

- miscellaneous materials

112) Fluorine and potassium were analysed in ZrO_2 used as ground material for industrial ceramic products (Galatanu et al.²⁶²). Bremsstrahlung of a betatron was used for activation. For fluorine analysis, batches of the material were irradiated with bremsstrahlung from 11.9 MeV electrons to avoid interference from the zirconium matrix; the most prominent possibly interfering zirconium reaction is $^{90}Zr(\gamma, n)^{89}Zr$ with a threshold energy of about 12 MeV. In previous experiments it was found that using this bremsstrahlung energy, there is no interfering photon radiation to be expected in the range between 400 and 700 keV of the resulting gamma-ray spectrum. Therefore, NaI spectroscopy was used to analyse the annihilation radiation of ^{18}F non-destructively. The maximum possible electron energy of the machine (26.5 MeV) was used to activate other batches of the analysis material for potassium determination. Because of multiple interference, high-resolution gamma spectrometry had to be used for measurement of the 2167 keV gamma-ray line of ^{38}K . A detection limit of about one mg was found for both elements analysed using the described procedure. This value does not agree with other sensitivity data reported in the literature. However, it may be considered reliable since it was obtained by experiment and the sensitivity calculation was carried out very conservatively.

113) The analysis of several toxic components of PVC material was reported by Kondo¹⁰⁷⁵. The analysis of toxic elements in plastic material is of importance because the material is in widespread daily use and incorporation of any of its components is likely. Frequently, children's toys are made of PVC and investigations have shown that both the toxic matrix and other components can be leached out and eventually incorporated by the child which might lead to severe illnesses and diseases. In the article of Kondo, the analysis of Zn, Cd, Ba and Pb in PVC sheets by photon activation is described. Pure elements (Zn, Cd and Pb) or stoichiometrically well-determined compounds (sodium chloride and barium nitrate) were used as reference materials. The samples were irradiated with 16 MeV bremsstrahlung (mean electron beam current: 20-30 microamperes) and measured with a 40 cm^3 Ge(Li)-detector. Because of the low activation energy there was no background radiation due to the matrix carbon and only relatively small contribution from ^{34m}Cl produced in the matrix chlorine. Moreover, some of the elements to be analysed could be measured after ^{34m}Cl had decayed to negligible activity and therewith, the gamma-ray spectra were not interfered by any matrix background activity. The analysed concentrations were between 0.06 and 1%.

114) The instrumental photon activation analysis of glass matrix was described by Hislop and Williams⁹⁵². NBS standard glass material was analysed. A synthetic multielement reference material was prepared by mixing oxides of as many as 39 elements with a synthetic average glass matrix. This reference material was already discussed in 6.2.4.3 about the analysis of biological material (Rev. 65). Sample and reference material were sandwiched together and irradiated with 35-45 MeV bremsstrahlung for one hour at a mean electron beam current of 5-10 microamperes. Another batch of the sample was irradiated with 17 MeV bremsstrahlung from an electron beam of 50-60 microamperes. Samples and reference materials were measured multiply in increasing intervals using a 40 cm³ Ge(Li)-detector. In the case of the lower energy activation, the special advantage is the low activity background contribution of the matrix.

As, Sr, Zr, Sb, Cs, Ce, Tm and Tl were analysed quantitatively in the NBS reference glass. However, the analysis of thulium using the 198 keV gamma-ray line seems somewhat questionable because of probable strong interference by ^{120m}Sb from antimony present in the sample. The obtained values and the certified data - if any available - agreed well within the precision of the method.

The analysis of glass matrix is also discussed in the forensic context in the following paragraph. More information about photon activation analysis of industrial products can be found in Ref's. 1076-1079.

A summary of several applications of photon activation analysis to industrial and raw material is given in Tab.6.2-8.

