

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 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

problem of contamination due to the packaging material which is in close contact with the sample during irradiation obviously is not a too serious one. Tracer experiments were carried out in the authors' laboratory to investigate the component exchange behaviour between the sample and the packaging material. According to the results, no significant contamination by ordinary household aluminium foil which generally has been used for sample wrapping could be detected. In a few cases, loss of elements to be analysed due to recoil into the wrapping material was reported in the literature (see 6.1 and 6.2.3.4).

Similarly, the contamination of liquid samples by the material of the container (typically PYREX glass) was restricted to very small traces of sodium, probably due to isotopic exchange in the glass surface. In photon activation analysis, as noted above, the most suitable material for packaging of solid samples and transportation to the irradiation position is aluminium since, on the one hand, it does not undergo a photonuclear reaction with significant activity yield (see chapter 5), and, on the other hand, the neutron reactions yield either short-lived nuclides (^{28}Al , ^{27}Mg) or moderate activities (^{24}Na). The samples are wrapped in aluminium foil and packed in aluminium rabbits for transportation in the pneumatic tube system (see chapter 3).

In the case of volatile components to be analysed (e.g. Hg) samples have to be irradiated in sealed high purity quartz vials or especially pretreated to avoid losses during irradiation. A method for prevention or at least reduction of mercury losses during bremsstrahlung exposure is described in the application section below (6.2.4). Although usually the sample rabbits are air-cooled during irradiation, one has to take into account a considerable heating of the sample during long-time (greater than 10 minutes) exposure. Moreover, damage may also occur to the samples by the incident radiation itself. This gains importance especially if either organic or liquid matrices have to be irradiated at short (up to 5cm) distances from the bremsstrahlung converter. During practical work it was found that in the case of short period (less than 10 minutes) irradiations organic material like plant or tissue matrix does not suffer too much from radiation damage, nor do water samples if they are irradiated in glass vials which are wrapped in aluminium foil. If these materials are irradiated for longer periods at small distance from the target, damage due to both heat and radiation becomes significant; in the case of organic matter the material structure is partly destroyed and volatile components are set free. Water will be partly decomposed and evaporised. A cooling of the sample during irradiation could reduce the evaporation of volatile components but not avoid radiation damage.

There is not much one can do to prevent damage of organic material; one has to select, with respect to the required analysis sensitivity, the shortest possible bremsstrahlung exposure period. For quantitative evaluation it is then necessary to determine the sample mass ahead of the irradiation to avoid errors due to uncontrolled losses of components. In the case of water samples it is useful to remove the irradiation position to 10-20 cm from the converter target and irradiate a larger volume. Thereby, heat and radiation damage are reduced and, by convection, heat is distributed over a large sample volume and hence rendered less harmful. Normally, the sample volume is restricted to a maximum of about 10 milliliters in the pneumatic tube rabbit. For more information about losses of sample components - particularly during sample preparation and irradiation - the reader might refer to⁸⁹²⁻⁸⁹⁴ and to paragraph 6.2.4.8, single element studies.

Larger vessels (100 ml maximum) can be exposed to the bremsstrahlung radiation using the rotating irradiation facility. But then, as explained above, one has to take into account significant flux gradients. Yet larger volumes, especially liquids, should be irradiated in a cylindrical container whose axis coincides with the bremsstrahlung radiation axis; about 1200 ml proved optimal for trace element determinations in water samples (see 6.2.4); yet larger volumes can be activated if required; using the irradiation facility in the authors' laboratory, up to seven liters have been irradiated, but then a considerably small fraction of the total sample volume is activated by the bremsstrahlung; in the case of such large volumes irradiated the exploitation of the photoneutrons as activating particles gain importance. Therefore, in any case, one has to carefully optimise the total sample mass or volume, respectively, according to the analyst's requirements; see also Ch.3.

Exposure periods have to be selected according to the half-lives of the reaction products under consideration and to the required analytical sensitivity, respectively; in the authors' laboratory a maximum of five hours has proven suitable for multitrace analysis of microgram amounts of components to be determined. The exposure times in the different application cases are given in the application section below. Sometimes, more than one exposure has been performed for convenient measurement of activation products with greatly different half-lives. Moreover, frequently several exposures have been performed using different activation energies to obtain a quasi-selective activation exploiting the difference in threshold energies. However, this is of questionable value if routine analyses of large series of samples have to be carried out. In this case it is of advantage to irradiate with maximum energy and to account for

first order interferences with correction calculations. Although thereby the integral uncertainty of the results is somewhat enhanced these correction routines are recommended to keep a reasonable time-schedule of the analysis task. To a certain extent, this also applies to the product activity measurement as is discussed in the next paragraph.

6.2.3.2 Preparation for counting and photon spectroscopy

Basically, the preparation of the irradiated sample for counting is done following the same procedures as usual in neutron activation analysis. However, in the authors' laboratory it has proven useful in many cases if solid powdered samples are irradiated, to mix the sample with cellulose powder and press it to a pellet of 15 to 20 mm diameter and less than 1 mm thickness. This geometry is particularly useful if both gamma spectroscopy and low energy photon spectroscopy are required (see 2.5); self-absorption of softer photon radiation to be evaluated for analysis is thus reduced. Liquid samples, if analysed purely instrumentally, have been filled into vessels shown in Fig.6.2.1.

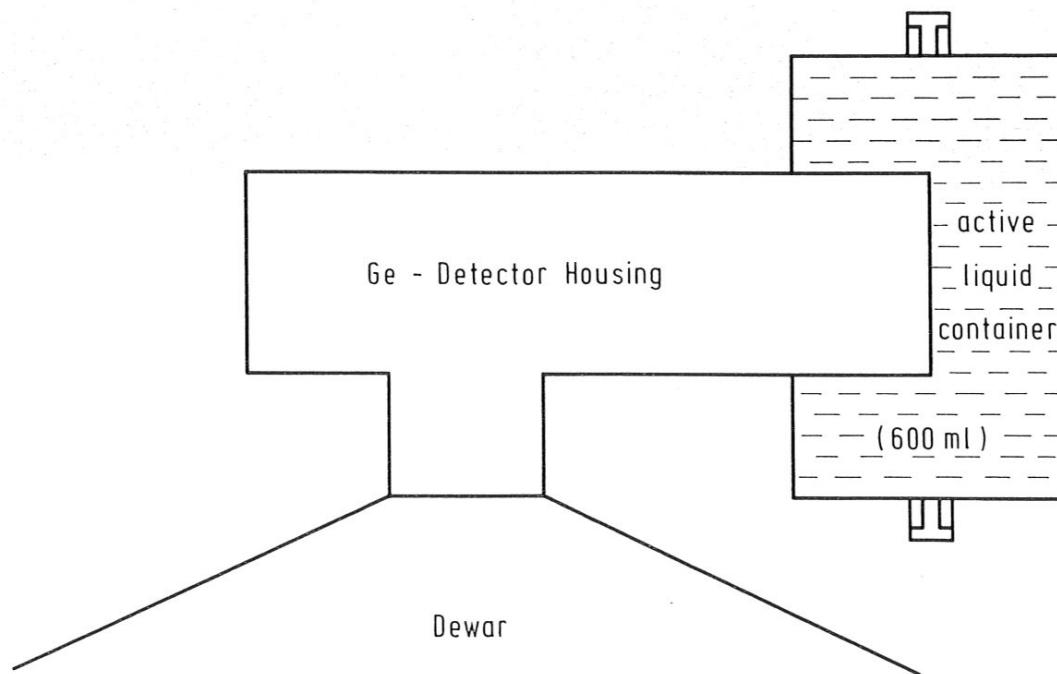


Fig. 6.2.1: Counting setup for radioactive liquid samples

Using these containments for counting, the detector crystal is partly surrounded by the sample. Thereby, considerable counting efficiency is gained compared with conventional counting vessels positioned in front of the detector. For counting it is of advantage to establish conditions in which the dead-time of the electronic equipment does not exceed about 10%. This can be realised by a proper measurement geometry or by a sufficiently long cooling period. By excessively high count rates, the resolution capability of the spectrometer is significantly reduced (see chapter 4). Moreover, laboratory experiments have clearly indicated that a dead-time of more than 10% registered by the electronic equipment implies considerable dead-time losses within the spectrometer which cannot be controlled and hence not be accounted for by live time counting (see Ch.4).

Nowadays, electronic equipment is available which provides fairly good gamma-ray peak shapes and spectral resolution in the case of high input pulse rates; additionally, as mentioned in chapter 4, new ways have been found concerning pile-up management and account for dead time losses due to the electronic equipment. Nevertheless, the mentioned uncontrolled pulse rate losses in the spectrometer, with help of any hardware, cannot be managed satisfactorily as yet, except - to a certain extent - by the use of an internal standard, as explained in 6.2.2. One disadvantage of photon activation analysis if short-lived product nuclides have to be measured is the large background activity of ^{15}O due to the oxygen contents which is mostly considerably high. Although 511 keV annihilation radiation exclusively is produced by oxygen, the detectability of other components with say minutes of half lives is severely hampered by the dead-time losses due to the integral input pulse rate and also in the case of softer photon radiation to be measured, by severe degradation of the signal-to-background ratio due to the Compton continuum, effected by annihilation radiation. This is, of course, especially true in the case of low concentrations to be analysed. Therefore, short-lived activities after photon activation usually are evaluated for analysis of major or minor components only, e.g. Si (^{28}Al , ^{29}Al), K (^{38}K), Fe (^{53}Fe). In order to reduce the mentioned interference, one should use a multiple step procedure beginning with a short period exposure, cooling and measurement followed by either a longtime reactivation of the same sample or of another batch of the material and one or more cooling and counting periods. However, in the case of large series of samples to be analysed one should generally strive for a minimum of irradiation and measurement steps during analysis, as noted above. In the case of say one single activation and one measurement interferences of various types have to be taken into account. The management of these interferences during analysis evaluation proce-

ture is described in detail in paragraph 6.2.3.3. As explained in chapter 4, in order to achieve maximum resolution capability of the spectrometer, it is recommended to collect the spectra in as many channels of the multichannel analyser memory as possible. However, it is recommendable to save a certain partition of the total memory for intermediate fast spectrum storage after counting. Moreover, the total storage area might be quickly consumed if more than one detector are connected to one multichannel analyser.

All in all, during practical instrumental multielement photon activation analysis, 2048 channels have proven to be a suitable storage size and meet the requirements of photon spectroscopy quasi-optimally, although in this case the maximum achievable energy resolution of modern semiconductor detectors cannot be exploited; an average gamma-ray line then contains 4 to 5 channels at about 2200 keV total energy range (see also Ch.4).

6.2.3.3 Data handling

At this point, no lengthy descriptions of spectrum processing and data evaluation computer programs are given but rather the basic principles of data handling in photon activation analysis. Although, as already noted, storage memory size is not the primary problem in modern multichannel analysers, space is limited and especially if large series of samples has to be analysed, spectra have to be dumped quickly on any data carrier which enables subsequent data processing by computer. Data frequently have been stored on punched paper tapes, but nowadays mostly more convenient carriers are in use, e. g. magnetic tape or magnetic disc. Although modern multichannel analysers, as described in chapter 4, usually are equipped with microprocessors and associated software, external data processing by computer is preferable. Small, easy-to-run computers are mostly used for spectra processing. Nowadays, a large variety of these machines are available, so that one can select a suitable unit which ideally meets the individual requirements. Moreover, many manufacturers supply the complete gamma measurement software for relatively moderate prices.

The first step of multi-component spectrum evaluation is the peak search and identification. It depends upon each analyst's personal philosophy if an automatic peak search program is used or if the qualitative evaluation is performed interactively. In the daily practice it has been shown that the reliability of a fully automatic peak search program decreases with the complexity of the spectrum. Moreover, these programs are mostly severely hampered if peaks are to be detected which are located in the close neighbourhood of either huge Compton

edges or other larger peaks. Since especially in photon activation analysis one has to be aware of complex spectra emitted by activated multi-component samples it is recommended to perform qualitative analysis interactively accompanied by visual control. Fully automatic programs should be used in the case of large series of routine analyses after having ascertained that the peak search routine operates reliably and the integration works precisely in any case. It also depends upon the individual analyst's philosophy in which way the net peak area is determined. Some describe the peak background by higher order function, but an extended investigation yielded no significant difference between the net peak areas obtained by linear or higher order background subtraction in the case of semiconductor spectra to be processed^{676,677}. In photon activation analysis, the peak assignment can easily be performed with help of photon energy compilations (e.g.⁶⁹⁰⁻⁶⁹²) or the tables in Ch.5 of this book or with nuclide libraries integrated in the microprocessor software of the multichannel analyser as explained in chapter 4.

Quantitative analysis evaluation

As already noted, element concentration data are obtained by activity comparison of the analysis sample with a reference material.

