

This chapter is intended to be referred to in the daily laboratory practice in photon activation analysis. It is divided into two separate sections, namely (6.1): the analysis of light elements emphasising carbon, nitrogen, oxygen and fluorine and (6.2): the the heavier elements from $Z=11$ (sodium) up to $Z=92$ (uranium). This is done because in photon activation analysis the above named four light elements normally are analysed by their active (γ,n) -products ^{11}C , ^{13}N , ^{15}O and ^{18}F , respectively. These are pure β^+ -emitters without any gamma emission (see Ch.2). Therefore, a multielement procedure, e.g. including high resolution photon spectrometry as described in 6.2 is not applicable. A decay curve analysis of the annihilation radiation has to be carried out. This implies peculiar problems which are very different from those encountered in instrumental multielement analysis as performed in the determination of the heavier elements; mostly a radiochemical separation of the above named nuclides from the irradiated matrix is required.

On the contrary, since the general availability of high-performance semiconductor spectrometers (see Ch.4), one normally strives for instrumental multielement procedures for heavier elements analysis in the different activation methods including photon activation. Thereby tedious radiochemical multicomponent separation procedures can be avoided which mostly are much more complicated and time-consuming than those discussed in Ch.6.1. Therefore, radiochemical separation methods are discussed in Ch.6.1 whereas they are just mentioned marginally in a few cases in 6.2 as they were reported in the literature inspected by the authors.

Furthermore, the data processing - be it decay curve analysis in light element determination or multi-component gamma spectrum analysis - is not discussed in detail in this chapter; the proper selection of adequate data processing methods is strongly dependent upon many parameters, e.g. rapidity requirement, available spectrometry hardware and computation hard- and software. Last not least, it is a question of each analyst's personal philosophy which data processing path to follow. This is touched on further in Ch's.4 and 6.2 in the gamma spectrum processing context.

Finally, this chapter is restricted to photon activation analysis procedures in which delayed activity counting is applied. Therefore, the analysis of deuterium, beryllium and fissile elements through photodisintegration methods is not

included; this method normally requires prompt neutron counting, thus it is not discussed any further. This also applies to any other method including prompt radiation counting (see e.g.⁶⁹⁴).

6.1 Light element analysis

Regarding the tables in Ch.5, it is obvious that virtually all elements of the Periodic Table can be activated by high energy photons, but not all of the product nuclides emit characteristic gamma radiation. Several are pure β^- -emitters (e.g. ^{35}S , ^{32}P) or decay exclusively by β^+ emission (e.g. ^{11}C , ^{15}O) or electron capture (e.g. ^{49}V). This applies in particular to the elements up to sulfur. There are several ways to perform photon activation analyses of these elements, namely:

- 1 - Two of the light elements (deuterium and beryllium) can be analysed by direct observation of the prompt neutron emission during photon exposure (photon disintegration)⁶⁹⁵⁻⁷⁰¹. As mentioned in the introductory paragraph, this application is not discussed in this book.
- 2 - β^- -emitters can be analysed by beta spectroscopy. However, in this case one has to be aware of matrix attenuation problems. Moreover, the majority of the materials to be analysed produces a multicomponent mixture of radionuclides, frequently including several β^- -emitters whose radiation components cannot be separated spectrometrically because of the continuous distribution of the beta radiation energy. Therefore it is necessary to perform a chemical separation of the components to be analysed prior to spectrometry. The product nuclides can then be retrieved and identified by their maximum β^- -energy which is characteristic.
- 3 - Since mostly neutron-deficient radionuclides are produced through photon activation (see Ch.2) it is possible to analyse several nuclei by characteristic X-rays effected by eventual electron capture decay. The special equipment required for X-ray spectrometry is described in detail in Ch.4. However, in the low atomic number region electron capture decay usually is of quite poor probability and therefore appreciable analytical sensitivity cannot be expected. Moreover, characteristic X-rays in the low Z region are extremely soft and thus experimental difficulties arise due to eventually poor effective detector sensitivity (see Fig's.4.6 and 4.7 in Ch.4) and also matrix attenuation problems (see also 6.2).
- 4 - The majority of the neutron-deficient product nuclides of low atomic number decay by β^+ -emission. The photon radiation effected by annihilation of a positron as it combines with a negative electron is not specific since it

is no nuclear radiation and its energy represents the rest energy of an electron exclusively ($E_0 = 511 \text{ keV}$; see Ch.2). Although not being gamma radiation, annihilation quanta can be analysed with normal gamma spectrometers since their unique energy falls well within the gamma energy range usually emitted by radionuclides (about 100-4000 keV). However, as also applies to pure β^- -emitters, a chemical separation after bremsstrahlung exposure is required in the most cases since normally several β^+ -emitters are produced in the sample matrix. Unlike gamma emitters, the product nuclei can only be retrieved by their half-lives obtained by decay-curve analysis.

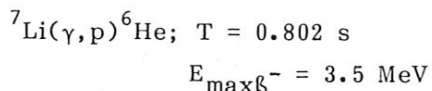
Among these possibilities the latter has been mostly applied for carbon, nitrogen, oxygen and fluorine analysis. In this chapter, these are discussed in more detail, too.

6.1.1 The analysis of light elements other than C, N, O and F

As already noted, other light elements than the above named ones have been analysed by photon activation in very few cases unless their product nuclides emit a well-measurable gamma spectrum. Several examples are given in the following paragraph. Since all yielded product nuclides are relatively short-lived, the determinations have to be carried out instrumentally.

Lithium

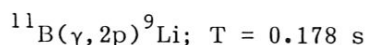
The non-destructive analysis of lithium by



and counting of the high energy β^- -radiation was proposed by Engelmann and Scherle⁷⁰². The measurable minimum concentration was claimed to be several hundred micrograms per gram. Due to the short half-life of the reaction product a fast sample transfer system must be available. The same procedure can be applied to the analysis of beryllium discussed below.

Boron

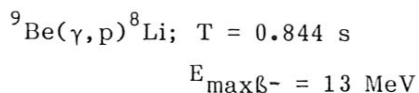
Using high bremsstrahlung energies, boron can be analysed by the reaction



and counting of the delayed neutrons emitted by ${}^9\text{Li}$. The delayed neutron counting method was first mentioned by Dorosh et al.⁷⁰³ and first applied to boron analysis by Engelmann and Scherle⁷⁰⁴. The intrinsic sensitivity is good - 50 nanograms were claimed as a detection limit - but the method is subject to interference by fissile elements eventually present in the sample.

Beryllium

Beryllium can be determined through



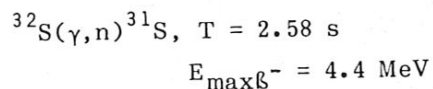
following virtually the same procedure as was proposed for lithium by Engelmann and Scherle in the publication quoted above⁷⁰². The particular advantage of the method in this application is the extremely high beta energy of the product nuclide which allows convenient quasi-selective activity counting. A sensitivity of a few hundred micrograms per gram were reported. Furthermore, it was proposed to improve selectivity and sensitivity by beta-gamma coincidence counting.

Phosphorus

Beresin et al.^{705,706} analysed phosphorus instrumentally in geological material by activation with betatron bremsstrahlung and subsequent scintillation counting of the 511 keV annihilation quanta due to ³⁰P decay. The evaluation was performed by complex decay function analysis. Interferences were minimised by proper selection of the irradiation energy (see also Ricci³²⁸, Katz and Penfold¹⁴²).

Sulfur

The photon activation analysis of sulfur was described by Engelmann and Scherle⁷⁰². The reaction



was applied using beta spectroscopy as described above for lithium and beryllium.

6.1.2 The analysis of carbon, nitrogen, oxygen and fluorine

Whilst the photon activation methods described above have been applied in a few cases only, the analytical interest was mainly concentrated on the analysis of the mentioned four elements. In the pioneer works on photonuclear activation analysis the determination of these were described (Basile et al.⁶, Beard et al.⁷⁰⁷, Albert et al.⁷⁰⁸. See also Ref's.⁸⁶⁸⁻⁸⁷⁰). (γ, n)-reactions yielding ^{11}C , ^{13}N , ^{15}O and ^{18}F , respectively, were used almost exclusively. The authors of this book could find but three papers in which other possibly usable photon reactions were mentioned, namely: $^{16}\text{O}(\gamma, 2n)^{14}\text{O}$ (gamma spectrometry; Bueno de Mesquita et al.⁷⁰⁹, $^{18}\text{O}(\gamma, p)^{17}\text{N}$ and $^{19}\text{F}(\gamma, 2p)^{17}\text{N}$ (both delayed neutron counting; Engelmann and Scherle^{702, 704}).