Tab.6.2-8: Instrumental photon activation analysis of raw materials and industrial products

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
Various metals	27 (50)	Ti, Ni, Zr, Ag	903	105
Bronze	70 (not given)	Eu, Gd	307	106
Copper ore	13.6 (not given)	Cu	1066	100
Various alloys	24 (not given)	Zr	1186	
Various metals	35 (50)	Ni, Tl, Pb	843	107
Ores and metals	5-40 (variable)	Noble Metals	1187	
Ores	25 (not given)	Nb, Ta	258	101
Ores	not given	Cu	256	
Ores	9 (30)	Au	283	96
Ores	5 (700)	W	1067	103
Copper ore	15-26 (not given)	Ti, Mo, Rh	1164	97
Glass	35-45 (5-10)	As, Sr, Zr, Sb, Cs, Ce, Tm, Tl	952	114
Ores	14.9 (not given)	Cu	255, 1192	
Rock samples, ores	14 (20)	Ag, Au	291	98
Minerals, ores	not given	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, Ce	1188	

Tab.6.2-8, continued

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
PVC	16 (20-30)	Zn, Cd, Ba, Pb	1075	113
Petroleum products	35-40 (100)	F, Pb	1189	
ZrO ₂	11.9, 26.5 (not given)	F, K	262	112
Various alloys	29.2 (35)	Ge, Zr, Nb, Mo	293	108
Platinum ore, copper	30 (150)	Noble Metals	155, 1071, 1072	109
Black Concentr.	6-8 (70)	Br, Rh, Ag, Ba, Ir, Pt, Au	921	102
Black Concentr.	35 (66)	Rh, Pd, Ag, Ir, Pt, Au	1065	99
Coke	16, 30 (200, 150) U		688	49
Coal	30 (30)	not clearly specified	1190	
Coal	21 (5)	Ca, Fe, Sr	296	111
Ores	8 (1000)	Au	290, 1191	
Phosphate rock, coal	18, 30 (60, 90)	Na, Mg, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sb, I, Cs, Ba, Ce, Pb, U	1068, 1073	104 110
Coal	up to 45 (50)	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Y, Zr, Sb, I, Ba, Ce, Pb, U	1074	

6.2.4.6 Analysis of archaeological material and forensic analysis

In this paragraph, only few works are reviewed since photon activation analysis has been applied to archaeometry and forensic science in very few cases as yet. Studying the literature about activation analysis application to these fields of science one will find classical thermal neutron activation clearly dominating. Furthermore, a good deal of the instrumental photon activation analysis work in archaeometry was performed in the laboratory of the authors of this book.

One special advantage of the method might become relevant in archaeometry and criminology, namely the possibility of non-destructive analysis in its very strict sense, i.e. the analysis of entire objects - also very large ones - without the necessity of sampling. On the one hand, analysing large objects, sampling bears the danger of non-representativeness and on the other hand it sometimes might cause damage devaluating the object under investigation. Moreover, using photon activation, a fairly homogeneous activation can be achieved in the most cases whereas in other techniques, e.g. thermal neutron activation or X-ray fluorescence analysis, frequently only small partitions of the object are comprised which - as in the case of sampling - might not be representative for the total. Finally, extremely long-lived radionuclides generally are not produced in excessive activities through photon activation. Therefore, objects which had been activated with photons may be returned in the collection or exposed in the public after appreciably short cooling time. This usually is not possible after exposure to high flux thermal neutrons. For instance, irradiating silver objects with photons of say 20 MeV maximum energy, mainly ^{106m}Ag will be produced which has a half-life of 8.3 days. Irradiating the same object in a nuclear reactor, however, ^{110m}Ag will be the most prominent product nuclide with a half-life of 250 days, and thereby the object may contain considerably high radioactivity for years. However, in several exceptional cases, this problem also might arise in photon activation as was demonstrated in another context by Kuttemperoor^{245,1080}.

In this paragraph, publications about the application of photon activation analysis to art and archaeology are reviewed first, and then forensic photoactivation studies are discussed.

- Art and archaeology

According to the literature accessible to the authors, photon activation analysis as applied in archaeological science was exclusively used for the analysis of metals and ceramic material up till now. Other materials of archaeological interest, e.g. glasses, dyes and organic matter, have, as far as the authors know, not yet been studied using photoactivation.

Among all archaeological materials pottery has been studied most since it was used in large quantities in all ancient cultural spheres and thus it is a good indicator for many questions of archaeological relevance. Furthermore, since the life time of ordinary household pottery objects usually has been comparatively short they have been reproduced in large series and therefore a lot of pottery fragments have been available to scientists for contemporary reference and research. Pottery material - at least the fine ware - may be considered fairly homogeneous within one specimen (Knoll et al.¹⁰⁸¹). It has been demonstrated that a sample of not less than about 50 milligrams taken from ancient Roman Red Ware (terra sigillata) normally represents the entire object quite accurately - as far as the elemental composition is concerned. In a few exceptional cases one might find slight differences in the elemental concentrations between the surface area and the bulk of a pottery sherd, e.g. caused by environmental influence during long-term burial (Segebade and Lutz^{156,1082-1084}, Lemoine et al.¹⁰⁸⁵). However, during studies of coarse ceramic ware in the authors' laboratory, a surprisingly homogeneous distribution of the elements throughout an entire specimen was stated. In this case larger samples had to be taken because of the coarse grain structure of the material under study.