Going out from equation 1.17 in chapter 1.3 the relation between the induced activity and the mass of the element to be determined is:

$$A(T_i, T_D) = \frac{m \cdot L \cdot h}{A_r} \cdot \varphi \cdot \sigma_{\text{eff}} \cdot (1 - e^{-\lambda \cdot T_i}) \cdot e^{-\lambda \cdot T_D} \quad (1.17)$$

which means that the induced activity stands in linear relationship to the mass of the irradiated element. Simultaneous irradiation of the analysis sample and the reference material assumed, the ratio between the activities of the element to be analysed in both materials immediately after irradiation, is:

$$\frac{A_S(T_i)}{A_R(T_i)} = \frac{m_S}{m_R} \quad (6.1)$$

S = analysed sample

R = reference material

Since one generally does not determine absolute element masses but rather component concentrations, m is thus replaced:

$$C = \frac{m}{M}$$

C = concentration of the component to be analysed

m = mass of the determined component

M = total mass of the sample

The concentration of the desired element in the sample is then expressed by:

$$C_S = \frac{A_S(T_i) \cdot M_R \cdot C_R}{M_S \cdot A_R(T_i)} \quad (6.2)$$

As explained in 5.3.1, the activity is determined by photopeak integration. Using equation 5.4 in paragraph 5.3.1 one obtains the relationship between the net photopeak integral and the activity:

$$I = A(T_i) \cdot \Theta \cdot \eta \cdot \frac{e^{-\lambda \cdot T_D}}{\lambda} \cdot (1 - e^{-\lambda \cdot T_c}) \quad (6.3)$$

where I is the photopeak integral.

In the case of each individual component to be determined, the photopeak emission probability (Θ), the spectrometer counting efficiency (η) and the decay constant of the product nuclide (λ) are identical for both the analysed sample and the reference material. Hence, the activity ratio of both can be expressed as:

$$\frac{A_S(T_i)}{A_R(T_i)} = \frac{I_S}{I_R} \cdot \frac{e^{-\lambda \cdot T_{D,R}}}{e^{-\lambda \cdot T_{D,S}}} \cdot \frac{1 - e^{-\lambda \cdot T_{C,R}}}{1 - e^{-\lambda \cdot T_{C,S}}} \quad (6.4)$$

Insertion into equation 6.2 yields:

$$C_S = \frac{C_R \cdot M_R \cdot I_S}{M_S \cdot I_R} \cdot \frac{e^{-\lambda \cdot (T_{D,R} - T_{D,S})} - e^{-\lambda \cdot (T_{D,R} - T_{D,S} + T_{C,R})}}{1 - e^{-\lambda \cdot T_{C,S}}} \quad (6.5)$$

C_S = desired component concentration in the analytical sample

C_R = known component concentration in the reference material

$M_{S/R}$ = mass of the sample/reference material

$I_{S/R}$ = net photopeak area of the product nuclide in the spectrum of the sample/reference material

λ = decay constant of the product nuclide

T_D = decay period

T_C = counting period

Remember: simultaneous irradiation of the sample and the reference material is still assumed and no internal flux monitor is used.

Let us consider now the application of an internal standard which is particularly useful in the case of non-simultaneous irradiation of the sample and the reference material, respectively. However, in this case the same electron energy must be assured in both irradiation cycles. The net peak areas of both the analysed nuclide in the sample and the reference material, respectively, and of the nuclide regarded in the internal standard are calculated using Eq's. 1.17 and 6.3. In combining the resulting four equations for the net peak area, the activating photon flux densities in both irradiations as well as the effective cross sections of the considered nuclear reactions are eliminated. The desired concentration value of the analysed component can then be calculated from the following expression:

$$C_S = \frac{C_R \cdot I_S \cdot I_{I,R} \cdot C_{I,S}}{I_R \cdot I_{I,S} \cdot C_{I,R}} \cdot \frac{e^{-\lambda_i \cdot T_{D,S}}}{e^{-\lambda_i \cdot T_{D,R}}} \cdot \frac{1 - e^{-\lambda_i \cdot T_{i,S}}}{1 - e^{-\lambda_i \cdot T_{i,R}}} \cdot \frac{1 - e^{-\lambda_i \cdot T_{C,S}}}{1 - e^{-\lambda_i \cdot T_{C,R}}} \cdot \frac{1 - e^{-\lambda_i \cdot T_{i,R}}}{1 - e^{-\lambda_i \cdot T_{i,S}}} \cdot \frac{1 - e^{-\lambda_i \cdot T_{C,R}}}{1 - e^{-\lambda_i \cdot T_{C,S}}} \cdot e^{-\lambda \cdot (T_{D,R} - T_{D,S})} \quad (6.6)$$

(Explanations see next page)

In the case of simultaneous irradiation of the sample and the reference material Eq.6.6 simplifies to:

$$C_S = \frac{C_R \cdot I_S \cdot I_{I,R} \cdot C_{I,S}}{I_R \cdot I_{I,S} \cdot C_{I,R}} \cdot \frac{e^{-\lambda_i \cdot T_{D,S}}}{e^{-\lambda_i \cdot T_{D,R}}} \cdot \frac{1 - e^{-\lambda_i \cdot T_{C,S}}}{1 - e^{-\lambda_i \cdot T_{C,R}}} \cdot \frac{1 - e^{-\lambda \cdot T_{C,S}}}{1 - e^{-\lambda \cdot T_{C,R}}} \cdot e^{-\lambda \cdot (T_{D,R} - T_{D,S})} \quad (6.7)$$

Index S = analysis sample data

Index R = reference material data

C = concentration of the element to be analysed

I = photopeak integral of the product nuclide

I_I = photopeak integral of the internal flux monitor

C_I = concentration of the internal flux monitor

λ = decay constant of the product nuclide of the element to be analysed

λ_I = decay constant of the internal standard product nuclide

T_i = period of bremsstrahlung exposure

T_D = decay period

T_C = counting period

Using this expression, spectroscopy data can easily be computed as fast and conveniently as the available hard- and software allow.

6.2.3.4 Error sources

In this paragraph, only those error sources are discussed which are typical for photon activation analysis; knowledge of the reader about accurate sampling, precautions against contamination and other general analytical laboratory techniques are assumed. Furthermore, as explained in chapter 4, errors due to malfunctions of the electronic system of the spectrometer nowadays are fairly unlikely to occur. Inconstancies occurring by any mischance mostly can be accounted for by using an internal standard or a reference pulser as demonstrated in chapter 4. More information about various error sources in photon activation analysis can be found in 6.1.

- Irradiation geometry and bremsstrahlung energy

As already noted in Ch's. 3, 6.1 and 6.2.2 the irradiation geometry is somewhat delicate due to the incident photon beam geometry. But, as explained above,

errors due to the sharp flux gradient can be avoided by using an internal standard. However, excessively different locations of the analysis sample and the reference material in the photon beam can cause errors due to the energy gradient which, although slight compared with the flux gradient (see Fig.6.2.2), cannot be accounted for by the internal monitor.

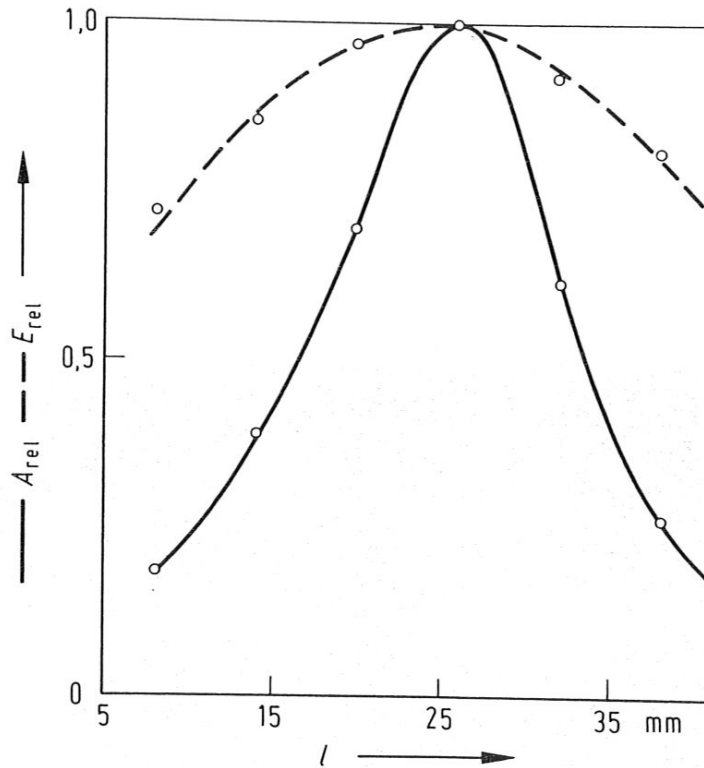


Fig. 6.2.2: Schematic representation of the flux gradient and the effective gradient of the activating photon energy perpendicular to the beam axis at a distance from the bremsstrahlung converter of 5 cm

This is particularly true in the case of analysis reactions with comparatively high threshold energies, e.g. $(\gamma, 2n)$ or $(\gamma, \alpha n)$. Fig.6.2.3 shows that at an incident energy of about 30 MeV a moderate electron energy shift would not have significant effect upon the activity yield of the internal flux monitor whereas the yield of the analytical reaction would be altered significantly.

However, reactions other than (γ, n) are used for analysis evaluation in very few cases only, but these reactions sometimes cause interference. Therefore,

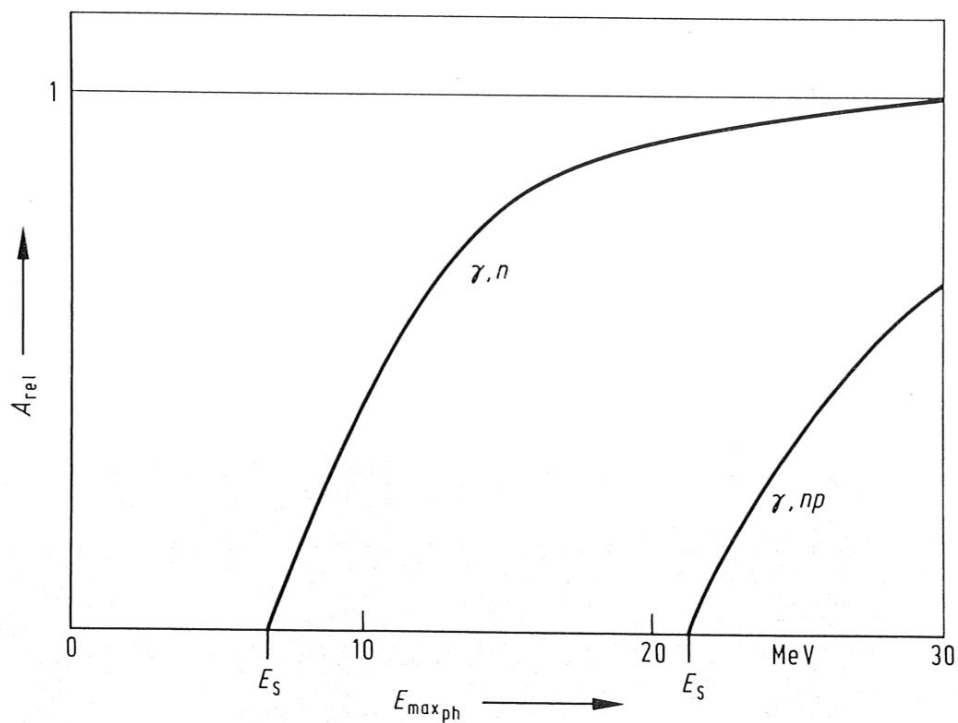


Fig. 6.2.3: Schematic typical yield curves for a (γ, n) and a (γ, np) -reaction

uncontrolled photon energy shifts, be they caused by inconstancies of the electron energy output of the accelerator or by mislocation of the sample in the irradiation position, might lead to incorrect values within the interference calculation process which is described below. To a certain extent, errors due to the irradiation geometry can be avoided by rotating the sample in the beam. See also 6.1.

- Matrix absorption

Another source of error in the irradiation phase is due to the absorption of the incident bremsstrahlung beam within the sample. In the case of thick sample layers of high density material irradiated the flux gradient along the beam axis due to the high attenuation might become significant, and, in the case of largely different reference material matrix, lead to uncomparable activation of both. This error is much more likely in thermal neutron activation analysis due to the large differences in the neutron absorption cross section of the ele-

ments, but in extreme cases - e.g. if lead or gold matrix is irradiated - it might gain significance also in photon activation analysis (see e.g. Reimers et al.⁸⁸⁴). In this case correction steps have to be inserted into the evaluation process (Lutz et al.⁷¹⁷).

- Damage by radiation and heat

Yet another error source in the irradiation step is due to the chemical effects of the incident radiation upon the sample material. Moreover, one has to be aware of significant heating of the sample in the irradiation position close to the bremsstrahlung converter, as was already explained in the preceding paragraph. This problem is common to all activation analysis methods and it becomes especially significant if organic matrix is activated¹¹²⁵. As touched on above, a special case in instrumental photon activation analysis as in almost every instrumental analysis method is the analysis of mercury because of the volatility of most of its compounds. In this case sealed vials have to be used for irradiation and measurement or the element has to be transferred into a compound which is able to stand irradiation and heat without being evaporated. Special procedures have been developed to "trap" the mercury, e.g. with sulphur compounds, during activation and thereby transform it into relatively stable and resistant HgS (see e.g. Raghi-Atri and Segebade⁸⁹⁶; see also 6.2.4.3 and 6.2.4.8 below).

As also briefly mentioned in the preceding paragraph, losses of several elements due to recoil from the sample into the wrapping material have been reported⁴⁹.

