Photon Activation Analysis

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In photon activation analysis (PAA), nuclides of the analyte elements in the material sample under study are converted to radioactive nuclides through exposure to high-energy photons. Characteristic radiation upon disintegration of these radionuclides (preferably γ quanta) is then measured with appropriate spectrometers. PAA is not an "absolute" method; hence, the samples under investigation have to be irradiated together with a comparative material sample (calibration material) with well-known chemical composition. After spectroscopic measurement of both samples, the quantitative evaluation is performed by comparison of the two resulting element spectra, basically following the same procedure as in most instrumental methods, e.g. ICP, AAS, etc. The particular advantages of this method are freedom from blank values; reduced danger of contamination; and, since frequent investigations can be carried out "nondestructively", easy handling of materials that are difficult to treat chemically, e.g. certain refractory metals, dusts, ashes, etc. Another advantage is the option to study very small samples (a few milligrams) as well as very large ones (up to kilogram amounts). Basically, there are no limitations concerning the nature of material studied but matrices like lead or other heavy elements raise the limit of detection considerably, and separation techniques have to be used.

1 INTRODUCTION

1.1 Basic Principle of Photon Activation Analysis

From the large number of analytical methods, activation analysis techniques are the only ones that are based on nuclear reaction. The material sample studied is exposed to high-energy radiation, which can be partly absorbed by a nucleus in the sample. Thus the nucleus is excited to a high-energy level, which can decay through quasi-prompt emission of a nuclear particle or photon. The product nuclide produced is mostly radioactive, and therefore emits delayed radiation. Both this and the aforementioned prompt radiation can be measured using appropriate radiation detectors. By evaluating the energy and the count rate of the particles detected, qualitative and quantitative analyses of the target material under study can be performed. Thus, it is clear that only isotopes of the elements can be determined directly and not the chemical species. A large variety of particles can be used for activation, namely, uncharged ones (neutrons and photons) or charged particles like protons, deuterons, tritons, and even heavier ones. Mostly thermal neutrons from nuclear research reactors are used since this technique offers the highest average analytical sensitivity. During photon activation, the target nucleus is activated by photonuclear reaction. This is induced to "normal"

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material at high energies, usually not below 10 MeV. The photonuclear reaction data of the elements suggest an activation energy around 30 MeV regarding analytical sensitivity and interfering reactions, respectively. This energy is best achievable with bremsstrahlung sources like high-power linear accelerators or microtrons.

Favorable irradiation parameters are 30-MeV electron energy at 100–150-μA mean electron beam current. With the help of suitable radiation spectrometers, e.g. high-resolution germanium detectors connected to appropriate pulse processing electronics, photon (γ or characteristic X ray) spectra can be measured.

1.2 Advantages/Drawbacks of Photon Activation Analysis; Scope of Application

Simultaneous multicomponent analyses can be carried out mostly without chemical separations, sometimes even nondestructively. Moreover, partly extreme sensitivities can be achieved, and some elements can be analyzed whose determinations are problematic using other techniques, e.g. light elements like carbon, nitrogen, oxygen, and fluorine. However, radiochemical separation steps are required in this case. A further advantage is the relative freedom from blanks in many cases; after bremsstrahlung exposure, undesirable surface contaminants can be removed from the sample and the recontamination that eventually occurs is inactive, and thus can be disregarded. Since the activation and measuring process is independent of the chemical status of the component studied, a large variety of matrices can be analyzed. Photon activation has been applied in several areas including

- geo- and cosmochemistry;
- environmental, biological, and medical science;
- raw material, industrial product, and high-purity material analysis;
- archeological and forensic science; and
- certification of reference materials.

The disadvantages of the method are common to all activation analysis techniques, e.g. the instrumental equipment costs. A high-performance germanium spectrometer costs US $40 000, and this does not include the permanent costs of maintenance and liquid nitrogen supply. The purchase price for an appropriate high-power photon source is in the million dollar range. Furthermore, a licensed radiation laboratory and additional personnel qualification are required for work with radioactivity. Finally, the handling of radioactive waste unavoidably produced during activation analysis might be problematic in some cases.

1.3 History of Photon Activation Analysis

The first photonuclear experiments were performed by Chadwick and Goldhaber(1) in 1934. They detected the photodisintegration process of deuterium bombarded with high-energy γ photons emitted from radionuclides. These can be used for photon activation in a few application cases only (Section 2.1.1). The first analytical application of photodisintegration apparently dates back to the late 1930s. This would make PAA contemporary with the other activation methods (Neutron activation: von Hevesy and Levy(2); activation with charged particles: Seaborg and Livingood(3)). However, there is no contemporary report available about this pioneering work. The first report about analytical use of γ-induced photoexcitation dates back to 1954.(4) Also, in 1954, the application of a betatron for PAA of oxygen was reported by Basile et al.(5) First, Geiger–Müller counters were used for radiation counting. Later, scintillation spectrometry, mostly using thallium-doped sodium iodide crystals was applied, and NaI(Tl) counters have been in use till now, particularly for the determination of light elements like C, O, N, and F. With these spectrometers, multicomponent γ spectrometry could be performed, and thus this was the beginning of instrumental multielement PAA. Since the beginning of the 1960s, high-resolution γ-ray spectrometry developed dramatically with the introduction of the Ge-based semiconductor detector and the multichannel analyzer. Data processing by computer was also introduced at this time. PAA has been applied to a large variety of materials as a complementary technique to neutron activation analysis (NAA). The analysis of light elements in many matrices, high-purity materials in particular, has been very important in the field of material science and technology and will be of interest in the future as well.

1.4 Basic Literature and Data Compilations

Engelmann(6) introduced PAA in "Advances in Activation Analysis" in which the principle of PAA and the application to light element analysis were explained in detail. "Photon Activation Analysis" by Segebade et al.(7) is a comprehensive textbook of PAA, containing more than 1200 literature references and many useful tables, such as a list of usable and competing photonuclear reactions as well as a list of γ-ray and X-ray energies. Kushelevsky(8) presented a short guide of PAA, in which the principles and applications of the method are concisely summarized. Toms(9) compiled the photonuclear reaction products and their γ-ray energies, while Williams et al.(10,11) collected γ-ray spectra of 40–44-MeV photon activation products. Lutz and Segebade(12) published a two-dimensional (half-life vs. γ-ray energy) map of photonuclear reaction products and Kato(13)

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obtained sensitivities of 71 elements in PAA using 30-MeV bremsstrahlung. An extended compilation of further basic literature on PAA can be found in the textbook of Segebade et al. (Ref. 7, p. 443ff). See Section 5.1.

2 PHOTON REACTION

The interaction of nuclei and photons usually occur at elevated photon energies. The cross section of this reaction is mainly dependent on the probability of photon absorption. A schematic representation of the cross section of the photon absorption is shown in Figure 1 (Ref. 7, p. 31).

2.1 Activating Photon Sources

2.1.1 Radionuclide Sources

The first photon reactions detected were induced by γ emission of radionuclides (Section 1.3). For the detection of deuterium, beryllium, and some fissile elements by photodisintegration, strong ^{124}Sb sources have been used almost exclusively.(14) However, other sources were also used in some exceptional cases. Also, radionuclide-induced photoexcitation of elevated nucleus energy states is restricted to a few advantageous cases. ^{24}Na, ^{60}Co, ^{116m}In, and ^{182}Ta have been used as sources of exciting γ emission (Ref. 7, p. 58). Higher energies can be achieved through γ radiation promptly emitted during nuclear reaction of some elements (Ref. 7, p. 57). However, for different reasons, these sources normally are of limited use for PAA.

2.1.2 Electron Accelerators

The disadvantages of the isotopic sources mentioned earlier can be eliminated by using bremsstrahlung beam produced by electron accelerators for photoactivation. The achievable photon fluxes usually outrange those of radionuclide sources by orders of magnitude. Moreover, the effective cross section is significantly enlarged since the bremsstrahlung energy is continuous with the electron energy. Finally, photon energies can be produced, which are much higher than obtainable, with any isotope or nuclear reaction source. Therefore, by activating with high-energy bremsstrahlung beam, photonuclear reactions can be induced in the target material, whereas – except very few cases – only isomeric-state excitation can be achieved by γ rays from isotopes (see the preceding text).

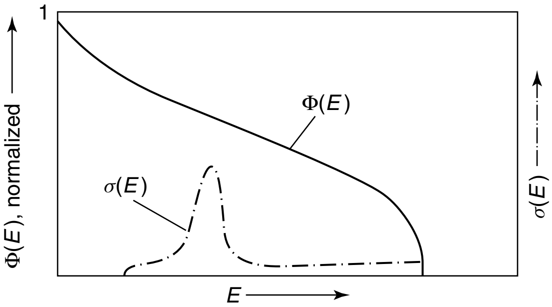

Figure 1 Bremsstrahlung continuum and photonuclear cross section. $\Phi(E)$, energy-differential bremsstrahlung photon flux density and $\sigma(E)$, energy-differential cross section. (Reproduced from Verlag Walter de Gruyter GmbH & Co. KG by permission of Segebade et al.(7)).

An accelerator is a device to accelerate charged particles such as electrons, protons, or heavier ions up to a kinetic energy through which they are enabled to induce reactions upon the electron shell or the nucleus of a target atom. In PAA, electrons produced by accelerator are absorbed by a layer of metal with high atomic number, usually tungsten, tantalum, platinum, or gold. About 50% of the kinetic electron energy is converted into bremsstrahlung, which is used for activation; the rest is converted into heat that makes cooling of the target and samples necessary. The bremsstrahlung beam is directed coaxially with the electron beam axis in forward direction. The apical angle is reversely proportional to the electron energy; at 30 MeV it is a few degrees,(8) thus producing an extremely inhomogeneous photon beam. One has to distinguish primarily between electrostatic (Cockcroft–Walton generator, Van de Graaff generator) and cyclic accelerators (linear accelerator, betatron, and microtron). Also, one has to distinguish between linear and circular machines, according to the accelerated particle path geometry. In static accelerators, electrons are accelerated by a constant high voltage potential. The maximum achievable particle energy is directly dependent on the maximum high voltage of the individual machine. In cyclic accelerators, electron energies are achieved by multiple application of comparatively low voltages upon the electrons. The maximum achievable energy is dependent upon various parameters.

The accelerators suitable for the production of bremsstrahlung usable for photon activation are Van de Graaff generator, linear accelerator, betatron, and microtron. However, in the majority of all applications, either linear accelerators or, to a lesser extent, microtrons have been used. Electron sources of comparatively low output energy (a few tens of megaelectronvolt) and high power (up to several tens of kilowatts) are most suitable for PAA. However, only a few types of accelerators are suitable for PAA, since modern accelerators are designed for the production of much higher energies to primarily meet the demands of nuclear and particle physicists.

