, not specified	not specified/ 0.2 µg/g	HgCl <sub>2</sub> added to support dissolution; 20 m/sep.	763
	b) inert gas oxid.fus.	Pb <sub>3</sub> O <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	He/400	1250/HF	molecular sieve	not specified/ 0.6 µg/g	simultaneous C and N analysis	742
Si	a) -----	-----	-----	-----	see Al b)	-----	-----	742
	b) Kjeldahl	NaOH melt/ Si <sub>3</sub> N <sub>4</sub>	N <sub>2</sub> /not given	1000/HF	acid, not specified	BN/0.3 µg/g	NH <sub>3</sub> precip. with tetra- phenylborate	730

Tab. 6.1-6, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp. (°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Si	c) Kjeldahl	KOH melt/ not given	Ar/300	500/not given	Ti-sponge	AlN 0.1 µg	10 m/separation	795
	d) inert gas oxid.fus.	Pb <sub>3</sub> O <sub>4</sub> -B <sub>2</sub> O <sub>3</sub> - Fe/N in Fe	He/200	1200/HF	molecular sieve	not specified/ 41 ng/g	10 m/separation	775
SiC					see Al b)			742
Ti	reduct. fusion	Pt	He/not	2300/HF	Ca filings	BN/ 10 ng/g	chemical yield: 98%; 4 m/separation	737, 800
Fe, Co, Ni, GaP, GaAs					see al b)			742
Ge	a)				see Si b)			730
Ge	b)				see Si b)			730
	c) inert gas oxid.fus.	Pb <sub>3</sub> O <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	He/100-150	ca.700/HF	molecular sieve	not specified/ 10 ng	10 m/separation; simult. C and N analysis	758

Tab. 6.1-6, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Zr	a)	Kjeldahl HF 10M	He/400		H <sub>2</sub> SO <sub>4</sub> dl.	not specified/ ca.1 µg/g	simultaneous C and N analysis	742, 763
	b)	inert gas Pt red.fus.	He/not given	2500/HF	Ca filings	BN/10 ng/g	chemical yield: 98%; 4 m/separation	737, 800
Nb	a)	-----	-----	-----	see Al b)	-----	-----	742
	b)	-----	-----	-----	see Ge c)	-----	-----	758
	c)	inert gas Pt or Fe red.fus.	He/not given	2200-2300/ HF	Ca filings	BN/10 ng/g	chemical yield: 98%; 4 m/separation	737, 800
Mo	a)	-----	-----	-----	see Al b)	-----	-----	742
	b)	-----	-----	-----	see Nb c)	-----	-----	737, 800
Ta	a)	-----	-----	-----	see Ge c)	-----	-----	758
	b)	-----	-----	-----	see Mo b)	-----	-----	737, 800

Tab. 6.1-6, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp. (°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
W	inert gas red.fus. or Ni-Sn	Pt or Fe	He/not given	2300/HF	Ca filings	BN/10 ng/g	chemical yield: 98%; 4 m/separation	737,800
Various chemicals	red. fus.		Ar/not given	2200- 2400/HF	Ti sponge	AlN/0.2 µg/g	10m/separation simultan. O <sub>2</sub>	891

## - Chemical interference

In the most cases instrumental analysis of nitrogen is not possible due to multiple uncorrectable chemical interference by matrix components (see e.g.<sup>726</sup>); furthermore, nitrogen analysis is interfered by oxygen and carbon activity. The decay curve of  $^{13}\text{N}$  lies between those of  $^{15}\text{O}$  and  $^{11}\text{C}$  and thereby it loses significance. Since the activation threshold of the nitrogen reaction is lower than that of carbon, the interference due to  $^{11}\text{C}$  might be excluded by activation at lower photon energies<sup>714,715</sup>, but this bears the penalty of poor sensitivity.

Tab.6.1-7: Bremsstrahlung-produced radionuclides with half-lives close to 10 minutes

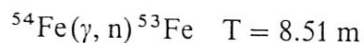
T(m)	Nuclide	Target	T(m)	Nuclide	Target	T(m)	Nuclide	Target
6.1	$^{82\text{m}}\text{Br}^1$	$^{81}\text{Br}$	7.6	$^{111\text{m}}\text{In}$	$^{112}\text{Sn}$	10.3	$^{95}\text{Y}$	$^{96}\text{Zr}$
6.26	$^{94\text{m}}\text{Nb}$	$^{95}\text{Mo}$	7.7	$^{38}\text{K}$	$^{39}\text{K}$ ,	10.5	$^{60\text{m}}\text{Co}^1$	$^{61}\text{Ni}$ ,
6.46	$^{78}\text{Br}$	$^{79}\text{Br}$			$^{40}\text{Ca}$			$^{59}\text{Co}$
6.6	$^{29}\text{Al}$	$^{30}\text{Si}$	8.2	$^{79}\text{As}$	$^{80}\text{Se}$	14.4	$^{112}\text{In}$	$^{113}\text{In}$ ,
6.7	$^{179\text{m}}\text{W}$	$^{180}\text{W}$	8.51	$^{53}\text{Fe}$	$^{54}\text{Fe}$			$^{114}\text{Sn}$
7.2	$^{105\text{m}}\text{Ag}$	$^{107}\text{Ag}$ ,	9.46	$^{27\text{m}}\text{Mg}^1$	$^{27}\text{Al}$	14.5	$^{131\text{m}}\text{Ba}$	$^{132}\text{Ba}$
		$^{106}\text{Cd}$	9.76	$^{62}\text{Cu}$	$^{63}\text{Cu}$	14.6	$^{101\text{m}}\text{Mo}^1$	$^{100}\text{Mo}$

<sup>1</sup>photoneutron-produced

Among the numerous interference sources (see e.g. Tab.6.1-7) impurities of copper and iron yielding  $^{62}\text{Cu}$  and  $^{53}\text{Fe}$ , respectively, are the most prominent ones; particularly the copper reaction



has a comparatively large integrated cross section so that very small traces of copper impurity in the sample can make precise and accurate instrumental nitrogen analyses impossible. This interference, and also the interference by



cannot be ruled out by energy selection since the threshold energies of both are close to that of the nitrogen reaction analytically exploited (10.84 MeV, 13.62 MeV and 10.55 MeV, respectively).

Quantitative interference yield assessments were published by Engelmann<sup>726,801</sup>. In radiochemical analysis chemical interference normally is excluded. The authors could not find any report about serious error of nitrogen analyses caused by contamination of the  $^{13}\text{N}$  activity fraction by other activities. Other sources of error might exist, particularly during Kjeldahl extraction. These are discussed below.

#### - Nuclear interference

Nuclear interference by neighbouring elements can be avoided in photon activation analysis of nitrogen more easily than it is possible in carbon determinations because of the lower reaction threshold of the nitrogen reaction. However, regarding the required sensitivity, one or several competing reactions (see Tab.6.1-8) might prove unavoidable since activations for trace analyses have to be carried out far above the giant resonance energy. Out of the reactions in Tab.6.1-8, No's. 2, 3 and eventually 16, 17 and 18 might interfere significantly if irradiations are carried out at around 30 MeV electron energy. The other reactions normally can be disregarded unless the target element is a main matrix component (see 6.1.2.5).

Tab.6.1-8: Nuclear reactions by which  $^{13}\text{N}$  is produced

No.	Reaction	Threshold (MeV) <sup>1</sup>	No.	Reaction	Threshold (MeV) <sup>1</sup>
1	$^{14}\text{N}(\gamma, n)^{13}\text{N}$	10.5	10	$^{24}\text{Mg}(\gamma, 2\alpha)^{13}\text{N}$	39
2	$^{16}\text{O}(\gamma, t)^{13}\text{N}$	25	11	$^{27}\text{Al}(\gamma, ^{14}\text{C})^{13}\text{N}$	25.6
3	$^{19}\text{F}(\gamma, ^6\text{He})^{13}\text{N}$	24.4	12	$^{27}\text{Al}(\gamma, 3\alpha 2n)^{13}\text{N}$	46
4	$^{19}\text{F}(\gamma, \alpha 2n)^{13}\text{N}$	25.4	13	$^{28}\text{Si}(\gamma, ^{15}\text{N})^{13}\text{N}$	26.9
5	$^{20}\text{Ne}(\gamma, ^7\text{Li})^{13}\text{N}$	27.3	14	$^{31}\text{P}(\gamma, ^{18}\text{O})^{13}\text{N}$	29
6	$^{20}\text{Ne}(\gamma, \alpha t)^{13}\text{N}$	29.8	15	$^{32}\text{S}(\gamma, ^{19}\text{F})^{13}\text{N}$	30
7	$^{23}\text{Na}(\gamma, ^{10}\text{Be})^{13}\text{N}$	27.5	16	$^{13}\text{C}(p, n)^{13}\text{N}$	2.5 <sup>2</sup>
8	$^{23}\text{Na}(\gamma, 2\alpha 2n)^{13}\text{N}$	36	17	$^{12}\text{C}(p, \gamma)^{13}\text{N}$	2.5 <sup>2</sup>
9	$^{24}\text{Mg}(\gamma, ^{11}\text{B})^{13}\text{N}$	28	18	$^{16}\text{O}(p, \alpha)^{13}\text{N}$	6.0 <sup>2</sup>

<sup>1</sup>taken out of Ref.<sup>754</sup> or calculated

<sup>2</sup>taken out of Ref's.<sup>56,858</sup>



Yield values of reactions contributing to the common  $^{13}\text{N}$  activity were published by Engelmann and co-workers<sup>23, 756-758</sup>. As an example, Engelmann et al.<sup>758</sup> found after activation with 30 MeV bremsstrahlung 780 micrograms of oxygen giving, by  $^{16}\text{O}(\gamma, t)$ , the same activity of  $^{13}\text{N}$  like 1 microgram of nitrogen.

- Other error sources

Error sources in the separation procedure of the radiochemical photon activation analysis of nitrogen - if performed by oxidising fusion - are less problematic than encountered in C or O analysis; elemental nitrogen gas is quasi-inert and not subject to adsorption during transport and incomplete collection in the sorbent to a significant degree as it might occur in the handling of  $^{11}\text{CO}_2$ . Consequently, the nitrogen carrier eventually used (see Tab.6.1-6) does not play such an important role as e.g. carbon-containing fluxes in the carbon analysis<sup>775</sup>. Sometimes oxidising fusion was found to be somewhat more efficient than reductive fusion<sup>777, 793</sup>.