Generally, before irradiating any material its resistance against radiation and heat must be assessed, not only regarding the accuracy of the analytical results but also for radiation protection reasons; in the case of some elements being volatilised during irradiation, e.g. mercury or iodine, contamination by their product nuclides of the working area might occur. Thereby, both the legal radiation protection requirements are affected and also spectroscopic interference by contamination of any samples to be measured may falsify the accurate data.

- Integral sample activity and composition of the sample

The first source of error in the spectroscopy step is excessive integral count rate of the sample due to the matrix activity (see Ch.4), especially if the

analytical sample and the reference material have essentially different matrix compositions. As already mentioned, differences in the signal-to-background ratio between both may falsify the analytical results. Electronically incorrect dead time losses within the spectrometer can be accounted for by using an internal standard, as mentioned above, but since the deviation due to bad signal-to-background ratio is contingent upon the signal energy and the internal standard generally is represented by only one photon energy, it cannot correct for this source of error. Hence the analyst has to care for similar integral activities of the sample and the reference material, preferably by selecting a reference material with similar matrix composition as already noted.

- Measurement geometry

The counting efficiency is strongly dependent on sample/detector geometry, particularly at low (up to 500 keV) photon energies and at short distances between the measured sample and the detector. Therefore, the counting geometry has to be kept as similar as possible for the analysis sample and the reference material, especially if they are, as is usually done, measured very closely to the detector; The internal standard cannot account for deviations due to changes in the absolute counting efficiency. Experiments have shown that at distances of more than 4 cm from the detector housing the sample geometry is not crucial if an internal standard is used (see Fig.6.2.4); If soft photon radiation is to be measured, however, differences in the measurement geometry should be avoided.

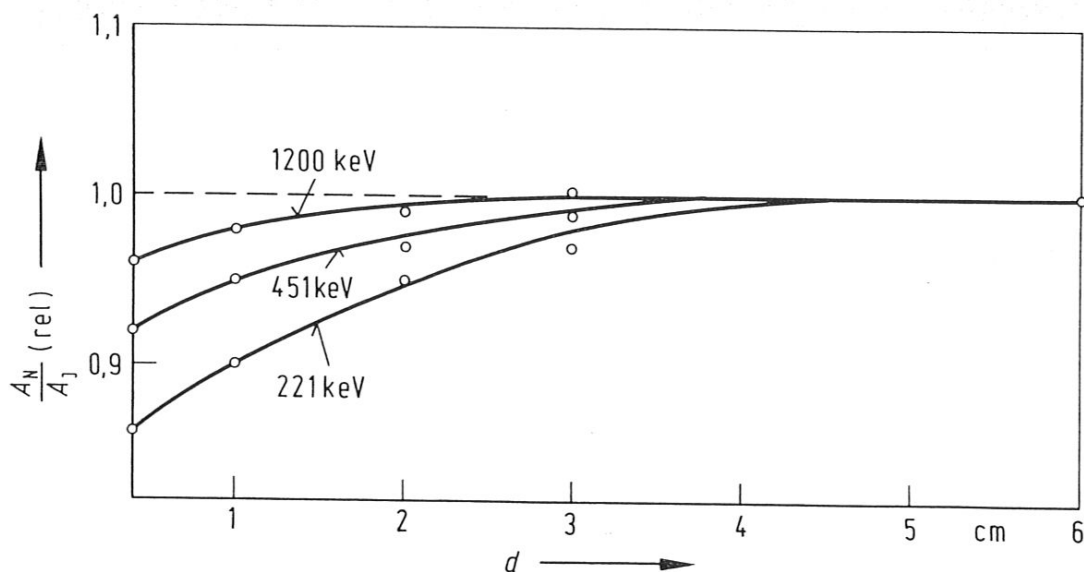


Fig. 6.2.4: Ratio between the net area of the analysed peak and the net area of the internal standard line as a function of the distance sample-detector entrance window

- Self-absorption

Errors due to self-absorption of photon rays within the sample matrix is only significant in the case of high density matrix material or in low energy photon spectroscopy. In the authors' laboratory powdered samples mostly are pressed into thin pellets (see 6.2.3.1). However, in extreme cases, e.g. if there is no reference material with similar matrix available, correction calculations of the self-absorption losses have to be performed (Reimers et al.¹¹⁸⁰, Lutz⁷¹⁴). The use of an internal standard cannot correct these count rate losses since they are, of course, strongly dependent upon the absorbed energy.

- Spectral interference

One can distinguish between three kinds of interference when using gamma spectroscopy and low energy photon spectroscopy.

- 1 - Competing reactions (first order interference), i.e. the production of the same activation product from different target nuclides;
- 2 - the spectral interference of radiation energies of different activation products due to limited spectrometer resolution (peak overlap);
- 3 - the production of the same activation product by secondary decay of nuclides by produced by two or more target elements.

Chattopadhyay and Jervis⁸⁸³ compiled some possibilities to reduce these interferences to an unavoidable minimum:

In the case of competing photonuclear reactions such as $^{56}\text{Fe}(\gamma, np)^{54}\text{Mn}$ and $^{55}\text{Mn}(\gamma, n)^{54}\text{Mn}$ (see below) the bremsstrahlung energy can be set below the threshold energy of the interfering reaction (in this example $E_{\text{th}}=20.9$ MeV for $^{56}\text{Fe}(\gamma, np)^{54}\text{Mn}$).

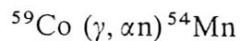
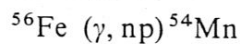
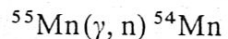
In the case of overlapping gamma-ray lines, several procedures were suggested. If the interference is due to a short-lived nuclide, it is either allowed to decay to negligible activity before measurement, or the contribution of the interfering activity is accounted for analysing the combined decay functions. If neither radiation energy nor half-life difference allow a separation, a different gamma-ray line must be used for analysis.

The third type of interference (not mentioned by Chattopadhyay and Jervis) is caused by secondary decay into a common product nuclide, e.g. $^{48}\text{Ti}(\gamma, p)^{47}\text{Sc}$, $^{48}\text{Ca}(\gamma, n, \beta^-)^{47}\text{Sc}$. This interference frequently can be avoided (in the above example by analysis of titanium using $^{49}\text{Ti}(\gamma, p)^{48}\text{Sc}$) or neglected due to poor activity yield.

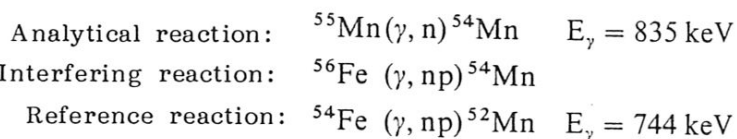
The various types of interference occurring in photon activation analysis, and methods to avoid or reduce them, were reported by many authors (see application section below). However, most of the proposed methods are rather time-consuming and require excessive working effort. Hence they can hardly be used in routine multielement analysis. In the authors' laboratory, considerable effort has been spent on the interference problem in photon activation analysis, and correction procedures have been developed which are integrated in the spectra processing and data evaluation computer programs (Segebade et al. 1959).

1 - Interference by competing reactions

As was shown in chapter 5, frequently common reaction products are formed by different elements during activation with high energy radiation through competing reactions. The probability of their occurrence and also their activity yields increase with the incident radiation energy.



If, as mentioned above, the electron energy is set below 21 MeV the 835 keV peak of ^{54}Mn would be exclusively due to manganese as a target element, but one would have to take into account a serious decrease of the integral analysis sensitivity. Using another reaction of the competing element as a reference the contribution of the interference to the common product activity can be calculated. This method can be used under the following conditions: (1) The activity yield ratio of the interfering and the reference reaction must be known. (2) Since the activities are determined in terms of photopeak integrals, both the absolute emission probabilities of all photon lines involved and the detector efficiency function must be known. These conditions fulfilled, the interference can be calculated. The interference case be the following:



Going out from equation 5.7 in paragraph 5.3.1

$$I = A(T_i) \cdot \Theta \cdot \eta \cdot \frac{e^{-\lambda \cdot T_D}}{\lambda} \cdot (1 - e^{-\lambda \cdot T_C}) \quad (5.7)$$

the peak area ratio of the interfering line and the reference line can be calculated:

$$\frac{I_{\text{int}}}{I_{\text{ref}}} = \frac{\Theta_{\gamma, \text{int}}}{\Theta_{\gamma, \text{ref}}} \cdot \frac{\eta_{\gamma, \text{int}}}{\eta_{\gamma, \text{ref}}} \cdot \frac{A_{\text{int}}(T_i)}{A_{\text{ref}}(T_i)} \cdot \frac{\lambda_{\text{ref}}}{\lambda_{\text{int}}} \cdot \frac{e^{-\lambda_{\text{int}} \cdot T_D}}{e^{-\lambda_{\text{ref}} \cdot T_D}} \cdot \frac{1 - e^{-\lambda_{\text{int}} \cdot T_C}}{1 - e^{-\lambda_{\text{ref}} \cdot T_C}} \quad (6.8)$$

where

int = interfering line data
 ref = reference line data

As explained in paragraph 5.3.1, from the single element activations, the ratio between the specific activities (N) of the product nuclides and the nickel monitor were calculated by:

$$N = \frac{a_{\text{el}}(T_i = 1 \text{ h})}{a_{\text{Ni}}(T_i = 1 \text{ h})} \quad (5.1)$$

$a_{\text{el}}(T)$ = activity of product nuclide, divided by mass of element, after 1 hour irradiation under standard conditions.

Since the interference and the reference reaction occur in the same element, the ratio between the N-values of both reaction can be expressed in terms of the activities:

$$\frac{N_{\text{int}}}{N_{\text{ref}}} = \frac{A_{\text{int}}(T_i = 1 \text{ h})}{A_{\text{ref}}(T_i = 1 \text{ h})} \quad (6.9)$$

Conversion of the activities for the actual analysis irradiation time, and insertion into equation 6.8 yields:

$$I_{\text{int}} = I_{\text{ref}} \cdot \frac{N_{\text{int}}}{N_{\text{ref}}} \cdot \frac{\Theta_{\gamma, \text{int}}}{\Theta_{\gamma, \text{ref}}} \cdot \frac{\eta_{\gamma, \text{int}}}{\eta_{\gamma, \text{ref}}} \cdot \frac{\lambda_{\text{ref}}}{\lambda_{\text{int}}} \cdot \frac{e^{-\lambda_{\text{int}} \cdot T_D}}{e^{-\lambda_{\text{ref}} \cdot T_D}} \cdot \frac{1 - e^{-\lambda_{\text{int}} \cdot T_C}}{1 - e^{-\lambda_{\text{ref}} \cdot T_C}} \cdot \frac{1 - e^{-\lambda_{\text{ref}} \cdot T}}{1 - e^{-\lambda_{\text{int}} \cdot T}} \cdot \frac{1 - e^{-\lambda_{\text{int}} \cdot T_i}}{1 - e^{-\lambda_{\text{ref}} \cdot T_i}} \quad (6.10)$$

T_i = actual exposure period

In the most cases the irradiation time is much shorter than the half-lives of product nuclides. Then equation 6.10 can be simplified to:

$$I_{\text{int}} = I_{\text{ref}} \cdot \frac{N_{\text{int}}}{N_{\text{ref}}} \cdot \frac{\Theta_{\gamma, \text{int}}}{\Theta_{\gamma, \text{ref}}} \cdot \frac{\eta_{\gamma, \text{int}}}{\eta_{\gamma, \text{ref}}} \cdot \frac{\lambda_{\text{ref}}}{\lambda_{\text{int}}} \cdot \frac{e^{-\lambda_{\text{int}} \cdot T_D}}{e^{-\lambda_{\text{ref}} \cdot T_D}} \cdot \frac{1 - e^{-\lambda_{\text{int}} \cdot T_C}}{1 - e^{-\lambda_{\text{ref}} \cdot T_C}} \quad (6.11)$$

The correction factor

$$V_1 = \frac{N_{\text{int}} \cdot \Theta_{\gamma, \text{int}} \cdot \eta_{\gamma, \text{int}}}{N_{\text{ref}} \cdot \Theta_{\gamma, \text{ref}} \cdot \eta_{\gamma, \text{ref}}} \quad (6.12)$$

was calculated for the most frequently occurring interfering reactions and is listed in table 6.2-2.