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Regardless of the type of activating radiation source, but accelerators in particular, should be equipped with a fast pneumatic sample transfer facility. Thus, short-lived radionuclides can also be measured (see e.g. Ref. 7, p. 90).

More recently, the problem of large-volume photon activation was accessed to improve the representativeness of results if large amounts of material have to be analyzed. An electron beam scanning facility was developed so as to create a large-volume bremsstrahlung field usable for activation of samples up to multikilogram amounts.(15)

2.2 Isomeric-state Excitation

The inelastic reaction that is expressed by (γ, γ') can be induced by the irradiation of low photon energies. Target nuclei are excited to isomer levels, subsequently decaying back into the ground-state isomeric transition (IT) by emission of γ radiation. The cross-section integrals of (γ, γ') reactions are very small, and only a few radioisotopes usable for PAA are available, e.g.

$$\begin{aligned} &{}^{107}\mathrm{Ag}(\gamma, \gamma')^{107\mathrm{m}}\mathrm{Ag}\text{–IT} \\ &\quad \longrightarrow {}^{107}\mathrm{Ag}\ (\text{half-life: } 44\,\mathrm{s},\ E\gamma: 93\,\mathrm{keV}) \end{aligned} \tag{1}$$

Using γ-ray sources for isomeric-state excitation, the analytical sensitivity frequently suffers from unsuitable energy of the activating radiation. Since the width of the isomeric resonance cross section is extremely small, the direct isomeric excitation is unlikely (Figure 1). Thus, only the Compton scattering due to the γ emission of the exciting source can be exploited.

2.3 Photonuclear Reaction

A photonuclear reaction is usually characterized by the "giant dipole resonance" also called *giant resonance*, because this type of reaction has the largest cross section among the various types of photonuclear reactions. When the wavelength of the photon becomes similar to the diameter of nucleus, the photon can be absorbed by the target nucleus through the electric dipole resonance mechanism with a high degree of probability. This phenomenon is interpreted by the fact that a collective oscillation of all protons against all neutrons is induced by the electromagnetic wave. The maximum cross-section region is located at about 14 MeV for heavy elements to about 25 MeV for light elements. After photon absorption, one or two neutrons and/or protons or higher-order particles can be released because the binding energy of one nucleon is about 10 MeV. At 60 MeV, where the wavelength approximately equals the diameter of the deuteron, a neutron–proton pair in a nucleus is likely to absorb the photon. As a result of this reaction, called *quasi-deuteron reaction*, a proton and neutron pair is emitted. In this energy region, two or more nucleons can also be released from the target nucleus by a direct process and many kinds of reaction products are formed. The cross sections of the direct process are much smaller than that of the giant resonance region. Above 150 MeV, the total photoabsorption cross section increases again because of the photomeson production. Various reaction products are then produced. However, the latter two types of photoreaction are not suitable for analytical purposes, but rather have to be considered as sources of interference.

2.3.1 Photoneutron Reaction

If the excitation energy of the nucleus is higher than the binding energy of a nucleon (neutron, proton) or a heavier particle, e.g. an α particle, a neutron or a charged particle may be emitted from the nucleus instead of electromagnetic radiation. Figure 2 schematically shows the total absorption cross section in the photon energy region up to 25 MeV for a nucleus with medium atomic number.

Below the nucleon emission threshold – $E_{\mathrm{th}}\ (\gamma, n)$ – only elastic and inelastic scattering contribute to the total photon absorption cross section, which exhibits a few isolated absorption lines in this region. At higher energy, the excited nuclear state may decay by photon or nuclear emission. Owing to the very short lifetime of levels above the nucleon emission threshold, the absorption lines become increasingly broad. At even higher energy, the nuclear level spacing is so small that the excited states partially overlap and the photon absorption leads to collective excitation of all nucleons. This is the giant resonance region mentioned earlier. The total cross section in this region is composed of the contributions of elastic and inelastic scattering and emission of a single nucleon, more than one nucleon, or a composite charged particle. For medium and heavy nuclei, the emission of protons and other charged particles is inhibited by an electrostatic potential wall called the *Coulomb barrier*. Here, the total photon absorption cross section is nearly completely given by the total photoneutron cross section. For analytical purpose, the simplest photoneutron reaction type (γ, n) is most important. Consequently, the giant resonance structure is clearly pronounced in the $(\gamma, 1n)$ cross sections, too. Of course, the resonance parameters are slightly different from those of the total photoneutron cross section.

The (γ, n) threshold shows a relatively smooth decrease from more than 15 MeV for light nuclei down to about 8 MeV for heavy nuclei. At several values of the atomic number, slight discontinuities exist that reflect the nuclear shell structure. For analytical purposes, the achievable specific saturation activity is an interesting value. It is

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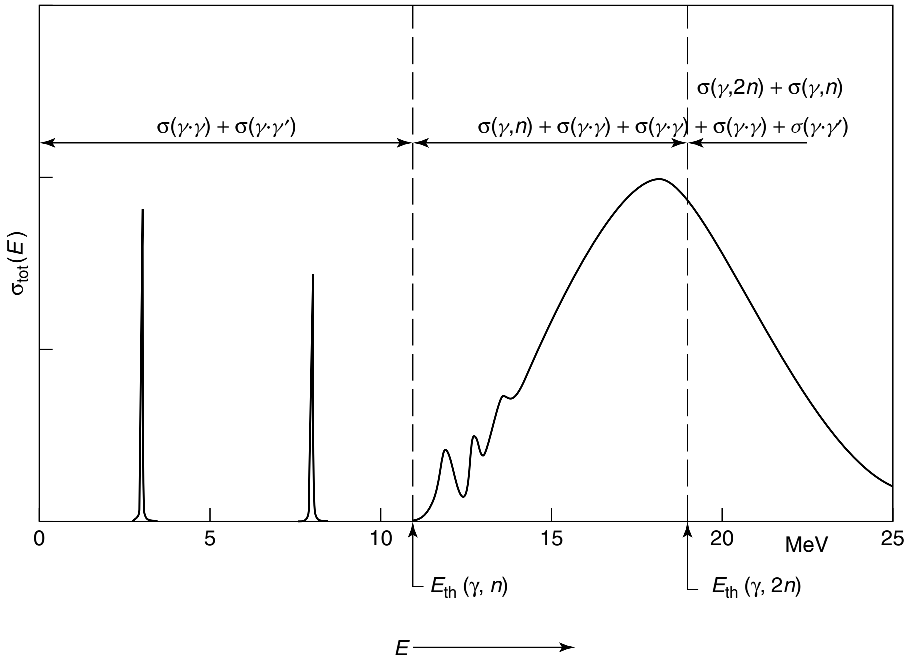

Figure 2 Total (γ, γ') and (γ, xn) absorption cross section, schematically. σ_{tot}, total photon absorption cross section and E_{th}, threshold energy. (Reproduced from Verlag Walter de Gruyter GmbH & Co. KG by permission of Segebade et al.$^{(7)}$).

proportional to the effective cross section of the nuclear reaction:

$$\sigma_{\text{eff}} = \int_{E_{\text{th}}}^{E_{\max}} f(E) \cdot \sigma(E)\,\mathrm{d}E \qquad (2)$$

where $f(E)$ is the normalized continuum of the activating photons (weighting function).

The bremsstrahlung-weighted cross section rapidly increases with the atomic number. For medium and heavy nuclei, it is approximately proportional to the square of the atomic number. Thus, by irradiating heavy elements in a photon beam much higher activities can be produced than in light elements.

2.3.2 Higher-order Photonuclear Reaction; Emission of Charged Particles

Sometimes no analytically suitable radionuclides are produced in a given element by (γ, n) reactions. Then higher-order reactions such as $(\gamma, 2n)$ or even $(\gamma, 3n)$ must be used. The threshold energies for $(\gamma, 2n)$ reactions, however, are nearly twice as high as those of (γ, n) reactions and the peak cross sections are considerably lower. Therefore, the achievable saturation activities and, consequently, the analytical sensitivity are much lower than for (γ, n) reactions. If an electron accelerator is used as a photon source, the induced activity can be increased by using a higher electron energy because the effective cross section increases with the bremsstrahlung energy due to a better overlap of the photon spectrum with the cross-section curve.

The emission of charged particles from an excited nucleus is hindered by nuclear forces and by the Coulomb barrier (Section 2.3.1). The attracting nuclear forces are responsible for the binding energy of the particle, which is identical with the threshold energy of the photonuclear reaction. Even if the photon energy exceeds the binding energy of the charged particle, its emission probability remains very low because it is enclosed in the Coulomb barrier. Nevertheless, there is a nonzero probability for the particle to be transmitted through this barrier by the quantum mechanical tunnel effect. As a consequence, the photonuclear cross section for charged reaction products slowly rises above the threshold and then strongly increases as the photon energy exceeds the coulomb barrier. Owing to the high effective threshold and the low cross section, it is difficult to observe $(\gamma$, charged particle$)$ reactions for heavy nuclei. In several advantageous cases, $(\gamma$, charged particle$)$ reactions have been utilized for the production of carrier-free radionuclides.$^{(16)}$

2.4 Photofission

If fissile nuclei are highly excited by photon absorption, de excitation by fission is an important reaction mechanism. Photofission contributes significantly to the total reaction cross section. In the practical analytical work, however, the fission products have to be considered as sources of interference.

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2.5 Neutron-induced Reaction

In practical PAA work, one sometimes encounters radionuclides that can only be attributed to neutron-induced reactions. The neutron source responsible for these reactions is the bremsstrahlung converter of the electron accelerator. In the heavy metal of the converter, photoneutrons are produced by the bremsstrahlung, thus yielding a considerable neutron flux density distributed isotropically(17) at the irradiation position of the sample. The shape of the neutron spectrum depends on the material in the vicinity of the bremsstrahlung converter. Besides the primary photoneutrons, a large low-energy partition is produced by moderation of the primary neutrons in the surrounding material. Therefore, two types of neutron-induced reaction may occur in the sample. Low-energy neutrons may be captured by (n, γ) reactions and neutrons with sufficiently high energy may induce threshold reactions, e.g. (n, p) or (n, α) processes. By (n, γ) reactions, in contrast to the complementary (γ, n) reactions, mostly neutron-rich β^- emitters are produced. This neutron reaction type is most frequently observed in PAA. In some cases, the respective product nuclides have been found analytically usable. For example, routine analyses of several elements in air dust filters have been carried out successfully by analyzing vanadium and manganese through activation with photoneutrons.(18) However, frequently neutron reactions appear as sources of interference.