6.1.2.1 Irradiation

In order to achieve the highest possible analytical sensitivity, the electron energy of the accelerator has to be adjusted well above the giant resonance excitation energy. However, as demonstrated in Ch.2, excessively high bremsstrahlung energy bears the danger of multiple interference by competing nuclear reactions or, in the case of instrumental analysis, by enhanced influence of other radionuclides. In the daily laboratory practice, electron energies around 30 MeV have been proven as a good compromise between achievable sensitivity and unavoidable interference by competing reactions (see Ch.2). This is also true for the analysis of heavier elements (see Ch.6.2). Selecting the bremsstrahlung energy, one has to consider the activation threshold of the interfering reactions. If the activation is carried out near the threshold energy of the interfering reactions, their contribution might vary greatly in the case of uncontrolled electron energy shift and thus render unreproducible. This problem arises also if internal monitors are used (see below).

As already explained in Ch.3, reproducibility of the electron energy is not always satisfactory if linear accelerators are used.

Other energies applied were reported by Voigt and Abu-Samra³⁰⁵ (70 MeV), Beard et al.⁷⁰⁷ (40 MeV), Scherle and Engelmann⁷¹⁰ (40-62 MeV; in this case other reactions than (γ, n) were used; see introductory paragraph), Vialatte⁷¹¹ (up to 40 MeV), Williams et al.⁷¹² (up to 40), Wilkniss et al.⁷¹³ (22 MeV), Kosta and Sluneko²⁴⁸ (19 MeV), Rocco et al.⁷¹⁴ (17-19 MeV), Schmitt et al.⁷¹⁵ (15 MeV). Yet other activation energies used are mentioned in papers quoted in the chapter about heavier element analysis (see 6.2). Many of these workers have

selected other energies to exclude interferences.

The exposure periods in the non-destructive approach have to be selected so that an optimum ratio is obtained between the activities to be measured for analysis and any interfering activity. In the case of radiochemical analysis irradiation times may be set as long as convenient and reasonable regarding both the concentration of the component to be determined and the half-life of the desired nuclide. For instance, in the authors' laboratory - if traces are determined - average exposure periods of five, twenty and forty minutes have been selected for the analysis of oxygen, nitrogen and carbon/fluorine, respectively.

- Error sources

Using excessively long irradiation periods one has to bear in mind eventually limited durability of irradiated matrices against heat and radiation attack. In critical cases, e.g. if no "thick" converter target (see Ch.3) is used and transmitted electrons hit the sample, countermeasures might become necessary, viz. cooling or reduction of the integral radiation flux by removing the sample to a farther distance or reduction of the electron beam current. For instance, alkali metals have been cooled during bremsstrahlung exposure by air jet or even liquid nitrogen (see also 6.2.2). Moreover, in several critical cases, the chemical reactivity of the matrix material is considerably enhanced by irradiation and the handling after bremsstrahlung exposure can render hazardous (see e.g. 6.1.4).

A thorough study about the proper irradiation conditions was undertaken by Engelmann^{24,45,716}.

Since the flux distribution - and to a lesser extent also the energy distribution of the activating photons - is inhomogeneous (see e.g.²⁸⁶) the standardisation of the integral photon flux received by the sample and the reference material is somewhat problematic if they are not located precisely at the same place in the beam axis. Experiments^{24,25,717,718} have indicated both a longitudinal and transversal gradient of flux and a transversal gradient of the bremsstrahlung energy (see also Ch.3).

A beam-steering system which enables proper adjustment of the electron beam on the target area is useful for establishing reproducible irradiation conditions.

If simultaneous irradiations of the sample and the reference material are performed or external flux monitors have been applied, the sample has been either sandwiched between a pair of those and irradiated coaxially with the photon beam or a rotating multi-sample irradiation assembly has been used. Thereby either the flux gradient within the sample has been monitored or a quasi-uniform irradiation geometry was enabled, respectively. However, a more efficient way of flux monitoring is the use of a matrix-inherent (or additive) internal standard (see below and also in 6.2.2).

Flux monitoring through electron beam current and position measurement is not sufficient since variation of the mean photon energy is not detected by this method²⁵.

Errors due to inhomogeneities in the composition of the sample and the reference material contribute to the common uncertainty of the results, but mostly cannot be exactly quantified; these errors were reported to amount to several per cent in critical cases⁴⁹.

Errors caused by geometrical non-congruency of the sample and the reference material can be ruled out by using internal standards as discussed below; otherwise similar shape and - in critical cases - similar matrix compositions have to be provided for samples and standards irradiated simultaneously. Similar matrix composition is required if material of large density and atomic number is analysed; in this case, particularly if large-volume samples are activated, the photon beam attenuation by matrix absorption might become significant (see 6.2.3.4 and also Lutz⁷¹⁷, Baker et al.⁷¹⁹).

Another error might be introduced by recoil of active light element isotopes from the close environment, e.g. the reference material, into the sample. This was evaluated quantitatively by Marsh⁴⁹; see also Schmitt⁷²⁰, Seitz⁷²¹. However, this interference generally can be avoided by insulating the different items to be irradiated simultaneously with help of any separating layer, e.g. aluminium foil. A thorough post-irradiation removal of the surface layer should also solve the problem of recoil contamination. Secondary activation through recoil particles is discussed in 6.1.2.5 below.

- Internal standards

Frequently internal standards for flux monitoring have been used. This is of particular importance if a considerable amount of material is removed during

post-irradiation surface treatment and, for any reason the sample cannot be reweighed, as was demonstrated by Lutz and DeSoete during analysis of carbon in sodium⁷²².

Usually the activity induced in a main matrix component, if activable, has been utilised. The specific activity of the element to be analysed is then normalised by the specific activity of the internal monitor element. In photon activation analysis this ratio, for several reasons, has to be predetermined utilising a reference material with known composition. Although being an elegant method for the implicate correction of flux variations and several other error sources (see 6.2.2) the use of internal standards might entail problems, e.g. if the half-lives of both components under consideration are greatly different. No significant photon flux variations with time during bremsstrahlung exposure can be tolerated. If both radionuclides have half-lives which are large compared with the irradiation period the influence of flux variations with time are of minor import.

Critical cases in this instance are analyses of carbon, or, even worse, oxygen in sodium using ^{22}Na as an internal monitor (see below in the concerning paragraphs).

Moreover, the accelerator electron energy must be considerably greater than the energies of the giant resonance maxima of both reactions involved. In the case of slight energy shift of the electron beam nearly equal activity variation of the two product nuclides can then still be expected. These energy variations might induce severe error if the activation is performed close above the threshold energy of one of the two reactions considered, or, even worse, near threshold. If linear accelerators are used, the analyst should bear in mind that an energy instability can amount up to $\pm 5\%$.

The eventual significant yield ratio variation of the internal monitor reaction and the analytically used one at small electron energy shifts was well demonstrated by the application of ^{18}F produced through $^{23}\text{Na}(\gamma, \alpha n)$ as an internal standard in oxygen analyses of sodium; experimentally determined quantitative results of this application, together with a thorough evaluation of the internal monitor technique as applied in light element photon activation analysis was published by Nordmann et al.⁷²³; see also Wilkniss⁷²⁴.

6.1.2.2 Surface treatment

Particularly for the analysis of ultratrace quantities a complete removal of the contamination from outer source onto the surface of the sample is essential. In critical cases this contamination can introduce deviations from the true value by orders of magnitude^{49,724}. Three of the light elements under study (C,N,O) are major atmospheric components and thus contamination is most likely. This problem is common to all analysis methods, especially the non-activation techniques. In activation analysis, however, the surface contamination problem can be solved more easily; once the surface is cleaned after activation a subsequent re-contamination may be disregarded since it is inactive and thus cannot interfere during measurement. This applies to all standard activation methods. In the case of light element analysis, the surface contamination removal might become problematic, e.g. in the 14 MeV-neutron activation analysis of oxygen yielding ^{16}N . Because of the short half-life of the product nuclide (7.13s) cleaning procedures consuming more than several seconds entail severe losses of sensitivity (Pauwels⁷²⁵, Engelmann⁷²⁶, particularly see the discussion after the presentation of the paper.). In charged particle activation analysis the surface contamination removal is a special problem since only a very small fraction of the sample surface is activated whilst the bulk remains untouched. Thus surface treatment must be optimised so that the contaminants are completely removed but the removal of an excessively thick surface layer is avoided⁷²⁷. In photon activation analysis, however, the problem of surface treatment is not too serious; the whole sample body is quasi-evenly activated and even the shortest half-life encountered in standard photon activation analysis of the light elements under study, namely about two minutes of ^{15}O , allows a reasonably thorough removal of surface contaminants after irradiation in almost every given case. Some workers have removed the very outer layer of their irradiated samples mechanically (see e.g. Mackintosh and Jervis (Ref.⁷²⁸, Nordmann et al.⁷²⁹, Pronman et al.⁷³⁰). However, this sometimes entails difficulties; depending upon the gross matrix composition, eventually excessive radioactivity after irradiation of the sample might render its mechanical handling hazardous so that it might have to be performed by manipulators behind lead shielding. Moreover, as was touched on above, some matrices might require special precautions against violent oxidation when exposed to the atmosphere, e.g. caesium; Nordmann et al.⁷²⁹ freeze-dried caesium samples in liquified nitrogen before bremsstrahlung exposure to prevent excessive heating during activation, and also after irradiation to facilitate mechanical surface treatment.