The analysis of metal objects entails essentially different problems which begin at the sampling stage. Possibly significant inhomogeneities caused by different reasons might have to be considered. First, metal objects might have been assembled by the producer using parts of differently composed metals, e.g. in order to achieve decorative variations of the colour. Instead, pottery specimens normally have been produced using one batch of clay material and then eventually have been painted.

Inhomogeneities of metal objects also might occur during the different processing steps of the metal alloy, e.g. segregation behaviour of certain components. Furthermore, the surface area composition might be altered by outer influence, e.g. long-term handling. This particularly applies to ancient coinage as is demonstrated in several papers reviewed below. Therefore, representative

sampling from metal objects might become extremely difficult compared with the sampling of pottery.

Furthermore, the matrix compositions of different kinds of pottery normally are quite similar in terms of elements present in the material. This is surely of advantage for the analyst's work although it might be a disadvantage for the archaeological part of the given task, e.g. classification or assignment of the object to certain cultural spheres or producers. The elemental composition of metal specimens, however, might differ by several orders of magnitude. Hence, the analytical procedure cannot be standardised which is possible and frequently done in ceramics studies. Thus in photon activation analysis as in most other instrumental techniques, large series of metal-based reference materials - at least one for each basic metal to be investigated - are required whereas theoretically one single multielement reference material can be used for pottery analysis (see also paragraph 6.2.2). In practice, however, the experienced analyst will strive to use more than one reference material. For instance, in the archaeometry section of the Brookhaven National Laboratory in Long Island, U.S.A., six different multielement reference materials have been used in routine pottery neutron activation analysis (Sayre¹⁰⁸⁶).

Another difference between pottery and metals concerning their analysis was already touched on above; whilst samples can be taken from pottery specimens without any restriction, this might not be allowed in the case of metal specimens, particularly precious metal objects. Therefore, for this and other reasons (homogeneity, see above), the non-destructive analysis might be required in the case of metal matrix under study. Instrumental photon activation analysis has proven to offer considerable advantages for the non-destructive analysis of metal specimens as was mentioned in the introductory part of this chapter. Finally, due to the different chemical behaviours (e.g. solubility) of metals and pottery, metals frequently have been studied using destructive techniques, e.g. wet chemistry, atomic absorption spectrometry, atomic emission spectrometry and others, whereas pottery almost invariably has been analysed by instrumental radiometric techniques, e.g. X-ray fluorescence or activation analysis, from the time of their general availability hitherto.

The publications reviewed in the following are not ordered by the material classes studied as is done in the other application subparagraphs but in a rough chronological order of their appearance.

115) Undoubtedly, the first application of photon activation to archaeology was reported by Voigt and Abu-Samra³⁰⁵. They analysed carbon in a Damascene steel sword using the reaction $^{12}\text{C}(\gamma, n)^{11}\text{C}$. This work is not reviewed here since it is concerned with the analysis of a light element and therefore is discussed in the preceding section about photon activation analysis of the light elements.

116) In a paper of Thompson and Lutz¹⁰⁸⁷ an instrumental photon activation analysis procedure is described with help of which ancient bronze artifacts were analysed. This work was carried out within a comparative analytical study in which many laboratories participated using different analytical techniques. The samples lay before as fine chips. 10-20 mg batches were wrapped into thin plastic foils and encapsulated in polyethylene rabbits. An NBS reference bronze was used as multielement reference material. 30 MeV bremsstrahlung was used for activation. The samples were irradiated for approximately one hour. After irradiation, the samples and reference materials were dissolved in HNO_3/HF mixture and diluted to a standard volume to provide a reproducible counting geometry. Ge(Li)-detectors with 47 and 60 cm^3 active volume were used for gamma spectrometry. The copper content of the samples and reference materials was used as an internal flux monitor selecting the induced ^{61}Cu activity. The copper concentration of the samples had been determined previously using thermal neutron activation analysis. Fe, Ni, Zn, Sn and Pb were analysed, but only for tin and lead definite results could be given since the concentration of the other elements were below the experimental detection limits (about 0.1 %). For tin comparative values were available which were obtained with help of instrumental neutron activation analysis in the same laboratory; the agreement was fairly good.