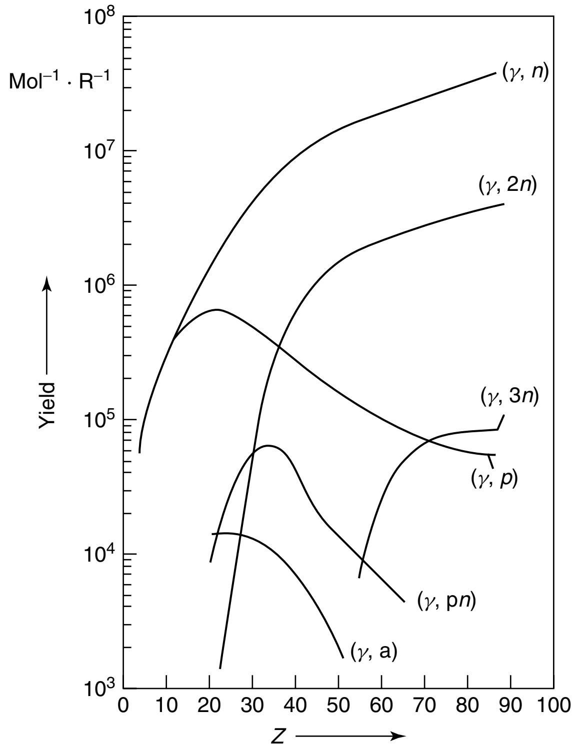

Figure 3 Yields of photonuclear reactions for 30-MeV bremsstrahlung as a function of the atomic number. (Reproduced from Verlag Walter de Gruyter GmbH & Co. KG by permission of Segebade et al.(7)).

2.6 Photonuclear Reaction Yields

The yield of a photonuclear reaction may be defined in many different ways with regard to the irradiation time and other physical irradiation parameters. In Figure 3, production rates of different photonuclear reaction types are plotted over the atomic number of the target element in order to compare the yields obtained by the different reaction types detected after exposure to 30-MeV bremsstrahlung.(13) Thus, the plotted curves represent the dependency of the effective reaction cross section at 30-MeV bremsstrahlung on the atomic number of the target nuclide. The yield curves for the photoneutron reactions – (γ, n); $(\gamma, 2n)$; $(\gamma, 3n)$ – monotonically rise with increasing atomic number. The (γ, n) yield is higher by more than a factor of 10 than the $(\gamma, 2n)$ yield and higher by about three orders of magnitude than the $(\gamma, 3n)$ yield. The yield of (γ, p) reactions is nearly comparable to the (γ, n) yield up to $Z = 20$, but for high atomic numbers the (γ, p) yield curve rapidly declines and falls below the $(\gamma, 3n)$ curve because of the increasing Coulomb barrier (Section 2.3.2). In the case of charged particle emission, the yield curve has a pronounced maximum and a monotonic decline toward higher atomic number. The yield values of $(\gamma, n\mathrm{p})$-, (γ, α)-, and $(\gamma, \alpha n)$ reactions are so small that they are rarely useful for analytical purpose but must be regarded as eventual sources of interference. Yield data collections for other activation energies were published by several authors, e.g. Oka et al.(19) and Kato et al.(20) Systematic studies at different activation energies were performed by Masumoto et al.(21) For analytical applications, however, it is more appropriate to refer to the activity at the end of fixed standard irradiation time and conditions, and for a standard target element mass. Compilations of such yield data were published by Engelmann(22) and Segebade et al. (Ref. 7, p. 305ff). These data were obtained by experiment. Calculated analytical sensitivities were published by Lutz.(23)

In order to achieve the highest possible analytical sensitivity, the electron energy of the accelerator has to be adjusted well above the giant resonance excitation energy. In the daily laboratory practice, electron energies around 30 MeV have been proven as a good compromise between achievable sensitivity and unavoidable interference due to complex spectra or by competing reactions, respectively.

2.7 Properties of Product Radionuclides

In Table 1, selection of photon reactions usable for PAA are compiled. Quasi-complete compilations can be found

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Table 1 Analytically usable photonuclear reactions; a selection

Element	Reaction	Half-life	E_{Ph} (keV)	S^a (μg)
C	$^{12}C(\gamma, n)^{11}C$	20 min	511^b	0.1
N	$^{14}N(\gamma, n)^{13}N$	9.96 min	511^b	0.02
O	$^{16}O(\gamma, n)^{15}O$	2 min	511^b	0.05
F	$^{19}F(\gamma, n)^{18}F$	110 min	511^b	0.001
Na	$^{23}Na(\gamma, n)^{22}Na$	2.6 years	1275	15
Cl	$^{35}Cl(\gamma, n)^{34m}Cl$	32 min	146	0.005
Ca	$^{44}Ca(\gamma, p)^{43}K$	22.2 h	372	0.5
Cr	$^{52}Cr(\gamma, n)^{51}Cr$	27.8 days	320	0.3
Ni	$^{58}Ni(\gamma, n)^{57}Ni$	36 h	1379	0.06
As	$^{75}As(\gamma, n)^{74}As$	17.77 days	596	0.05
Zr	$^{90}Zr(\gamma, n)^{89}Zr$	78.4 h	909	0.03
Cd	$^{116}Cd(\gamma, n)^{115}Cd$ $^{115}Cd(\beta^-)^{115m}In$	53.38 h	336	0.05
Sb	$^{123}Sb(\gamma, n)^{122}Sb$	2.7 days	564	0.01
I	$^{127}I(\gamma, n)^{126}I$	12.8 days	388	0.04
Ce	$^{140}Ce(\gamma, n)^{139}Ce$	137.5 days	166	0.06
Tl	$^{203}Tl(\gamma, n)^{202}Tl$	12.2 days	440	0.04
Pb	$^{204}Pb(\gamma, n)^{203}Pb$	52.1 h	279	0.1
Bi	$^{209}Bi(\gamma, 3n)^{206}Bi$	6.24 days	804	10
U	$^{238}U(\gamma, n)^{237}U$	6.75 days	59.5^c	0.001

[a] Sensitivity at standard conditions (Ref. 7, p. 305ff).
[b] To be measured after radiochemical separation.
[c] To be measured with a low-energy photon (LEP) spectrometer (Section 3.1.3).

in Segebade et al.,(7) p. 171ff. See Section 5.1. From the elements H to B, no analytically useful radionuclides are produced. From carbon, nitrogen, oxygen, and fluorine, pure β^+ emitters are produced by (γ, n) reactions. These radionuclides do not emit nuclide-specific γ rays and can be analyzed only by means of the unspecific 511-keV annihilation radiation, which originates from positrons emitted by neutron-deficient radioactive nuclei absorbed in the surrounding material. In the annihilation process, the positron captures an electron from the material, thus forming the so-called positronium, which then decays by conversion of the positron and electron rest mass (511 keV each) into two 511-keV photons simultaneously emitted into opposite directions. Since only this radiation is available for the analysis of the light elements up to fluorine, in general, a chemical separation of these elements must be performed (Section 4.1).

In the case of medium and heavy elements, however, the radionuclides produced by photonuclear reactions emit – with very few exceptions – γ radiation, which is characteristic for the nuclide. Owing to the specific γ radiation, an instrumental multielement analysis of medium and heavy elements using high-resolution γ-ray spectroscopy becomes possible. By photoneutron reactions, in general, neutron-deficient nuclides are produced from the nuclides of the target element. Their predominant decay mode for low atomic number is β^+ emission, which leads to excited states of the decay product accompanied by subsequent γ-ray emission or without γ emission directly to the ground state (as in the case of ^{11}C, ^{13}N, ^{15}O, ^{18}F, see preceding text). Neutron-deficient radionuclides with medium and high atomic number decay through two competing modes, namely, β^+ emission and electron capture (EC). EC, in general, also leaves the decay product in an excited state, which returns to the ground state through γ-ray emission. Instead of positron emission, the nucleus captures an orbital electron – predominantly a K electron – thus leaving an electron hole in the K shell. When this hole is subsequently filled by an electron from a higher shell, characteristic X radiation is produced or an Auger electron is emitted. For heavy nuclei, X-ray emission is favored. The X-ray energy is proportional to the square of the atomic number. In the case of heavy elements, X-ray spectroscopy can be used as an alternative to conventional γ-ray spectroscopy because the X-ray photons have a conveniently high energy (about 100 keV) and the emission probability is sufficiently high (Section 3.1.3).

In the case of a target element having several stable isotopes, this series of isotopes may be interrupted by one or more β^--emitting radionuclides, which can be produced from this element through photoneutron reactions and analyzed by conventional γ-ray spectroscopy. The most important production mode of β^--active radionuclides in PAA, however, is the (γ, p) reaction, which reduces the number of protons in the nucleus so that a neutron-rich radionuclide is generated. In most cases, these radionuclides can be analyzed by γ-ray spectroscopy. There are only a few unfavorable cases in which the reaction product does not emit nuclide-specific γ rays. In general, the nucleus originating from a photonuclear reaction is not produced in its ground state but in an excited state. The excitation energy of the produced nucleus is released by γ-ray emission. Since the lifetimes of the excited states are generally very short, this so-called prompt γ radiation is emitted almost immediately after the formation of the product nucleus, thus leaving the nucleus in its ground state. If the ground state of the product nucleus is unstable, a radionuclide is produced that is transformed into a decay product. Like the photonuclear reaction, the radioactive decay of the product nucleus leads to excited states of the decay product. It is the de excitation γ radiation of the decay product, which is normally analyzed. In practice, the prompt γ radiation from the photoreaction product is not used for analytical purpose. However, if the reaction product has an isomeric state with sufficiently long half-life, the analysis of the γ radiation from the reaction product can be performed in the laboratory after irradiation. Particularly simple is the case in which the reaction product is a stable nuclide with an isomeric state. With a certain probability, by the reaction

$$^{136}\mathrm{Ba}(\gamma, n)^{135\mathrm{m}}\mathrm{Ba{-}IT} \longrightarrow {}^{135}\mathrm{Ba} \tag{3}$$

The product is formed in the isomeric excited state with 29-h half-life. The 268-keV γ radiation from the transition to the ground state of ^{135}Ba can be measured conveniently off-line.

In other cases, the reaction product having an isomeric state is unstable. The isomer originating from the photonuclear reaction can decay to its (unstable) ground state, accompanied by γ emission and then the ground state is transformed subsequently into an excited state of the decay product, followed by γ-ray emission.

$$^{45}\mathrm{Sc}(\gamma, n)^{44\mathrm{m}}\mathrm{Sc{-}IT} \longrightarrow {}^{44}\mathrm{Sc}{-}\beta^{+} \longrightarrow {}^{44}\mathrm{Ca} \tag{4}$$

Even longer decay chains might occur.

Sometimes the isomeric reaction product directly transforms into the decay product; then only the γ radiation from the de-excitation of the decay product is observed.

$$^{103}\mathrm{Rh}(\gamma, n)^{102\mathrm{m}}\mathrm{Rh{-}EC} \longrightarrow {}^{102}\mathrm{Ru} \tag{5}$$

Isomeric states exist only in medium and heavy nuclides.