In the case of chemical etching it is recommendable to remove the gross surface contamination prior to activation either mechanically by shearing or chemically by etching. However, mechanical pre-irradiation treatment seems preferable. Marsh⁴⁹ found that etching prior to bremsstrahlung exposure removes minute impurity but roughens the surface of the sample and probably opens micro-cracks, thus increasing the danger of surface recontamination. Pre-irradiation purification is of particular importance if, for any reason, a thorough post-activation surface treatment is not possible (Williams et al.⁷¹²). The etching procedures and the chemicals used therein are, of course, contingent upon the chemical behaviour, particularly the chemical attackability, of the sample matrix. Furthermore, different bulk materials require different surface layer thicknesses removal (Rook et al.⁷³¹). Therefore, the total duration of the etching process has to be carefully selected with respect to the minimum removed layer thickness required and unavoidable loss of sample material. This is of special importance if the samples cannot be reweighed after etching⁷¹². One elegant way out in critical cases is the use of a matrix activity as an internal radiation flux monitor (see above and 6.2.2). Pronman et al.⁷³⁰ reported results of a thorough study about the surface layer thickness to be separated from the sample matrix for complete removal of the outer contamination by light elements. For more information about quantitative considerations and experimental results the reader may refer to Evshanov et al.⁷³², Chapyshnikov et al.⁷³³, Wasserman et al.⁷³⁴, Pauwels⁷²⁵, Marsh⁴⁹, Kapitsa et al.^{289,735}, Lutz and DeSoete⁷²², Quaglia et al.⁷³⁶, Schmitt and Fusban⁷³⁷, Rook et al.⁷³¹. The latter described a thorough study on surface contamination treatment with respect to adsorbed, re-adsorbed and active atom recoil-caused radioactive contamination; see also Guardipee⁷³⁸. An "electropolishing" procedure (removal of a partition of the very outer surface layer including any contaminant by electrolysis making the sample the anode versus a platinum cathode) was developed in the Harwell photon activation analysis laboratory (Hislop et al.⁷³⁹, Williams et al.⁷¹² and other papers cited therein). Engelmann reported ultrasonic bath-aided etching of metals after bremsstrahlung exposure¹⁷; see also Schmitt and Fusban^{737,800}.

A particular problem is the contamination by active atom recoil. However, normally serious recoil activities remain on the very outer surface of the sample and thus are easily removable⁴⁹; see also above 6.1.2.1, error sources section). In Tab. 6.1-1 etching media are listed which have been most frequently recommended in the literature accessible to the authors. Surface treatment procedures recommended by the Reference Bureau of the European Communities (BCR) can be found in Ref.⁷⁴⁰.

Tab.6.1-1: Surface contamination removing agents; etchings carried out at room temperature unless stated

Etchant ¹	Material	Remarks	Ref.	Etchant ¹	Material	Remarks	Ref.
HCl	Cr	1M, boiling	781, 784	H ₂ SO ₄	Ni	dilute	739, 818
	Steel	3M	712		Mo	4:3 w.H ₂ O or 1:3, methanolic	749
	Zn	dilute	750				
	Cd	dilute	750				
	In	70-90°C	289, 734, 851	HClO ₄	Steel	conc'd., boiling	735, 851
				HF	Be	1M	17, 49
HNO ₃	Mg	1M, methanolic	750, 781				
	Ni	3M, boiling	750, 781	HCl:HNO ₃	Steel	45:5:50 w. H ₂ O, boiling	712
	Cu	4:1 w.H ₂ O, boiling	712		Au, Mo	3:1, hot	750
	Cu, Sn	conc'd.	289, 735, 851	HNO ₃ :HF	various	4:1	848
	Zn	1M, boiling	750, 781		Si	3:1.5:5.5 w.H ₂ O	781
	Zn/Mg/ Te all.	3M	750, 781		Si	1:1 w.H ₂ O	795
	Se	boiling	810		Si	prior to activ'n.	769
	Ag, Ag/Zn	2M, boiling	750, 781		Ti, W	1:1, 3M each	285

¹In the case of electropolishing: etchant plus electrolyte^{712, 739};
all etchant compositions given in v/v

Tab.6.1-1, continued

Etchant ¹	Material	Remarks	Ref.	Etchant ¹	Material	Remarks	Ref.
HNO ₃ :HF	Fe	9:1 w.H ₂ O	285	Br ₂ : CH ₃ OH	InP	1.5:0.8	712,850, 854
	Ge	3:1	712				
	As,GaAs	3:1:2 w. H ₂ O	712	H ₂ O	Li		851
	Refract. metals	1:1, ultra- son.bath	737	H ₂ O, HOac.	Li	sequent ^y .	732,852 853
	Zr	1:1:8 w.H ₂ O	781	CH ₃ OH	Li		49
HNO ₃ : H ₂ SO ₄	Mo	0.5:4.5:5 w.H ₂ O	781	C ₂ H ₅ OH	Na	90% 96%	756 732,852 853
	Mo	1:4.5:4.5 w.H ₂ O	285			90%, triply etched	722,743, 744,815
H ₂ SO ₄ : H ₃ PO ₄	Steel	1:4.3:1.4 w.H ₂ O	712	Various organic solvents	Na	sequent ^y .	852,853
HNO ₃ : H ₂ SO ₄ : H ₃ PO ₄	Al, Al/mg	0.5:2:7	781,797				
HNO ₃ :HF: H ₃ PO ₄	Si	1:1:1	849				
KOH	Nb	melted KOH	293				

¹In the case of electropolishing: etchant plus electrolyte^{672,732};
all etchant compositions given in v/v

After post-irradiation surface treatment the residual activity of the desired nuclides are measured either instrumentally or after radiochemical separation. The separation procedures are discussed in the single elements section below.

6.1.2.3 Activity counting

The common photon energy produced in the positron emission of the nuclides under study (511 keV) is well measurable by scintillation detectors. Since in every positron annihilation two 511 keV photons are emitted simultaneously in opposite directions, there is the possibility of very efficient background suppression by coincidence counting using NaI(Tl)-crystal detectors arranged in a proper geometrical setup (Fig.6.1.1).

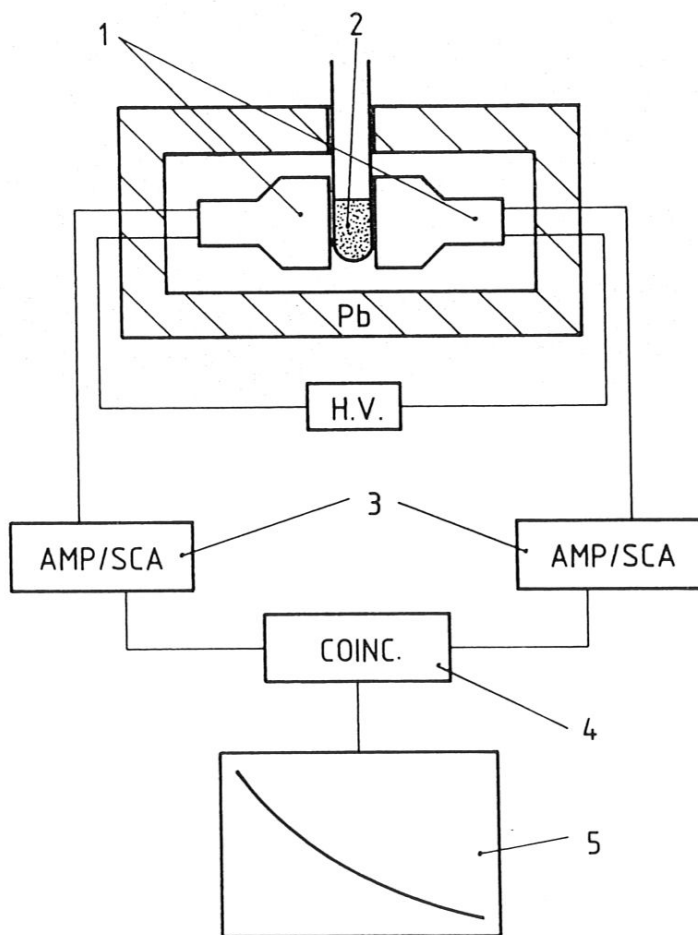


Fig. 6.1.1: γ - γ coincidence measurement setup: explanations see text

NaI-detectors (1) have been used almost exclusively to measure the desired activity (2). The authors could find only very few reports about other counting methods after activation (see e.g.^{6,730}). The pulse height windows of single channel analysers (3) are adjusted to screen out the 511 keV full energy peak. The pulses from the single channel analyser outputs are then fed into a coincidence pulse processing unit (4). In the case of coincidentally absorbed annihilation quanta in both detectors, the coincidence unit will issue a pulse signal which can then be processed further (5) in any desired manner, e.g. by multichannel scaling.