117) Segebade et al.^{156,1082-1084,1088} made large-scale investigations on ancient Roman pottery. Studying various aspects concerning this material, the analytical procedure was virtually the same in each of the above cited works. 50-200 mg batches of the pulverised material were taken and wrapped in aluminium foil. Depending upon the number of the available gamma spectrometers, sets of several samples were irradiated simultaneously for 2-6 hours with 30 MeV bremsstrahlung at 150 microamperes mean electron beam current. A standard clay served as multielement reference material (Knoll et al.¹⁰⁸¹). After irradiation, the samples were mixed with about 200 milligrams of cellulose powder and pressed into large, thin pellets. Each sample was measured several times after increasing cooling periods. Both gamma-ray spectrometry and low energy photon measurement were used for activity counting. With this procedure, the following 27 elements could be analysed: Na, Mg, Si, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni,

Zn, As, Se, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, Ce, Pb and U. The accuracy of some of the obtained data was checked by an interlaboratory Round Robin analysis of a similar material, using X-ray fluorescence analysis, instrumental neutron- and photon activation and 14 MeV neutron activation. The comparison of the results yielded good agreement of the photon activation data with those obtained by the other methods.

118) The analysis of precious metal coins and a silver vase as reported by Reimers et al.^{884,1180} had to be carried out non-destructively for the reasons mentioned in the introductory part of this paragraph. Copper, silver and gold were analysed in the coins, and gold in the silver vase using activation with 30 and 15 MeV bremsstrahlung and subsequent gamma-ray spectrometry with a Ge(Li)-detector. During this work, several problems had to be solved. First, for most of the specimens, no adequate reference material was available. Using an external flux monitor, small discs of the pure elements to be analysed could serve as standards. Second, self-absorption during gamma spectroscopy had to be considered. Since gamma-ray lines of high energies (greater than 1000 keV) were used for analysis, this correction could be performed quite easily and accurately. Third, the integral matrix activity had to be kept as low as possible so that the objects could be returned into the collection quasi-immediately after analysis. This was accomplished by holding the activating photon flux as low as the required sensitivity allowed. Therefore, trace components could not be analysed, but their determination was not required in this case. Finally, a spectral interference had to be eliminated: ^{105}Ag , produced through $^{107}\text{Ag}(\gamma, 2n)$ emits a gamma-ray line which partly overlaps the peak used for gold analysis. This interference is significant in the analysis of less than 1% of gold in silver matrix. A gold concentration beneath this level was expected to be present in the vase. Therefore, the object was irradiated with 15 MeV bremsstrahlung to avoid the interfering silver reaction which has a threshold energy above 15 MeV. Whilst the coins could be measured readily after activation, the measurement of the vase had to be performed with a modified procedure. A small spot within the activated area of the object was screened out with a lead collimator fixed to the detector housing. For one set of the analysed coins, comparative analysis results obtained by 14 MeV neutron activation analysis lay before. The agreement was satisfactory except for several copper values; the copper was rather low-concentrated in the coins and therefore, the analysis had to be carried out close to the experimental detection limit. The accuracy of the concentration data for the other set of coins could only be estimated by summing up the obtained values and checking the difference to 100% since no comparative data were available. The largest difference to 100% was 2.8%. Hence, with re-

spect to the precision requirements, the quality of these values could also be considered satisfactory. However, there was no possibility to check the quality of the results for the silver vase.

In this work, several advantages of instrumental photon activation analysis were demonstrated; several difficulties could be avoided as they arise in the analysis of gold matrix in using other analysis methods, particularly thermal neutron activation (Sayre¹⁰⁸⁹, Meijers¹⁰⁹⁰).

119) The comparison of results of ancient bronze analyses was reported by Neider et al.⁵⁸. 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 hours with 30 MeV bremsstrahlung (mean electron beam current: 150 microamperes). The resulting gamma radiation was measured several times after different cooling periods with a 50 cm³ Ge(Li)-detector. A certified standard bronze was used as a multielement reference material. Fe, Ni, Cu, Zn, As, Ag, Sn, Sb and Pb were analysed both by instrumental photon activation analysis as described and also by atomic absorption spectrometry. The comparison showed satisfactory agreement in the most cases.