3 RADIATION SPECTROMETRY

At the time before the invention of energy-discriminating devices, a separation of the components to be determined from the sample matrix was necessary, followed by separate measurements of the analytes using either gas counters or neutron detection methods. After the advent and general availability of photon spectrometers, almost invariably, these devices have been utilized for activation analysis since most of the product nuclides of any nuclear activation process emit typical photon spectra including γ and specific X radiation, which can easily be discriminated. Thus, multielement analyses became possible. Product nuclide radiation other than photons have been used in exceptional cases only, e.g. if the product nuclide does not emit specific photon energies (Section 3.4).

3.1 Photon Spectrometry

Two basic principles of photon counting have been in use, namely the detection by scintillators exploiting the radioluminescence effect and the detection by semiconductor crystals. By both detector types, photons are converted into electric pulses whose heights are quasi-linearly dependent on the energies of the absorbed photon quanta – at least in the energy region of interest in PAA (5–3000 keV). The pulses are then amplified, reshaped, and finally discriminated by their heights with the help of electronic devices. These are discussed separately in the following sections. The resulting spectra are then processed by computer.

To summarize, the parts of a photon spectrometer necessary for activation analysis are as follows:

1. *Detector*: scintillation crystal plus photomultiplier or semiconductor crystal; operating voltage supply.
2. *Preamplifier*: voltage or charge sensitive, plus power supply.
3. *Linear spectroscopy amplifier*: including baseline restorer, pileup rejector, and pulse shaping unit.
4. *Analog-to-digital converter* (ADC; see below, Section 3.2.3) .
5. *Pulse-height analyzer* plus data storage and data output unit, which is coupled to a data dumping unit or processing device, e.g. computer.

There are various other hardware setups for special procedure requirements, but the instrumentation that is normally needed consists of those listed earlier.

In recent years, the so-called analog electronic described earlier is being replaced by digital signal processing (DSP) systems. In these systems, the signal from the preamplifier is directly digitized. All other

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pulse-shaping processes are then done by using digital processing algorithms.

3.1.1 Scintillation Detectors

Light flashes are produced upon absorption of high-energy radiation by several materials via secondary electrons from photoelectric effect, Compton scattering, or interactions due to pair production (Section 3.2). This so-called radioluminescence is measured (and analyzed in favorable cases) using appropriate light detectors connected to pulse processing electronics. Fundamental work on the theory and practice of inorganic scintillators by Hofstadter and McIntyre(24) yielded that thallium-activated sodium iodide single crystals were the most suitable scintillators for γ detection. Light flashes are produced if X rays or γ photons are absorbed within the crystal. These flashes produce photoelectrons in a photocathode. The electrons are directed to a photomultiplier, which is connected to an operating voltage of about 1 kV. By secondary electron emission, the incident electron pulses whose heights show a linear dependency upon the energy of the incoming photons are amplified and then can be processed in the following electronic system of the spectrometer. In PAA, until now, scintillation detectors have been used particularly during light element analysis (Section 4.1).

3.1.2 Semiconductor Detectors

The most convincing advantage of semiconductor detectors is their excellent spectral resolution power as compared with that of scintillation crystals (see Figure 4). Until now, the energy resolution of high-purity germanium single crystals is superior to all other materials tested as yet. However, this and most of the other usable semiconductor detectors require cooling (mostly using liquid-nitrogen-operated cryostats), which complicates the handling of these detectors. The first operating lithium-drifted germanium detectors were developed by different working groups in the beginning of the 1960s using the ion drift process.(25)

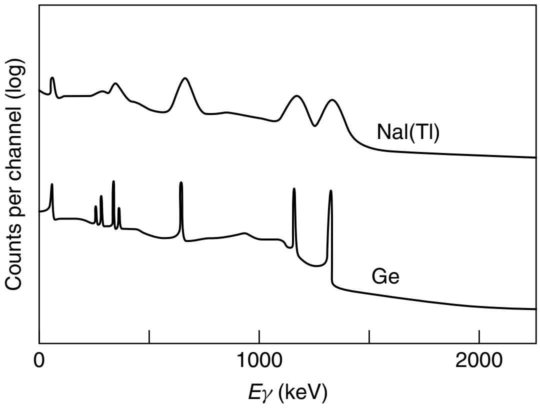

Figure 4 NaI(Tl) and Ge spectrum of ^{133}Ba, ^{137}Cs, and ^{60}Co. (Reproduced from Verlag Walter de Gruyter GmbH & Co. KG by permission of Segebade et al.(7)).

The operational principle of a semiconductor detector is comparable to that of an ionization chamber or a proportional gas counter. The radiation enters an electrically isolating single crystal – usually silicon or germanium – of which two oppositely located areas are used as electrodes to which an operating voltage is connected. If a photon interacts with the detector material, the resulting electrons from photoelectric or other interaction processes will produce a large number of subsequent pairs of electrons and electron defect holes. This cascade process is continued until the electrons have lost their energies insofar as they cannot produce any more charge carriers. Therefore, to a large extent, the number of the charge carriers (and thereby the height of the resulting electric pulse at the output) is exclusively dependent upon the energy of the absorbed incident radiation, not upon its kind. This is true since the energy, which is necessary to create an electron–electron defect hole pair, is independent from the kind and energy of the incident radiation. Also, thereby, as is the case in scintillation detectors, the resulting pulse height is proportional to the incident photon energy in the case of total absorption within the detector crystal.

3.1.3 Low-energy Photon Detectors

In PAA radionuclides, decaying by EC is produced predominantly during photon bombardment of medium-to-high Z elements. Since these products usually emit highly intensive X-ray fluorescence, the measurement of soft photon radiation using a LEP (low energy photon) diode is useful (Section 2.7). In this case, thin planar semiconductor crystals are used (Ge, Si, and, more recently, CdTe and CdZnTe(26)). The detector housing is equipped with a thin (several tenths of millimeters) beryllium window to allow the access of soft radiation to the detector crystal. The relatively small detector crystals have considerably better energy resolution capabilities than larger coaxial ones. However, the absolute resolution capacity rapidly decreases with increasing incident photon energy. Anyway, their resolution performance is brilliant and, therefore, they are especially suitable for characteristic X-ray spectra measurements. One problem in LEP spectroscopy is the strong self-absorption of the soft radiation within the measured sample. Therefore, one has to follow special precautionary measures to prevent erroneous data evaluation.

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3.2 Photon Counting Electronics

The standard components of electronic operation control, signal processing, and data acquisition and processing are (Section 3.1) detector operation bias supply, linear pulse preamplifier, spectroscopy pulse processor (also called *spectroscopy amplifier*), ADC, and pulse-height analyzer (single or multichannel operation). For the performance of the spectrometer, the main sources of deterioration are the electronic noise of the whole system and the instability of the pulse-amplifying units. Therefore, major attention has been paid to the noise level and the long-term operation stability of all spectrometry components. Furthermore, counting losses due to the dead time of the spectrometer (i.e. the time period in which the system processes a signal and cannot accept another) have to be accounted for. There are different approaches to the dead time handling at high count rates,(27) but in the routine procedure the best strategy is not to exceed a certain count rate, which is dependent upon the integral performance of the spectrometer (Ref. 7, p. 150f.).

3.2.1 Preamplifier

The primary purpose of the preamplifier is to optimize the coupling of a detector output to the rest of the spectrometer. More exactly, it provides the accurate analog conversion of the burst of electrons, resulting from absorption of the radiation energies in the detector, into a signal that can be conveniently transmitted to the measurement system. Another task of the preamplifier, especially its pulse entrance unit, is to minimize any source of noise, which may degrade the energy resolution capacity of the spectrometer. Briefly summarized, the preamplifier is used to derive a stable, precise, reproducible, and undisturbed output signal from the detector.

3.2.2 Spectroscopy Amplifier

The major role of the spectroscopy amplifier is to convert the preamplifier output signal into a form, which is most suitable for the subsequent ADC signal input. The most important features required are as follows:

Amplification: while the amplification level of the preamplifier is constant the output level of the spectroscopy amplifier can be selected so as to determine the energy range to be processed.
Baseline restoring: the output baseline level (usually at zero voltage) must be restored for each pulse so as to provide a reference level for the subsequent processing step (pulse-height analyzing and eventual digitization).
A *pole/zero cancellation* is provided, which enables monotonic return of the output pulse to zero baseline reference level so as to avoid undesired influence of over- or undershoot of the output pulse upon the height of a subsequent one.
Pulse shaping: Optimum system energy resolution requires a quasi-Gaussian-shaped amplifier output signal with adjustable half width; for different reasons, 4 μs is the best selection for standard γ-spectroscopy.
A *pileup rejection* circuit is included in high-quality amplifiers to avoid interference of sequential pulses interfering with previous ones. At high count rates, subsequent pulses are automatically inhibited until the output pulse has recovered to the baseline level.

To summarize, linear spectroscopy amplifiers are used to convert incoming pulses from the preamplifier into, ideally Gaussian-shaped, noise-free pulses whose heights are proportional to the photon energy incident to the detector. These pulses should arise on a stable, adjustable baseline. The amplifier should be able to process a count-rate range up to at least $5 \times 10^4\,\mathrm{s}^{-1}$ without any kind of pulse quality degradation.

3.2.3 Pulse-height Analyzer and Analog-to-digital Converter/Multichannel Analyzer

A pulse-height discriminator is required to keep track of the spectral distribution of the radiation. Nowadays, two types are used, namely single- and multichannel analyzer.

The differential pulse-height discriminator, also called *single-channel analyzer*, is used to trigger the data output device by pulses whose heights fall within an adjustable “window” (also called *channel*) between two pulse-height (or energy) levels, mostly utilizing an anti-coincidence mechanism. Using a single-channel analyzer, all signals outside the window are discarded. In PAA, these devices are used for the analysis of the light elements (C, N, O, F) where only the 511-keV annihilation radiation signals are processed after chemical separation of the above-mentioned elements from the matrix (Section 4.1). In this case, the window is permanently positioned to measure the 511-keV annihilation line.

If more than one pulse height (or radiation energies, respectively) have to be measured, a *multichannel spectrometry system* has to be used. This contains the following elements:

1. a quantizing and digitizing device (ADC) that associates each incoming signal with a specific amplitude channel (see the preceding text);
2. a data storage device (memory), which keeps track of the number of signals that fall in each of the amplitude channels;
3. a display service that allows immediate visual inspection of the collected data; and

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4. a data output facility of any kind, which allows either data storage on any carrier or immediate data processing.

Modern multichannel analyzers are integrated in a standard PC, either as external unit connected via serial, parallel, or universal serial bus (USB) input or as plug-in card. The number of pulse-height channels is selectable, usually starting at 2^8 up to 2^{15} (256 to about 34 000). The output data range ("conversion gain") of the ADC has to be set accordingly.