The spectroscopy equipment is discussed in more detail in Ch.4. The described counting setup basically has been applied almost invariably hitherto. Differences have appeared in the crystal size. This depends upon the counting efficiency requirement of the given task. Engelmann⁷²⁶ used two sets of differently sized NaI-crystals: a pair of 1.75" x 2" crystals for routine analyses and two 3" x 4" detectors for analyses close to the detection limit. A quasi-fully automated counting system was described by Engelmann¹⁷.

Environmental background pulse rates are low; a few pulses per second have been reported as an upper value. Sometimes well-type crystals for 4- π -counting have been used abandoning the advantage of high-performance background suppression in favour of enhanced counting efficiency⁷¹⁹.

As mentioned in the introductory paragraph, the above described counting procedure bears the penalty of non-selectiveness (see Ch.2). Therefore, one has to select between two kinds of analysis:

a) One can rely upon the resolution of a complex decay function into its components of half-lives, two, ten, twenty and 112 minutes for the analysis of oxygen, nitrogen, carbon and fluorine, respectively, obtained graphically or by computer program⁷⁴¹. This is only possible in high purity material whose matrix does not produce an excessive background radiation. Moreover, the material must be free from elements which produce positron emitters with similar half-lives as the component to be determined, e.g. the analysed sample must be free from phosphorus in the case of oxygen measurement, from copper if measuring nitrogen, and from silver if carbon is to be analysed. Furthermore, all other β^+ -emitters can interfere, if present in relatively large amounts (Engelmann⁵⁰, see also above 6.1.2.5). Finally, if one of the light elements is present in excessively larger concentrations than the other, their signals might lose all significance and thus cannot be resolved from the major component; this has

frequently been observed during instrumental nitrogen analysis. Both the activities of the analysed elements and the unavoidable matrix background should all be of the same order of magnitude. In Fig.6.1-2 a complex decay-curve (1) and its computer-resolved components due to ^{15}O (2), ^{13}N (3), ^{11}C (4) and a long-lived unidentified background (5) is shown.

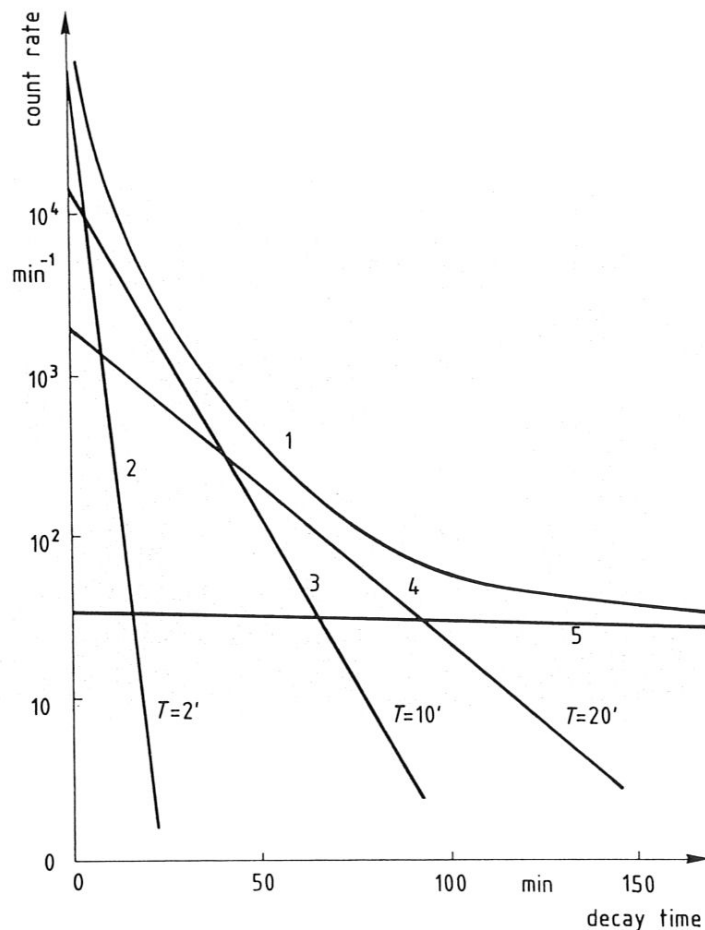


Fig. 6.1.2: Deconvolution of a complex decay curve (1) of positron emitters into 4 exponential components (2-5); explanations see text

b) Normally if traces of the named elements are to be determined, the non-destructive approach is barely suitable. In this case a radiochemical separation of the activated element from the matrix is required. In paragraphs 6.1.3 ff. both methods - instrumental and radiochemical analysis - are discussed as they have been applied in the authors' laboratory or were reported in the literature.

- Error sources

Since the measured radiation does not directly originate from nuclear decay but from delayed annihilation, complete annihilation of the positrons within a defined and reproducible spatial area must be ascertained since otherwise a constant actual radiation source geometry cannot be assumed. Engelmann¹⁷ found that a layer of 2 mm of copper wrapped around the source was thick enough to completely absorb (and subsequently convert) the positrons with the highest energy encountered throughout the study.

Samples mostly are measured as closely as possible to the detector(s) so as to provide maximum counting efficiency. However, in the close vicinity to the detector the sample normally cannot be regarded as a point radiation source and therefore the actual counting efficiency is strongly dependent on the geometrical shape of the source. Thus, in order to achieve comparable countings, the shapes of sample and reference material must not be greatly different. This might become problematic, e.g. if small pellets of reference material are measured non-destructively whilst the activity of the sample to be counted has been collected by a liquid or solid sorbant which usually is of greater volume. In this case a correction factor has to be determined previously (see also the reference material section 6.1.2.4) below.

In the non-destructive approach, in critical cases an error can be introduced by matrix absorption of the annihilation quanta if high Z material of large volume is analysed. In this case the reference material must have a similar matrix composition and the problem of similar volumes has to be handled very accurately.

Too high photon emission rates of the sample might create dead-time problems of the counting equipment; this is frequently the case in instrumental analysis.

Finally, one cannot be sure about the absolute radiochemical purity of the counted fraction in every case (see also 6.1.3 ff); therefore it is essential to perform a decay-curve analysis also if a separated fraction is counted to minimise the probability of error due to interference.

6.1.2.4 Reference materials

The question of reference materials in light element photon activation analysis is comparatively easily solved; since normally only one or two components are analysed simultaneously, pure elements or simple compounds can well serve as reference materials, e.g. graphite in the case of carbon analysis. Frequently the reference material has been selected so that it bears a component usable as internal standard, e.g. sodium carbonate in the case of carbon determination in sodium; ^{22}Na has been used for internal standardisation^{722,742-745}.

Normally the reference material does not have to pass the separation procedure, unless the chemical yield of the separation method has to be monitored. This is, however, better performed with help of a certified reference material having the same or a similar matrix composition as the analysed sample. Many kinds of reference species are commercially available which contain various certified concentrations of the components to be analysed and can be supplied with almost every desired matrix composition⁷⁴⁶⁻⁷⁴⁸.

Primary standards are recommendable as reference materials in any case. Since those usually contain large concentrations of the desired element they can be counted after separation and counting of the sample to be analysed. The total mass of the analysed element in the reference material is best selected so that it can well be measured after a cooling period which about equals the separation period of the unknown sample.

As mentioned above, the analyst has to provide the same counting geometry for the reference material as used for the analysed sample i.e. the same shape and volume. This can be performed practically by dissolution or mathematically by a correction factor previously obtained by experiment⁷⁴⁹⁻⁷⁵¹; see also above 6.1.2.3. The reference materials generally used are specified for every element to be determined in the concerning paragraph below.

6.1.2.5 Interferences

There are two mechanisms in photon activation analysis of the light elements by which interference is introduced, namely the signal overlap due to other activities than the desired ones (chemical interference) and the interference by competing nuclear reaction (nuclear interference).

- Chemical interference

Chemical interference is of particular importance in non-destructive analysis by photon activation since a large number of neutron-deficient radionuclides decay by positron emission. In some cases this type of interference might also occur in radiochemical analysis. In critical cases radiochemical impurity of the desired activity fraction was reported^{734,737}.