120) The results of a comparison study on different analytical techniques applied to the analysis of ancient Roman brass coins perhaps elucidates the difficulties of sampling in ancient coinage studies (Carter et al.¹⁰⁹¹; see also Ref.¹⁰⁹²). In the photon activation analysis procedure, the samples were irradiated as such without any treatment before or after activation with 30 MeV bremsstrahlung. The exposure periods varied, depending upon the mass of the samples (400 mg to 5 g), between 1 and 3 hours. After a cooling period of about five days, the ⁶⁴Cu activity originating from copper which was present in the matrix at 70-80% had decayed to negligible level. measurements were performed with both a large volume coaxial Ge(Li)-detector and a small planar low energy photon diode. Standard bronzes, brasses and copper specimens with certified element concentrations were used as multi-element reference materials. Since none of them were available with a shape similar to the analysed fragments (roughly a quarter-circle being about 1 mm thick) the matrix copper was used as an internal flux monitor. In the fragments, the copper content had been determined previously by wet chemistry analysis (gravimetry). These values were considered most reliable compared with the results of instrumental methods. Cr, Mn, Ni, Zn, Ge, As, Se, Ag, Sn, Sb, Te, Au, Tl, Pb, Bi and U were analysed by instrumental photon activation analysis; out of these, Ni, Zn, Ag, Sn, Sb and

Pb were included in the intercomparison procedure. The applied methods in the intercomparison study were: wet chemistry, wavelength-dispersive X-ray fluorescence spectrometry, tube-excitation source energy-dispersive X-ray fluorescence analysis, radionuclide excitation source energy-dispersive X-ray fluorescence analysis, atomic absorption spectrometry, instrumental neutron- and photon activation analysis. Among these only photon activation analysis comprised the entire sample whereas all others could only analyse greater or smaller subsamples of it. Hence, some of the disagreements between the obtained results surely are due to inhomogeneities in the material (Caley¹⁰⁹³) which were also detected during microstructural studies of the objects. However, in general - with a few exceptions - the agreement of the photon activation analysis results with the consensus values calculated from all obtained data was good. It became evident that none of the participating methods outstood all others in every relevant aspect; the particular advantage of instrumental photon activation analysis as performed in the described case is its analysing the entire object. However, in several disadvantageous cases, this does not guarantee usable and representative analytical results.

121) Ancient Roman copper coins were analysed using instrumental photon activation analysis and wavelength-dispersive X-ray fluorescence analysis as reported by Segebade et al.¹⁰⁹⁴. The activation analysis procedure was essentially the same as applied in the work on the brass coins reviewed above. However, high-energy gamma spectrometry was used only, and the coins were counted first after a week's decay period and then once more after 20 days. Two different reactions of the matrix copper were used for internal flux monitoring, namely, in the first measurement $^{65}\text{Cu}(\gamma, n)$ yielding ^{64}Cu , and in the second measurement $^{63}\text{Cu}(\gamma, \alpha n)^{58}\text{Co}$ since after the second cooling period ^{64}Cu had decayed to non-detectable activity. Mn, Fe, Ni, Zn, As, Se, Ag, Sn, Sb, Te, Au, Pb and U were analysed by photon activation. The agreement with the comparative X-ray fluorescence values covered a wide range from "very bad" to "excellent". In the work reviewed above about the brass coins (Rev.120) the specimens were sacrificed by cutting them into suitably-sized pieces which were then abraded and polished to create optimal conditions for X-ray fluorescence spectrometry. Thereby one could assume a surface representing a fairly good cross section of the bulk material. The copper coins, however, were analysed as such without any pretreatment exceeding a careful mechanical removal of outer surface contaminants. Thus, the topographies of the coins were inconstant and the conditions for X-ray fluorescence were not optimal. This might partly explain the disagreements between some of the results obtained by both methods.