If nitrogen separation after Kjeldahl is used the analyst eventually has to be aware of more sources of error, besides the insufficient rapidity of the method. Anyhow, as also recommended for any other radiochemical separation procedure, the chemical yield should be determined prior to analysis evaluation by use of either tracer methods with doped samples or, more efficiently as mentioned in 6.1.3.3, by analysis of certified reference materials. If yields other than 100% are obtained this might have the following reasons (see also 6.1.3.3):

- a) The sample was not completely decomposed; this has frequently occurred during Kjeldahl separation, but sometimes was also observed in heat extraction (see Ref.<sup>742</sup>). It has been noted<sup>775</sup> that Kjeldahl separation sometimes is incomplete if nitrogen lies before as nitride of certain elements, e.g. Al, Ti, V, Zr, Nb. The decomposition of these compounds sometimes is extremely difficult. This error source can mostly be circumvented by proper reselection of the separation conditions (flux, extraction temperature etc.).
- b) Radionitrogen did not appear as a unique compound; this has frequently been encountered during Kjeldahl separation, but also in oxidising fusion. Whilst the gas mixture after Kjeldahl extraction can contain elemental nitrogen, ammonia and hydrazine in various ratios<sup>795</sup>, the gas extracted by oxidising fusion frequently contains nitrogen oxides. The easiest method to avoid radionitrogen losses is to convert all radionitrogen compounds into elemental

nitrogen gas by oxidising or reducing media, respectively, and collect it with appropriate agents as described in 6.1.4.2.

- c) Radionitrogen was not completely collected in the absorption vessel; this might be due to the production of more than one  $^{13}\text{N}$ -containing compounds as explained above. Otherwise, if radionitrogen was collected as metal nitride, the adsorption temperature might not have been properly adjusted or, and this might occur as well if molecular sieve collection is applied, the residence period of the nitrogen gas in the collecting vessel was insufficient. This might also be the case if  $^{13}\text{N}$  was absorbed as ammonia after Kjeldahl separation.
- d) The case of radioactive contamination of the counted fraction after separation is discussed in detail in 6.1.3.3, error sources section.

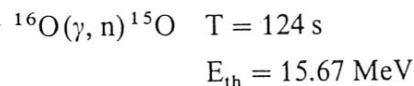
Normally, if heat extraction has been used, yields around 100% have been reported. However, as already mentioned, the Kjeldahl separation procedure sometimes shows up as troublesome in terms of incomplete extraction or excessively long duration, resulting in eventually inaccurate or unprecise results, respectively. However, Kjeldahl separation, being the first of all nitrogen separation methods applied in photon activation analysis, is still used successfully in many cases nowadays. See e.g.<sup>891</sup>.

#### 6.1.4.4 Sensitivity

For some general remarks about the achievable sensitivity the reader might refer to 6.1.3.4. For the standard activation conditions described above (one half-life exposure to 30 MeV bremsstrahlung, mean electron beam current 100 microamperes; total decay period 15 min) from 60 nanograms to five micrograms, quasi-peaking at one microgram have been reported as a detection limit in instrumental nitrogen photon activation analysis. In the radiochemical approach from 10 to 700 nanograms have been found, mainly around 50 nanograms.

### 6.1.5 Oxygen

Oxygen was the first element to be analysed with help of photonuclear activation. Basile et al.<sup>6</sup> analysed oxygen in organic matter using the reaction



induced by 18.6 MeV bremsstrahlung from a betatron. The intrinsic sensitivity of detection about equals that of nitrogen discussed above. However, achieving appreciable sensitivity of oxygen analysis in the radiochemical approach is somewhat problematic; with respect to the comparatively short half-life of  ${}^{15}\text{O}$  all post-irradiation treatment steps, viz. sample transfer and uncapsulating, surface contamination removal, separation of radiooxygen from the matrix, collection in the absorption containment and eventual transport to the detector system, must be kept as short as possible. Instrumental analyses, however, are less problematic than those of other light elements, e.g. nitrogen; according to the literature reviewed by the authors, there are more reports about successful instrumental photon activation determinations of oxygen than of any other of the light elements. This is explained further below in the instrumental analysis section.

The above named photoneutron reaction has been exploited for analysis almost exclusively, using coincidence annihilation quanta counting as also applied for the other light elements. The authors could find only very few reports about other reactions and/or counting procedures used in photon activation analysis of oxygen. In the pioneer work cited above<sup>6</sup> the authors applied positron counting, and so did Chepel et al.<sup>802</sup> analysing oxygen in organic material. Measurement of the photoneutrons promptly emitted during photon activation of oxygen was proposed<sup>694,803</sup>. However, in this approach the analyst is confronted with the surface contamination problem as in conventional analysis. The same problem arises in the method described by Scherle and Engelmann<sup>710</sup>, who measured the delayed neutrons emitted by  ${}^{17}\text{N}$  produced through  ${}^{18}\text{O}(\gamma, p)$ . However, using this method it is possible to determine the isotopic concentration ratio of  ${}^{18}\text{O}/{}^{16}\text{O}$  which sometimes is of import, e.g. during biological research work.

Oxygen can be analysed by nuclear methods, photon activation in particular, more favourably than with other techniques, with respect to rapidity, sensitivity and relative freedom from error sources<sup>802,803</sup>.

## 6.1.5.1 Non-destructive analysis

Although instrumental photon activation analysis of oxygen is subject to interference of any kind to a lesser extent, it can only be carried out in very special cases, namely normally in high purity matrices. This is true in particular, if trace analysis is required.

The application of this technique to oxygen analyses in organic matter offers itself since the activation of the matrix carbon can be excluded by selection of an electron energy not exceeding 18.7 MeV (see above, Basile et al.<sup>6</sup>). However, serious decrease of sensitivity has to be taken into account as a consequence since the cross section maximum of the oxygen reaction is located at a relatively high photon energy. Moreover, chemical interference induced by other elements might be unavoidable also at low bremsstrahlung energies; see 6.1.5.3 and Tab.6.1-9.

Tab.6.1-9: Bremsstrahlung-produced radionuclides with half-lives close to 2 minutes

T(m)	Nuclide	Target	T(m)	Nuclide	Target	T(m)	Nuclide	Target
0.99	<sup>25</sup> Na	<sup>26</sup> Mg	1.7	<sup>57</sup> Mn	<sup>58</sup> Fe	3.4	<sup>140</sup> Pr	<sup>141</sup> Pr
1.02	<sup>201m</sup> Pb	<sup>204</sup> Pb	2.1	<sup>75</sup> Ga	<sup>76</sup> Ge	3.75	<sup>52</sup> V	<sup>53</sup> Cr
1.02	<sup>86m</sup> Rb	<sup>87</sup> Rb	2.246	<sup>28</sup> Al	<sup>29</sup> Si	3.8	<sup>121m</sup> In	<sup>122</sup> Sn
1.03	<sup>141m</sup> Nd	<sup>142</sup> Nd	2.3	<sup>149m</sup> Pr	<sup>150</sup> Nd	3.9	<sup>79m</sup> Se	<sup>80</sup> Se
1.075	<sup>17</sup> F	<sup>19</sup> F	2.3	<sup>119</sup> In	<sup>120</sup> Sn	4.16	<sup>89m</sup> Zr	<sup>90</sup> Zr
1.08	<sup>91m</sup> Mo	<sup>92</sup> Mo	2.41	<sup>108</sup> Ag	<sup>109</sup> Ag	4.2	<sup>122m</sup> Sb	<sup>123</sup> Sb
1.18	<sup>14</sup> O	<sup>16</sup> O	2.5	<sup>30</sup> P	<sup>31</sup> P	4.3	<sup>77m</sup> Br	<sup>79</sup> Br
1.2	<sup>114</sup> In	<sup>115</sup> In	2.5	<sup>53m</sup> Fe	<sup>54</sup> Fe	4.4	<sup>118m2</sup> In	<sup>119</sup> Sn
1.2	<sup>111m</sup> Ag	<sup>112</sup> Cd	2.55	<sup>137m</sup> Ba	<sup>138</sup> Ba	4.69	<sup>109m</sup> Pd	<sup>110</sup> Pd
1.68	<sup>185m</sup> W	<sup>186</sup> W	2.6	<sup>99</sup> Nb	<sup>100</sup> Mo			

Instrumental photon activation analyses of oxygen were also reported by Breger et al.<sup>804</sup> (semiconductor material), Beard et al.<sup>7</sup> (beryllium), Gilman and Isserow<sup>762</sup> (beryllium), Evshanov et al.<sup>732</sup> (alkali metals and alkaline earths), Holm and Sanders<sup>805</sup> (sodium), Engelmann et al.<sup>806</sup> (sodium), <sup>17,24,726,761,764</sup> (beryllium), <sup>788</sup> (<sup>16,18</sup>O isotopic ratio determination), Albert et al.<sup>708,763</sup> (beryllium), Persiani et al.<sup>768</sup> (caesium), Mackintosh and Jervis<sup>728</sup> (lead/ bismuth mixtures), Kusnetsov et al.<sup>807</sup> (iodine compounds), Marsh<sup>49</sup> (lithium and beryllium), Berry<sup>867</sup> and others.

#### 6.1.5.2 Radiochemical analysis

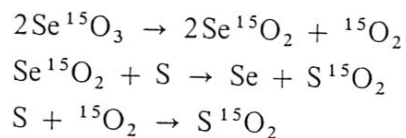
Two basic methods are available for chemical separation of radiooxygen, namely first, the classical reductive fusion carried out under vacuum or inert gas atmosphere and second, isotopic exchange separation; the latter is preferably used for oxygen analysis in alkali metals.

##### - Reductive fusion

The apparatus setup is the same as utilised for oxidising fusion under vacuum or inert gas (see Fig.6.1.4). Graphite crucibles are used to provide a reducing environment so that, initiated by heating, all matrix-inherent oxygen is converted to carbon monoxide. This is carried by a vector gas through the further processing stations as described above in the oxidising fusion context (see 6.1.3.2). Inactive oxygen, either inherent to the graphite crucible or the vector gas or the flux metal eventually added, serves as a carrier so as to obtain complete recovery of radiooxygen in the collecting sorbant (e.g. ascarite; see 6.1.3.2). Platinum has been used frequently as a flux in reducing fusion<sup>772, 773, 789</sup> but other, less expensive media might serve as well in many cases (see e.g.<sup>737</sup>). Since graphite crucibles are used as combustion vessels, there is the possibility of different ways of heating exploiting the electrical conductivity of graphite; except the above described furnaces (resistance or induction furnace; eventually gas burner) other principles have been used, namely direct current carbon arc heating<sup>716, 773, 775, 789, 808</sup> or high-current impulse heating<sup>733, 774, 809</sup>.

Nitrogen can be analysed simultaneously (see e.g.<sup>737</sup>). However, reviewing the relevant literature, nitrogen has mostly been analysed by oxidising fusion, simultaneously with carbon as described in 6.1.3.2. In several critical cases, incomplete extraction of nitrogen during reductive fusion was observed (Ref.<sup>793</sup> and the relevant literature cited therein).

The above described procedure is not applicable for all matrix materials. For instance, oxygen analyses of selenium carried out as described lead to insufficient results. Gosset and Engelmann<sup>810</sup> described a method in which selenium-inherent oxygen - most probably present as  $\text{SeO}_2$ , but possibly as  $\text{SeO}_3$  - is extracted with elemental sulphur either in the melt or in the vapour phase.