The corrected analysis peak area is calculated by:

$$I_{\text{corr}} = I_{\text{meas}} - I_{\text{ref}} \cdot V_1 \cdot \frac{\lambda_{\text{ref}}}{\lambda_{\text{int}}} \cdot \frac{e^{-\lambda_{\text{int}} \cdot T_D}}{e^{-\lambda_{\text{ref}} \cdot T_D}} \cdot \frac{1 - e^{-\lambda_{\text{int}} \cdot T_C}}{1 - e^{-\lambda_{\text{ref}} \cdot T_C}} \cdot \frac{1 - e^{-\lambda_{\text{ref}} \cdot T}}{1 - e^{-\lambda_{\text{int}} \cdot T}} \cdot \frac{1 - e^{-\lambda_{\text{int}} \cdot T_i}}{1 - e^{-\lambda_{\text{ref}} \cdot T_i}} \quad (6.13)$$

where

I_{corr} = corrected analysis photopeak integral

I_{meas} = measured gross photopeak integral

V_1 = correction factor (see eq.6.12)

Tab.6.2-2: Interferences in photon activation analysis of heavier elements ($Z \geq 21$) and correction factors

Analytical reaction	Photon energy (keV)		Interfering reaction	Photon energy (keV)		Reference	Photon energy (keV)		Correction factor		Remarks	
$^{52}\text{Cr}(\gamma, n)^{51}\text{Cr}$	320	320	$^{56}\text{Fe}(\gamma, \text{cn})^{51}\text{Cr}$ $^{148}\text{Nd}(\gamma, n)^{147}\text{Nd}$	320	320	$^{54}\text{Fe}(\gamma, \text{np})^{52}\text{Mn}$	744	744	7.07E-1	7.07E-1	a	
				319	319		147Nd	1434	1434	1.09	1.09	a
				835	835		$^{54}\text{Fe}(\gamma, \text{np})^{52}\text{Mn}$	744	1434	(2.9E-1)	(2.9E-1)	1.52E-1
$^{55}\text{Mn}(\gamma, n)^{54}\text{Mn}$	835	835	$^{56}\text{Fe}(\gamma, \text{np})^{54}\text{Mn}$	835	835	$^{54}\text{Fe}(\gamma, \text{np})^{52}\text{Mn}$	744	744	4.84E+2	4.32E+2	a	
$^{59}\text{Co}(\gamma, n)^{58}\text{Co}$	811	811	$^{60}\text{Ni}(\gamma, \text{np})^{58}\text{Co}$	811	811	$^{58}\text{Ni}(\gamma, n)^{57}\text{Ni}$	1378	1378	7.57E-2	8.01E-2	a	
			$^{63}\text{Cu}(\gamma, \text{cn})^{58}\text{Co}$	811	811	$^{65}\text{Cu}(\gamma, n)^{64}\text{Cu}$	1346	1346	3.53E-1	3.38E-1	a	
			$^{48}\text{Ca}(\gamma, n)^{47}\text{Ca}$	808	808	^{47}Ca	1297	1297	1.64E-1	1.14E-1	a	
			$^{97}\text{Mo}(\gamma, \text{p})^{96}\text{Nb}$	810	810	^{96}Nb	569	569	1.57E-1	2.04E-1	a	
			$^{107}\text{Ag}(\gamma, n)^{106\text{m}}\text{Ag}$	808	808	$^{106\text{m}}\text{Ag}$	717	717	1.70E-1	1.33E-1	a	
							1046	1046	(2.9E-1)	(2.9E-1)	1.99E-1	1.99E-1
$^{65}\text{Cu}(\gamma, n)^{64}\text{Cu}$	1346	1346	$^{66}\text{Zn}(\gamma, \text{np})^{64}\text{Cu}$	1346	1346	$^{66}\text{Zn}(\gamma, n)^{65}\text{Zn}$	1116	1116	5.80E-5	5.92E-5	a	
$^{68}\text{Zn}(\gamma, \text{p})^{67}\text{Cu}$	185	185	$^{69}\text{Ga}(\gamma, 2n)^{67}\text{Ga}$	185	185	$^{68}\text{Zn}(\gamma, \text{p})^{67}\text{Cu}$	185	185	2.34E-4	2.41E-4	a	
								299	299	2.77	2.78	a
$^{69}\text{Ga}(\gamma, 2n)^{67}\text{Ga}$	299	299	$^{136}\text{Ce}(\gamma, n)^{135}\text{Ce}$	300	300	^{135}Ce	606	606	(3.33)	2.78	a, c	
								166	166	2.47E-4	2.17E-4	a

Tab.6.2-2, continued

Analytical reaction	Photon energy (keV)	Interfering reaction	Photon energy (keV)	Reference	Photon energy (keV)	Correction factor		Remarks
						V_0 or V_1 , respectively calcul.	exper.	
$^{75}\text{As}(\gamma, n)^{74}\text{As}$	596	$^{44}\text{Ca}(\gamma, p)^{43}\text{K}$	594	^{43}K	618	1.59E-1	1.68E-1	a
$^{76}\text{Se}(\gamma, n)^{75}\text{Se}$	136	$^{58}\text{Ni}(\gamma, p)^{57}\text{Co}$	136	^{57}Co	122	1.26E-1	1.18E-1	a
$^{89}\text{Y}(\gamma, n)^{88}\text{Y}$	1836	$^{90}\text{Zr}(\gamma, np)^{88}\text{Y}$	1836	$^{90}\text{Zr}(\gamma, n)^{89}\text{Zr}$	909	8.83E-4	1.25E-3	a, d
$^{93}\text{Nb}(\gamma, n)^{92\text{m}}\text{Nb}$	935	$^{54}\text{Fe}(\gamma, np)^{52}\text{Mn}$	936	^{52}Mn	744	7.47E-1	9.13E-1	a
					1434	1.27	1.41	a
$^{107}\text{Ag}(\gamma, n)^{105}\text{Ag}$	345	$^{106}\text{Cd}(\gamma, p)^{105}\text{Ag}$	345	$^{116}\text{Cd}(\gamma, n, \beta^-)^{115\text{m}}\text{In}$	336	1.50E-1	1.44E-1	a
$^{127}\text{I}(\gamma, n)^{126}\text{I}$	389	$^{89}\text{Y}(\gamma, 2n, \text{EC})^{87\text{m}}\text{Sr}$	388	^{87}Y	485	1.14	1.15	a
				$^{89}\text{Y}(\gamma, n)^{88}\text{Y}$	898	5.01E-2	7.09E-2	a
$^{133}\text{Cs}(\gamma, n)^{132}\text{Cs}$	668	$^{127}\text{I}(\gamma, n)^{126}\text{I}$	666	^{126}I	1836	8.31E-2	1.30E-1	a
	29.78	$^{130}\text{Ba}(\gamma, p)^{129}\text{Cs}$	29.78	$^{136}\text{Ba}(\gamma, n)^{135\text{m}}\text{Ba}$	32.19	--	6.09E-2	b, e
$^{136}\text{Ba}(\gamma, n)^{135\text{m}}\text{Ba}$	268	$^{136}\text{Ce}(\gamma, n)^{135}\text{Ce}$	265	^{135}Ce	389	4.15E-1	4.69E-1	a
				$^{149}\text{Ce}(\gamma, n)^{139}\text{Ce}$	166	5.45E-4	5.31E-4	a
$^{140}\text{Ce}(\gamma, n)^{139}\text{Ce}$	33.44	$^{133}\text{Cs}(\gamma, n)^{132}\text{Cs}$	33.6	^{132}Cs	29.78	1.86E-1	2.04E-1	b, f

Tab.6.2-2, continued

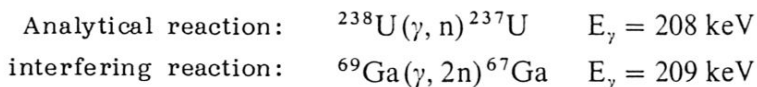
Analytical reaction	Photon energy (keV)		Interfering reaction	Photon energy (keV)		Reference	Photon energy (keV)	Correction factor		Remarks
								V_0 or V_1 , calcul.	V_1 , exper.	
$^{148}\text{Nd}(\gamma, n)^{147}\text{Nd}$	38.72	38.7	$^{140}\text{Ce}(\gamma, n)^{139}\text{Ce}$	38.7	^{139}Ce		33.44	6.06E-2	5.04E-2	b
	91.1	91.3	$^{68}\text{Zn}(\gamma, p)^{67}\text{Cu}$	91.3	^{67}Cu		166	(1.9E-1)	1.43E-1	b, c
	531	531	$^{48}\text{Ca}(\gamma, n)^{47}\text{Ca}$	531	^{47}Ca		93.3	4.40E-1	4.27E-1	b
		528	$^{116}\text{Cd}(\gamma, n, \beta^-)^{115\text{m}}\text{In}$	528	$^{115\text{m}}\text{In}$		1297	4.95E-3	4.71E-3	a
							336	(5.5E-1)	3.66E-1	a, c
$^{197}\text{Au}(\gamma, n)^{196}\text{Au}$	66.83	66.99	$^{198}\text{Hg}(\gamma, n)^{197}\text{Hg}$	66.99	^{197}Hg		68.81	5.52E-1	5.92E-1	b
$^{198}\text{Hg}(\gamma, n)^{197}\text{Hg}$	68.81	68.89	$^{203}\text{Tl}(\gamma, n)^{202}\text{Tl}$	68.89	^{202}Tl		70.82	5.51E-1	5.95E-1	b
$^{203}\text{Tl}(\gamma, n)^{202}\text{Tl}$	70.82	70.83	$^{204}\text{Pb}(\gamma, n)^{203}\text{Pb}$	70.83	^{203}Pb		72.87	5.57E-1	5.89E-1	b
	440	439	$^{70}\text{Zn}(\gamma, n)^{69\text{m}}\text{Zn}$	439	$^{66}\text{Zn}(\gamma, n)^{65}\text{Zn}$		1116	2.25E-2	2.34E-2	a
		440	$^{148}\text{Nd}(\gamma, n)^{147}\text{Nd}$	440	$^{68}\text{Zn}(\gamma, p)^{67}\text{Cu}$		185	9.09E-2	9.41E-2	a
					^{147}Nd		531	1.18E-1	9.37E-2	a
$^{204}\text{Pb}(\gamma, n)^{203}\text{Pb}$	72.87	72.80	$k\alpha_2$ Pb backgr.	72.80	$k\alpha_1$ Pb backgr.		74.97	5.57E-1	5.97E-1	b
	279	276	$^{134}\text{Ba}(\gamma, n)^{133\text{m}}\text{Ba}$	276	$^{136}\text{Ba}(\gamma, n)^{135\text{m}}\text{Ba}$		268	3.36E-1	3.37E-1	a
$^{238}\text{U}(\gamma, n)^{237}\text{U}$	208	209	$^{69}\text{Ga}(\gamma, 2n)^{67}\text{Ga}$	209	^{67}Ga		299	1.90E-1	1.90E-1	a

Remarks to Tab.6.2-2

- a - radiation measured with large-volume coaxial Ge-detector.
- b - radiation measured with planar Ge low-energy photon diode.
- c - calculated V-value is uncertain; tabulated nuclear data vary strongly.
- d - if cooling period is ≥ 5 d, additional interference from $^{90}\text{Zr}(\gamma, 2n, \text{EC})^{88}\text{Y}$ becomes significant.
- e - V_0 -value cannot be calculated because both interfering line and reference energy are emitted by different product nuclides (with similar half-lives).
- f - X-rays of xenon may also be emitted by activation products of barium possibly present in the sample.

2 - Overlapping photon energy lines

If the interfering nuclide emits another line besides the interfering one the correction is somewhat simpler than the above evaluated for competing reactions. The interference case be the following:



Reference energy: 299 keV of ^{67}Ga

The contribution of the interfering nuclide to the peak used for analysis can be calculated from the peak area of a second line emitted by the interfering nuclide as a reference. Using equation 5.5 in Ch.5, one can calculate the ratio V_0 between the interfering peak area and the reference peak area:

$$V_0 = \frac{I_{\text{int}}}{I_{\text{ref}}} = \frac{\Theta_{\gamma, \text{int}} \cdot \eta_{\gamma, \text{int}}}{\Theta_{\gamma, \text{ref}} \cdot \eta_{\gamma, \text{ref}}} \quad (6.14)$$

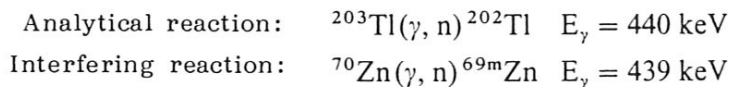
I_{int} = net peak area of the interfering energy $E_{\gamma, \text{int}}$
 I_{ref} = net peak area of the reference energy $E_{\gamma, \text{ref}}$

The corrected analysis energy line is then calculated by

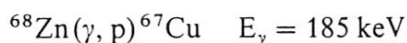
$$I_{\text{corr}} = I_{\text{meas}} - V_0 \cdot I_{\text{ref}} \quad (6.15)$$

I_{meas} = area of the interfered peak to be used for analysis
 V_0 = values are compiled in Tab.6.2-2 for the most frequently occurring interferences.

If there is no reference line available, e.g. in the following case:



the above described procedure for competing reactions has to be used taking



as a reference reaction. This procedure can be used for correction of any kind of spectral interference, since the correction equation for overlapping photon rays is a simplified version of the somewhat complicated one for correction of competing reaction interferences; in the case of $N_{\text{int}} = N_{\text{ref}}$ and $\lambda_{\text{int}} = \lambda_{\text{ref}}$ (i.e. in the case of identical nuclides interfering and being used as a reference for correction) equation 6.13 simplifies into equation 6.15. The values in Tab.6.2-2 designated as "calculated" were evaluated from literature data for emission probabilities and from the measured efficiency function of the detector used. The values designated as "experimental" were calculated from the results of single element irradiations. The V_0 and V_1 values compiled in Tab.6.2-2 are valid under the following conditions:

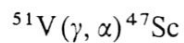
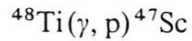
- a) maximum energy of activating bremsstrahlung: 30 ± 2 MeV,
- b) well-known detector efficiency function

In general, there is a satisfactory agreement between calculated and experimentally determined correction factors. Deviations of V_0 and V_1 from the accurate value may be caused by:

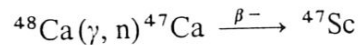
- a) uncontrolled shift of the electron energy of the accelerators; cross sections of analysis, reference and interfering reactions have different energy dependencies,
- b) dependency of the relative detector efficiency function on the counting geometry,
- c) errors caused by complex production paths of the product nuclides, e.g. ${}^{89}\text{Y}(\gamma, n){}^{88}\text{Y}$ interfered by ${}^{90}\text{Zr}(\gamma, np){}^{88}\text{Y}$ and also by ${}^{90}\text{Zr}(\gamma, 2n, \text{EC}){}^{88}\text{Y}$,
- d) poor accuracy of the tabulated nuclear data used for interference calculation.