122) Going out from these results, Segebade and Carter¹⁰⁹⁵ undertook systematic studies about the macroscopic homogeneities of several of these coins, using instrumental photon activation analysis. No absolute concentrations of components were analysed, but relative areal distributions of Ag, Au, Pb and Bi. Therefore, no reference material was needed. The coins were irradiated for six hours with 30 MeV bremsstrahlung at 150 microamperes mean electron beam current. After seven days decay time the coins were scanned two-dimensionally in front of a Ge(Li)-detector. This detector was equipped with a lead collimator which screened out a small spot of the coin surface. Since an apparent mass determination of the analysed partition was not practical (due to the very irregular topography of the objects) the obtained activities were normalised by the ⁵⁸Co activity produced in the matrix (see above). As a result, the Noble Metals appeared to be distributed very homogeneously, whereas locations with abnormally high bismuth concentrations were found distributed irregularly over the coins, and lead showed a pronounced concentration gradient across the total coin body.

123) The work reviewed next combines both fields of science discussed in this paragraph, namely archaeometry and forensic science. Lead and copper in tin vessels were analysed using instrumental photon activation analysis (Segebade, Ref.¹⁰⁹⁶). These vessels were offered for sale and declared as late medieval works or as produced shortly thereafter. By stylistical check some of them were suspected to be recent forgeries. Studying medieval regulations concerning the purity requirements of the basic material, the concentrations of lead and copper appeared to be useful fingerprints for genuinity assessment; at least these data were expected to serve as additional indicators along with the stylistical investigations. Samples of 50-200 milligrams were taken from most of the twenty objects under study. The others were analysed non-destructively as also performed in the above discussed analysis of a silver vase reported by Reimers et al.^{884,1180}; see Rev.118. The irradiations were conducted with an electron linear accelerator using 30 MeV electron energy at 150 microamperes mean electron beam current. The average exposure time was one hour, in the case of non-destructive analysis 2.5 hours since the objects had to be removed from the beam converter to comprise a large area of the specimens. Gamma measurements were carried out with a standard Ge(Li) spectrometer. The copper concentrations ranged between 0.1 and 1%, and lead between 0.5 and 7%. The particular problem in this case was due to the tin matrix. The resulting spectra were extremely complex because of the large number of photonuclear reactions of tin (see Ch.5). Due to the relatively high concentrations to be analysed, instrumental photon activation analysis could be applied in this case, but for event-

ual trace analyses in tin matrix one would either have to insert a chemical separation step into the analysis procedure or another technique would be the method of choice, e.g. neutron activation analysis.

As a result, several of the objects could be clearly identified as forgeries since the concentrations of the major constituents of the alloy (tin, copper and lead) did essentially differ from the material compositions indicated by the hallmarks imprinted on the vessels.

- Forensic analyses

Photon activation analysis has been applied least to forensic science as yet. However, it is an interesting fact that photoactivation of heavier elements was one of the first to be applied - if not the very first - to crime detection.

124) As early as 1964, Bryan et al.^{1097,1098} analysed lead in moonshine whiskey using bremsstrahlung activation. It is furtherly interesting to note that this pioneer work was performed without any sample treatment prior to or after irradiation. The samples were irradiated with 25 MeV bremsstrahlung of a 45 MeV electron linear accelerator for one hour. After a cooling period of about three days they were counted for ten minutes with a NaI spectrometer. Parallel colorimetric analyses were also carried out. The agreement of the results was acceptable. See also Ref.¹⁰⁹⁹.

In the same paper, the photon activation analysis of glass samples, also carried out purely instrumentally, was reported. Ten different samples of automobile glasses (lights, windshields etc.) were irradiated and counted multiply after several decay periods with a scintillation spectrometer. Because of the multiple peak overlap interferences in the complex resulting spectra, no absolute quantitative analysis was attempted, but glass samples from the same source could be clearly identified by the gamma spectrum pattern.

In the analysis of glass matrix, photon activation is superior to neutron activation because of the usually high sodium content of glass. In another report of this group (Settle¹¹⁰⁰), the glass analysis procedure used was described in somewhat more detail. See also Ref's.^{1101,1102}.