Sulfur oxide produced thus ( $\text{S}^{15}\text{O}^{16}\text{O}$  or other isotopical composition) is then collected in any appropriate sorbant, e.g. hydrogen peroxide, whilst residual sulfur vapour is collected in an ice-cooled trap. This method is applicable to all matrix elements whose sulphides are chemically more stable than their oxides.

Reductive fusion extraction cannot be used for oxygen analysis in alkali metals. Oxygen, if present as alkali oxide will not undergo the above named chemical reaction. Therefore, other ways have to be used for oxygen separation (see below).

#### - Oxygen in alkali metals

The classical procedures of oxygen separation from alkali metals, viz. amalgamation<sup>811</sup>, isolation with help of alkyl halides<sup>812</sup>, vacuum distillation of sodium metal<sup>813</sup> and other methods<sup>814,815</sup>, are not applicable for radiochemical photon activation analysis. In the most cases this is due to the short half-life of  $^{15}\text{O}$  and the considerable time-consumption of the above named methods, respectively.

The technique described by Lutz<sup>815</sup> has been applied, eventually with slight procedural variations, in almost all cases. It is based upon isotopical exchange between inactive oxygen and radiooxygen. The apparatus setup is presented in Fig.6.1.6. After irradiation and surface contamination removal the sodium is brought into the reaction flask(1) which contains several tens of milliliters of sodium hydroxide solution where the sodium is dissolved. Nitrogen gas atmosphere is provided to exclude atmospheric oxygen access. The matrix-inherent oxygen including radiooxygen is converted to sodium hydroxide.  $^{15}\text{O}$  then exchanges with inactive oxygen in a water molecule to form  $\text{H}_2^{15}\text{O}$ . By heating with a gas burner, water including radiooxygen-containing water is distilled into a cooled trap (2) which contains a few milliliters saturated sodium hydroxide solution. Eventually occurring contamination by radionitrogen-containing ammonia (see preceding paragraph about nitrogen analysis; error sources section)

is removed by boiling. The distillate should now contain radiochemically pure  $\text{H}_2^{15}\text{O}$ . It is adjusted to standard volume if necessary and then counted as described in the paragraphs above.

Frequently the matrix activity of the residue in the reaction vessel (1) has also been diluted to a standard volume and aliquots have been measured to obtain an internal photon flux monitor as also described above in 6.1.2.1, internal standards section; see also<sup>815</sup>. The described procedure allows a separate determination of carbonate-bound oxygen; however, there are some limitations due to the chemical behaviour of the carbonates. This is discussed further below in the error sources section 6.1.5.3.

Basically, this method is applicable to all alkali metals, but sometimes further countermeasures against too violent reaction of the metal with water might be necessary, e.g. in the case of caesium analysis as described by Nordmann et al.<sup>729</sup>; see also<sup>816</sup>. The described method can be applied to radiochemical analysis of materials whose elemental forms are readily hydrolysable.

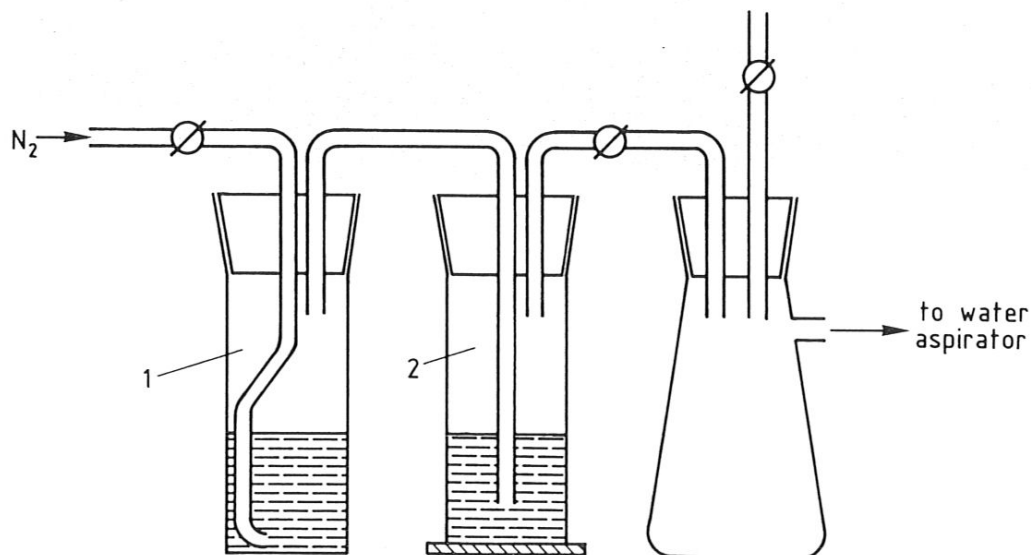


Fig. 6.1.6: Apparatus for separation of radiooxygen from alkali metals (after Lutz<sup>815</sup>); explanations see text

In Tab.6.1-10 some examples of radiochemical oxygen analyses are summarised.



Tab.6.1-10: Examples of radiochemical photon activation analysis procedures for oxygen determination

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp. (°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Li	H <sub>2</sub> <sup>15</sup> O- distill.	water	-/gas burner	-/gas burner	not specified	B <sub>2</sub> O <sub>3</sub> /0.2 µg 6 m/separation	chemical yield: 60%; 6 m/separation	851, 852
Na	a) -----	-----	-----	-----	see Li	-----	-----	851, 852
	b) H <sub>2</sub> <sup>15</sup> O- distill.	water-NaOH	-/gas burner	-/gas burner	NaOH satur.	NaOH/1 µg	reference mat. also sep'd.; <sup>22</sup> Na as intern. stand.; 4 m/separation	815
	c) dto.	water-NaOH/ Na <sub>2</sub> CO <sub>3</sub>	-/vacuum distill.	liq.N <sub>2</sub> cold trap	NaOH/ 0.1 - 0.5 µg/g	NaOH/ 0.1 - 0.5 µg/g	chemical yield: 50%; <sup>22</sup> Na as intern. stand.; 2 m/separation	723, 742, 743, 818
Al	red.fus. Fe	Cu, Ni or given	He/not given	2200/HF ascarite	ascarite	not specified/ ca 1 µg/g		711, 742
Si	a) -----	-----	-----	-----	see Al	-----	-----	742
	b) red.fus. flux	Fe/O <sub>2</sub> in flux	He/not given	2000/HF ascarite	ascarite	Al <sub>2</sub> O <sub>3</sub> / not given	chemical yield: 100%	859
Ti	a) red.fus.	Ar/700	2800-3000/ pulse curr.	KOH powder	B <sub>2</sub> O <sub>3</sub> /0.07 µg	chemical yield: 100%; tot. anal. duration: 30m		733

Tab.6.1-10, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Ti	b) red.fus.	Pt	He/not given	2300/HF	ascarite	Al <sub>2</sub> O <sub>3</sub> / 0.02 µg/g	4 m/separation	737, 800
V	red.fus. (vacuum)	Fe-Ni or Pt/O <sub>2</sub> in flux		2500/HF	gas chamber	B <sub>2</sub> O <sub>3</sub> / 0.5 µg/g	§ <sup>+</sup> measured w. plastic scintillation counter; 4 m/separation	730
Fe	a) red.fus.	Fe-Sn/ O <sub>2</sub> in flux	Ar/700	2800-3000/ pulse curr.	KOH powder	B <sub>2</sub> O <sub>3</sub> / 0.07 µg	chemical yield: 100%; tot. anal. duration: 30m	733
	b) red.fus.	Sn	Ar/not given	2000/ pulse curr.	Cu at 1000°C	B <sub>2</sub> O <sub>3</sub> /0.15 µg	chemical yield: ca.100%; rad.chem. purity also at 860 high C conc. of the sm.	719, 783,
	c) red.fus.	Fe/ O <sub>2</sub> in flux	Ar or He/ several l/m	2000/HF	ascarite	mica/0.01 µg	5 m/separation	758
	d) red.fus.	Ni-Fe/ O <sub>2</sub> in flux	Ar/700	3000/ pulse curr.	KOH powder	B <sub>2</sub> O <sub>3</sub> /2 ng	eventually simult. N and O anal.; 2.5 m/separ <sup>n</sup> .	289, 735, 860
	e) red.fus.	not speci- fied/O <sub>2</sub> in flux	He/400	200/HF	Hopcalite	BeO/0.2 µg	6-8 m/separation	712

Tab.6.1-10, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Co					see Al			742
Ni	a)				see V			730
	b)				see Al			742
	c)				see Fe e)			712
Cu	a)				see Fe d)			289, 735
	b)	red.fus flux	Ni/ O <sub>2</sub> in Ar/700	2800-3000/ pulse curr.	KOH powder	B <sub>2</sub> O <sub>3</sub> /0.07 µg	chemical yield: 100%; tot. anal. duration: 30m	733
	c)	red.fus.	He/not given	1300/HF	ascarite	BeO/not given	4 m/separation	55, 861
	d)				see Fe a)			733
	e)				see Al			742
	f)				see Fe e)			712

Tab.6.1-10, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
GaP	red.fus.	Cu, Ni or Fe	He/not given	1250/HF	ascarite	not specified/ ca 1 µg/g		742
GaAs	red.fus.	Cu-C/ O <sub>2</sub> in flux	He/400	200/HF	Hopcalite	BeO/0.1 µg	6-8 m/separation	712
Ge	a)				see Fe e)			712
	b)	sulfur vapour separ <sup>n</sup> .	He/not given	1200/res.	soda lime	BeO/0.2 µg	residual gaseous species caught by molecular sieve	712
As					see Ge b)			712
Se	sulfur vapour separ <sup>n</sup> .	SeO <sub>2</sub>	Ar/200	400/res.	H <sub>2</sub> O <sub>2</sub> or soda lime	not specified/ 0.05 µg/g	6-7 m/separation	742, 810
Zr	red.fus.	Pt	He/not given	2500/HF	ascarite	Al <sub>2</sub> O <sub>3</sub> / 0.02 µg/g	4 m/separation	737, 800
Nb	a)	red.fus. Pt or Fe	He/not given	2200-2300/ HF	ascarite	Al <sub>2</sub> O <sub>3</sub> / 0.02 µg/g	4 m/separation	737, 800