3 - Secondary decay interference

This type of interference does not occur very frequently and can be mostly avoided by selection of another reaction for analysis evaluation. An example: ${}^{47}\text{Sc}$ is produced by direct activation of either titanium or vanadium:



It may be also produced by β^- -decay of ${}^{47}\text{Ca}$ produced through activation of calcium



In order to assess the activity yield ratio of the contributing reactions one has to compare the activity functions of the common product nuclide produced by the different mechanisms. The activity function of ${}^{47}\text{Sc}$ produced by titanium and vanadium can be simply derived with help of the activation equation (see Ch.1). The decay function of the ${}^{47}\text{Sc}$ activity produced by calcium is somewhat more complex. It is characterised thus: ${}^{47}\text{Sc}$ is produced by immediate decay of ${}^{47}\text{Ca}$ during activation of ${}^{48}\text{Ca}$. After the irradiation period (i.e. the "mother" activity of ${}^{47}\text{Ca}$ has reached its maximum) the ${}^{47}\text{Sc}$ activity ("daughter") increases on to a maximum and then decays along an equilibrium function between ${}^{47}\text{Ca}$ and ${}^{47}\text{Sc}$ (see Fig.6.2.5; Ref. 897,1200).

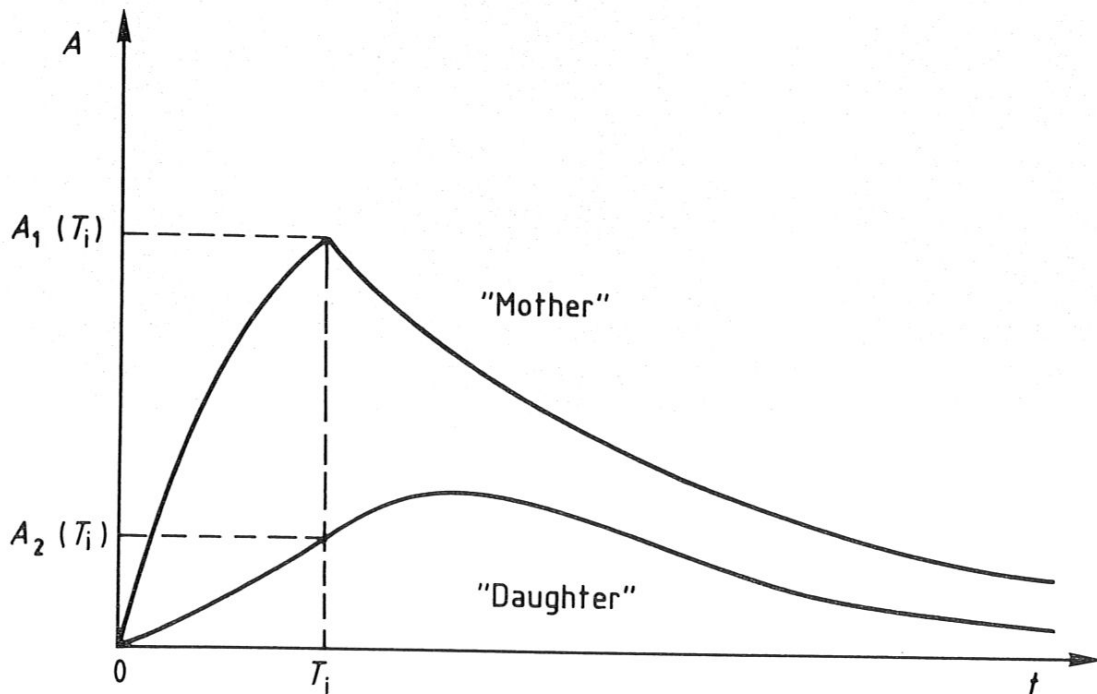


Fig. 6.2.5: Activity as a function of time for the mother (A_1) and the daughter (A_2) nuclide during complex decay; T_i = end of irradiation

The activity function of the daughter nuclide during irradiation

Going out from equation 1.1 in 1.3 the number of produced nuclei is given by

$$\frac{dN}{dt} = \dot{N}^+ - \lambda \cdot N(t) \quad (1.1)$$

Hence, both nuclei numbers within a mother-daughter decay scheme are described by

$$\frac{dN_1}{dt} = \dot{N}_1^+ - \lambda_1 \cdot N_1 \quad (6.16)$$

$$\frac{dN_2}{dt} = \dot{N}_2^+ - \lambda_2 \cdot N_2 \quad (6.17)$$

where index 1 stands for the mother and index 2 for the daughter. The solution of equation 6.16 yields

$$N_1(t) = \frac{\dot{N}_1^+}{\lambda_1} \cdot (1 - e^{-\lambda_1 \cdot t}) \quad (6.18)$$

In the decay scheme the decay rate of the mother equals the product rate of the daughter:

$$\dot{N}_2^+ = \lambda_1 \cdot N_1(t) \quad (6.19)$$

Thus, for the time interval between zero and the end of irradiation (T_1) the number of daughter nuclei as a function of time is given by the differential equation:

$$\frac{dN_2(t)}{dt} + \lambda_2 \cdot N_2(t) - \dot{N}_1^+ \cdot (1 - e^{-\lambda_1 \cdot t}) = 0 \quad (6.20)$$

The solution of this equation yields:

$$N_2(t) = \frac{N_1^+}{\lambda_2} \cdot \left(1 - \frac{\lambda_2}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_1 \cdot t} + \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_2 \cdot t} \right) \quad (6.21)$$

At the end of the exposure period the number of daughter nuclei is ($t=T_i$):

$$N_2(T_i) = \frac{\lambda_1}{\lambda_2} \cdot N_1(T_i) \cdot \frac{1 - \frac{\lambda_2}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_1 \cdot T_i} + \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_2 \cdot T_i}}{1 - e^{-\lambda_1 \cdot T_i}} \quad (6.22)$$

In the diagrams in Figs. 6.2.6 - 6.2.9 activities are plotted. Therefore, using the relationship

$$A_2(T_i) = \frac{\lambda_2}{\lambda_1} \cdot \frac{N_2(T_i)}{N_1(T_i)} \cdot A_1(T_i) \quad (6.23)$$

we obtain from Eq.6.22:

$$A_2(T_i) = A_1(T_i) \cdot \frac{1 - \frac{\lambda_2}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_1 \cdot T_i} + \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_2 \cdot T_i}}{1 - e^{-\lambda_1 \cdot T_i}} \quad (6.24)$$

The activity function of the daughter nuclide after irradiation

After irradiation, the mother activity will decay following the function:

$$N_1(t) = N_1(T_i) \cdot e^{-\lambda_1 \cdot (t-T_i)} \quad (6.25)$$

Since, as noted above, the production rate of the daughter activity equals the decay rate of the mother activity, the number of daughter nuclei as a function of time can be expressed as follows:

$$\frac{dN_2}{dt} - \lambda_1 \cdot N_1(T_i) \cdot e^{-\lambda_1 \cdot (t-T_i)} + \lambda_2 \cdot N_2(t) = 0 \quad (6.26)$$

The solution of equation 6.26 yields:

$$N_2(t) = \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot N_1(T_i) \cdot (e^{-\lambda_1 \cdot (t-T_i)} - e^{-\lambda_2 \cdot (t-T_i)}) + N_2(T_i) \cdot e^{-\lambda_2 \cdot (t-T_i)} \quad (6.27)$$

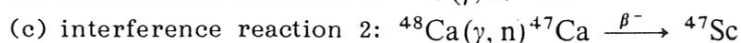
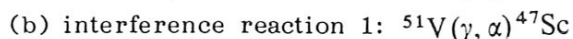
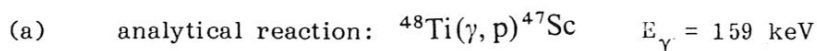
$t-T_i$ is the decay period (see chapter 1.3). Using equation 6.27 the activity of the daughter nuclide after the decay time T_D is obtained:

$$A_2(t) = \frac{\lambda_2}{\lambda_2 - \lambda_1} \cdot A_1(T_i) \cdot (e^{-\lambda_1 \cdot T_D} - e^{-\lambda_2 \cdot T_D}) + A_2(T_i) \cdot e^{-\lambda_2 \cdot T_D} \quad (6.28)$$

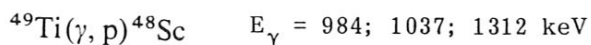
Using this equation, the interfering contribution originating from complex decay of activation products can be calculated.

As far as it is known to the authors no correction routine has been worked out as yet for this interference type. At this point, however, some examples are discussed. This is done in the following manner:

The interference case be the above named with ^{47}Sc as the common product nuclide:



First, alternative analysis reactions will be given, in this case:



Then the activity functions of all participating nuclides will be represented graphically, starting immediately after the exposure period of equal masses of all elements involved. In the figures below, the relative activity yield after

one hour bremsstrahlung activation (see chapter 5) is plotted over the decay time (see Fig.6.2.6).

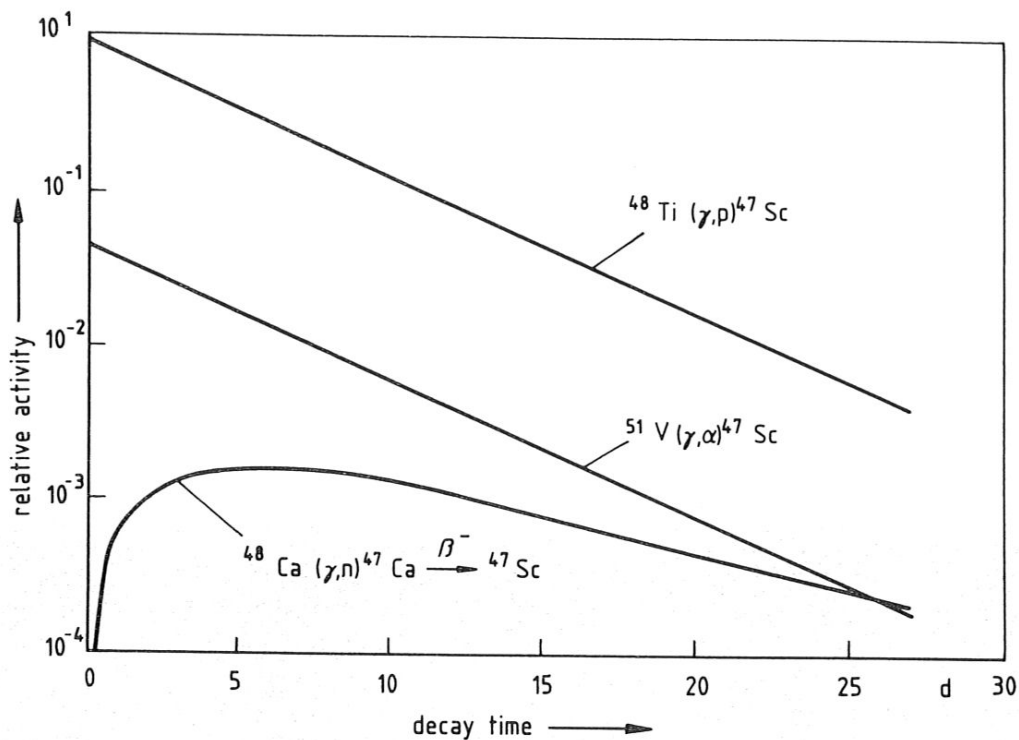


Fig. 6.2.6: Complex decay functions of ^{47}Sc ; decay curves of ^{47}Sc produced through three different reactions

Hereby it is obvious that the competing reaction (b) can be neglected if vanadium is present in amounts comparable to those of titanium and calcium. However, titanium can be determined by reaction (1) if the cooling time is kept very short.

- $^{87\text{m}}\text{Sr}$

(a) analytical reaction: $^{88}\text{Sr}(\gamma, n)^{87\text{m}}\text{Sr}$ $E_\gamma = 388 \text{ keV}$

(b) interfering reaction 1: $^{89}\text{Y}(\gamma, np)^{87\text{m}}\text{Sr}$

(c) interfering reaction 2: $^{89}\text{Y}(\gamma, 2n)^{87}\text{Y} \xrightarrow{\text{EC}; \beta^+} ^{87\text{m}}\text{Sr}$

Alternative analytical reactions:



If cooling periods are kept short, the interference reaction (c) can be neglected in the most cases, whereas reaction (b) yields considerable activities (see Fig.6.2.7).