3.3 Pulse-height Spectrum

Three relevant processes for photon detection can be distinguished, namely, (i) the photoelectric effect, (ii) the Compton scattering, and (iii) the pair production. The probability of their occurrence within a given element is contingent upon the energy of the incident photon. Among these, the photoelectric effect is of major analytical interest, while all others, if occurring, have to be considered as sources of interference.

In the *photoelectric process,* all of the energy of the incident photon is absorbed by a bound electron of a target atom reappearing as kinetic energy of this electron as it is ejected from the atom. The energy of the ejected electron will then equal the difference between the energy of the incident photon and the binding energy of the level from which the electron was ejected. If the incident photon energy exceeds the K shell binding level, interaction will take place principally with electrons of this shell. As a result of this process, the atom is left with a vacancy in this shell, resulting in the emission of specific X-ray quanta or Auger electrons. In the low photon energy region, the photoelectric effect dominates. It is probable that a fraction of the above-mentioned X rays will escape from the detector. In this case, signals that are representative of the full incident photon energy minus the emitted X-ray energy will be detected. The important characteristic of the photoelectric effect is that monoenergetic photons, which interact by the photo process, will produce monoenergetic photoelectrons within the detector volume that results, through different subsequent processes within the detector, in a uniform, discrete signal which can then be processed. However, this signal might be produced not only by a single photoelectric event but will also appear always if the total incident photon energy is absorbed by the detector body. This might as well occur by a sequence of different mechanisms.

In the *Compton scattering process,* incident photons are scattered by target atom electrons accompanied by a partial energy loss. In this process, scattering generally occurs with electrons, which can be regarded as essentially free, and the energy of the incident photon is distributed between the target electron and the scattered photon. This distribution does not have a fixed value but ranges within a relatively large energy interval, depending on the incoming photon energy. Thus, the Compton process results in a broad electron energy distribution, and therefore, detector pulses originating from Compton scattering cannot be used for evaluation of photon spectra measured after activation, but rather are sources of interference, as noted earlier.

Pair production: if the incoming photon has an energy that exceeds the electron/positron pair rest mass ($= 1022\,\mathrm{keV}$), then production of this pair becomes possible. This process occurs in the coulomb field in the close neighborhood of the nucleus. The incident photon ray disappears and the pair is created. Its total energy equals the energy of the primary photon, and the kinetic energy of both particles equals their total energy minus their rest energy ($2m_ec^2 = 1022\,\mathrm{keV}$). Since the positron is unstable, as it comes to rest in the field of an electron, annihilation of the two particles occurs with the emission of two photons, the energy of which is equal to the rest mass equivalent of the pair ($2 \cdot 511\,\mathrm{keV}$). Interaction by the pair process in a detector will, therefore, result in an energy loss equal to the incident photon energy minus 1022 keV, if both 511-keV annihilation quanta escape from the detector. If only one of them escapes, a signal representative of the total incident photon energy minus 511 keV will appear.

Consequently, various kinds of interaction of photon rays, in energies exceeding 1022 keV, within a detector body will generally result in a quite complex pulse amplitude spectrum containing signals representative of any energy from zero up to full energy of the primary photon. Moreover, it is rendered even more complex by other effects, e.g. due to the close environment of the detector (Ref. 7, p. 109ff).

Other signals also appear that are not due to the measured sample activity at all; they originate from external radiation penetrating the detector shielding or from radioactive contamination within the shielding material. These signals are called *external background*. This background has to be known very well to avoid misinterpretations of pulse-height spectra obtained from unknown samples.

3.4 Nonphoton Measurement

Radiation other than γ, annihilation quanta, or X-ray fluorescence has been applied for PAA in a few exceptional cases only. Neutron counting has been used for the detection of photodisintegration of beryllium and some fissile elements (Section 2.1.1). Oxygen and fluorine were detected by delayed neutron counting.(28)

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Recently, phosphorus and nitrogen were determined by β^+ spectroscopy using a twin plastic scintillation spectrometer.(29)

4 ANALYTICAL APPLICATION

4.1 Analysis of Light Elements

The interest of PAA was mainly concentrated on the determination of carbon, nitrogen, oxygen, and fluorine. In the pioneer works on photonuclear activation analysis, the determination of these were described.(5,30) (γ, n) reactions yielding ^{11}C, ^{13}N, ^{15}O, and ^{18}F, respectively, have been used almost exclusively. Others have been applied in very rare cases only.(28) Since the named activation products emit β^+ radiation only, usually the 511-keV annihilation quanta are counted. However, the analyte nuclides normally have to be separated from the sample matrix after activation. In several advantageous cases, instrumental procedures can be applied(31) (see also Ref. 7, p. 326). Detailed descriptions of the PAA of light elements can be found in Segebade et al.,(7) p. 313ff.

4.1.1 Irradiation

Exposure periods are dependent upon the half-lives of the respective product nuclides. Typical values are 5 min for oxygen, 20 min for nitrogen, and ≥40 min for carbon or fluorine, respectively. Other values might be selected regarding particular conditions, e.g. radiolytical behavior of the sample matrix or the expected contents of the analytes. Since the bremsstrahlung beam exhibits a sharp radial and a slight axial flux gradient (Section 2.1.2), one has to take measures to provide equal dose rates received by the sample and the calibration material. This can be accomplished by rotating exposure positions or by flux monitors (Section 4.3).

4.1.2 Surface Treatment

Particularly for the analysis of ultra trace quantities, a complete removal of the contamination from outer source onto the surface of the sample is essential. In critical cases, this contamination can introduce deviations from the true value by orders of magnitude.(32) Three of the light elements under study (C, N, O) are major atmospheric components and thus contamination is most likely. In activation analysis, the surface contamination problem can be solved easily; once the surface is cleaned after activation, a subsequent recontamination may be disregarded since it is inactive and thus cannot interfere during measurement. Details about surface treatment are given in Segebade et al.,(7) p. 321ff.

4.1.3 Radiochemical Separation

4.1.3.1 Carbon Total combustion of the sample in a stream of oxygen (oxidizing fusion) is the fastest method of carbon separation.(33) The element may be present in almost any form, free carbon or chemically bound. Detailed descriptions of this procedure are given in Segebade et al.,(7) p. 337ff. However, other methods might be necessary depending upon the physicochemical nature of the sample matrix, e.g. separation of $^{11}CO_2$ by strong acids after combustion and subsequent absorption in alkali hydroxide solution. This can be applied in the determination of carbon in alkali metals.(34) Using heat extraction, carbon and nitrogen can be determined quasi simultaneously (Section 4.1.3.2). Detection limits for PAA of carbon varying from 1 to 500 ng have been reported.

4.1.3.2 Nitrogen In metals, nitrogen is normally present elementally; during heat extraction, mostly no chemical reaction of nitrogen takes place. It is evolved as N_2 or $^{13}N_2$ from the melted matrix. It can be analyzed simultaneously with carbon by oxidizing fusion under oxygen or inert gas atmosphere(35) or simultaneously with oxygen by reductive fusion under vacuum or inert gas atmosphere.(36) Radionitrogen can be collected with hot metal wire or granulate, e.g. calcium or titanium.(37) Sometimes, the Kjeldahl method has also been applied; ammonia is produced by dissolving the sample and reduction of the nitrogen. $^{13}NH_3$ is then collected with acids. Detection limits reported range from 10 to 700 ng for the radiochemical approach (Ref. 7, p. 359).

4.1.3.3 Oxygen Heat extraction using oxidizing fusion can also be used for simultaneous determination of oxygen and nitrogen. One difficulty of PAA of oxygen is due to the short half-life of ^{15}O (122 s). Thus, the procedure must be carried out quickly. Heat extraction with reductive fusion is used most favorably for radiooxygen separation. Graphite crucibles are used to provide a reducing environment so that, initiated by heating, all matrix-inherent oxygen is converted to carbon monoxide. This is carried by a vector gas through further processing steps (removal of particulate matter, undesired gases and water, oxidizing of $C^{15}O$ to $C^{15}OO$, and collection of carbon radiooxide with alkali media). Oxygen in alkali metals was applied by Lutz,(34) exploiting an isotopic exchange process between inactive and radiooxygen forming $H_2^{15}O$, which is then distilled and collected by saturated NaOH solution. Detection

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limits ranging from 10 to 300 ng have been reported for radiochemical PAA of oxygen.

4.1.3.4 Fluorine Other than the above-mentioned product nuclides, ^{18}F cannot be mobilized by normal heat extraction. Distillation procedures have been utilized normally. Intrinsically, the PAA of fluorine is the most sensitive among all light elements. Limits of detection in the subnanogram region have been achieved under practical laboratory conditions. Radiofluorine has been separated from any matrix mostly by distillation of hydrofluoric or fluorosilicic acid with various radiofluorine contents, e.g. $H_2Si^{18}F_2F_4$. Fluorine (including radiofluorine) is evolved by dissolution of the sample in a strong, concentrated acid, typically sulfuric or perchloric acid. After addition of some inactive fluorine compound, which serves as a carrier, hydrofluoric acid thus produced is either distilled as such or as fluorosilicic acid by vapor distillation. Frequently, radiofluorine has been preconcentrated before measurement, typically by precipitation as $Pb^{18}FC1$ or calcium radiofluoride. Different analytical procedures were reported in Wilkniss et al.[(38)] Reported detection limits vary between subnanogram amounts and 100 ng for the radiochemical approach.

4.1.4 Coincidence Annihilation Quanta Spectroscopy

The common photon energy produced in the positron emission of the nuclides under study (511 keV) is well measurable by scintillation detectors. Since in every positron annihilation two 511-keV photons are emitted simultaneously in opposite directions, there is the possibility of very efficient background suppression by coincidence counting using NaI(T1) crystal detectors arranged in a proper geometrical setup (Figure 5). Environmental background values of a few pulses per second have been reported.

The pulse-height windows of the single-channel analyzers (7) are adjusted to screen out the 511-keV full-energy peak. The pulses from the single-channel analyzer outputs are then fed into a coincidence pulse-processing unit (8). In the case of coincidentally absorbed annihilation quanta in both detectors, the coincidence unit will issue a pulse signal, which can then be processed further (9) in any desired manner, e.g. by multichannel scaling. Instrumental approaches, e.g. using computer-operated deconvolution of the multicomponent decay function are possible in a few favorable cases only (Ref. 7, p. 326).

The analytical results of annihilation radiation spectroscopy are eventually subject to several kinds of error sources. These are discussed in Section 4.4.