Tab.6.1-10, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Nb	b)	-----	-----	-----	see V	-----	-----	730
Mo	a)	red.fus. Sn	Ar/not given	2000/pulse current	ascarite	B <sub>2</sub> O <sub>3</sub> /0.15 µg	see Fe b)	719, 783
	b)	red.fus. Pt or Fe	He/not given	2200-2300/ HF	ascarite	Al <sub>2</sub> O <sub>3</sub> / 0.02 µg/g	4 m/separation	737, 800
	c)	-----	-----	-----	see Fe e)	-----	-----	712
Ag	-----	-----	-----	-----	see Al	-----	-----	742
In	a)	red.fus. Ni-Cu/ O <sub>2</sub> in flux	Ar/700	3000/pulse current	KOH powder	B <sub>2</sub> O <sub>3</sub> /2 ng	see Fe d)	289, 851
	b)	red.fus. Cu, Ni or Fe	He/not given	1250/HF	ascarite	not specified/ ca. 1 µg/g	-----	742
InP	a)	-----	-----	-----	see In b)	-----	-----	742
	b)	red.fus. Cu-C/O <sub>2</sub> in flux	He/400	2000/HF	Hopcalite	BeO/ not given	6-8 m/separation	712

Tab.6.1-10, continued

Matrix	Method	Flux or solvent/ carrier	Vector gas/ flow rate (ml/m)	Fusion temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Sn	a)				see Fe d)			289, 735
	b)				see In b)			742
Cs		H <sub>2</sub> <sup>15</sup> O- distill. Cs <sub>2</sub> CO <sub>3</sub>	water-NaOH/ vacuum distill. cold trap	liq. N <sub>2</sub>	CsOH/ 0.1 µg/g		6-7 m/separation; react. vessel cooled by liq.N <sub>2</sub> ; <sup>130</sup> Cs and <sup>132</sup> Cs as int. standard	72, 729, 743
Hf					see Al			742
Ta	a)				see V			730
	b)				see Nb a)			737, 800
W		red.fus. Pt, Fe or Ni-Sn	He/not given	2300/HF	ascarite	Al <sub>2</sub> O <sub>3</sub> / 0.02 µg/g	4 m/separation	737, 800
Pb, Pb-Sb					see In b)			742
(many matrices)		red.fus. various/ O <sub>2</sub> in flux	Ar/700	3000/ pulse curr.	KOH powder	not specified/ 0.1 µg	1.5-2 m/separation	862

## 6.1.5.3 Reference materials; error sources

## - Reference materials

In the instrumental analysis of oxygen, frequently mylar has been used as a reference material. This can also be applied for simultaneous carbon and oxygen determination (see 6.1.3.3). Since one strives for non-destructive reference material measurement in radiochemical oxygen photon activation analysis, materials have been selected whose non-oxygen components do not interfere; boron trioxide and beryllium oxide have been favoured (see Tab.6.1-10).

In alkali metal analysis appropriate oxides, hydroxides, or carbonates have been selected since they usually have to pass the separation procedure so as to obtain the chemical separation yield (see below). Moreover, the cation is selected so that it can serve as internal photon flux monitor.

For more general information about the reference materials see 6.1.2.4 and 6.1.3.3.

## - Chemical interference

Due to frequent chemical interference instrumental analysis of oxygen (as well as of any other of the light elements) is possible only in a few favourable cases. In Tab.6.1-9, a selection of possibly interfering nuclides produced through bremsstrahlung activation are listed. Out of these, several have been studied in more detail since they frequently interfere.

a) Interference by  $^{30}\text{P}$ 

At normal, say 30 MeV, bremsstrahlung energies  $^{30}\text{P}$  can be produced at significant levels by



The influence by sulphur and chlorine, respectively, can be minimised by irradiation at lower energies. However, this entails severe loss of sensitivity.



Moreover, the interference by phosphorus cannot be outwitted thereby. This source of interference was studied thoroughly by Engelmann and co-workers<sup>17,45,723,726,806</sup>; see also<sup>21,142,728</sup>.

b) Interference by  $^{38}\text{K}$

This interference is of particular relevance during instrumental oxygen analysis in lithium or sodium, since the according target element, namely potassium, is likely to be present as matrix contaminant in considerable amounts.  $^{38}\text{K}$  can also be produced in calcium containing matrix by  $^{40}\text{Ca}(\gamma, np)$ . Although being quite different in half-lives, the decay functions of  $^{15}\text{O}$  and  $^{38}\text{K}$  cannot be properly resolved if trace oxygen is to be analysed. Engelmann and Loeuillet<sup>806</sup> recommended anti-coincidence counting referring to the characteristic gamma-ray line of  $^{38}\text{K}$ . This method can well be applied in other interference cases but, as already was mentioned in other context<sup>805</sup>, requires additional hard- and software effort.

c) Interference by aluminium

If oxygen is analysed non-destructively in aluminium several nuclides were found to interfere, e.g.  $^{27}\text{Mg}$ ,  $^{24}\text{Na}$  and  $^{28}\text{Al}$ . The latter can be produced by  $^{27}\text{Al}(n, \gamma)$  as well as by silicon mostly present in normal aluminium, through  $^{29}\text{Si}(\gamma, p)$ . Also copper is frequently present in considerable concentrations, hence  $^{62}\text{Cu}$  must eventually be taken into account as source of error. See also Ref's. 711,817.

Although the gamma signals of the above mentioned radionuclides are discarded to a large extent by coincidence counting their integral activity creates dead-time problems and quasi-coincidentally absorbed gamma-rays might produce a considerable background.

The above mentioned interference sources normally are relevant only in instrumental photon activation analysis of oxygen. However, also in the radiochemical approach frequently impurities of the counted fraction have been complained. Radioactive contaminants sometimes pass the purification steps unretained and thus radiochemical purity of the counted fraction cannot be assumed. Frequently contaminations by the light element product nuclides have been observed.  $^{13}\text{N}$  compounds can be expelled from the collecting agent by reduction to ammonia and subsequent evaporation (see e.g.<sup>818</sup>), but thereby the total decay period is considerably prolonged and consequently there has to be taken into account a

significant loss of sensitivity.

A particular problem is the contamination by  $^{11}\text{C}$ . Since this is, as is radiooxygen, absorbed as  $\text{CO}_2$  an interference in the case of large carbon excess in the sample seems unavoidable (see e.g. Ref's. <sup>55,711,819</sup>). Baker et al. <sup>719</sup> proposed selective sorption of  $^{15}\text{O}$  by isotopic exchange and quantitative retention of radiooxygen in hot cuprous oxide. Hislop and Williams <sup>776</sup> presented a method with help of which all of the desired components ( $^{11}\text{C}$ ,  $^{13}\text{N}$ ,  $^{15}\text{O}$ ) can be efficiently separated. They used copper metal at  $600^\circ\text{C}$  (to reduce radionitrous oxide) and Hopcalite at  $650^\circ\text{C}$  (to separate  $^{11}\text{CO}_2$  and  $\text{C}^{15}\text{O}_2$ ) to enable selective absorption of the different active components from a helium gas stream, whereby radiocarbon oxide passes the Hopcalite trap unabsorbed,  $\text{C}^{15}\text{O}_2$  is quasi-completely retained and the elemental radionitrogen passes both sorbants and is caught by molecular sieve. Hopcalite also serves as an additional purifying agent (see also 6.1.3.2, oxidising fusion section).

Chepel et al. <sup>802</sup> used beta spectroscopy for discrimination between  $^{11}\text{C}$  and  $^{15}\text{O}$ , exploiting the different maximum beta energies (960 keV and 1732 keV, respectively; the  $^{11}\text{C}$  activity was used as an internal photon flux monitor). An additional advantage of the method is the high counting efficiency of the detector chamber used (80-85% for  $^{15}\text{O}$ ). This method was also used by Pronman et al. <sup>730</sup>.

Other sources of chemical interference were mentioned by Lutz <sup>815</sup> ( $^{22}\text{Na}$ ), Evshanov et al. <sup>732</sup> ( $^{21}\text{Na}$ ), Wasserman et al. <sup>734</sup> (indium isotopes), Baker et al. <sup>719</sup> ( $^{18}\text{F}$ ), Kapitsa et al. <sup>289</sup> (indium isotopes).

#### - Nuclear interference

Excluding competing reactions by irradiating at lower bremsstrahlung energies is possible but can be achieved in a limited number of cases only; on the one hand, the activation threshold is somewhat lower than that of the carbon reaction (15.67 MeV compared with 18.72 MeV, respectively), thus chemical interference through carbon can be excluded. The competing reactions with the highest integrated cross sections at energies below 30 MeV (Nos. 2 and 3 in Tab.6.1-11) are unlikely to interfere, both because of the low concentration levels in "normal" matrices and fluorine, normally also does not interfere because of the relatively high activation threshold of the interfering reaction. On the other hand, irradiating at less than 30 MeV might entail crucial loss of analytical sensitivity. A quantitative yield assessment of the interference by fluorine after 30 MeV bremsstrahlung irradiation was performed by Fusban et al. <sup>820</sup>. They

found a fluorine-produced apparent oxygen concentration of 1.6% of the fluorine content.

Nordmann et al.<sup>723,743</sup> examined the matrix influence in the oxygen determination in sodium, but, according to the reaction threshold values given in table 6.1-11, this can be neglected at electron energies around 30 MeV.

Tab.6.1-11: Nuclear reactions by which  $^{15}\text{O}$  is produced

No.	Reaction	Threshold (MeV) <sup>1</sup>	No.	Reaction	Threshold (MeV) <sup>1</sup>
1	$^{16}\text{O}(\gamma, n)^{15}\text{O}$	15.7	9	$^{27}\text{Al}(\gamma, 2\alpha n)^{15}\text{O}$	47.9
2	$^{19}\text{F}(\gamma, tn)^{15}\text{O}$	27.4	10	$^{28}\text{Si}(\gamma, ^{13}\text{C})^{15}\text{O}$	27.5
3	$^{20}\text{Ne}(\gamma, \alpha n)^{15}\text{O}$	20.4	11	$^{28}\text{Si}(\gamma, 3\alpha n)^{15}\text{O}$	39.7
4	$^{23}\text{Na}(\gamma, ^8\text{Li})^{15}\text{O}$	33.3	12	$^{31}\text{P}(\gamma, ^{16}\text{N})^{15}\text{O}$	33
5	$^{23}\text{Na}(\gamma, \alpha tn)^{15}\text{O}$	37.8	13	$^{32}\text{S}(\gamma, ^{17}\text{O})^{15}\text{O}$	28
6	$^{24}\text{Mg}(\gamma, ^9\text{Be})^{15}\text{O}$	28.1	14	$^{35}\text{Cl}(\gamma, ^{20}\text{F})^{15}\text{O}$	31.8
7	$^{24}\text{Mg}(\gamma, 2\alpha n)^{15}\text{O}$	29.7	15	$^{36}\text{Ar}(\gamma, ^{21}\text{Ne})^{15}\text{O}$	27.4
8	$^{27}\text{Al}(\gamma, ^{12}\text{B})^{15}\text{O}$	33.4	16	$^{15}\text{N}(p, n)^{15}\text{O}$	20 <sup>2</sup>

<sup>1</sup>taken out of Ref.<sup>754</sup> or calculated

<sup>2</sup>taken out of Ref.<sup>858</sup>

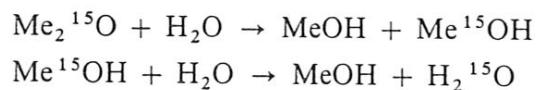
#### - Other error sources

Since the separation procedure using heat extraction is very similar and the purification and sorption step are the same as used in carbon analysis, error sources due to radiochemistry are about the same in oxygen and carbon determinations. Hence, the reader might refer to 6.1.3.3, error sources section.