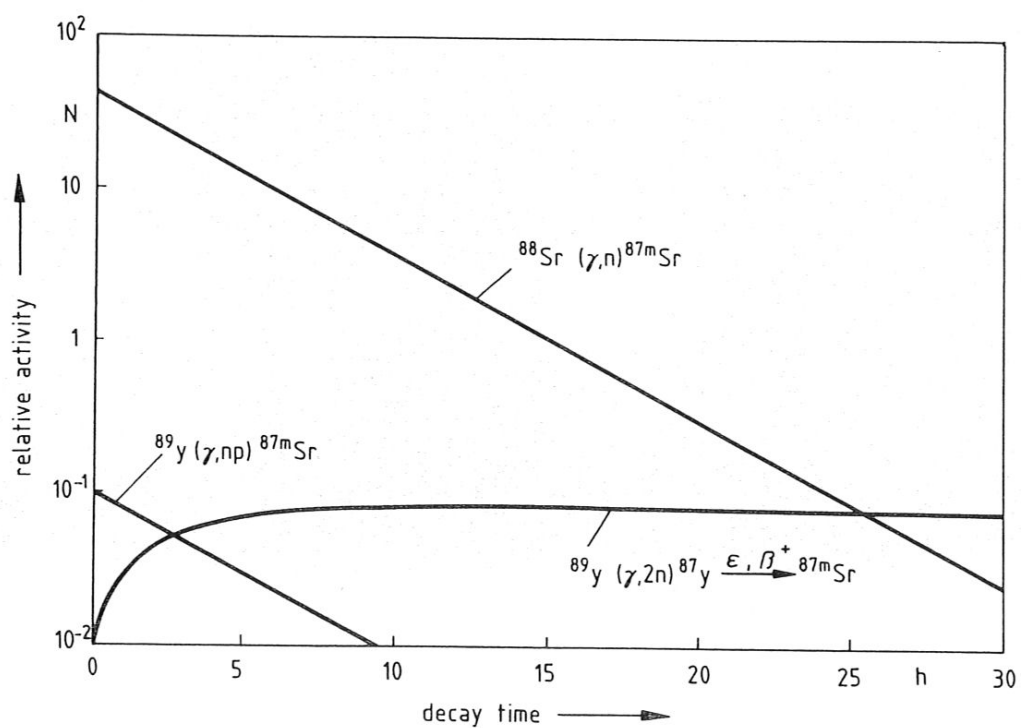


Fig. 6.2.7: Complex decay functions of ${}^{87\text{m}}\text{Sr}$

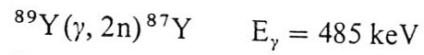
- ${}^{88}\text{Y}$

(a) analytical reaction: ${}^{89}\text{Y}(\gamma, n){}^{88}\text{Y} \quad E_\gamma = 898; 1836 \text{ keV}$

(b) interfering reaction 1: ${}^{90}\text{Zr}(\gamma, np){}^{88}\text{Y}$

(c) interfering reaction 2: ${}^{90}\text{Zr}(\gamma, 2n){}^{88}\text{Zr} \xrightarrow{\text{EC}} {}^{88}\text{Y}$

alternative analytical reactions:



Interference reaction (c) becomes significant after long cooling periods; considerable activity is yielded by reaction (b) (see Fig.6.2.8).

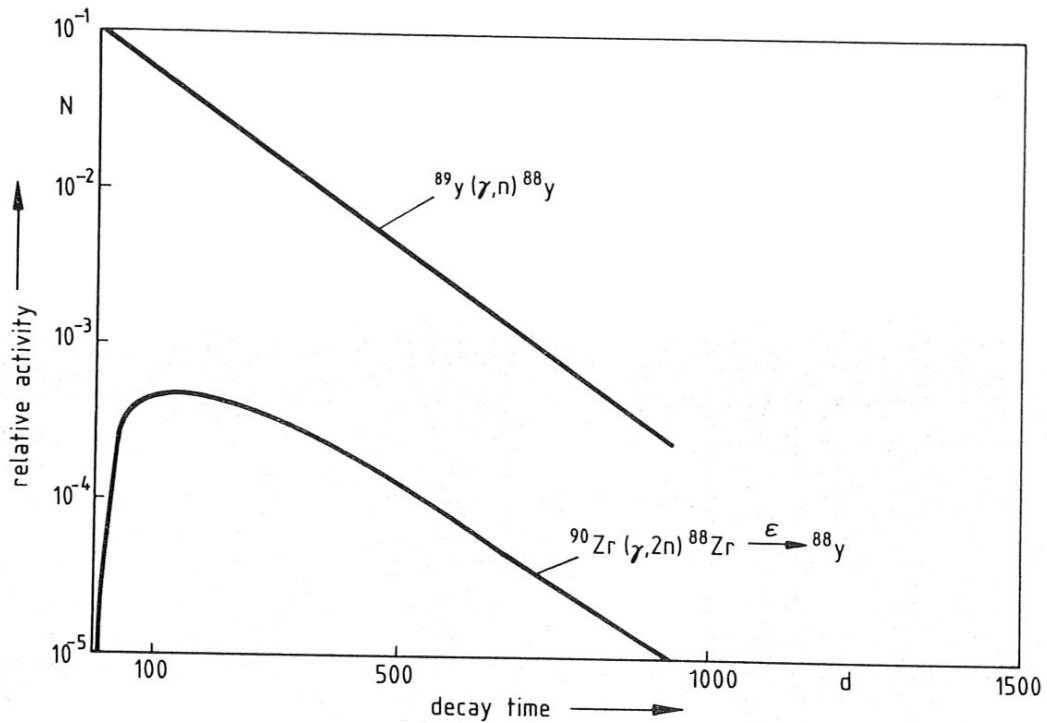


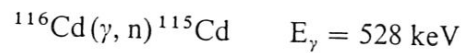
Fig. 6.2.8: Complex decay functions of ^{88}Y

- $^{115\text{m}}\text{In}$

(a) analytical reaction: $^{116}\text{Cd}(\gamma, n)^{115}\text{Cd} \xrightarrow{\beta^-} ^{115\text{m}}\text{In} \quad E_\gamma = 336 \text{ keV}$

(b) interfering reaction: $^{116}\text{Sn}(\gamma, p)^{115\text{m}}\text{In}$

alternative analytical reaction:



In this special case the secondary decay product is used for analysis and the direct (γ, p) -reaction interferes. This time it is easy to avoid the interference by simply allowing the ^{115m}In due to tin target to decay to quasi-zero activity (see Fig. 6.2.9).

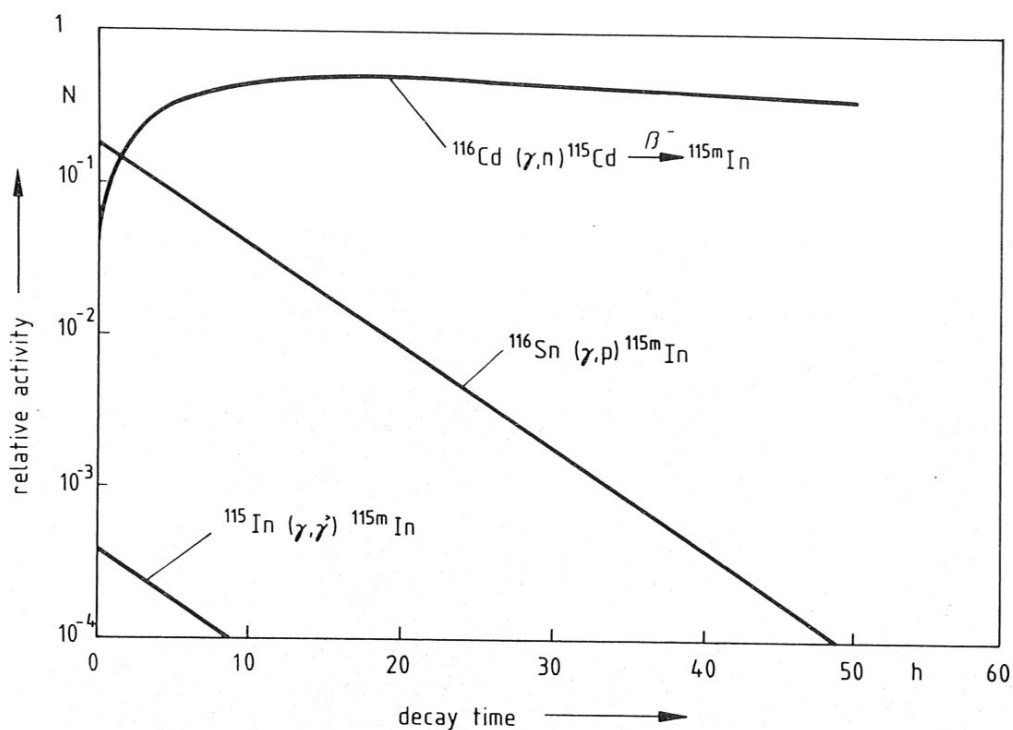


Fig. 6.2.9: Complex decay functions of ^{115m}In

- Interference by neutron or proton reactions

photoneutrons may induce reactions which interfere with photonuclear processes. This also a first order interference as explained above, but it can hardly be corrected quantitatively since the neutron flux distribution is essentially different from that of the bremsstrahlung radiation and the flux density of the photoneutrons is dependent upon many parameters which cannot be controlled. However, neutron reactions interfere in a few cases only and mostly it is possible to select another analytical reaction which is not interfered. One can as well reduce or completely suppress interfering reactions by neutrons wrapping the samples into cadmium foil or mixing the samples with lithium salts to absorb thermal neutrons.

Furthermore, reactions with photoprotons produced either in the converter target or in the sample matrix may also induce interfering reactions in a few cases (see Ch.6.1)

- Variations in the isotopical abundance

On the one hand, in activation analysis normally the reaction of only one stable isotope is evaluated analytically. On the other hand, there are only 21 "pure" elements containing only one naturally occurring isotope and the quantitative isotopical composition of the other elements frequently varies depending upon the deposit or provenience of the material. Thereby, miscalculations during analysis evaluation might be introduced. Furthermore, the isotopical composition of an element within one sample might be falsified by isotopic diffusion effects, particularly in metal matrix⁸⁹⁸⁻⁹⁰². However, in photon activation analysis frequently more than one isotope can be analysed, and thereby questionable values may be verified. In this case, however, a reference material of well-known isotopical composition must be available.

All in all, the interference management in instrumental photoactivation analysis is a complex problem and is discussed by many analysts in the concerning recommended literature compiled below.

6.2.4 Applications

In this paragraph photon activation analysis procedures applied to different material classes are described. Examples of analysis are discussed referring to the literature available to the authors. The different areas of application are distinguished by the scientific background of the analysed sample. However, the problems concerning the analytical procedure are emphasised rather than the scientific context of the analysed object.

Different element groups are of special interest in each field of application. This spectrum has varied due to advanced research, e.g. in environmental science. The list of elements and compounds known to be hazardous or harmful to man and nature has become very large and is still rapidly growing. Moreover, frequently the relevance of certain components in a given material seems to rise along with its improving determinability. Hence, the determination of an increasing number of elements and compounds is required in almost every field of science with chemical analysis involved. However, in instrumental photon activation analysis - as in every other analytical technique - the analysis of each element in any matrix entails particular problems which are due to the physical and chemical behaviour of both. Therefore, in the following and particularly in paragraph 6.2.4.9, these problems are discussed in relevant cases, primarily based upon practical experience in the analytical laboratory.

6.2.4.1 Systematic compilations

In this paragraph the most relevant photonuclear data compilations with analytical background without regard to a special application are discussed. This is no analytical application in the common sense, of course. However, since the major part of this book consists of a data compilation it might be of interest to discuss other ones comparatively which comprise a reasonably large list of elements without regard to special analytical problem.

Systematic investigation work on photonuclear reactions, as already mentioned in chapter 2, has become possible with the maturity of high energy bremsstrahlung sources with large output power. The first systematic investigations were primarily concerned with the giant resonance within the photonuclear cross section function. According to the literature accessible to the authors, the first systematic work with an analytical background was performed comparatively late, namely in 1964 by Schweikert and Albert⁹⁰³. There is a previous paper (McGregor Ref.⁴³) in which activity yields are presented for a large number (84) of ra-

dionuclides produced through photonuclear reactions, but this is of minor interest in the present context, since it has no analytical background but is an article on radionuclide production and the yield data given are not based upon practical measurement but are calculated theoretically.

There was another earlier systematic listing available to the authors (Kurz⁹⁰⁴) but this is a private communication and not available to the public, hence it is not included in this compilation.

Two other earlier papers (Otvos et al.²¹¹, Lukens et al.¹²¹) give specific activity yields of photonuclear processes yielding metastable isomeres by (γ, γ^-) -reactions. However, at this point only those methods are discussed which can be applied to the majority of elements; the photonuclear isomeric state excitation can be applied to a limited number of elements only. Therefore, this special application will be discussed seperately later on in this paragraph.

1) In the report cited above (Schweikert and Albert⁹⁰³) excitation functions and analytical sensitivities at an incident maximum bremsstrahlung energy of 27 MeV and 50 microamperes mean electron beam current are presented for a selected series of elements. This work contains a lot of fundamental facts and data concerning photon activation analysis, e.g. sensitivity assessments, interference sources etc.. It also shows, based upon experimental results, that the optimum bombardment energy - with respect to both activity yields of the desired nuclides and yields of unwanted reactions - is around 25 to 35 MeV as explained in chapter 2. However, the presented sensitivity data were obtained with help of NaI(Tl) spectrometers which can hardly be used in multielement analysis work.