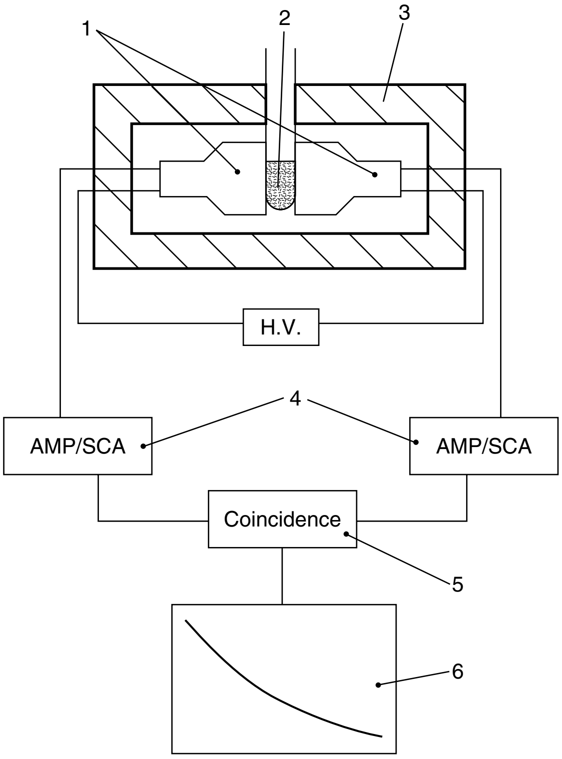

Figure 5 Photon coincidence measurement setup: 1, NaI(Tl) detectors; 2, radioactive sample; 3, lead shielding; 4, spectroscopy amplifier/single-channel analyzer; 5, coincidence pulse processing unit; 6, multichannel scaler. (Reproduced from Verlag Walter de Gruyter GmbH & Co. KG by permission of Segebade et al.[(7)]).

4.2 Multielement Analysis

In this section, only the solid samples are discussed; liquid or gaseous material has been analyzed by PAA in rare cases only. These analyses demand special procedures (Ref. 7, p. 410ff).

Multielement determinations of heavier elements using photon activation can be carried out radiochemically, analogous to the light element analyses described earlier, or instrumentally, i.e. without chemical separation steps. Normally, NaI(Tl) spectrometry, owing to poor energy resolution capacity, is unsuitable in this case. High-resolution semiconductor spectrometry has to be applied instead (Section 3.1.2 ff). In the following, the general analytical procedure is summarized. More details are given in Segebade et al.,[(7)] p. 410ff.

4.2.1 Sample Preparation, Transfer, and Irradiation

In PAA using an accelerator source with endstanding converter, various sample sizes and geometries can be exposed (Section 6). However, in most cases, an analysis of comparatively small samples is required, typically some tens of milligrams. If the samples are compact pieces,

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generally no special precautions have to be undertaken against surface contamination, since it can easily be removed after activation, especially in the case of metals to be analyzed. 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 analyzed, a postirradiation purification is not normally possible. Therefore, it is of use to run blanks if available. For different reasons, the most suitable material for packaging of solid samples and transportation to the irradiation position is aluminum (Ref. 7, p. 410ff). The samples are wrapped in aluminum foil and packed in aluminum rabbits for transportation in the pneumatic tube facility. Because of the radial and axial flux gradient of the activating beam, external (e.g. metal foils between the different material batches(39)) or internal flux monitors (Section 4.3) have to be applied. Also, these monitors correct for errors due to partial absorption of the activating photon beam by the sample matrix.

In special cases, samples cannot be unpacked after exposure, e.g. if the matrix was partly decomposed radiolytically or by heat during activation. In this case, the sample has to be wrapped in high-purity aluminum foil prior to irradiation and later measured. Thus, no interference will occur during spectroscopy.

Typical exposure periods vary between minutes (for short-lived products) and up to 5 h (for product half-lives of several hours and more). However, special irradiation parameters (irradiation periods, distance from the converter, eventual cooling, etc.) have to be set in critical cases, e.g. during analysis of the material that is subjected to radiolytical or thermal decomposition (e.g. organic/biological matrix) or volatile components (e.g. mercury compounds). These problems are discussed in detail in Segebade et al.,(7) p. 410ff.

4.2.2 Preparation for Counting – Photon Spectroscopy

The total decay period from the end of exposure to the start of measurement is dependent upon several parameters: the half-lives of the nuclides to be measured, the total activity of the sample, the time required for the sample preparation procedure, and eventually more. Compact samples are unpacked, and the surface is cleaned with appropriate agents (Ref. 7, p. 321ff). Powdered samples are unwrapped and transferred to an appropriate container for activity counting. Frequently, it has proven useful to mix the sample with cellulose powder and press it to a pellet of 15–20 mm diameter and less than 1 mm thickness. This geometry is of advantage, particularly, if both γ spectroscopy and LEP spectroscopy are required; self-absorption of softer photon radiation to be evaluated for analysis is thus reduced. Moreover, highly reproducible sample geometry is thus provided. The distance from the detector head has to be selected according to the total dead time of the spectrometer, however, at least several centimeters, depending upon the size and shape of the counting crystal. At smaller distance, geometry-related measurement errors increase dramatically. γ spectra should be collected in at least 4096 channels of the multichannel analyzer, but for X-ray fluorescence spectra 1024 channels are sufficient; the ADC range (conversion gain) has to be set accordingly. At lower channel numbers, loss of spectral resolution capacity is significant. The counting period has to be selected with respect to the activities to be counted. Starting with a few minutes for short-lived nuclides up to one day or more might be necessary, depending upon the activity of the respective analytes. Sometimes more than one measurement after stepwise increasing cooling periods might be performed so as to exclude spectral interference by short-lived nuclides. However, in the analytical practice, this procedure is frequently of doubtful value because of the excessive total time consumption, particularly if large series of samples have to be analyzed. In this case, other strategies will have to be found (Section 4.4.2).

The spectrum files should be stored immediately on appropriate mass storage devices, e.g. data CDs or USB solid-state storage devices (“data sticks”).

4.2.3 Spectrum Processing

Computer programs are used for processing the spectral data obtained by the multichannel analyzer. Usually the tasks of these programs are

- peak detection;
- peak centroid location;
- calculation of the respective radiation energy;
- net peak integration;
- peak multiplet unfolding;
- eventually peak assignment to radionuclides; and
- creation of a result file.

4.3 Calibration and Quality Control

The quantitative result of PAA is obtained by the number of counts within the spectral signals (peak areas) of the respective activation products. Going out from the general equation of nuclear activation,

$$A(t_\mathrm{i}, t_\mathrm{d}) = \frac{m \cdot L \cdot \Theta}{A_\mathrm{r}} \int_{E_\mathrm{th}}^{E_\mathrm{max}} \varphi(E) \cdot \sigma(E)\,\mathrm{d}E \cdot (1 - \mathrm{e}^{-\lambda \cdot t_\mathrm{i}}) \cdot \mathrm{e}^{-\lambda \cdot t_\mathrm{d}} \tag{6}$$

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The peak area is defined by

$$P(t_\mathrm{i}, t_\mathrm{d}, t_\mathrm{c}) = \frac{m \cdot L \cdot \Theta \cdot \eta \cdot h}{A_\mathrm{r}} \cdot \int_{E_\mathrm{th}}^{E_\mathrm{max}} \varphi(E) \cdot \sigma(E)\,\mathrm{d}E \cdot (1 - \mathrm{e}^{-\lambda \cdot t_\mathrm{i}}) \cdot (\mathrm{e}^{-\lambda \cdot t_\mathrm{d}}) \cdot \frac{(1 - \mathrm{e}^{-\lambda \cdot t_\mathrm{c}})}{\lambda} \tag{7}$$

where $A(t_\mathrm{i}, t_\mathrm{d})$ is the radioactivity after exposure and decay period, m is the sample mass, L is the Avogadro's constant, Θ is the abundance of the isotope under study, A_r is the relative atomic mass, E_th is the threshold energy of the regarded photoreaction, E_max is the maximum energy of the bremsstrahlung continuum, $\phi(E)$ is the energy-differential photon flux density, $\sigma(E)$ is the energy-differential cross section of the regarded photoreaction, λ is the decay constant of the product radionuclide, t_i is the exposure period, t_d is the decay period, $P(t_\mathrm{i}, t_\mathrm{d}, t_\mathrm{c})$ is the full-energy net peak area ("photopeak") after exposure, decay, and spectrum collection period, η is the counting efficiency of the spectrometer at the regarded energy, h is the emission probability of the regarded energy signal, and t_c is the counting period.

Since several of the parameters herein are not known with the required precision or not at all, the quantification has to be performed with the help of calibration materials usually irradiated simultaneously. In this case, the expression used for calculation of the analyte concentration is

$$c_\mathrm{S} = \frac{c_\mathrm{Cal} \cdot m_\mathrm{Cal} \cdot P_\mathrm{S}}{m_\mathrm{S} \cdot P_\mathrm{Cal}} \cdot \frac{\mathrm{e}^{-\lambda(t_\mathrm{dCal} - t_\mathrm{dS})} \cdot \mathrm{e}^{-\lambda(t_\mathrm{dCal} - t_\mathrm{dS} + t_\mathrm{cCal})}}{1 - \mathrm{e}^{-\lambda \cdot t_\mathrm{cS}}} \tag{8}$$

where (Index S) denotes sample-related quantities, (Index Cal) denotes calibration material-related quantities, c denotes the contents of analyte, m is the mass, and P is the net peak area.

Quality control can be carried out using different procedures, synchronous analysis of a control material, e.g. appropriate certified reference material, and use of an internal monitor (IM)$^{(40)}$ (see also Ref. 7, p. 418f). The former procedure should be applied in every analytical method; the other is of particular advantage in PAA because of the pronounced inhomogeneity of the activating photon beam and other eventual sources of error.

4.3.1 *Internal Monitor*

The IM is a component of both the sample and the calibration material; thus, it is subjected to the same procedure as these. The following conditions must be fulfilled:

1. the IM must not be an analyte;
2. the contents of the IM must be known in the sample/calibration material with high precision;
3. the IM must undergo the same type of photoreaction as the analytes; and
4. no interference must occur between the energies emitted by the activated IM and those of the analytes;
5. the emitted energy of the IM must be located in the region of the emissions of the analytes, and the IM signals must be strong enough to provide a minimum statistical error.

If the following conditions are fulfilled several sources of error can be ruled out, namely:

1. deviations due to the inhomogeneity of the activating beam;
2. deviations due to differences in size/shape between the samples and the calibration materials;
3. matrix absorption of the activating beam if large samples and/or material of average high atomic number is analyzed;
4. errors due to loss of material before, during, or after exposure; and
5. (within limits) error sources due to irregularities during radiation spectroscopy, errors due to dead time losses, and errors due to matrix absorption during counting.

Moreover, taking into account a slightly increased uncertainty of the result, samples and calibration materials can be irradiated nonsimultaneously.