125) According to the authors' knowledge, there was no further application of photon activation to forensic analysis published until 1980 when Kanda et al., Ref.¹¹⁰³, also reported the analysis of glass samples in forensic context (hit-

and-run cases in traffic accidents). The suitability of the method using high resolution gamma spectrometry was examined analysing an NBS reference glass sample. A multi-element reference material was prepared by adding known amounts of compounds of the desired elements to a synthetic glass matrix. The samples were powdered, wrapped into aluminium foil and pelletised. Samples and reference materials were sandwiched and then sealed in a silica tube. The irradiation was conducted with 30 MeV bremsstrahlung at 100 microamperes mean electron beam current. After irradiation, the samples were repacked and counted several times after increasing cooling periods with standard Ge(Li) spectrometers. Na, Mg, Ca, Sc, Ti, Mn, Co, Ni, As, Rb, Sr, Y, Zr, Nb, Sb, Cs and Ce were analysed. The reported sensitivities were between 400 ng/g (for Y and Cs) and 0.035% (for Ca). As far as certified NBS-values or other comparative data were available, good agreement was stated.

In Tab.6.2-9, a summary of papers about photon activation analysis in archaeology and forensic science is presented.

Tab.6.2-9: Instrumental photon activation analysis of archaeological and forensic material

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
Bronze	30 (not given)	Fe, Ni, Zn, Sn, Pb	1087	116
Pottery	30 (150)	Na, Mg, Si, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, Ce, Pb, U	156, 1081-1084, 1088	117
Noble Metal objects	15, 30 (150)	Cu, Ag, Au	884, 1180	118
Bronze	30 (150)	Fe, Ni, Cu, Zn, As, Ag, Sn, Sb, Pb	58	119
Brass coins	30 (150)	Cr, Mn, Ni, Zn, Ge, As, Se, Ag, Sn, Sb, Te, Au, Tl, Pb, Bi, U	1091	120
Copper coins	30 (150)	Mn, Fe, Ni, Zn, As, Se, Ag, Sn, Sb, Te, Au, Pb, U	1094	121
Copper coins	30 (150)	Ag, Au, Pb, Bi	1095	122
Tin objects	30 (150)	Cu, Pb	1096	123
Whisky	25 (500)	Pb	1097	124
Glass	25 (500)	Na, Zn, As, Sr, Y, Zr, Sn (Nb, Mo)	1100	
Glass	30 (100)	Na, Mg, Ca, Sc, Ti, Mn, Co, Ni, As, Rb, Sr, Y, Zr, Nb, Sb, Cs, Ce	1103	125

6.2.4.7 Comparison studies; analysis of reference materials

There are not too many papers to be found in the literature which deal with the analysis of reference materials or intercomparison studies exclusively; mostly these are performed along with other analyses. Therefore, most of the publications discussed in this paragraph are reviewed in other context in the preceding paragraphs or in the following final one. At this point the results of the comparison with either certified or recommended data or results of other analyses of the same material are presented only and the reader may find more detail on the scientific background and the analysis procedure in the concerning paragraphs.

Studying the literature one can differentiate roughly between four material classes analysed by instrumental analysis for comparison studies. First, rocks, ashes, dusts and related matter, second, metal-based material, third, organic-based material and finally, glasses. Since several specific reference materials (e.g NBS-SRM) have been analysed by many working groups it is practical to combine these results. Since every experienced analyst uses certified multielement reference materials, either exclusively or as secondary standard, many comparative data obtained by instrumental photon activation analysis and other techniques can be found in the application section of this book. In this paragraph, only a few examples were given to demonstrate accuracy and precision achievable in instrumental photon activation analysis. Moreover, materials of widespread use are focussed, so as to supply the reader of this book with concentration data of many components in these specimens which are not given by the producer, be it as certified or recommended values.

On reviewing the literature, it appears that within the material category named first (rocks, ashes etc.) fly ash was studied most, particularly the NBS-reference coal fly ash (NBS-SRM 1633). Unfortunately, this material ran out of stock, hence the concentration data might be of limited practical use for the analyst; nonetheless, the comparison elucidates the quality of photon activation analysis results.

In the following tables, all concentration values are given in micrograms per gram unless stated otherwise.

In the leading explanatory paragraph, the sources of the data presented in the table are given, followed eventually by several remarks about these sources or the concerned material.