Due to the lack of higher resolution detectors and appropriate electronic equipment at that time scintillation spectrometers were also used in most of the compilations which are cited in the following (the first quasi-complete compilation of photonuclear activation products measured by high resolution spectrometry was published - as far as the authors know - in 1972).

2) According to the literature accessible to the authors, the first catalogue of photonuclear reactions comprising all elements except a few (namely those which are not included in chapter 5 of this book, too) was published by Oka et al.⁹⁰⁵. This paper offers a lot of fundamental data for photon activation analysis purpose. Irradiations were carried out with an electron linear accelerator using 20 MeV bremsstrahlung from a 2mm platinum converter. The mean electron beam current was 40 microamperes. Gamma spectroscopy was performed using

a 3" x 3", NaI crystal spectrometer. Following data are presented: The most prominent photonuclear reactions of the target element, half-life of the product, its most prominent gamma-ray energy, activity yield data in terms of photopeak counts per time and target element mass (these data were normalised to a standard bremsstrahlung dose rate received by the sample), detection limits, and products from other reactions which had been detected. As an immediate aid for the analyst to the determination of experimental conditions, the photopeak count rates were plotted over the gamma-ray energy for all elements included.

3) Another paper of the same authors¹⁴⁵ presents absolute disintegration rates of the photonuclear reaction products for a selected number of target elements. The experimental conditions were apparently the same as applied in the work cited previously. In both works, no chemical separation was performed after bremsstrahlung exposure.

4) In 1968, the same working group published an article in which some (γ, p)-reactions induced under the above named conditions were evaluated (Oka et al., Ref.⁷⁹⁸). Chemical separations of the product nuclides from the target matrix had to be carried out in some cases. In this paper, the influence of interfering reactions with photoneutrons was discussed somewhat extendedly, whereas in the paper of Schweikert and Albert⁹⁰³(Rev.1) these interferences and those by secondary reactions with photoprotons were just listed without further evaluation.

5) In the same year, again by the Tohoku University group, a report was published in which a selected number of elements yielding short-lived (10 s to 1 m half-life) photonuclear reaction products was evaluated⁹⁰⁷. As noted above concerning the metastable isomere formation, the quasi-selective production of short-lived nuclides is a very special application and is discussed separately in this paragraph.

6) Analytical sensitivities for a selected number of elements after exposure to 30 MeV bremsstrahlung (mean electron beam current = 5 microamperes) were given in the review article of Baker⁴⁶. One millimeter tungsten was used as a converter target, hence it was not a "thick" one to absorb all incident electrons. Moreover, apparently no photon flux or dose rate measurements were made. Therefore, these yield data are not comparable to those obtained using other machines and conditions.

7) Baker et al.⁹⁰⁸ published a catalogue of gamma-ray spectra from bremsstrahl-

ung-produced radionuclides including all elements from sodium through bismuth. Essentially, this compilation is laid out very similar to the one by Oka et al.⁹⁰⁵ cited above (Rev.2); the major difference is that Baker et al. presented plots of all spectra obtained and that they used 30 MeV bremsstrahlung excitation.

8) 35 MeV bremsstrahlung was used in the work reported by Debrun and Albert⁸⁴³, where a number of selected elements were investigated.

9) In the compilation of Adams and Dams⁹⁰⁹ a list of neutron deficient nuclides was given, which can be produced through photon activation. However, this list is not complete since it comprises only (γ, n) and $(\gamma, 2n)$ products and does not contain any quantitative yield information. Moreover, the presented data are not based upon experimental results but on theoretical considerations exclusively.

10) The sensitivity data presented by Lutz¹⁴⁶ are also theoretically calculated ones. Activity yields in terms of disintegrations per time and target mass were given for three different incident bremsstrahlung energies (25, 30, 35 MeV). The values, as noted, were calculated but based upon experimentally determined cross section data of photonuclear reactions; these data do not include every photon reaction detected after irradiation by the mentioned energies (e.g. photoproton reactions etc.).

11) Bendel and Numrich⁴⁸ reported experimentally obtained yield data of photon reactions for a limited number of elements. Their major concern was the analysis of the 511 keV annihilation quanta with help of scintillation detectors.

12) A comprehensive survey on the possibilities of photon activation analysis with a betatron as exciting radiation source was given by Kusnetzow^{243, 253, 910}. He pointed out advantages and limitations of activation at lower energies (up to about 26 MeV). The experimental irradiation periods and energies were varied according to the properties of the expected product nuclides; the specific activities were normalised to several standard exposure periods. Measurements were carried out with a NaI spectrometer. Activities with half-lives of less than six seconds and greater than some tens of days were not included. The data compilation is somewhat similar to that of Lutz¹⁴⁶(Rev.10) cited above, but it is less complete due to the less powerful bremsstrahlung source used and some other limitations. It can well be used for general information about the use of betatrons for photon activation analysis.

13) The first systematic compilation of photonuclear reaction data using high energy bremsstrahlung activation and high resolution gamma spectrometry - as far as it is known to the authors - was published by Kato and Oka⁹¹¹. Yield data were given for 52 elements irradiated with 30-72 MeV bremsstrahlung from an electron linear accelerator. Different reaction types were taken into consideration and discussed in detail with respect to their usability for activation analysis or as a source of first order interference. The presented results were obtained by experiment exclusively and were presented as yield values plotted over the incident bremsstrahlung energy. For a selected number of reactions numerical yield data were tabulated. It was concluded that photon activation in combination with high resolution spectrometry and eventual chemical separation can be used for trace component analysis well below the microgramm range.

14) A very extended review on photon activation analysis was given by Sluneko and Kosta⁵². This article includes a table of the analytically relevant photonuclear reactions observed after bremsstrahlung exposure plus a lot of data important for the analysis (see also chapter 1) most of them based upon experiment. This compilation comprises all elements up to bismuth. Following data were tabulated: photonuclear reaction, natural abundance of the isotope involved, half-life of the product nuclide, its decay mode, most prominent gamma-ray lines of the product (up to five ones), threshold energy of the reaction, energy of the cross section function maximum, cross section integral, analytical sensitivity data for different experimental conditions and some additional remarks. The literature on photon activation analysis through 1970 was thoroughly reviewed.

15) In the tables of Galatanu and Grecescu⁹¹², photonuclear reaction products were listed by the order of the most prominent gamma-ray energies. Following data are given: gamma-ray energy (no characteristic X-rays were included although the tables cover energies from 6 to 3300 keV), product radionuclide, isotope abundance of the target nuclide, half-life of the reaction product, other analytically relevant gamma-rays emitted from the product nuclide if any present. One compilation of the (γ, n) products and another of (γ, p) products were presented. These tables are useful for a first rough qualitative checkout of an unknown gamma-ray spectrum of a photon-activated sample. The compilation is one of the first containing gamma-ray tables usable for photon activation analysis using high resolution gamma spectrometry.

16) The data collection of Toms^{913,914}, as well as those by Galatanu and Grecescu cited above (Rev.15) was not obtained through experiment but from

literature sources. All elements through bismuth irradiated with bremsstrahlung energies up to 60 MeV were considered. The entire collection was divided into two parts, each containing two tables, the first ordered by the atomic number of the target nucleus, and the second ordered by the gamma-ray energies emitted by the residual nuclei. Following data were given: photon reaction, threshold energy, half-life of the activation product, its decay mode, gamma energies, and, as an information about the activity to be expected, the product of the natural abundance of the target isotope and the emission probability of the listed gamma-ray energy; with known integrated effective cross-section this intensity factor can be used for convenient calculation of residual activities. The first part includes all reactions which yield nuclei with up to one day half-life, the second part lists all reactions yielding half-lives from one day to one year. Following reaction types were considered: (γ, n) , $(\gamma, 2n)$, (γ, p) , (γ, np) , (γ, α) , $(\gamma, \alpha n)$, $(\gamma, 2p)$, (γ, T) , $(\gamma, {}^3\text{He})$.

17) In the same year, a data compilation was published which meets nearly all requirements of practical photon activation analysis work, namely the tables of Kato¹³⁷. The general layout is very similar to earlier systematic work of the Tohoku research group¹⁴⁵(Rev.3),⁹⁰⁵(Rev.2),⁹⁰⁶(Rev.4),⁹⁰⁷(Rev.5),⁹¹¹(Rev.13), but is modified to the optimum parameters of today's photon activation analysis work, namely: Maximum energy of the bremsstrahlung continuum = 30 MeV (comprehensive data were given also for other energies), photonuclear reactions which are relevant for photon activation analysis (i.e. those which had been detected during experiment) without half-life limitations. The table was organised thus: target element, reaction, half-life of the product, gamma-rays observed, photo-peak count rate (which was called "activity", but given in counts per minute per milligramm) and analytical sensitivity were listed in the main table. The yield data are normalised to one hour bremsstrahlung irradiation at 30 MeV electron energy and a dose rate of 4.41 million roentgens per minute received by the target element and to a fixed counting geometry. Like in the tables of Toms cited above^{913,914}(Rev.16) only the most prominent gamma-ray energies were listed. No emission probabilities were given. Also, some reaction types frequently occurring at the named irradiation conditions were excluded, e.g. (γ, γ') , $(\gamma, \alpha n)$ and reactions with photoneutrons. However, at least the inclusion of the latter is a question of each author's personal philosophy (see chapter 5).

The tables of Kato are a valuable tool for practical photon activation analysis work since they present results obtained exclusively by experiment and thus contain relevant data without being overloaded with information of no use for

the analyst.

18) Comprehensive yield data for a selected number of elements irradiated with 110 MeV bremsstrahlung were given by Ricci⁹¹⁵. The tables present interference-free sensitivity yields, but an interference-free analysis using the named incident radiation energy can be expected in a few exceptionally favourable cases only. If so, however, the analytical sensitivity is improved significantly due to higher reaction yields.

19) The compilation and Anderson et al.⁹¹⁶⁻⁹¹⁸ presents the gamma-ray spectra of all elements with a few exceptions after exposure to 40-44 MeV bremsstrahlung. All gamma-rays which had been observed were listed and the spectra taken with a semiconductor detector after several different decay periods were plotted. This presentation mode allows a valuable first checkout of the spectrum to be expected after irradiation of a given element. Activity yields in terms of specific count rates after flux normalisation were given for the product nuclide to be used most suitably for non-destructive analysis (which does not necessarily have to be the one with the highest reaction yield; see Ch.5). Energy and flux behaviour of the incident photon beam was monitored by irradiation of pure iron and quantitative evaluation of different photonuclear reactions induced in the iron. These reactions were so selected that no interference by photon neutrons were possible or relevant. Sensitivities of other occurring reactions were given to enable approximate interference estimation and assessment of the other activities in the spectrum. First order interference by competing reactions could be evaluated quantitatively by irradiating the batches of element samples in series of adjacent atomic numbers so that their receiving equal doses of bremsstrahlung with identical energy distribution could be assumed (in our work, sets of elements which undergo competing reactions were irradiated and measured separately, see chapter 5). The data were presented thus:

The catalogue is divided into three parts of which the second and the third one were published four years later than the first. The first includes all elements up to molybdenum, the second those from ruthenium to uranium. In the third part all gamma-ray lines observed were listed by the order of their energies. One table was presented in which the most relevant first order interference reactions were listed. The contribution of each to the common activity was quantified. In the main part of the catalogue, the reactions of each element were presented in single data sheets including one or a set of spectrum plots so as to represent the gamma-ray spectrum of the concerned element after different cooling periods. First, all nuclides observed and reactions by which they are

produced were given, including their half-lives. Then specific activity yields for one or more reactions were presented and finally all gamma-ray energies detected. Each energy was attributed to the emitting radionuclide or marked as not identified in the case that it could not be assigned for sure to either one of the product nuclides quoted or to background activity.

This way of presentation is very favourable for practical evaluation work. The search for the desired data in this catalogue is not as time-consuming as in other comparable tabulations. Moreover, it is - as far the authors know - the first data collection intended for photon activation analysis in which also fissile elements were considered and evaluated (thorium, uranium). Also reactions due to photoneutrons were given.

20) Within a large-scale multi-element photon activation analysis work Kato et al.⁹¹⁹ presented a comprehensive study of photonuclear reaction yields after exposure of single elements to 60 MeV bremsstrahlung. As noted above, interference problems gain significance at this incident energy. First order interference was evaluated quantitatively and the method was applied to a large variety of samples. This work is discussed further in paragraph 6.2.4.4; see Rev.95.

21) An extensive study of reaction yields with 30 to 68 MeV bremsstrahlung was published by the Tohoku working group (Masumoto et al.¹⁴⁷) with the major aim to evaluate quantitatively interferences by competing reactions in multi-element photon activation analysis. In this work also interferences due to neutron reactions were included.

22) The work of Lutz and Segebade⁹²⁰ was performed to be used for quick qualitative analysis of an unknown spectrum after 30 MeV bremsstrahlung activation. Maps of diagrams are presented in which the energies of photon activation product nuclides were plotted over their half-lives. Whilst gamma energies can be determined very precisely with help of modern photon spectrometers (see chapter 4) it is scarcely possible to assess half-lives accurately with help of a few measurements, particularly of multi-component spectra. Therefore, energies were plotted on a linear scale and half-lives on a logarithmic one. Energies were obtained by experiment but no yield data were given and the half-lives were taken out of literature sources.