The analytical result is obtained by modifying Equation (4) to

$$c_\mathrm{S} = \frac{c_\mathrm{Cal} \cdot P_\mathrm{S} \cdot P_\mathrm{ICal} \cdot c_\mathrm{IS}}{P_\mathrm{Cal} \cdot P_\mathrm{IS} \cdot c_\mathrm{ICal}} \cdot \frac{\mathrm{e}^{-\lambda_\mathrm{I} \cdot t_\mathrm{dS}}}{\mathrm{e}^{-\lambda_\mathrm{I} \cdot t_\mathrm{dCal}}} \cdot \frac{1 - \mathrm{e}^{-\lambda_\mathrm{I} \cdot t_\mathrm{cS}}}{1 - \mathrm{e}^{-\lambda_\mathrm{I} \cdot t_\mathrm{cCal}}} \cdot \frac{1 - \mathrm{e}^{-\lambda \cdot t_\mathrm{cS}}}{1 - \mathrm{e}^{-\lambda \cdot t_\mathrm{cCal}}} \cdot \mathrm{e}^{-\lambda(t_\mathrm{dCal} - t_\mathrm{dS})} \tag{9}$$

where (Index I) denotes IM-related quantities.

Modified procedures of the IM methods are application of the standard addition method$^{(41)}$ or the stable isotope dilution method.$^{(42)}$

IMs can be inherent (an *à-priori* component of the materials involved, e.g. a matrix element of high-purity material$^{(43)}$) or additive monitors added to powdered or liquid samples.$^{(40)}$ Thus, it is clear that the IM method cannot be applied in every case since additive monitors are not possible if compact samples are studied, e.g. metals.

4.4 Error Sources

4.4.1 *Competing Reactions*

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. For instance, carbon is analyzed by $^{12}C(\gamma, n)^{11}C$. The reaction threshold energy is about 19 MeV. Hence, in order to achieve satisfactory sensitivity, one has to irradiate at energies well above this threshold, e.g. 30 MeV. At this energy, however, ^{11}C may also be produced in considerable amounts by $^{16}O(\gamma, \alpha n)^{11}C$ having a threshold energy of about 26 MeV. This interference has to be taken into account in almost every case, since (i) it cannot be outwitted by chemical means; (ii) oxygen is quasi-omnipresent, mostly in considerable amounts; and (iii) reduction of the bremsstrahlung energy does rule out the interfering reaction, but entails a loss of sensitivity of the carbon analysis, which can amount to orders of magnitude (Ref. 7, p. 750f). Competing reactions and their quantitative contributions obtained by experiment at 30-MeV activation energy are given in Segebade et al.,(7) p. 300ff. The contribution of the interference to the common product activity can be calculated using another reaction of the competing element as a reference. This procedure is described in detail in Segebade et al.,(7) p. 425ff. for 30-MeV activation. Another similar type of interference is the secondary decay into a common product:

$$
\begin{aligned}
&^{48}\mathrm{Ti}(\gamma, \mathrm{p})^{47}\mathrm{Sc}\\
&^{51}\mathrm{V}(\gamma, \alpha)^{47}\mathrm{Sc}\\
&^{48}\mathrm{Ca}(\gamma, n)^{47}\mathrm{Ca}\text{–}\beta^{-} \longrightarrow {}^{47}\mathrm{Sc}
\end{aligned}
\tag{10}
$$

This type of interference is discussed in Segebade et al.,(7) p. 433ff.

4.4.2 Spectral Signal Interference

If the energies of spectral signals are close to one another so that the resolution capacity of the spectrometer is unable to separate them clearly, there are several options to separate the overlapping peaks:

1. If the half-lives of the nuclides involved are different enough, one can carry out more than one measurement so that for later measurements, the short-lived contributors would have decayed to insignificant activities and would not interfere any more. This procedure provides highest quality of the analytical results. However, it is mostly not useful in the practical routine analysis (Section 4.2).
2. 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:

   Analytical reaction: $^{238}U(\gamma, n)^{237}U$ $E\gamma$: 208 keV
   Interfering reaction: $^{269}Ga(\gamma, 2n)^{267}Ga$ $E\gamma$: 209 keV
   Reference energy of ^{267}Ga: $E\gamma$: 299 keV

   However, many experimental parameters have to be known with high precision (e.g. the efficiency function of the spectrometer used) or have to be kept constant, respectively (e.g. the counting geometry applied). Yet more complicated is the procedure if the interfering nuclide does not emit usable reference energy.

   Analytical reaction: $^{203}Tl(\gamma, n)^{202}Tl$ $E\gamma$: 440 keV
   Interfering reaction: $^{70}Zn(\gamma, n)^{69m}Zn$ $E\gamma$: 439 keV
   Reference energy: none

   In this case, the interference has to be corrected like a competing reaction (Section 4.4.1).
3. If the peaks involved overlap only partly, they might be integrated separately using a deconvolution routine. This procedure is usable only if enough data points are available. One has to take into account a certain deterioration of the results that, upon any manipulation of the raw spectral data, cannot be avoided. Nonetheless, frequently in the routine case, this is the only usable strategy since it is simple and can be performed without significant time consumption.

4.4.3 Other Error Sources

To summarize all interfering influences already mentioned,

- fissile material (Section 2.4);
- photoneutrons (Section 2.5);
- matrix absorption during spectroscopy (Section 3.1.3);
- dead time (Section 3.2);
- satellite signals due to high energies (Section 3.3);
- matrix absorption during activation (Sections 4.1 and 4.2); and
- measurement geometry, contamination, and radiolytical/thermal disintegration (Section 4.2).

Furthermore,

1. *Recoil nuclei*: An error might be introduced by recoil of active light element isotopes from the close environment, e.g. the calibration material, into the sample.(44) This can be generally avoided by insulating the different items with the help of aluminum foil. A thorough postirradiation removal of the surface layer should also solve the problem of recoil contamination.
2. *Secondary activation*: Secondary reactions with charged particles are induced by promptly emitted protons, deuterons, or α particles owing to photonuclear reactions within the sample matrix. Among

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these, protons theoretically might introduce significant interfering activity during activation, e.g.

Analytical reaction: $^{19}\mathrm{F}(\gamma, n)^{18}\mathrm{F}$
Interfering reaction: $^{18}\mathrm{O}(\mathrm{p},n)^{18}\mathrm{F}$

In critical cases, significant yields might be reached.(45)

3. *Inhomogeneity of the sample*: Errors due to inhomogeneity in the composition of the sample and the reference material contribute to the common uncertainty of the results, but mostly cannot be exactly quantified; these errors might amount to several percentage in critical cases.
4. *Unreliable isotopic abundance*: The quantitative isotopical compositions of many elements frequently vary depending upon the deposit or prominence 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 matrix.(46) However, in some cases, more than one isotope can be analyzed, and thereby questionable values may be verified. In this case, however, a reference material of well-known isotopical composition must be available.
5. *Location of positron annihilation*: In annihilation quanta, counting the effective location and geometry of the radiation source mostly is not clearly defined, since the location of the actual annihilation process is dependent on the energy (and thereby the mass range) of the positrons. Engelmann(47) found that a layer of 2 mm of copper wrapped around the source was thick enough to completely absorb (and subsequently convert) the positrons with the highest energy encountered throughout the study. Thus, defined radiation source geometry could be created.

4.4.4 Counting Statistical Uncertainty

The counting statistical uncertainty is common to all measurement results that are based on number of events distributed statistically (in radiation measurement: numbers of counts obtained during spectroscopy). In the first approximation, it can be defined simply by the square root of the count number. However, in radiation counting, the signals due to a radionuclide (e.g. counts collected in the γ peak) are associated with background signals in the same energy region emitted by different sources (mostly due to Compton events, Section 3.3). These have significant influence upon the statistical uncertainty. The absolute total statistical uncertainty can be obtained, according to the Gaussian statistical uncertainty propagation, by

$$U_{\mathrm{stat}} = \sqrt{A_{\mathrm{net}} + A_{\mathrm{Bgr}}} \tag{11}$$

where U_{stat} denotes total statistical uncertainty, A_{net} denotes net peak counts; and A_{Bgr} denotes background count integral underneath the peak.

5 EXAMPLES OF APPLICATION

In this section, PAA is discussed as it is applied to different groups of material. Most of these material classes require particular handling during analysis, depending upon the properties of the respective matrix, the elements of interest, and their concentration ranges. The following fields of application are discussed: (i) systematic studies, (ii) environmental analysis, (iii) biological material, (iv) geochemical studies, (v) raw materials and industrial products, and (vi) archeological material. An extended review of publications on these and other areas of application of PAA can be found in Segebade et al.,(7) p. 443ff.

5.1 Systematic Studies

Photonuclear data compilations with analytical background without regard to a special application are discussed here. This is not an analytical application; in the general sense; however, it might be of interest to refer to compilations that comprise a reasonably large list of elements without regard to special analytical problem. Systematic investigation work on photonuclear reactions has become possible with the maturity of high-energy bremsstrahlung sources with large output power. Thus, the first systematic work with an analytical background was performed comparatively late, in 1964, by Schweikert and Albert.(48) This work contains a lot of fundamental facts and data concerning PAA, 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 25–35 MeV.

For further examples, see Table 2.