In the purely instrumental approach, the chemical interference is of complex nature. The different sources can be distinguished thus:

- a) Interference by β^+ -emitting radionuclides with half-lives close to that of the nuclide to be analysed. A selected number of those are given in the concerning paragraphs below. If one or more of these are due to a major or minor matrix component, a non-destructive trace analysis forbids itself unless this interference can be outwitted by activation at lower energy (see below).
- b) Interference by any other β^+ -emitters; if these have half-lives significantly lower than that of the desired component, they can be allowed to decay before counting and thus can be disregarded. If β^+ -emitting nuclides are produced whose half-lives are longer than the analysed one, the desired decay function can be resolved from that of the interfering activity unless the interference is produced in excessive activity levels. In this case the signal to be analysed might lose any significance and cannot be retrieved.
- c) Interference by any other photon-emitting nuclides; normally, using a gamma-gamma coincidence spectrometer described above, this interference problem can be considered as a minor one. The interfering spectrum - either full energy signals in the close vicinity to 511 keV or originating from Compton signals due to higher energies - are almost completely discarded by the coincidence pulse analyser.

In advantageous cases an interfering background can be subtracted with help of another gamma-ray line emitted by the interfering nuclide²⁸⁷. This can be done mathematically by calculating the background counts by the well-known ratio between the positron emission and the other gamma-ray line (reference energy) previously determined by experiment (see also Ch. 6.2.3.4) or electronically by an additional coincidence unit which inhibits the edition of a signal in the case of coincidentally registered pulses originating from the analysed energy

(511 keV or energies nearby) and the reference gamma energy of the interfering nuclide. However, in the case of complex background interference this procedure costs additional hardware effort and is of doubtful value regarding the quality of the final result. Moreover, if the matrix activity is excessively high, one has to be aware of dead-time and pile-up problems in the spectrometer (see Ch.4). Therefore, a radiochemical separation is recommended in these cases. As demonstrated in Ch.2, sometimes it is possible to exclude interferences by irradiating at lower energy if the reaction threshold of the interfering component is higher than that of the analysed one. This also applies to the nuclear interference discussed below. However, considerable loss of sensitivity has mostly to be taken into account. As already noted, there are only few - preferably high purity - matrices, in which purely instrumental photon activation analyses of the light elements are possible. In this case the absence of any potentially interfering components must be ascertained previously by fullscale trace analysis⁷⁵². In other material the mentioned interferences can be ruled out quite efficiently by radiochemical separation and careful purification of the components to be counted, usually performed in their gas-phase with help of dust filters, acid scrubbers etc. Moreover, undesired volatilisation and gettering effects can be avoided by flux-aided low temperature extraction as is described further in 6.1.3.2. The radiochemical purity of the counted source can be confirmed by recording the decay function.

- Nuclear interference

The nuclear interference can be much more of a problem than the chemical discussed above. An example:

Carbon is analysed by $^{12}\text{C}(\gamma, n)^{11}\text{C}$. The reaction threshold energy is about 19 MeV^{753, 754}. Hence, in order to achieve satisfactory sensitivity, one has to irradiate at energies well above this threshold, say 30 MeV. At this energy, however, ^{11}C may also be produced in considerable amounts by $^{16}\text{O}(\gamma, \alpha n)^{11}\text{C}$ having a threshold energy of about 26 MeV. This interference has to be taken into account in almost every case, since:

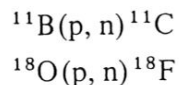
- 1 - it cannot be outwitted by chemical means,
- 2 - oxygen is quasi - omnipresent, mostly in considerable amounts,
- 3 - reduction of the bremsstrahlung energy does rule out the interfering reaction, but entails a loss of sensitivity of the carbon analysis which can amount to orders of magnitude⁷⁵⁰.

Major attention has to be paid to competing reactions due to matrix components (see e.g.⁷⁵⁵). For instance, in the case of carbon analysis in sodium the matrix might interfere significantly. As obvious by reaction No.8 in Tab.6.1-4 in 6.1.3.3, ^{11}C might be produced also by sodium at activation energies around 30 MeV. Although being produced with low cross section near threshold, ^{11}C due to the sodium matrix might contribute significantly to the common carbon activity because of its high excess in mass and thus in number of target nuclei, as was demonstrated through experiment by Nordmann et al.⁷⁴⁴. The quantitative contribution of the interference strongly depends upon the electron energy. Experimentally determined values given in the inspected literature vary considerably; this is not only due to the different electron energies used, but also caused by unavoidable uncontrolled shift of the beam parameters during sample exposure, particularly, if linear accelerators have been used (see also 6.1.2.1 and Ch's.2 and 3). Since the above named competing reactions often are induced at photon energies close to their activation thresholds, small energy drift might cause great variations of the interference activity yields (see 6.1.2.5). Yield values were reported by Engelmann and co-workers^{23,24,744,756-759}, Lutz and Masters⁷⁵⁰, Hislop and Wood⁷⁴⁹ and others. As an example, Engelmann and co-workers have found 50 micrograms nitrogen or 1000 micrograms oxygen to produce the same ^{11}C activity as 1 microgram carbon, respectively, during exposure to 30 MeV bremsstrahlung.

The most of the possibly interfering reactions given in Tables 6.1-4, 6.1-8, 6.1-11 and 6.1-14 normally might be disregarded, but need be investigated when analysing new matrices.

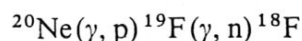
- Interference by secondary reaction

Secondary reactions with charged particles are induced by promptly emitted protons, deuterons or alpha particles due to photonuclear reactions within the sample matrix. Among these, protons theoretically might introduce significant interfering activity during activation e.g.



interfering with the analysis of carbon or fluorine, respectively. The significance of this type of interference is strongly dependent upon the nuclear data

of the matrix material in terms of effective integrated photoproton cross section at the given irradiation energy. Furthermore, it is of course a function of the cross section of the interfering proton reaction and several other nuclear parameters. In critical cases, significant yields might be reached (see e.g.^{760,877}). Moreover, these reactions cannot be avoided by suitable selection of the electron energy since normally in the low atomic number region (γ, p)-reactions have lower thresholds than (γ, n). However, normally secondary reactions due to photoprotons do not induce significant interfering activities in the case of light element analysis⁷¹². Engelmann¹⁷ did not detect any interference due to charged particle recoil activity. The occurrence of interfering reaction chains is thinkable, e.g.



interfering with the fluorine determination⁴⁵. In practice, however, this kind of reaction will be scarcely detectable.

Reactions due to photoneutrons are more likely to interfere, but this is only true for the analysis of heavier elements; although the photoneutron flux may be considerably high (see Ch. 3, 6.2) there is no danger of interference since neutron reactions yielding ^{11}C , ^{13}N , ^{15}O and ^{18}F have extremely small cross sections at photoneutron energies.

The different sources of interference are discussed for each element to be determined in the relevant paragraphs below.

6.1.2.6 Sensitivity

The intrinsic sensitivity is primarily dependent upon the integrated effective reaction cross section (see Ch. 2). To a great extent, the sensitivities achievable in photon activation analysis of the light elements are dependent upon irradiation and machine parameters of the accelerator, viz. electron energy, electron beam current, distance of the irradiation position from the bremsstrahlung converter target, construction of the converter, exposure time, all these summarised as: integral activating photon flux received by the sample at the given energy. However, the dependency of the induced activity on the electron energy can be exploited for achievement of higher sensitivity only within limits; as already noted, the quality of the results obtained through activation with excessively high bremsstrahlung energies might be degraded by enhanced

chemical and nuclear interference (see 6.1.2.5). Furthermore, sensitivity can be influenced by the sample mass selected, chemical efficiency of the separation method as well as its time consumption and - within limits - the counting period.

As already stated in 6.1.2.2, post-irradiation removal of the active surface contamination is essential in high-sensitivity non-destructive or radiochemical analysis.

The achievable sensitivity is greatly influenced by the counting properties of the gamma spectrometer used for activity measurement, viz. size and geometry of the scintillation crystal(s), background suppression measures and the quality of the electronic pulse processing units. The latter, however, are less complex than those required in instrumental multi-component spectrometry and thus usually do not appear as major sources of error and deterioration. As already noted, mostly coincidence counting has been applied. Although a lower count yield is achieved than in counting e.g. with a single well-type crystal, this method is preferable in the most cases since a much higher signal-to-background ratio can be achieved. This factor much more determines the quality of the results and with it the sensitivity of the method than the absolute count rate does.

Finally, the gross matrix composition of the sample takes influence upon the sensitivity, particularly in the case of purely instrumental analysis. The tables in Ch.5 may be consulted in order to estimate the resulting matrix activities after irradiation both qualitatively and quantitatively. The behaviour of the matrix components against heat and radiation attack can be taken from paragraph 6.2.4.8.

- Instrumental analysis

In the case of analysis without chemical separation the matrix composition is a determining factor in the sensitivity assessment, as was touched on above in 6.1.2.3. Even if the sample matrix does not contain considerable amounts of interfering positron emitters after activation, an eventually excessively high integral gamma emission rates of the active matrix components unavoidably enhance the background count rate and thereby degrade the achievable signal-to-background ratio, even if a coincidence counting spectrometer is used. Therefore, it might be of no use to increase the activating photon flux or the electron energy. As already mentioned, acceptable sensitivities in the purely

instrumental approach are achievable only in a limited number of cases.