The error caused by pre-irradiation contamination is probably more problematic in oxygen analysis than in the determination of the other light elements because of the ubiquitous nature of oxygen. In critical cases an efficient post-irradiation treatment of the sample is difficult or impossible, e.g. in the analysis of caesium or other alkali metals<sup>768,818,821</sup>. See also Pauwels<sup>725</sup>. Special storage and sampling procedures might be required in some cases<sup>818,821</sup>.

A particular problem is the recovery of radiooxygen during analysis of alkali metals. The chemical yield values given in Tab. 6.1-10 refer to the following

extraction process:



However, a part of the material-inherent oxygen might be present as carbonate. This oxygen does not undergo the isotopic exchange process described above, as was found by Hislop et al.<sup>818</sup>, Nordmann et al.<sup>723</sup> and others. The latter proposed a separate carbonate-bound indirect oxygen analysis.

#### 6.1.5.4 Sensitivity

The general remarks given in 6.1.3.4 also apply to oxygen analysis; hence it is recommended to study the named paragraph. The intrinsic sensitivities of oxygen analysis at different bremsstrahlung energies is given in Tab.6.1-12.

According to the comparatively short half-life of  $^{15}\text{O}$  the total cooling period takes much more influence upon the achievable analytical sensitivity than it does in the analysis of the other light elements. As touched on in the preceding paragraph, the oxygen analysis of alkali metals using the method of Lutz (Ref.<sup>681</sup>) is somewhat problematic in terms of sensitivity. The decay of radiooxygen during separation and its radiochemical recovery result in an effective yield (Nordmann et al.<sup>723</sup>) which normally is far beneath unity. Therefore, the sensitivity of radiochemical photon activation analysis of oxygen, particularly performed in alkali metal matrix, is limited.

For instrumental oxygen analyses detection limits between 10 and 5000 nanograms have been found. Because of the above mentioned strong dependency of the analytical sensitivity upon various experimental parameters a consensus value can hardly be named. The average of the values reported in the literature reviewed by the authors is about one microgram. The agreement in radiochemical analysis is comparable to that in other light element photon activation analyses performed radiochemically; detection limits from 10 to 300 nanograms were found, quasi-peaking at 50 ng.

All in all, the oxygen analysis is a special problem, independently upon the analytical technique applied. In comparison to other methods, photon activation

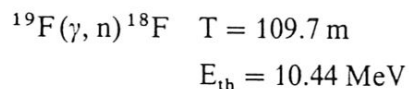
analysis appears to offer a high degree of reliability in the trace concentration level in any material<sup>822</sup>.

Table 6.1-12: Intrinsic sensitivity of oxygen detection by photon activation analysis, normalised to 100 microamperes mean electron beam current and two minutes exposure period as a function of the electron energy (after Nordmann et al.<sup>723</sup>)

$E_{e^-}$ (MeV)	sensitivity ( $\mu\text{g O}$ )
30	0.12
35	0.055
40	0.029
45	0.020
50	0.015
55	0.011
60	0.009

### 6.1.6 Fluorine

Among the light elements under investigation, fluorine was studied the least. Whilst the other elements can be analysed quasi-simultaneously, e.g. after separation by heat extraction and selective collection, fluorine has to be handled differently because of its peculiar chemical nature. The only common property - in radiochemical terms - is its being a pure  $\beta^+$ -emitter and thus radiochemical separation is necessary in the most cases.  $^{18}\text{F}$  produced through



cannot be mobilised by normal heat extraction. Distillation procedures have been normally applied as is demonstrated in 6.1.6.2. Intrinsically, and mostly in the laboratory practice as well, the photon activation analysis of fluorine is the most sensitive amongst all light elements. The comparatively long half-life of the product nuclide permits thorough post-irradiation surface treatment (although surface contamination is not of as problematic nature in fluorine analysis as in the determination of other light elements, e.,g. oxygen), and efficient radiochemical separation. In the authors' laboratory, a limit of detection of about one nanogram was achieved under practical laboratory conditions (see Ref.<sup>60</sup>).

As usual in light element photon activation analysis, radiofluorine normally is analysed by annihilation photon counting. The authors could find but two messages about another technique applied, namely delayed neutron counting of  $^{17}\text{N}$  produced through  $^{19}\text{F}(\gamma, 2p)^{17}\text{N}$ <sup>710,823</sup>.

#### 6.1.6.1 Non-destructive analysis

Perhaps more than other light elements, fluorine is subject to multiple interference during instrumental analysis after photon activation. In several advantageous cases an instrumental analysis is possible exploiting the comparatively low activation threshold.

There are very few reports about non-destructive photon activation determinations of fluorine; almost all of them were performed at bremsstrahlung energies between 12 and 18 MeV to exclude interfering activity. However, the sensitivity

is thereby limited; in advantageous cases 20 ng were reported as detection limit, normally several hundred micrograms were found (see below).

According to the literature accessible to the authors instrumental fluorine analysis by photon activation was first proposed by Albert<sup>763</sup>. He claimed 0.2 micrograms per gram as a detection limit for instrumental fluorine photon activation analysis in aluminium.

Engelmann and Albert<sup>24,45,726</sup> reported instrumental simultaneous analysis of fluorine and carbon in high purity beryllium using 28 MeV bremsstrahlung irradiation. An intrinsic sensitivity of 20 nanograms was found. They proposed instrumental fluorine analysis in several other high purity material using different bremsstrahlung energies (Li, Be, B, Si, W at 30 MeV; Na and Ca at 25 MeV).

Andersen and co-workers<sup>824,825</sup> reported instrumental photon activation analysis of F in biological material (teeth). 12 MeV bremsstrahlung was used for activation to avoid serious interference by chlorine. See also<sup>826</sup>.

Fluorine in organic and inorganic matrices was analysed instrumentally by Kosta and co-workers<sup>57,248</sup>. Multiple possible chemical interference was found after activation with 18.7 MeV bremsstrahlung of a betatron. In Ref.<sup>57</sup> photon activation analysis of fluorine is reviewed.

Simultaneous instrumental photon activation analysis of fluorine and nitrogen in air dust filters was published by Schmitt et al.<sup>715</sup>. They used irradiation with 15 MeV bremsstrahlung to exclude in particular interference by oxygen and carbon.

Relative age determinations of fossile materials were reported by Meijers<sup>787</sup>. Nitrogen and fluorine were analysed by instrumental photon activation analysis using exposure to bremsstrahlung of about 19 MeV (to exclude the interfering carbon reaction). The common decay function of the annihilation peak was followed for 50 hours. The components due to  $^{13}\text{N}$  and  $^{18}\text{F}$  were separated and the weight ratio between nitrogen and fluorine was used as an indicator of the relative age of the sample. See also 6.1.4.1 and<sup>827,828</sup>.

#### 6.1.6.2 Radiochemical analysis

Radiochemical separations of  $^{18}\text{F}$  have been performed during fluorine analysis by photon activation and determinations of other elements by charged particle reactions as well, e.g. oxygen analysis by proton activation using  $^{18}\text{O}(\text{p},\text{n})^{18}\text{F}$ . The radiochemical separation of the isotope is not at all influenced by the way of its production. Therefore many of the examples given in the following were performed with charged particle activation analysis.

Radiofluorine has been separated from any matrix mostly by distillation of hydrofluoric or fluorosilicic acid with various radiofluorine contents. The distillation method for fluorine separation has been well-established for a long time in conventional and radioanalytical chemistry<sup>829-834</sup>.

Fluorine (including radiofluorine) is evolved by dissolution of the sample in a strong, concentrated acid, typically sulphuric or perchloric acid. After addition of some inactive fluorine compound which serves as a carrier, hydrofluoric acid thus produced is either distilled as such or as fluorosilicic acid by vapour distillation. Frequently radiofluorine has been preconcentrated before distillation and thereafter before measurement; typically this has been performed by precipitation as  $\text{Pb}^{18}\text{FCl}$  or calcium radiofluoride. The radiation source thus prepared is then measured, normally by annihilation photon coincidence counting analysing the decay curve for confirming the radiochemical purity of the source.

In several cases the distillation method might not be readily applicable for different reasons, e.g. volatility of any matrix component.

In the following, according to the literature accessible to the authors, examples of other techniques hitherto applied to radiofluorine separation are briefly summarised. See also Tab.6.1-13.

Combined precipitation and extraction of the matrix after dissolution in aqua regia was performed to separate the desired radiofluorine from gallium arsenide by Bailey and Ross<sup>835</sup>. After addition of a fluoride carrier, gallium was extracted by ethyl ether, and arsenic was precipitated subsequently with silver nitrate as  $\text{Ag}_3\text{AsO}_4$ . After filtration radiofluorine could be either counted readily or after precipitation with lanthanum nitrate solution. Extraction techniques were also applied by Bock et al.<sup>836,837</sup>. Various precipitation techniques, either precipitating the matrix as described above or the radiofluorine



were reported by Wilkniss and Born<sup>838</sup>, Nordmann and Engelmann<sup>839</sup> and Gosset et al.<sup>840</sup>. An amalgamation method for separation of radiofluorine from gold matrix was reported by Wilkniss and Born<sup>838</sup>. Wilkniss<sup>841</sup> proposed to separate  $^{18}\text{F}$  from irradiated sea water by quasi-selective absorption in calcium sulphate followed by purification using extraction techniques or sublimation of ammonium radiofluoride.

Frequently several of the mentioned separation techniques have been combined in one procedure or have been used for pre- or post-irradiation treatment, e.g. as preconcentration steps followed by distillation. In Tab.6.1-13 several of the radiofluorine separation procedures are summarised as they have been hitherto applied, particularly in photon activation analysis of fluorine in the ultra-trace level.