More systematic compilations can be found in the recommended literature below. In the following, several compilations will be reviewed in which special groups of elements are focussed.

a) Isomeric state excitation

As explained in chapter 2, the (γ, γ') -reactions usually have very low threshold energies but also extremely small integrated cross sections. Therefore, isomeric states of many isotopes can be produced with help of gamma radiation from radionuclide sources. More efficiently, bremsstrahlung from small electron accelerators like Van de Graaff generators have been used. The advantage of the method is its relative freedom from interfering reactions. Since the irradiation energy can be set well below the threshold of almost any photoneutron reaction.

23) Lukens et al.¹²¹ pointed out that in the atomic number region between 5 and 32 no interference due to activation by neutrons which are unavoidably present around operating accelerators can occur; by photoneutrons from low energy electron accelerators no isomeres with suitable half-lives can be formed and the concerned isotopes in this atomic number regions have no sufficient fast neutron cross sections to undergo detectable (n, γ) -reactions. In this work, all elements with few exceptions were investigated. During this work several isomeric states were detected which had been unknown thereto. It was found that the method is potentially useful for the analysis of Se, Sr, Y, Rh, Ag, Cd, In, Ba, Lu, Hf, Ir, Pt, Au and Hg. Minimum concentrations detectable of about 4 to 100,000 micrograms per gram were stated if the following parameters are used: irradiation (1 hour maximum) with 3 MeV bremsstrahlung at 1 milliamper electron beam current; counting with a 3" x 3" well-type NaI crystal.

24) Lukens¹²⁴ reported photoreaction yields for a selected number of elements irradiated with 15 MeV bremsstrahlung of a linear accelerator (electron pulse current = 400 milliamperes, 1 hour sample exposure, measurement by scintillation spectroscopy). At this energy frequently both (γ, γ') and (γ, n) -reactions by neighbouring stable isotopes lead to the formation of isomeres; since (γ, n) -reactions generally have considerably higher cross section integrals, the intrinsic sensitivity under the reported conditions is greater than achievable by (γ, γ') -reactions only; detection limits ranging from 0.04 to 40 micrograms were reported.

25) More recently, the production of metastable isomeres by 6 to 8 MeV bremsstrahlung activation was reported (Breban et al.⁹²¹). Ge, Se, Br, Sr, Y, Zr, Rh, Ag, Cd, In, Sn, Te, Ba, Yb, Hf, W, Os, Ir, Pt, Au, Hg and Pb were studied. The authors used a 14 MeV electron linear accelerator equipped with a platinum bremsstrahlung converter. Irradiations were carried out at 7 MeV elec-

tron energy. Two semiconductor detectors were used for product activity measurement; one conventional coaxial gamma detector and a low energy photon diode so as to be able to, as efficiently as possible, detect all photon energies emitted by the irradiated samples. Spectra were stored in a 4096 channel pulse height analyser. Detection limits ranging from 0.25 (gold) to 25,000 (tin) micrograms per gram were claimed. The influence of several irradiation (e.g. electron energy) and measurement (e.g. sample geometry) parameters were studied and evaluated thoroughly. It was concluded that from the 23 above listed elements at least 18 are well determinable under the described conditions. The authors outlined that analyses free from interference due to photoneutrons can only be achieved at incident photon energies not exceeding 7 MeV; in the application examples reported (Noble Metals analyses) at these energies negligible but detectable activities of neutron activation products were observed (^{28}Al , ^{104}Rh , ^{198}Au).

All in all, there is not too much experimental variation possible in the isomeric state excitation analysis. Therefore, no further publications on this subject are reviewed at this point; More about this method can be found in the recommended literature cited below. Also, the metastable isomere excitation with help of isotope gamma-rays, particularly with ^{60}Co sources, are not discussed here; and extended review about this method can be found in the report of Law and Iddings (Ref.¹⁸⁹; see also chapter 2).

b) Production of short-lived isotopes

Frequently, the excitation of metastable isomeres discussed above coincides with the production of short-lived (up to minutes half-lives) nuclides. Systematic work about the analysis with help of short-lived product nuclides is presented separately since it implies several experimental details different from those usually applied in "normal" photon activation analysis. Moreover, several advantages can be stated for the analytical application of short-lived activation products. These are not discussed here but in the other application paragraphs below.

26) The Tohoku research group published an article about the formation of short-lived product nuclides through 20 MeV bremsstrahlung activation (Oka et al.⁹⁰⁷, Rev.5). This work includes (γ, n) products with half-lives from 10 seconds to about 1 minute. Irradiations were one minute long and subsequent gamma spectrometry was carried out using scintillation crystal counting. Under these conditions, only seven radionuclides were found to be promising, namely ^{23}Mg ,

^{75m}Ge , ^{77m}Se , ^{91m}Mo , ^{139m}Ce , ^{141m}Nd and ^{158m}Tb . For the analysis of the corresponding target elements limits of detection were calculated between 0.5 and 4.5 micrograms. In the case of both ground state and metastable isomere production possible the induced activity yields were evaluated comparatively. It is interesting to note that using different excitation energies, there were no significant variations observed in the isomeric yield ratios.

27) Cyclic photon activation was reported to be suitable for activation analysis measuring short-lived nuclides (Kondo⁹²²). Samples of a selected series of elements (sixteen in total) were irradiated (14 MeV bremsstrahlung; exposure time = 28 seconds) and measured (transfer time = 2 seconds; counting period = 28 seconds) multiply; generally five cycles were run. Measurements were carried out by Ge(Li)-spectrometry. Sensitivities in the low microgram regions were obtained.

28) In 1978, the same author⁹²³ published a report about the same subject; the number of elements studied was extended. In total, 27 nuclides with half-lives ranging from 0.8 seconds to 32 minutes were analysed. It was found that maximum analysis sensitivity is achievable by optimising the cycle schedule (exposure, sample transfer, measurement, cycle frequency) according to the half-life of the measured product nuclide.

29) More recently, an extended investigation about the use of short-lived radionuclides in activation analysis was reported (Dams⁹²⁴). Besides photon activation analysis also activation with thermal and fast reactor neutrons, 14 MeV neutrons and charged particles was included. Single and cyclic activations were applied. Radionuclides with half-lives from 10 microseconds to 1 hour were considered; in some exceptional cases also longer or shorter-lived reaction products were included. Only those reactions were taken into account by which gamma-emitting nuclides are produced; no characteristic X-ray measurement was considered. Bremsstrahlung energies varying from 4 to 35 MeV were considered as activating radiation. All naturally occurring elements from $Z = 9$ (Fluorine) to 92 (Uranium) with a few exceptions were studied and sensitivity values were given for normalised activation conditions, in the case of photon activation: (low energy photons) bremsstrahlung produced by 4 to 6 MeV electrons at 1 milliampere striking a gold target. (High energy photons) bremsstrahlung produced by an 25 to 35 MeV electron beam (mean electron beam current = 100 microamperes) impinging on a tungsten converter of 6 mm thickness (irradiation period = 1 minute, no cooling period). The counting period varied depending upon the half-life of the expected product nuclide. As a result, following elements were

reported to be efficiently determinable by photon activation analysis using short-lived activation products: Mg, Si, S, Cl, K, Cr, Fe, Zn, Ge, Se, Br, Rb, Y, Zr, Mo, Ag, Sn, Sb, Ba, Pr, Nd, Ho, Er, Yb, Hf, W, Ir, Au, Tl and Pb.

At the end of this review on systematic compilations it should be mentioned that there were also published studies of special element groups. At this point, only one of these is discussed, namely the investigation of the Rare Earth elements by photon activation analysis. This is done because the analysis of the Rare Earth element group by neutron activation - although of partly dramatic intrinsic sensitivity - is subject to certain limitations due to several nuclear properties of these elements.

30) Kato and Voigt³⁰⁶ compiled the production rates of Rare Earth nuclides by 70 MeV bremsstrahlung from an electron synchrotron. Activity measurements were performed by Ge(Li) spectroscopy. Nine different reaction types were detected in total. Yield data were normalised to 30 minutes irradiation time and a standard bremsstrahlung dose rate received by the sample; this was obtained with help of copper flux monitors.

Further systematic studies can be found in Ref's. ^{24,116,925-948,974}.

6.2.4.2 Environmental analysis

On reviewing the accessible literature about multi-element photon activation analysis it is interesting to note that about half of all papers published deals with environmental analysis or analyses performed in an environmental context. This might be due to different reasons, e.g. that the development of the multielement photon activation analysis technique falls within the time of general major environmental attention and concern of scientists. Another reason might be that several elements of environmental interest (e.g. lead) can be performed most advantageously by instrumental photon activation analysis in trace quantities within routine analysis procedure. Also the fact that several elements of large abundance in nature (e.g. sodium) do not form isotopes which produce interfering high matrix activities certainly plays a role in this question.

In the following, analyses of samples originating from the different environmental spheres (e.g. air, water, soil) are discussed. Sampling and sample preparation problems are not discussed in too much detail; although being determining among the different analysis procedure steps, they are not the authors'

major concern at this point.

Another remarkable finding is the fact that most of the environmental applications refer to atmosphere, soil and biological matrix. Water and water-related analyses have rarely been performed, presumably due to experimental difficulties. However, as explained above in paragraph 6.2.3, as compared with instrumental neutron activation analysis, liquids generally can be analysed more advantageously by photon activation analysis.

In the following, analyses of air particulate and of soils are discussed separately; other applications like analysis of water and pollutants produced within industrial processes are discussed jointly. Biological matrix analysis - be it carried out in an environmental or any other context - are not described here but in paragraph 6.2.4.3.

- The analysis of atmospheric particulate

Among all papers on environmental photon activation analysis inspected by the authors, about 50% are concerned with the analysis of air particulate material. One problem in the analysis of air particulate is the proper selection of the filter material with respect to its behaviour during the analysis procedure. Since one strives for a purely instrumental analysis and thus the particulate matter is not removed from the filter, the following questions have to be answered:

- 1 - How is the stability behaviour of the filter material during bremsstrahlung exposure?
- 2 - Of which nature is the background radiation after activation of a blank filter due to its elemental matrix composition?
- 3 - What is the contamination level of the elements of interest in the blank filter and how homogeneous is the quantitative distribution of this contamination among the filters?
- 4 - Can the filters be prepared before bremsstrahlung exposure or measurement in any way (e.g. pelletised)?

These questions are best answered running blanks before definite selection of the filter material especially the filter matrix activity after activation

often creates serious difficulties since generally very small amounts of material to be analysed are collected on a filter, typically 5 to 20 mg in total. Frequently glass fibre filters are used for air particulate sampling. This material is unsuitable for instrumental activation analysis; the spectrum to be analysed is then superimposed upon a very high matrix background and thereby would lose all significance. Different materials have proven suitable during practical work; in the following review they are mentioned in every given case.

31) One of the first papers on instrumental photon activation analysis of air particulate was published by Aras et al.⁹⁴⁹. This article is discussed in somewhat more detail than the following ones since all problems arising during photon activation analysis of instrumental air particulate were investigated thoroughly and discussed extensively in this paper; many authors of later publications refer to this work since it gives valuable hints, useful for the analyst who is engaged with instrumental air particulate activation analysis.

Samples were taken at two residential areas near Washington, D.C., one of them in close vicinity of a highway and several parking lots so that primarily automotive exhaust was to be expected in the air dust. The air particulate was collected on polystyrene filters. One eighth of the filter was used for one single analysis; it was folded and pressed to a pellet of 1 cm diameter and several mm thickness. The reference material was synthesised using appropriate compounds of the elements to be analysed and was also pressed into pellets. Blank filter portions were also pelletised and irradiated simultaneously with the analysed samples and reference materials to provide blank values. Copper discs which were placed between the pellets were used as photon flux monitors. 35 MeV bremsstrahlung from a water-cooled tungsten converter target at a mean electron beam current of 50 microamperes of a linear accelerator was used for activation. The irradiations lasted several hours. Two spectra were taken after cooling times of one hour and one day, respectively, with a 55 or a 65 cm³ Ge(Li) detector. Due to the high pulse rate of the 511 keV annihilation radiation - mainly originating from ¹¹C produced in the filter matrix - only those nuclides could be measured in the first counting period whose energies are above 511 keV and thus not interfered by the Compton continuum associated with the annihilation radiation. These nuclides (target nuclides) were: ^{34m}Cl (³⁵Cl), ⁶³Zn (⁶⁴Zn), ^{204m}Pb (²⁰⁴,²⁰⁶Pb), ⁵⁶Mn (⁵⁷Fe). Also some product nuclides of reactions with photoneutrons were observable, e.g. ⁵⁶Mn (⁵⁵Mn); this can also be produced by (γ ,p)-reaction of ⁵⁷Fe as quoted above. ²⁴Na (²³Na) which can also be produced by (γ ,p) reaction of ²⁵Mg. ⁸⁰Br (⁷⁹Br) which is also possibly produced through (γ ,n) reaction of ⁸¹Br. ⁸²Br (⁸¹Br) was also visible. However,