- Radiochemical analysis

The major problem in the instrumental procedure mentioned above - the matrix activity of the sample - does not show up as serious in the radiochemical approach. However, it should not be completely neglected. There are several cases in which matrix activity possibly might influence the count rate during measurement of the desired light element activities - in spite of multiple decontamination measures. Generally, however, a high radiochemical purity of the counted fractions containing ^{11}C , ^{13}N , ^{15}O or ^{18}F , respectively, can be achieved.

This might lead to the assumption that it is of advantage in any case to provide maximum achievable photon flux received by the sample during activation. Basically this is true, but one has to bear in mind different durabilities of the irradiated materials against radiation and heat; partial or complete damage of the sample unavoidably leads to incorrect results. Moreover, in disadvantageous cases the matrix might gain excessive integral activity so that, for radiation protection reasons, its further processing might be problematic. Finally, to a certain extent, the geometry of the counted fraction is of importance; higher sensitivity can be achieved with relatively small samples than with large volumes to be counted. Therefore, mostly solid-state collectors with a large effective surface (e.g. ascarite) rather than liquid ones (e.g. base solution) have been applied hitherto. In the separation step one has to find an optimum between high-yield separation and fast performance, particularly in oxygen analysis because of the relatively short half-life of ^{15}O .

The achieved and achievable sensitivities are explicitly given for each element in the concerning paragraphs below. They are valid for the following irradiation parameters: 30 MeV electron energies, mean electron beam current 100 microamperes, exposure period of one half-life of the nuclide under consideration, total decay period including all treatment steps after activation: 15 min. (oxygen analysis: 5 min.).

6.1.3 Carbon

The photonuclear reaction used for carbon analysis is



The threshold energy for this reaction is 18.72 MeV (Howerton et al.⁷⁴⁴). The integrated cross section is comparably small (the maximum value of the cross section in the center of the giant resonance is about seven millibarns) and therefore intrinsically the above named reaction is one of the least sensitive among all elements. However, by virtue of fast and efficient separation procedures and low-background counting very low detection limits can be achieved. Moreover, trace determinations are favoured by the conveniently long half-life of ^{11}C . In the authors' laboratory a limit of detection as small as 20 nanograms was achieved under normal laboratory conditions (Segebade et al.⁶⁰).

6.1.3.1 Non-destructive analysis

There are only few matrices which enable the photon activation analysis of carbon (as well as the other mentioned light elements) without a radiochemical separation after bremsstrahlung exposure or at least a post-activation treatment (e.g. removal of surface contamination). The pioneer work about light element photonuclear activation analysis was performed without chemical separation. Basile et al.⁶ used direct positron counting after betatron bremsstrahlung activation. Exploiting the different activation threshold energies oxygen was analysed separately from the other light elements using bombardment with bremsstrahlung of about 19 MeV maximum energy. Carbon was analysed by activation with higher bremsstrahlung energies.

Obviously, the first application of annihilation quanta counting after bremsstrahlung exposure was performed by Beard et al.⁷⁰⁷ in 1957. For light elements analyses in high purity beryllium they used a linear accelerator as bremsstrahlung source. The 511 keV radiation was counted with two large NaI crystals in coincidence as described above. Carbon and oxygen were separated by decay function analysis. The maximum achievable sensitivity of the method was estimated about 1 microgram per gram for carbon and oxygen. 0.1-1 microgram per gram appears to be a consensus range of detection limit for instrumental analysis of the light elements in high purity beryllium (Engelmann⁵⁰ and the literature cited therein, particularly Ref.32, see also⁷⁶¹). Instrumental carbon analyses

by photon activation also were described by Gilman and Isserow⁷⁶², Albert et al.^{708,763}, Engelmann et al.^{17,726,761,764-766}, Sadvorny et al.⁷⁶⁷ (all high purity beryllium), Persiani et al.⁷⁶⁸ (caesium), Mackintosh and Jervis⁷²⁸ (Bi/Pb mixture), Sharma et al.⁷¹⁸ (pure compounds), Voigt and Abu-Samra⁵ (steel), Beresin et al.⁷⁰⁵ (geological material), Hislop and Wood⁷⁴⁹ (vanadium), Marsh⁴⁹ (beryllium, lithium), Helbig et al.⁷⁶⁹ (silicon), Davidson et al.⁷⁷⁰ (coal), Kasymov et al.^{872,873}, Spring and Nikkinen⁸⁷⁵ (organic matter) and many others.

6.1.3.2 Radiochemical analysis

As is also true for surface treatment, the separation technique within radiochemical analysis procedure has to be performed according to the physicochemical properties of the sample matrix so as to ensure quantitative separation of the element to be determined from the matrix.

Oxidising fusion or oxidising dissolution have been applied in all cases as far as it is known to the authors. The fusion conditions of course, differ strongly. Temperatures ranging from slight heating with a gas burner⁷²² to approximately 2000°C with either resistance or induction furnaces (see e.g.⁷¹⁹) have been utilised.

- oxidising fusion

The total burn of the sample in a stream of oxygen is the fastest method of carbon separation⁷⁷¹. The element may be present in almost any form, be it as free carbon or chemically bound. In many cases a suitable flux is necessary to support rapid melting of the sample. This is necessary in particular during analysis of refractory metals since their melting points are extremely high. Platinum has been used frequently as a bath metal^{717,737,772,773} and in particular⁷⁷⁴). Excessively high extraction temperatures have to be avoided in any case to provide minimal volatilisation of crucible and prevent undesirable release of sample components and thus reduce gettering of radiocarbon oxide (see Ref's.^{774,775}).

Unlike conventional techniques the radiochemical analysis does not require fluxes with as low as possible and reproducible contents of the determined element. Frequently fluxes have been used whose inherent carbon has been utilised as an inactive carrier to ensure quantitative transport of the ¹¹CO₂ to the absorbant. Prior to its absorption the gas has to be cleaned from any unwanted

component, e.g. dust of any kind and provenience. After quantitative transfer of the $^{11}\text{CO}_2$, the sorption vessel is readily counted using the spectrometer described above.

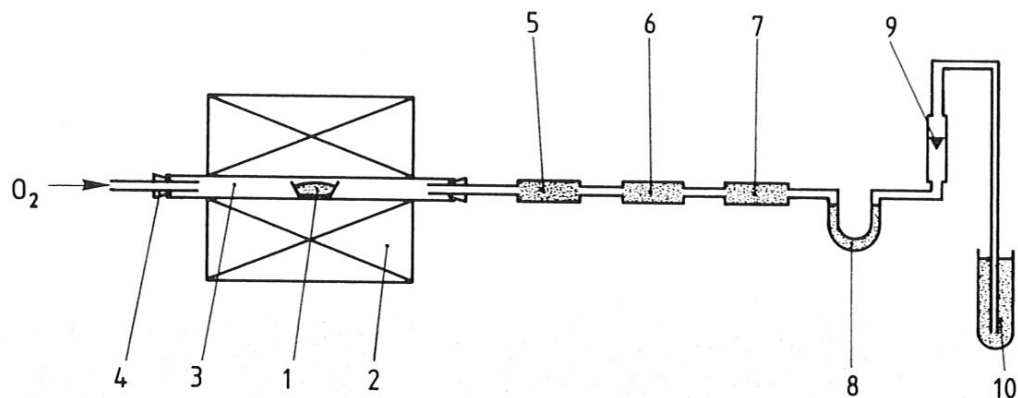


Fig. 6.1.3: Oxidation fusion apparatus for separation of radiocarbon; explanation see text

The irradiated sample (eventually together with a flux) - after surface decontamination - is placed in a boat (1) or crucible which is pushed into the hot zone of a furnace (2) where it is heated to the temperature needed for complete combustion of the sample. The material of the boat or the crucible must be selected with respect to its physico-chemical behaviour against the sample matrix material under the required reaction conditions. Silica⁷¹⁹ has been used as well as alumina or zircon⁷⁵¹. The total sample mass is somewhat limited due to its eventual exothermic oxidation. Excessive sample mass might cause melting of the boat and damage of the reaction tube (3). After closing the tube (4) the sample-flux mixture is heated to the desired temperature. The premelting sometimes is performed in inert atmosphere to prevent early oxidation. The melted sample is then burned under a controlled (9) flow of oxygen passed through the tube. A typical flow-rate is several hundred milliliters per minute⁷⁵⁰. The gas

stream coming from the reaction tube outlet is lead through several cleaning traps to remove undesirable contamination, e.g. silica-wool⁷⁵⁰ or an acid scrubber⁷³⁷ for gas-borne particulate (5), MnO_2 for absorption of SO_2 , Br_2 , F_2 ⁷¹⁹, silver wool for halogens^{756,775} (6) (see also below in the section about carbon analysis in alkali metals). Desiccating agents, e.g. $\text{Mg}(\text{ClO}_4)_2$ ⁷¹⁹ dry the gas stream (7). Eventually residual CO is then oxidised in cuprous oxide, Schütze-reagent (iodine pentoxide on silica gel) or other oxidants (8). The gas flow at the outlet is controlled by flow-meter (9). The evolved $^{11}\text{CO}_2$ plus carrier gas can then be trapped either by a liquid nitrogen-cooled multiloop trap⁷¹⁹ or by chemical absorption in any alkaline sorbant (10). The latter collection method has been preferred by the most workers. Sodium hydroxide or ascarite (NaOH sorbed in asbestos) have mostly been used as collectors. A thorough study of the CO_2 sorption mechanism was carried out by Marschal et al.⁷⁷⁵. The sorption vessel is then transferred to the gamma spectrometer where the annihilation quanta are counted. Usually a coincidence setup (Fig.6.1.1) is used.