Tab. 6.1-13: Examples of radiochemical photon activation analysis procedures for fluorine determination

Matrix	Method	Solvent/ carrier	Measured rad.source	Reference mat./ detection lim.	Remarks	Reference
Li <sub>2</sub> CO <sub>3</sub>	distillation as H <sub>2</sub> <sup>18</sup> F <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	Na <sup>18</sup> F in NaOH		used for carrier-free <sup>18</sup> F-prod'n.; estim'd. achievable chem. yield: 70%	834
Be	distillation as H <sub>2</sub> Si <sup>18</sup> F <sub>6</sub>	H <sub>2</sub> SO <sub>4</sub> 1:1/ LiF	Pb <sup>18</sup> FCl precipitate		β <sup>+</sup> -counting of <sup>18</sup> F; 3-4 h/separ'n.	831
Na	precipitation as Ca <sup>18</sup> F <sub>2</sub>	NaOH/ NaF	Ca <sup>18</sup> F <sub>2</sub> precipitate		purified by precipitation and ion exch.; chemical yield: 82%	839
Al	a) distillation as H <sub>2</sub> Si <sup>18</sup> F <sub>6</sub> b) see a)	H <sub>2</sub> SO <sub>4</sub> -HgCl <sub>2</sub> / NaF	Pb <sup>18</sup> FCl precipitate		purif'd. by precipitation as Ca <sup>18</sup> F <sub>2</sub> ; chemical yield: 60%	830
		H <sub>2</sub> SO <sub>4</sub> / NaF	see a)	NaF/41 ng		843
Si	distillation as H <sub>2</sub> Si <sup>18</sup> F <sub>6</sub>	KOH melt/ KF	Ca <sup>18</sup> F <sub>2</sub> precipitate		2 h/separation; chem. yield: 20%	833
Fe, Ni,						
Cu	a) distillation as H <sub>2</sub> Si <sup>18</sup> F <sub>6</sub>	HF-HNO <sub>3</sub> / NaF	Pb <sup>18</sup> FCl precipitate		see Al a); active matrix metals precipitated as hydroxides	830
Cu	b) -----			see Al b)	-----	843

Tab 6.1-13, continued

Matrix	Method	Solvent/ carrier	Measured rad.-source	Reference mat./ detection lim.	Remarks	Reference
GaAs	extraction and precipitation of the matrix	HCl-HNO <sub>3</sub> / fluoride; not specif'd.	residual sol'n. or La <sup>18</sup> F <sub>3</sub>		Ga extr'd. with ether, As precip'd. with Ag <sup>+</sup> or <sup>18</sup> F precipitated with La(NO <sub>3</sub> ) <sub>3</sub> ; chemical yield: 80%	835
Zr				see Al a)		830
Pt	distillation as H <sub>2</sub> Si <sup>18</sup> F <sub>6</sub>	HF-HNO <sub>3</sub> - HCL/NaF	Pb <sup>18</sup> FCI precipitate		see Al a); active matrix precip'd. with ammonia/hydrazine hydrochl. as elemental radioplatinum	830
Au	a) distillation as H <sub>2</sub> Si <sup>18</sup> F <sub>6</sub>	HF-HNO <sub>3</sub> / NaF	Pb <sup>18</sup> FCI precipitate		see Al a); active matrix separ'd. by extr'n. with ethyle acetate	830
	b) precipitation of matrix gold	HBr-Br <sub>2</sub> / NaF	Pb <sup>18</sup> FCI precipitate		radiogold precip'd. with Zn; <sup>18</sup> F precon'd. as Ba <sup>18</sup> F <sub>2</sub> , distilled as H <sub>2</sub> <sup>18</sup> F <sub>2</sub> ; chemical yield: 60-90%	838
	c) amalgamation of matrix gold	Hg/ NaF	Pb <sup>18</sup> FCI precipitate		chemical yield: 60-90%; 45 m/separation	838
Pb	distillation as H <sub>2</sub> Si <sup>18</sup> F <sub>6</sub>	HClO <sub>4</sub> / NaF	Pb <sup>18</sup> FCI precipitate	NaF/41 ng		843

Tab.6.1-13, continued

Matrix	Method	Solvent/ carrier	Measured rad.source	Reference mat./ detection lim.	Remarks	Reference
Th	distillation as $H_2Si^{18}F_6$	$H_2SO_4$ / NaF	$Pb^{18}FCl$ precipitate			829
U plus fission products	distillation as $H_2Si^{18}F_6$	$HCl-H_2O_2$ / NaF	$Pb^{18}FCl$ precipitate		chemical yield: 25%; 2 h/separation	838
water	a) distillation as $H_2Si^{18}F_6$	$H_2SO_4$ / NaF	$Pb^{18}FCl$ precipitate	NaF/ 50 ng	chemical yield: 60%	713, 844, 863, 864, 865
	b) extraction and sublimation	HCl/ NaF	$NH_4^{18}F$ solution		extr'n. with trimethyle chloro- silane; sublimation as $NH_4^{18}F$ after selective sorption in $CaSO_4$ ; chemical yield: 90%	841
rock material	a) distillation as $H_2Si^{18}F_6$	$HClO_4$ / $CaF_2$	distillate or $Ca^{18}F_2$ precip.	$CaF_2$ / 2 ng	sample fused in NaOH after irr'n.; chem. yield: 70%; 3 h/separation	846
	b) see a)	see a)	$Ca^{18}F_2$ precipitate	teflon/ not given	sample fused in $Na_2CO_3-Na_2O_2$ after irradiation	832
urine	distillation as $H_2Si^{18}F_6$	$H_2SO_4$ / not spec'd.	$Mg^{18}F_2$ precipitate	fluorine standard solution/ 10 ng	radiofluorine preconcentrated on anion exchange resin	842

Tab. 6.1-13, continued

Matrix	Method	Solvent/ carrier	Measured rad. source	Reference mat./ detection lim.	Remarks	Reference
petroleum products of $\text{Ca}^{18}\text{F}_2$	precipitation of $\text{Ca}^{18}\text{F}_2$	$\text{HNO}_3$ / fluoro- aniline	$\text{Ca}^{18}\text{F}_2$ precipitate	fluorine standard solution/ 5 ng/g	sample mineralised by method of Parr-Wurtzschmitt <sup>880</sup> after irr'n.; chemical yield: 79%	840

### 6.1.6.3 Reference materials; error sources

#### - Reference materials

In non-destructive photon activation analysis of fluorine any stoichiometrically well-determined fluorine compound might serve as reference material. Teflon has frequently been used (see e.g. Ref's.<sup>248,827</sup>). In the case of non-destructive analysis of fossil bones, fluoro-apatite was tested<sup>827</sup> to provide a quasi-constant signal-to-background ratio since this compound is somewhat similar to the bone-forming hydroxyle apatite. However, severe fluorine losses were observed after several re-irradiations, probably due to radiolytically induced partial decomposition.

In the radiochemical approach, unlike in the analysis of the other light elements, the reference material normally has to pass the separation procedure since complete or well reproducible recovery of radiofluorine cannot be assumed in every case, no matter which technique is applied. Normally, alkaline or alkaline earth fluorides have been utilised. It is interesting to note that obviously no attempt was hitherto made to apply the internal standard technique in radiochemical fluorine photon activation analysis; no mention could be found in the literature accessible to the authors.

#### - Chemical interference

Due to the relatively low reaction threshold many interferences by other sample components can be ruled out by activation at low energy, without crucial loss of sensitivity. However, interference by several abundant elements, e.g. chlorine or nitrogen (see e.g. Ref.<sup>842</sup>), can hardly thereby be avoided since they have similar activation thresholds. Andersen<sup>824</sup> minimised interference of chlorine by irradiation at 12 MeV. In the instrumental approach its contribution to the decay function has to be resolved mathematically. This might be problematic if chlorine is present in excessive amounts because the relatively long (32 minutes) half-life of  $^{34m}\text{Cl}$  eventually does not permit sufficient decay time. Significant interference by Cl, Cr, Zn and in particular Br during instrumental photon activation analysis of pharmaceuticals and other organic-based material were found by Kosta and Slunecko<sup>248</sup>. Interference by  $^{45}\text{Ti}$  during instrumental fluorine analysis in Ti-bearing material was found by the same authors<sup>57</sup>.

By chemical separation, however, many of these and other chemical interferences

can be avoided, but, particularly if distillation of  $\text{H}_2\text{F}_2$  or  $\text{H}_2\text{SiF}_6$  is applied, several undesired components tend to be carried into the distillate. This might particularly happen if either the dissolving acid is added or the distillation is carried out too rapidly, as was noted by Thomas et al.<sup>834</sup>.

Frequently, other radiohalogens were found to degrade the radiochemical purity of  $^{18}\text{F}$  (Refs. 831, 834, 835 and others). However, these can be separated easily by an intermediate scavenging precipitation with  $\text{Ag}^+$  after distillation, eventually after reduction to the corresponding halogenides<sup>843</sup>. Gold was found to be carried through easily into the counted fraction<sup>830, 838</sup>. It can be separated prior to radiofluorine distillation by extraction, precipitation or amalgamation<sup>830, 838</sup>.

Precipitation has also been applied for removal of other impurities<sup>830</sup>. Pre- or post-irradiation treatment by ion exchange was applied to either preconcentrate the fluorine prior to activation (see Ref.<sup>842</sup>) or remove eventually interfering activities after activation<sup>839</sup>.

Radiochemical impurity of the counted source was detected after radiofluorine separation by extraction techniques<sup>836</sup>. Depending upon the sample composition, several active matrix components were found in the counted fraction.

#### - Nuclear interference

The relatively low threshold energy of the photo reaction used for fluorine analysis can be used to rule out nuclear interference (as well as chemical interference as is described above). Possibly competing reactions are most likely due to neon or sodium (see Tab. 6.1-14), their threshold energies being around 20 MeV. However, running the accelerator at electron energies lower than 20 MeV, both interference sources can be excluded without severe loss of sensitivity. Therefore, many of the workers cited in this paragraph, have performed their activations at electron energies around 20 MeV. Quantitative interference yields were given by Engelmann<sup>726, 757</sup>. Debrun and Albert<sup>843</sup>, Wilkniss and Linnenboom<sup>724, 844</sup>, Reed<sup>832, 845</sup> and others. The interfering radiofluorine contribution of sodium was monitored by Hislop et al.<sup>846</sup> irradiating a sodium standard along with the samples to be analysed.