5.2 Environmental Analysis

On reviewing the accessible literature about multielement PAA, it is interesting to note that about half of all articles published deals with environmental analysis or analyses performed in an environmental context. This might, among other reasons, be due to the fact that several elements of environmental interest (e.g. lead) can be performed most advantageously by instrumental

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Table 2 Typical application examples of PAA

Application	Elements determined	Remarks	References
Systematic	(Almost all)	γ and LEP* spectrometry	49
	(Almost all)	40–44 MeV activation	10,11
	(Almost all)		13
Light elements	C, N, O, F	All techniques	50
	C, N	Molten salts separation	37
	C, N, O, P	γ- and β spectroscopy	29
Environmental	(30 elements)	Soil material	51
	Cl, Ca, Cr, V, Mn, Fe, Co, Ni, Zn, As, Se, Br, Mo, Cd, Sn, Sb, Tl, Pb, U	Airborne particulate; activation with photons and photoneutrons	18
	Cr, Co, Ni, Zn, As, Rb, Sr, Y, Zr, Nb, Cs, Ce, Pb	Internal monitor and internal flux monitor technique	52
Geological	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, Ce	Standard rock material	53
	Ca, Ti, Ni, As, Rb, Zr, Ce, Pb	Sediment (certified reference material)	54
Biological	Mg, Na, Cl, K, Ca, Mn, Fe, Zn, As, Rb, Sr, Zr, Sb, I, Cs, Tl		55
	Mg, Cl, Ca, Cr, Fe, Ni, Zn, Sr, Sn, Pb	Betatron irradiation at 18 (in vivo) and 33 MeV	56
	Ca, Rb, Sr	Plant material; 35–40 MeV	57
Industrial products	Sm, Eu, Gd, Dy	Boron carbide	58
	Na, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Ag, Cd, Sn, Sb, Ba, Ce, Pb, U	Electronic waste material	15
Archeological, forensic	Cu, Ag, Au	Gold coins	59
	Pb	Moonshine whiskey; 25-MeV irradiation	60

* LEP = Low Energy Photon

PAA 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. Most of the environmental applications refer to atmosphere, soil, and biological matrix. Among all papers about environmental PAA inspected by the authors, about 50% are concerned with the analysis of air particulate material. A Round Robin Program of air particulate analysis was reported by Cawse.(61) Air particulate was collected on cellulose air dust filters in an industrial town and in a nonurban site. Analyses of the deposits were carried out using instrumental NAA, wavelength-dispersive X-ray fluorescence spectrometry, flame atomic absorption analysis, colorimetry, and instrumental PAA. Within the program, 38 elements were analyzed, among them the following ones by photon activation: Na, Mg, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Rb, Sr, Zr, Nb, Mo, Cd, Sn, Sb, TI, and Pb. A synthetic mixture of simple compounds of all elements detected in a preliminary qualitative filter analysis served as multielement calibration material. In order to assess the accuracy of the method, a certified multielement reference material (NBS-SPM 1571, orchard leaves) was analyzed separately. Concerning instrumental PAA, the result of the intercomparison study indicated that this method stands out among other instrumental techniques in the analysis of Ni, Sb, and Pb. Less satisfactory accuracy and precision was observed for Fe, Cd, and Zn. The agreement of the results of PAA and the other methods applied was good in most cases.

For further examples, see Table 2.

5.3 Biological Material

Frequently, analyses of biological material are performed within an environmental context. Components are of particular interest, and hence their analysis is demanded, which have been known as *toxic*. One of them is lead. The specific advantage of PAA, as compared with neutron activation, is the detectability of several elements of biological significance such as lead, which cannot or hardly be analyzed by neutron activation. Moreover, the recovery of trace elements in organic and biological matrix using conventional noninstrumental techniques is troublesome in many cases, as reported in a paper about a systematic study of trace determination of elements in organic and biological matrix (Gorsuch, Ref. 62). Hislop and Williams(63) reported a purely instrumental multicomponent PAA of blood, urine, and bone samples. No trace components could be detected after short, say hours, decay periods except strontium in bone ash and urine. Activities resulting from C, Na, Mg, Cl, and Ca dominated in these spectra. The other trace elements determinable could be measured after about four days of

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decay period. These were rubidium in blood and urine and zinc in bone. For these and also for Ni, As, Sr, Zr, Mo, Cd, Sb, Cs, Ce, Hg, Tl, Pb, and Bi, limits of detection in biological matrix were determined.

For further examples, see Table 2.

5.4 Geochemical Studies

In these studies, mostly rock and mineral material, water-related material, and cosmogenic samples are analyzed. Usually, the problems arising in geochemical application of PAA are somewhat different from those in the other fields of science discussed until now. Frequently, concentrations to be determined are not as small as, for example, in environmental or biological analyses. In most cases in the geology and mining industry, a sensitivity as high as 1 mg is quite satisfactory. If a trace analysis is required, there is mostly the possibility of irradiating larger samples (Section 2.1.2). However, in many cases, particularly during analysis of rock- and ore-related material, the handling of matrix component activities after irradiation might be cumbersome. In comparison to analyses of biological/organic samples, geological material is normally heat and radiation resistant but produces a high background activity, whereas organic-based material might be damaged but usually does not contain long-lived matrix activities after activation. Analyses of sea sediments were reported by Masumoto and Suzuki.(64) Major attention was directed to the analysis of nickel. A special background suppressing method was developed using a $\gamma - \gamma$ coincidence configuration (Section 4.1) with a Ge and a NaI detector. In this manner, interfering activities, which do not emit annihilation radiation (e.g. ^{24}Na) could be gated off. Nickel was analyzed in offshore sea sediments, sampled from depths between 90 and 900 m, and several certified reference materials. A standard rock material was used as control material. Comparison of the concentration data obtained for the standard rock materials with literature data yielded satisfactory agreement in most cases. The described method is particularly useful if a material has to be analyzed, which contains elements in large concentrations whose reaction products are β^- emitters, e.g. Mg (^{24}Na), Ca (^{43}K,^{47}Ca), and Ti (^{46,47,48}Sc).

For further examples, see Table 2.

5.5 Raw Materials and Industrial Products

A lot of different properties are comprised in this class of materials; therefore, common features like a similar matrix as for organic materials cannot be assumed. Consequently, an appropriate analysis procedure has to be found in every individual case, e.g. for ores, metals, fuels, semiconductors, ceramics, glasses, etc. Moreover, the lists of elements of interest are largely different in every case. Reviewing the respective literature, the analysis of ores and ore-related products has been found to dominate. In this case, noble metals are frequently of major interest. The analysis of gold and silver in rocks and ores was reported by Kapitsa et al.(65) A microtron was used for irradiation at different energies, namely 9 MeV (average electron beam current: 30 μA) and 14 MeV (20 μA). With the help of the lower energy, activities due to isomeric-state photoexcitation were produced (^{107m}Ag, ^{109m}Ag, ^{197m}Au; Section 2.2) and by irradiation at the higher energy, (γ, n) reactions were affected. The isomers could be measured fairly interference-free with an NaI spectrometer, whereas the photonuclear products had to be counted with a semiconductor detector because of the somewhat more complex γ-ray spectra due to reaction products of other elements present in the samples (Ba and Pb).

For further examples, see Table 2.

5.6 Archeological Material

According to the literature accessible to the authors, PAA as applied in archeological science was exclusively used for the analysis of metals and ceramic material until now. Other materials of archeological interest, e.g. glasses, dyes, and organic matter, except one recent work about ancient American obsidian artifacts,(66) have not yet been studied using photoactivation. Among the metallic materials, copper-based metals (unalloyed copper, bronze, brass, and alloys with noble metals) have been studied most by PAA. The comparison of results of ancient bronze analyses was reported by Neider.(67) This work was performed within the preliminary studies of a large-scale investigation work about medieval bronze objects. Small samples (10–50 mg) were drilled out of the objects (fountain decorations) and irradiated for 1–4 h with 30-MeV bremsstrahlung (mean electron beam current: 150 μA). The resulting γ radiation was measured several times after different cooling periods with a 50-cm^3 Ge(Li) detector. A certified standard bronze was used as a multielement calibration material. Fe, Ni, Cu, Zn, As, Ag, Sn, Sb, and Pb were analyzed both by instrumental PAA and by atomic absorption spectrometry. The comparison showed satisfactory agreement in most cases.

For further examples, see Table 2.

In Table 2, publications are compiled that describe typical examples of application of PAA to systematic study, light elements, environmental material, geological and maritime samples, biological material, industrial products, and archeological and forensic studies. The activation energy applied is around 30 MeV or as indicated.

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6 COMPARISON WITH OTHER ACTIVATION METHODS

In this section, only basic procedures of the activation analysis methods (thermal NAA and activation analysis with charged particles comparison of photon activation analysis (CPAA)) as well as comparison of PAA with other methods are considered; special techniques like nuclide source applications and 14-MeV-NAA are not discussed.

6.1 Neutron Activation

6.1.1 Irradiation

High-energy photons from an electron accelerator have high-penetration capability, so large material layers (or many samples, respectively) can be activated mostly without crucial attenuation of the activating beam. Thermal neutrons, however, can be absorbed strongly by different elements. Thus, in this case, the areal distribution of the induced activities is extremely inhomogeneous, which might lead to miscalculations of the results. On the other hand, the bremsstrahlung photon field is focused and thus much more inhomogeneous than the quasi-isotropically distributed achievable thermal neutron field of a nuclear reactor. Hence, it is necessary to use flux monitors of any kind in PAA. However, many samples can be activated simultaneously in a reactor as well.

6.1.2 Nuclear Reactions

Predominantly, photonuclear reactions of the (γ, n) type are induced during bremsstrahlung exposure, giving rise to activation products that decay by β^+ emission or by electronic capture, respectively. Both kinds usually emit well-measurable γ-ray spectra. However, several reaction types can be induced by photon irradiation, depending upon the incident energy. This can give rise to interference through competing reactions. In contrast, (n, γ) reactions occur during thermal neutron almost exclusively, mostly producing β^-- and γ-emitting nuclides.

6.1.3 Sensitivity and Applicability

In many cases, the intrinsic analytical sensitivity of NAA is greater than that of PAA by orders of magnitude due to large activation cross sections. However, many elements can be determined by PAA that do not produce analytically usable neutron activation products, e.g. the light elements C, N, O, F, and P. Conversely, this is also true for PAA; for instance, no practically usable photoreactions are available for Al, V, La, and Th. Thus, NAA and PAA supplement one another in many cases. Both methods can be applied to the trace analysis of a large variety of matrices. A particular advantage of PAA as compared to NAA is its applicability to the analysis of material with excessively large neutron absorption cross sections, e.g. boron-containing matrices.

6.2 Activation with Charged Particles

6.2.1 Irradiation

Usually protons, deuterons, tritons, α, and ^{3}He particles are used for activation in CPAA. Since these are strongly absorbed in a target material, the method is particularly suitable for surface-related analyses. Thus, surface contamination is more critical than in PAA and NAA. Moreover, the predominant reaction type and the activity-induced type are dependent upon the penetration depth; thus, a quasi-homogeneous activation as achievable in NAA and PAA cannot be assumed in any case, and stacks of samples normally cannot be irradiated. Finally, the unavoidable heating of the sample might be more critical than in the other activation methods, e.g. during analysis of organic matter.

6.2.2 Nuclear Reactions

Like in PAA, during exposure to charged particles, several reactions can be induced giving rise to interference. The probability of interference increases with the atomic number of the element exposed, and therefore CPAA is normally unsuitable for analysis of heavier matter. Using deuterons or ^{3}He particles, some reactions can be induced at low excitation energies. Both kind and energy of the particle for bombardment can be selected quasi freely.

6.2.3 Sensitivity and Applicability

In contrast to PAA and NAA, CPAA has been utilized predominantly for the analysis of light elements, e.g. impurities in semiconductor material and other industrial products. Since the geometry of the sample is critical, its general applicability is limited. Moreover, due to the high probability of competing reactions, heavy elements usually cannot be determined. However, the general sensitivity is comparable to that of PAA.

RELATED ARTICLES

Instrumental Neutron Activation Analysis
Charged Particle Activation Analysis
Inductively Coupled Plasma Mass Spectrometry in Environmental Analysis
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Energy Dispersive, X-ray Fluorescence Analysis
Activation Analysis of Large Samples

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