Another technique frequently applied is the fusion separation consisting of melting the sample in a mixture of oxidising chemicals under a stream of inert gas or oxygen⁷²⁷. This method has been mainly performed for a simultaneous analysis of carbon and nitrogen^{758,775}; see Fig.6.1.4.

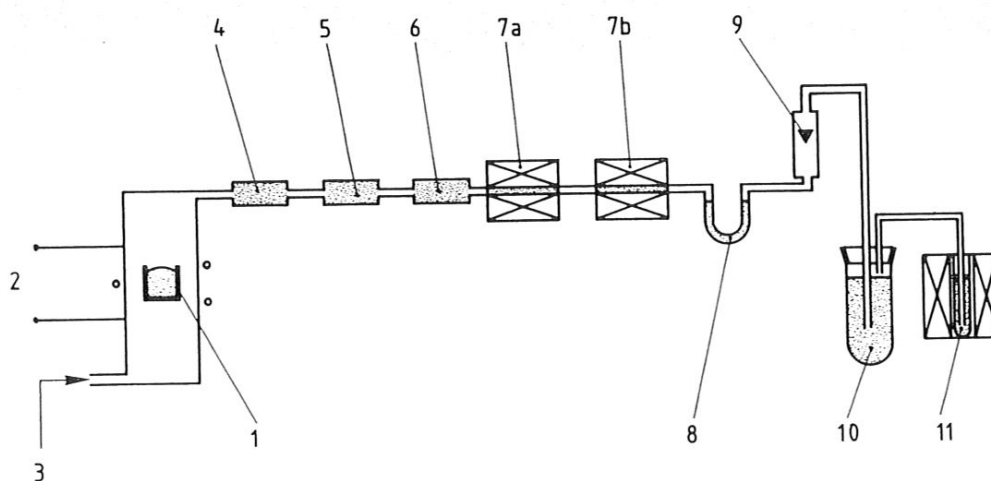


Fig. 6.1.4: Oxidising fusion apparatus used for separation of radiocarbon and radionitrogen under oxygen or inert gas flow; explanations see text

The sample and the oxidising mixture, e.g. Pb_3O_4 plus B_2O_3 ⁷⁵⁸ is placed into a crucible (1) which is heated under inert gas atmosphere by an induction furnace (2). The gas flow (3) is adjusted to 100-200 ml/min.⁷⁵⁸. The extracted gas is then cleaned as described above (4,5,6). Copper, heated to about 500°C (7a) reduces nitrogen oxides to N_2 . CO is oxidised with CuO (7b). Finally, after oxidation of any eventually residual CO by Schütze-reagent or Hopcalite (8; a mixture of manganese dioxide, cuprous oxide and silver oxide; Hopcalite can also serve for selective sorption of ^{15}O ; see⁷⁷⁶ and below in 6.1.5) the gas mixture contains carbon dioxide, elemental nitrogen and carrier gas only. The further processing of N_2 containing radionitrogen is described in the next paragraph. The carbon dioxide containing radiocarbon is then trapped and counted as described above.

As touched on above, a mixture of lead tetroxide and boron trioxide has frequently been used as an oxidising melt^{775,777-780}, but others have been reported as well (e.g.^{781,891}). The melt has a multiple function, e.g. as to provide an oxidising environment of the sample, to prevent the formation of a passivating oxide layer, to ascertain proper heat transport and more.

Marschal et al.⁷⁷⁵ and Fedoroff et al.⁷⁸¹ published thorough studies about the separation mechanisms in the different oxidising melted media.

- Carbon in alkali metals

The analysis of carbon in alkali metals basically is performed as done in other matrix, namely by oxidising fusion. However, due to the peculiar physico-chemical behaviour of the alkalines, the analysis procedure has to be somewhat modified. Bock et al.⁷⁵⁶ reported inert gas fusion with an oxidising flux for simultaneous separation of ^{11}C and ^{13}N from sodium. The apparatus setup is similar to that used for other matrices (see above; oxidising melt fusion).

Mostly, however, the system described by Lutz and DeSoete⁷⁷² which is based upon a method proposed by Kallmann and Liu⁷⁸² has been used with a few modifications according to the different analysis requirements. This separation system is illustrated in Fig.6.1.5.

After irradiation and surface treatment the sample, together with a carrier-bearing substance, e.g. inactive sodium carbonate, is transferred into a silica crucible (1) which is then introduced into the combustion flask (2). The sample is heated slightly under oxygen flow. During combustion the connection between

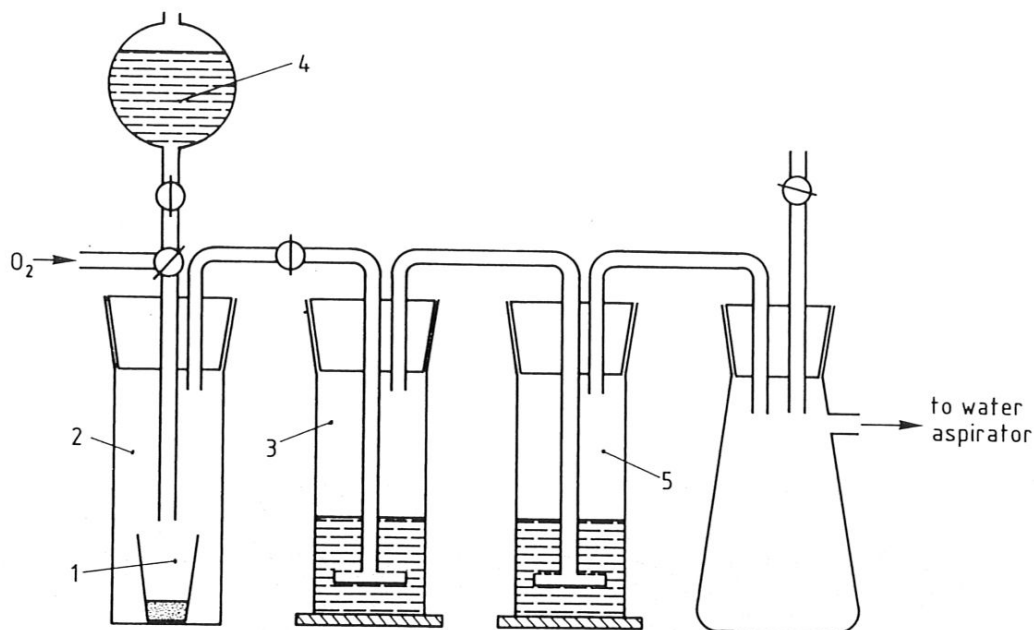


Fig. 6.1.5: Apparatus used for separation of radiocarbon from alkali metals (after Lutz and DeSoete⁷²²); explanations see text

the reaction vessel and the first absorption bulb (3) is closed by a stopcock which is re-opened after complete combustion. Dilute sulfuric acid (4) is then slowly added. $^{11}CO_2$ is thereby evolved; the inactive CO_2 due to the sodium carbonate carrier assists in complete flushing of all radiocarbon dioxide from the combustion flask. The first absorption bulb (3) contains a cleaning agent, e.g. boric acid to absorb radiofluorine. As described in 6.1.2.1 (internal standards), radiofluorine produced from matrix sodium (see Tab.6.1-14) sometimes has been used as an internal monitor, but normally appears as a source of interference during light element analysis of sodium. It can as well be absorbed by other agents (see 6.1.3.3, error sources).

The second absorption bulb (5) contains a CO_2 sorbent, e.g. sodium hydroxide solution, where all carbon dioxide is completely absorbed. This is then counted as described above.

As already noted, multiple variations of the above described setups have been worked out and reported. In Tab.6.1-2 examples of the different applications of oxidising fusion for photon activation analysis of carbon are summarised comprehensively including several relevant information.