Whilst the interfering activity due to neon normally can be disregarded<sup>844</sup> and the sodium influence can either be avoided or accounted for, the interference through proton reaction of oxygen sometimes is a serious problem; because of

Tab.6.1-14: Nuclear reactions by which  $^{18}\text{F}$  is produced

No.	Reaction	Threshold (MeV) <sup>1</sup>	No.	Reaction	Threshold (MeV) <sup>1</sup>
1	$^{19}\text{F}(\gamma, n)^{18}\text{F}$	10.5	9	$^{28}\text{Si}(\gamma, 2\alpha n)^{18}\text{F}$	40.3
2	$^{20}\text{Ne}(\gamma, np)^{18}\text{F}$	21.1	10	$^{31}\text{P}(\gamma, ^{13}\text{C})^{18}\text{F}$	28.5
3	$^{23}\text{Na}(\gamma, \alpha n)^{18}\text{F}$	21	11	$^{31}\text{P}(\gamma, 3\alpha n)^{18}\text{F}$	40.7
4	$^{24}\text{Mg}(\gamma, ^6\text{Li})^{18}\text{F}$	29	12	$^{32}\text{S}(\gamma, ^{14}\text{N})^{18}\text{F}$	29.7
5	$^{24}\text{Mg}(\gamma, \alpha np)^{18}\text{F}$	30.4	13	$^{32}\text{S}(\gamma, 3\alpha np)^{18}\text{F}$	47.3
6	$^{27}\text{Al}(\gamma, ^9\text{Be})^{18}\text{F}$	29.4	14	$^{35}\text{Cl}(\gamma, ^{17}\text{O})^{18}\text{F}$	29
7	$^{27}\text{Al}(\gamma, 2\alpha n)^{18}\text{F}$	31	15	$^{35}\text{Cl}(\gamma, 4\alpha n)^{18}\text{F}$	47.6
8	$^{28}\text{Si}(\gamma, ^{10}\text{B})^{18}\text{F}$	34.4	16	$^{18}\text{O}(p, n)^{18}\text{F}$	2.0 <sup>2</sup>

<sup>1</sup>taken out of Ref.<sup>754</sup> or calculated

<sup>2</sup>taken out of Ref's.<sup>847, 858</sup>.

the ubiquitous nature of oxygen it can hardly be circumvented by any experimental means. Wilkniss and co-workers<sup>760, 844</sup> found no secondary proton-produced radiofluorine in sea-water samples irradiated with bremsstrahlung energies of 22 MeV or less. However, the picture might change at higher activation energies and/or in another matrix. Therefore, interference of fluorine analysis due to activation with photoprotons needs investigation when analysing new matrices. Valuable information about this problem, mainly based upon experimentally obtained results, was given by Wilkniss and co-workers<sup>760, 844, 847</sup>, and by Engelmann<sup>45</sup>.

#### - Other error sources

If the well-established steam-distillation technique is applied for radiochemical analysis of fluorine, there are hardly other error sources thinkable than the above mentioned ones, nor were any detected in the laboratory, as far as it can be taken out of the literature reviewed by the authors. Difficulties caused by matrix absorption arose when positron counting was used for radiofluorine activity measurement<sup>831</sup> since a solid-state radiation source was counted (no significant self-absorption was detected during positron counting in the gas-phase, e.g. of radiocarbon dioxide or radionitrogen; see Ref.<sup>730</sup>.)

The incomplete radiofluorine recovery might also cause error; the reference material might behave differently during separation and a constant chemical yield cannot be assumed in this case. This might lead to erroneous analytical values.



To a certain extent, the sources of error mentioned in the carbon context (6.1.3.3, other error sources) also apply to fluorine determination; however, in radiochemical fluorine photon activation analysis these are not very likely to occur - at least, if the distillation procedure is applied.

#### 6.1.6.4 Sensitivity

As touched on in the introductory section fluorine can be analysed with one of the highest sensitivities encountered among all elements determinable by photo-nuclear activation. However, the sensitivity frequently is degraded by incomplete radiofluorine recovery; see also Tab.6.1-13.

In instrumental analysis detection limits from 20 to 2000 nanograms were reported; 20 nanograms may be regarded as a quasi-consensus value among the very few published results of instrumental fluorine photon activation analysis.

In the radiochemical approach from less than one to 100 nanograms have been achieved as a detection limit, quasi-peaking at 5 nanograms.

The analysis of fluorine can be performed more sensitively - in comparison with the other light elements - for several reasons:

- The target nuclide has 100 per cent natural abundance.
- The reaction has the lowest threshold energy.
- Assuming 30 MeV electron energy, the reaction has the largest effective cross section.

The relatively long half-life also supports the achievement of extreme sensitivity since the sample can be treated thoroughly after bremsstrahlung exposure without severe loss of radiofluorine activity.



## 6.2 Single and multielement analysis (Z greater than 10)

### 6.2.1 Introduction

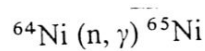
As already mentioned, this chapter deals with purely instrumental analysis. In the application section below, a few exceptions are left. Analyses are also described which involve radiochemical treatment. However, in these discussions emphasis is not placed upon the radiochemistry part of the concerned papers. There is no point in giving lengthy descriptions of radiochemical separation procedures which sometimes are used in photon activation analysis of the heavier elements, since there is no essential difference between the radiochemistry of photon activated elements and those activated by reactor neutrons. Therefore, detailed information on radiochemical analysis can be found, excellently described, in the literature on conventional neutron activation analysis.

Since photon activation analysis is frequently compared with neutron activation analysis as a complementary method - in some cases as a competing method - a short summary of the differences in the application of both is given.

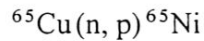
First, there is a number of organic matrices which are more resistant against photon than against neutron exposure (see below paragraphs 6.2.4.4 and 6.2.4.5). Second, there is a good number of elements beyond Ne which can be determined more advantageously by photon activation analysis than by classical activation with reactor neutrons. The following circumstances apply:

- Neutron activation provides less intrinsic sensitivity than photon activation in the analysis of: Mg, Ca, Te, Ge, Y, Zr, Sn.
- Neutron activation leads to product nuclides with inconveniently short half-lives: Mn, Nb, Rh, I.
- Neutron activation of Si, Tl, Pb, Bi yields nuclides with unsuitable radiation properties (e.g. beta radiation exclusively or too soft photon rays).
- The matrix may contain elements with large neutron absorption cross sections which consequently enhance flux depressions. Examples are: Li, B, Be, Cd, Noble Metals.

- Some matrix components gain an unconventionally high radioactivity level under neutron bombardment. Examples are: Na, Noble Metals, Rare Earth elements.
- Sometimes the neutron activation product is interfered by either a competing reaction or by a secondary decay interference, for example: Nickel is analysed by neutron activation through the reaction



which is subject to interference by copper probably present in the sample which undergoes the reaction



Instead, the product nuclide of the most prominent photonuclear reaction product of nickel, namely  ${}^{57}\text{Ni}$ , cannot be produced by any other element at bombarding photon energies less than 45 MeV.

- The irradiation position in a nuclear research reactor is too small for the non-destructive investigation of a relatively large object. The normal general layout of a linear accelerator allows the irradiation of very large objects whereas the total sample volume in neutron activation analysis in nuclear reactors normally is restricted to some tens of milliliters.
- The irradiation of large volume liquid samples in a reactor is hampered by any reason; very often nuclear reactor operation staffs refuse an irradiation of a liquid because of severe contamination in the case of sample rabbit damage or leakage. Moreover, as already mentioned, the total volume of the liquid sample is restricted for reasons of the construction, and hence the sensitivity for some components of interest might turn insufficient. Instead, in photon activation analysis with a linear accelerator, contaminations in the case of accidental fracture of the liquid sample containment during irradiation is less harmful because of the relatively good accessibility of the contaminated area close to the bremsstrahlung converter.

### 6.2.2 Reference materials and radiation monitoring

Basically, there is no difference in the required properties of the reference materials used in photon activation analysis compared with those used in other instrumental analytical methods. In most of these methods (e.g. X-ray fluorescence analysis, atomic absorption spectrometry, neutron activation analysis) the problem of reference materials generally has to be handled more conservatively than in photon activation analysis. As mentioned in 6.2.1, flux gradients of the incident activating radiation due to matrix absorption is much less probable during photon bombardment than is the case e.g. during thermal neutron activation. Therefore, differences in the matrix compositions and in the matrix densities of the analysis sample and the reference material are less harmful in photon activation analysis. However, it is of advantage to use reference materials in photon activation analysis whose matrix compositions are at least somewhat similar to those of the samples to be analysed (see also 6.1).

Self-absorption of low energy gamma-rays to be measured might be troublesome in the case of excessively different matrix densities of sample and reference material. Moreover, largely different matrix compositions might cause significant differences in the signal-to-background ratios within the photon spectrum of sample and reference material which can be a serious source of error. This is to be especially considered if primary standards (pure elements or their simple chemical compounds) are used as reference, minor components or traces being analysed.

Another source of error might be due to different behaviours of different matrices under high energy radiation bombardment. As an example, if organic matter is to be analysed, it might be of doubtful use to select e.g. a rock material as a reference. Whilst the organic matrix mostly is partially damaged during irradiation, the inorganic matter remains, macroscopically regarded, untouched. This might lead to miscalculations caused by eventual loss of volatile components of the organic sample matrix. Generally, as in many other instrumental analytical methods, certified multielement reference materials are used in photon activation analysis; a large variety with both different matrix compositions and different trace element concentrations are offered by many producers. There are very few cases in which no reference material is available, whose matrix composition and/or trace component concentration range is suitable for the given task. In these cases one might consider the production of a "lab-made" synthetic reference material by mixing suitable chemicals viz. oxides or halogenides. However, since both homogenisation and homogeneity con-

trol of large batches of candidate reference materials is very difficult, tedious and time-consuming, only small quantities of such synthetic materials can be produced; generally the total mass is limited to some tens of grams<sup>882</sup>. However, due to the sensitivity of photon activation analysis for the determination of the majority of the elements, this method might be suitable because generally only some tens of milligrams of both analysis sample and reference material is required for one multielement analysis.

In the conventional application of activation analysis, the induced activities are normalised by the mass of the sample and the reference material. One hereby assumes equal incident radiation doses at equal activation energy for both sample and reference material. To a certain extent, this can be realised by application of a constant geometry and simultaneous activation of both. However, there are certain limitations:

As is especially true in the case of photon activation analysis, since the radiation of almost any source cannot be considered homogeneous regarding both energy and flux density (see e.g.<sup>286</sup>), it is very difficult to ascertain that sample and reference material receive equal integral activating radiation doses (see 3.3.1). Due to the flux gradient, even small geometrical differences between sample and reference material during activation can cause severe differences in the bremsstrahlung radiation doses received and, consequently, deviations of the analytical data from the accurate values (see Ch's. 3 and 6.1). This problem is prominent to every analytical method based upon activation, and is due to both the irradiation geometry and the attenuation of the radiation in the various materials to be activated.

In photon activation analysis, there are different measures with help of which one could overcome this problem. First, one could irradiate at a large distance from the bremsstrahlung converter; this was done in the non-destructive analysis of ancient Noble Metal coins (Reimers et al.<sup>884,1180</sup>). Second, one could select a lower electron energy so as to enlarge the apical angle of the photon beam (see Ch.3). Using any of these aids one has to take into account serious decrease of integral and element-differential analytical sensitivity.

A more elegant way out is the use of an internal monitor for inter-sample flux gradient correction. The use of these internal standards is a well-known technique and has been applied frequently in instrumental neutron activation analysis, but also in X-ray fluorescence analysis, atomic absorption spectroscopy, gas chromatography, high performance liquid chromatography, and thin layer

chromatography. The application in photon activation analysis has also been reported by several workers (see 6.1 and 6.2.4.8). In the authors' laboratory it has been applied successfully both to 14 MeV neutron activation analysis and in photon activation analysis. When using an internal standard one can distinguish between two basic cases:

- a) A matrix component with well-known concentration is used as an inherent standard.
- b) An element is added to the sample and - if necessary - to the reference material so as to obtain an additive internal standard.