Tab.6.1-2: Examples of radiochemical photon activation analysis procedures for carbon determination

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus.temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Na	a) Na ₂ CO ₃	O ₂ /slow	950/gas burner	NaOH, 20%	Na ₂ CO ₃ , Na ₂ C ₂ O ₄ / 0.5 µg	quartz crucible; ²² Na, ²⁴ Na as internal standard; 15 m/separation	76, 742, 722, 743, 744
	b) Pb ₃ O ₄ -B ₂ O ₃ - NaCl-KCl/ C in steel add.	He/400	1000/HF	ascarite	RM not given/ 0.01 µg/g	²² Na used as internal standard; simultan. C and N analysis	756
Mg		air/100	not given/ gas burner	KOH, 12M	RM not given/ 0.01 µg	sample diss.in H ₂ SO ₄ /KIO ₄ ; H ₃ PO ₄ as complexing agent	781
MgO	Na ₃ B ₄ O ₇	O ₂ /400	1250/resist.	liqu. N ₂ or ascar. compounds/	graphite, org. 0.005 µg	Pt-boat; also applied to anal. of CaO, Al ₂ O ₃ ; about 20 m/separation	719, 783
Mg/Al	NaOH-NaNO ₃ - NaF	air/not given	not given/ gas burner	KOH, 12M	graphite/ 0.02 µg	Ni-crucible; 10 m/separation	855
Al	a) Pb ₃ O ₄ -B ₂ O ₃	He/400	1250/HF	ascarite	RM not given/ 40.1 µg/g	simultan. C and N analysis	759
	b) -----	-----	-----	-----	-----	-----	-----
				see Mg/Al	-----	-----	855

Tab.6.1-2, continued

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus.temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Si	a)	-----	-----	see Al a)	-----	-----	742
	b)	Pb ₃ O ₄ -B ₂ O ₃ - PbO ₂ /SiC	O ₂ /130 1000/resist.	KOH, 15%	spectr.graph./ 5 µg/g	quartz boat; Ba ¹¹ CO ₃ precip. 10 m/separation	769
	c)	KOH	Ar/300 500/not given	KOH, 12M	graphite/ 0.01 µg	Ni crucible; simultaneous C and N determination	795
	d)	-----	-----	see Al a)	-----	-----	759, 775
	e)	Pb ₃ O ₄ -B ₂ O ₃	O ₂ /not given	Ba(OH) ₂	graphite, poly- ethylene/ 0.1 µg/g	-----	730
K	-----	-----	-----	see Na a)	-----	-----	742
Ti	a)	NaOH-NaNO ₃	air/not given	KOH, 12M	graphite/ 0.02 µg	Ni crucible; 10 m per separation	781, 855
	b)	Fe/C in flux	O ₂ /not given	1350/resist.	ascarite graphite/ 0.03 µg	alumina crucible	737, 800

Tab.6.1-2, continued

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus.temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
V	a)	O ₂ /250	1200/resist.	ascarite	graphite/ 20 µg/g	silica boat	749
	b) Sn	dto.	1600/resist.	dto.		dto.	749
Cr	a)	Fe O ₂ /50	not given/HF	ascarite	graphite/ 1 µg/g	zircon boat	751
	b)	NaOH-NaNO ₃ / Na ₂ CO ₃ air/200	not given/ gas burner	KOH/12M	graphite/ 0.03 µg	Ni crucible; ¹¹ CO ₂ evolved by neutr. with HNO ₃ ; 20 m/separation	781,784, 855
Fe	a)	Sn/low alloy steel O ₂ /400	1150-1350/ resistance	liquid N ₂ or ascar. comp./0.005 µg	graphite, org. 20 m/separation	fire-clay boat; about 20 m/separation	719,783
	b)	Fe carbonyl O ₂ /50	not given/HF	ascarite	graphite/ 0.02 µg/g	zircon boat	751,874
c)		O ₂ /ab.200	1300/resist.	NaOH/3M	graphite/ 0.04µg	ceramic boat; several minutes/separation	750
d)	Fe/C in flux	Ar/50	not given/HF	KOH, ascarite	graphite/ 0.01 µg/g	alumina crucible	285

Tab.6.1-2, continued

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus. temp. (°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Fe	e)			see Al a)			759
	f)	Pb ₃ O ₄ -B ₂ O ₃ -Fe/ C in Fe	Ar/50 not given/HF	KOH, 12M	graphite 0.02 µg	alumina crucible; 10 m/separation	855
	g)	O ₂ /not given	not given/ not specified	ascarite	graphite/ 0.001 µg		856
	h)	O ₂ /200-250	1100-1270/ resistance	ascarite	Lavsan(similar to Mylar)/ 0.13 µg	multiple pre- and post-ir- radiation purification of the gas stream	857
Co				see Al a)			759
Ni	a)			see Al a)			759
	b)			see Fe f)			855
	c)	Pb ₃ O ₄ -B ₂ O ₃ -Fe	Ar/50 not given/HF	ascarite	graphite/ 0.4 µg/g	zircon crucible	751
	d)	Pb ₃ O ₄ -B ₂ O ₃ / SiC	Ar/100 1000/HF	ascarite	not specified/ 0.01 µg		848

Tab.6.1-2, continued

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus.temp.(°C)/ furnace	Sorbant detection lim.	Reference mat./ Remarks	Reference
Ni	e)			see Fe h)		857
Zn	a)	O ₂ /ab.200	850/resist.	NaOH, 3M graphite/ 0.04 µg	ceramic boat; combustion contr. by humidity of O ₂ stream ⁷⁷⁶	750
	b)			see Mg/Al		855
Zn/Ag		air/100	not given/ gas burner	KOH, 12M not specified/ 0.01 µg KIO ₄	sample dissolved in H ₂ SO ₄ / KIO ₄	781
Zn/Mg/Te				see Mg/Al		855
GaP	a)			see Al a)		759
	b)	Na ₂ CO ₃ -Na ₂ O C of Na ₂ CO ₃	N ₂ -O ₂ / not given	Ba(OH) ₂ graphite, polyethylene/ 0.1 µg/g	¹¹ CO ₂ evolved by acid neutralisation	730
GaAs	a)			see Al a)		759
	b)			see GaP b)		730

Tab.6.1-2, continued

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus.temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
GaAs c)				see InP			854
Ge a)	Pb ₃ O ₄ -B ₂ O ₃ -Fe/ C in flux	He/150	700/HF	ascarite	Mica/ 0.01 µg	10 m/separation; simult. C and N analysis	758
b)				see GaP b)			730
c)				see Al a)			759
Se				see Mg/Al			855, see also 801
Zr a)	Fe-Bi/ C in flux	O ₂ / not given	1350/resist.	ascarite	graphite 0.03 µg	alumina crucible	737, 800
b)	air/100		not specified/ gas burner	KOH, 12M	not specified/ 0.01 µg	sample diss. in H ₂ SO ₄ -KIO ₄ ; NaF as complexing agent	781
Nb				see Ti b)			737, 800
Mo a)	O ₂ /400		1250/resist.	liquid N ₂	graphite, org. or ascar. compounds/ 0.005 µg	fire clay boat; about 20 m/separation	719, 783

Tab.6.1-2, continued

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus.temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Mo	b)			see Ni c)			751
	c) Pb	O ₂ /ab.200	1250-1300/ resistance	NaOH, 3M 0.04 µg	graphite/ 20 m/separation	ceramic boat; about	750
	d)			see Fe d)			285
	e)			see Mg/Al			855
	f)			see Fe f)			855
	g)			see Zr a)			737, 800
	h)			see Fe h)			857
Ag	a)			see Fe f)			855
	b)	not given	not given/ gas burner	KOH, 12M 0.02 µg	graphite/ KIO ₄	sample dissolved in H ₂ SO ₄ -	855
	c) Pb	O ₂ /200	1100/resist.	NaOH, 3M 0.04 µg	graphite/ minutes/separation	ceramic boat; several	750

Tab.6.1-2, continued

Matrix	Flux/ carrier	Vector gas/ flow rate (ml/m)	Fus.temp.(°C)/ furnace	Sorbant	Reference mat./ detection lim.	Remarks	Reference
Cd	Pb	O ₂ /ab.200	930/resist.	NaOH, 3M	graphite/ 0.04 µg	ceramic boat; several minutes/separation	750
InP	Fe/ C in flux	O ₂ /not given	1300/not specified	ascarite	graphite/ 0.002 µg		850, 854
Cs	Na ₂ CO ₃	O ₂ /slow	not given/ gas burner	NaOH, 20%	not specified/ 1 µg/g	silica crucible; sample transfer under inert atm.; 132Cs as internal standard	742, 743
Ta	a)	-----	-----	see Ge a)	-----	-----	758
	b)	-----	-----	see Ti b)	-----	-----	737, 800
W	a)	-----	-----	see Mg/Al	-----	-----	855
	b)	-----	-----	see Ti b)	-----	-----	737, 800
Au	Pb	O ₂ /ab.200	1250/resist.	NaOH, 3M	graphite/ 0.04 µg	ceramic boat; several minutes/separation	750
Various chemicals	KIO ₃ - K ₂ Cr ₂ O ₇	Ar/not given	2200-2400/ HF	KOH, 12M	not given/ 0.2 µg/g		891