In both cases, the concentration calculation is then performed by normalising the measured activities by the activity of the internal standard instead of the sample mass as done in classical evaluation procedure. This method automatically corrects for flux gradients during irradiation. It cannot correct for serious shifts of the electron energy of the linear accelerator in the case of non-simultaneous irradiation of the analysis sample and the reference material.

There are some cases in which this method cannot or should not be applied. e.g. if a nondestructive analysis (in the very strict sense) is to be performed, or in the case of compact metal sample matrix. Powdered samples, however, like soils, rock material, dusts, clays, ashes etc. can easily be mixed with a compound of nearly any element to be used as an internal standard, and this is true in particular for liquid samples. The advantage of this method is the free choice of an element which - with respect to its photonuclear data - offers maximum convenience to the analyst. The desired properties of this element are the following:

- a) It does not, of course, have to be determined itself in the sample,
- b) Its concentration inherent to the sample has to be negligible compared with the added amount,
- c) its total concentration in the sample should be large enough to yield high count rate, but must not cause excessive count rate of the counting equipment during product activity spectroscopy,
- d) it should emit a simple spectrum, ideally containing a single line which is located in a favourable energy region so as to avoid interference of other

$\gamma$ -ray lines analysed and to achieve optimal signal-to-background ratio.

All in all, it is not possible to find an element which meets all these requirements completely, so one has to agree to some compromises. For many materials to be analysed, three elements were found optimal, namely scandium, yttrium and samarium.

Tab. 6.2-1: Photonuclear reactions used for internal monitoring

No.	Reaction	Threshold (MeV)	Half-life	$E_{\gamma}$ , keV (I% <sup>1</sup> )	Remarks
Y1	$^{89}\text{Y}(\gamma, n)^{88}\text{Y}$	11.86	108 d	898 (93) 1836 (100)	
Y2	$^{89}\text{Y}(\gamma, 2n)^{87}\text{Y}$ $^{87}\text{Y} \quad ^{87\text{m}}\text{Sr}$	21.05	80.3 h (2.81 h)	485 (96) 388 (83)	interferes with 388 keV of $^{126}\text{I}$ from iodine
Y3	$^{89}\text{Y}(\gamma, 2n)^{87\text{m}}\text{Y}$	21.05	13 h	381 (74)	
Y4	$^{89}\text{Y}(\gamma, np)^{87\text{m}}\text{Sr}$	18.58	2.81 h	388 (83)	interferes with $^{87\text{m}}\text{Sr}$ from strontium
Sc1	$^{45}\text{Sc}(\gamma, n)^{44}\text{Sc}$	11.32	3.92 h	1157 (100)	
Sc2	$^{45}\text{Sc}(\gamma, n)^{44\text{m}}\text{Sc}$ $^{44\text{m}}\text{Sc} \quad ^{44}\text{Sc}$	11.32	2.44 d (3.92 h)	271 (86) 1157 (100)	271 keV interferes with 269 keV of $^{135\text{m}}\text{Ba}$ from barium
Sc3	$^{45}\text{Sc}(n, \gamma)^{46}\text{Sc}$	---	84 d	889 (100) 1121 (100)	reaction is due to photoneutrons
Sm1	$^{154}\text{Sm}(\gamma, n)^{153}\text{Sm}$	7.80	46.75 h	103 (28)	suitable when using LEPS

<sup>1</sup>emissions per hundred disintegrations



## a) Yttrium

The reaction Y1 in table 6.2-1 is the most prominent one. The half-life is conveniently long, and the gamma emission is in a favourable energy range. If bremsstrahlung of more than 22 MeV is used for activation - which is generally the case - the other yttrium reactions listed in table 6.2-1 become significant and might cause interference. Yttrium has been used as an internal standard in the case of long-time (greater than 1h) irradiation and long-time (greater than 3h) measurement. It cannot be used if yttrium, strontium or iodine have to be analysed in the sample (see chapter 5).

## b) Scandium

The use of scandium as an internal standard is somewhat more complicated and restricted to fewer cases since two quasi-competing photonuclear reactions are excited during activation and also a neutron reaction occurs yielding significant product activity (Sc3 in table 6.2-1). Scandium is used in the case of short-time (less than 1 h) irradiation and short-period measurement after a cooling period not exceeding 7 hours. After this decay period up to 36 h the activity contribution of the secondary decay of  $^{44m}\text{Sc}$  into  $^{44}\text{Sc}$  becomes significant and the decay function is complex. After a cooling period of more than 36 h the  $^{44}\text{Sc}$  activity out of the secondary decay dominates and can be used for internal standardisation as well. The application is limited to measurements after a decay period not exceeding 14 days. The  $^{46}\text{Sc}$  activity as a neutron activation product cannot be used for internal standardisation.

## c) Samarium

Samarium, due to its soft gamma emission after photon activation (see chapter 5), is used in the case of low energy photon spectroscopy of the product activity.

The internal standard method has been extended to the use as a single comparator as applied sometimes in instrumental neutron activation analysis. This method was evaluated and critically discussed by Girardi et al.<sup>885</sup> and also reported by Neitzert and Lieser<sup>886</sup>, and by Alian et al.<sup>887</sup>. Difficulties arise in the case of application to photon activation analysis. First, since not all machine parameters of the accelerator are explicitly determinable, and consequently, the physical data of the photon radiation are not known completely (see chapter 5). Second, many photonuclear data of the reactions used for analysis of the elements are unknown as yet. Therefore, the procedure described by Girardi et al.<sup>885</sup> has to be modified in some details. For instance, the k-value which depends on the integrated photonuclear activation cross section cannot be

determined theoretically in many cases, but by experiment (simultaneous irradiation of the comparator element and a reference sample containing known concentration of the element to be analysed). Once this value is determined, one can activate and measure long series of analysis samples containing the internal standard and occasionally a reference material, also containing a known concentration of the internal standard. Using this method one can avoid the necessity of simultaneous irradiation of the analysis sample and the reference material. This procedure is of special advantage if one has to analyse product nuclides with half-lives of only a few minutes, e.g.  $^{29}\text{Al}$ ,  $^{38}\text{K}$ ,  $^{137\text{m}}\text{Ba}$ .

The procedure for calculation of the analysis results for both the conventional evaluation and for the application of an internal standard is described in paragraph 6.2.3.3 below. During long-period practical analysis work the use of internal standards in photon activation analysis has proven to be a useful tool to make analysis procedures more convenient and to improve accuracy and precision of the obtained data (Segebade et al.<sup>60</sup>; see also Ch.6.1). It should be applied particularly in the following cases:

- a) Analysis sample and reference material do not have the same size and shape.
- b) They cannot be irradiated simultaneously.
- c) The irradiation geometry cannot be kept identical for the sample and the reference material during simultaneous irradiation, e.g. by spontaneous misfunction of the sample rotating assembly.

The internal standard also corrects for inconstancies of the integral counting efficiency of the spectrometer, be they due to inconstant high voltage supply of the detector or to counting errors caused by incorrecable dead-time losses.

Following disadvantages have to be mentioned:

- a) The element selected to serve as an internal standard cannot be analysed.
- b) In the case of nuclear interference (see tab. 2) the concentration data of other components might be incorrect.
- c) Neutron reactions cannot be used for analysis unless there is also an internal neutron flux monitor provided both in the sample and in the reference material.

- d) The internal standard cannot correct deviations due to inconstant measurement geometry. This is discussed further in 6.2.3.4.

The application of additive internal standards in instrumental multielement photon activation analysis was also reported by Yagi and Masumoto<sup>888-890,1206</sup>.

Frequently in activation analysis, also external flux monitors have been used to correct for varying activating flux densities. Generally discs, sheets or wires are used which match with the sample geometry. In photon activation analysis this has been done in the analysis of ancient Noble Metal coinage (see Reimers et al.<sup>884,1180</sup>).

In this case the samples were located at a comparatively large distance from the bremsstrahlung converter namely about 50 cm and hence the photon field was fairly homogeneous. Copper discs with the shape of the coins and the reference material discs, respectively, were used as monitors. In the normal case, however, samples are irradiated at a distance of a few centimeters and the use of an external flux monitor would bear the danger of inhomogeneous activation of the sample and the monitor. Therefore, it would not yield any improvement of the initial situation.

All in all, compared with other instrumental radiometric analysis methods, the correct irradiation geometry in photon activation analysis is of medium problematic nature; it has to be handled more conservatively than in neutron activation analysis since the incident radiation is concentrated in a comparatively narrow beam (see chapter 3), whereas neutron radiation is distributed isotropically around the source with respect both to the energy spectrum and the flux density.

On the other hand, in other techniques like charged particle activation analysis or X-ray fluorescence analysis the irradiation geometry is much more a problem than in photon activation analysis. This is due to the extremely small penetration depth of soft X-rays and charged particles in most materials. However, in any of these methods, the use of internal standards will most probably yield maximum accuracy and precision of the obtained analytical data.

### 6.2.3 General analytical procedure

At this point, the laboratory procedure generally used in photon activation analysis is described. The procedure as applied in the authors' laboratory is taken as a model; procedures followed in other photon activation analysis laboratories, if essentially different, are described in the application section below. Differences to the procedures used in other activation analysis techniques are emphasised. No detailed descriptions of procedures used in individual cases are given; if they are necessary for better understanding of the problem, they are summarised in the concerning paragraphs in 6.2.4.

#### 6.2.3.1 Sample preparation, transfer and irradiation

As mentioned in chapter 3, the quasi-free choice of the irradiation volume enables the photon activation analyst to perform non-destructive analyses of large samples more often than e.g. in neutron activation analysis. Large objects, e.g. machine parts or large volume liquid or gas containments can be placed in front of the converter target. Of course there are several limitations due to the spacial distribution of the photon radiation, but in many cases one is interested to analyse a small area within a large object without being allowed to take a sample. Positioning the area of interest of the object in front of the bremsstrahlung source one can easily activate this spot and no damage occurs to the object.

However, in the most cases an analysis of comparatively small samples is required, typically some tens of milligrams. If samples lie before as compact pieces generally no special precautions against surface contaminations have to be undertaken since they can easily be removed after activation. This is especially true in the case of metals to be analysed. Measures for surface contaminations removal are extensively described and discussed in chapter 6.1 on the light elements analysis. The contamination problem in the analysis of the heavier elements generally is not as serious; the most frequent contaminants normally are atmospheric oxygen, nitrogen and carbon (as  $\text{CO}_2$ ). Contaminations due to atmospheric particles normally do not occur in activation analysis to a significant extent since the atmosphere in a radiochemical laboratory is purified from dust by air conditioning. The main source of contamination by heavier elements is due to abrasion of the tools used in the different phases of sample preparation (storage vessels, mills, tools for batching etc.). In the case of powdered materials to be analysed a post-irradiation purification normally is not possible. Therefore, it is of use to run blanks if available. However, the