- Analysis of NBS-SRM 1633 (coal fly ash)

Explanations to Tab.6.2-10:

- a - Certified or recommended (in brackets) values
- b - Chattopadhyay and Jervis⁸⁸³
- c - Paciga et al.¹¹⁰⁴
- d - Chattopadhyay and Jervis¹¹⁰⁵
- e - Roberts et al.⁹⁷⁵
- f - Öndov et al.^{1002,1003}
- g - Kato et al.⁹¹⁹
- h - Kato et al.⁹⁵⁶
- i - Chattopadhyay³³⁰
- j - idem, photon activation³³⁰
- k - idem, neutron activation³³⁰
- l - Jervis et al.¹⁰¹⁸
- m - Segebade et al.¹⁵⁷
- n - Segebade and Fusban⁶⁸⁸

Another compilation of comparative concentration values obtained from the analysis of coal fly ash (BCR No.38) using various methods including photon activation analysis can be found in Ref.¹¹⁰⁶; see also¹¹⁰⁷. This report contains the results of a certification campaign initiated by the European Community Reference Bureau (BCR).

Tab.6.2-10; values given in $\mu\text{g/g}$ unless stated

El.	a	b,c,d,e	f	g,h	i,j,l	k	m
Na	--	3400 \pm 300	--	3860 \pm 130	3300 \pm 150	3200 \pm 300	--
Mg%	--	1.48 \pm 0.01	--	1.50 \pm 0.01	1.50 \pm 0.15	1.68 \pm 0.21	--
Si%	--	--	21 \pm 2	--	20 \pm 1.6	--	--
Cl	--	19.6 \pm 0.1	--	--	25 \pm 7	32 \pm 10	--
K%	(1.72)	--	--	1.59 \pm 0.05	1.60 \pm 0.06	1.69 \pm 0.13	--
Ca%	--	3.92 \pm 0.28	5.3 \pm 0.5	5.1 \pm 0.03	4.4 \pm 0.4	4.5 \pm 0.5	--
Sc	--	20.7 \pm ?	--	--	27 \pm 2	25.5 \pm 2	--
Ti	--	7320 \pm 40	7300 \pm 300	7660 \pm 70	7250 \pm 360	7300 \pm 280	--
V	214 \pm 8	208 \pm 12	--	--	210 \pm 12	220 \pm 15	--
Cr	131 \pm 2	131 \pm 6.1	--	142 \pm 9	131 \pm 6	135 \pm 6	--
Mn	493 \pm 7	495 \pm 25	--	491 \pm 10	495 \pm 15	500 \pm 15	--
Fe%	6.14 \pm 0.01	6.08 \pm 0.52	--	4.24 \pm 0.19	6.1 \pm 0.2	6.2 \pm 0.4	--
Co	(38)	35.4 \pm 2.8	--	42 \pm 3	40 \pm 2	42 \pm 1.6	--
Ni	98 \pm 3	96.8 \pm 3.2	92 \pm 6	96 \pm 3	97 \pm 5	95 \pm 9	100 \pm 7
Cu	128 \pm 5	--	--	--	--	--	140 \pm 20
Zn	210 \pm 20	214 \pm 16	216 \pm 25	--	215 \pm 20	200 \pm 20	205 \pm 20
As	61 \pm 6	60.7 \pm 2.6	61.5 \pm 3.0	65 \pm 1	60 \pm 2.6	59 \pm 4	63 \pm 4
Se	9.4 \pm 0.5	9.48 \pm 0.8	--	--	9.5 \pm 0.8	9.8 \pm 1	10.0 \pm 0.9
Br	--	--	--	--	--	11.2 \pm 3.5	--
Rb	(112)	--	125 \pm 10	95 \pm 1	120 \pm 10	116 \pm 10	--
Sr	(1380)	1373 \pm 95	--	1244 \pm 6	1370 \pm 120	1500 \pm 180	--
Y	--	--	62 \pm 10	67 \pm 1	60 \pm 8	--	--
Zr	--	301 \pm 22	301 \pm 20	298 \pm 6	300 \pm 20	310 \pm 20	--
Mo	--	1.52 \pm 0.15	--	--	0.5 \pm 0.08	--	--
Ag	0.03 \pm 0.02	1.32 \pm 0.13	--	--	0.4	0.1	--
Cd	1.45 \pm 0.06	1.52 \pm 0.07	--	--	1.5 \pm 0.1	--	1.2 \pm 0.2
In	--	0.28 \pm 0.03	--	--	0.29 \pm 0.06	0.32 \pm 0.08	--
Sn	--	12.5 \pm 1.2	--	--	12 \pm 1	10.2 \pm 1.4	--
Sb	--	7.14 \pm 0.56	7.0 \pm 1.1	7.1 \pm 0.7	7.1 \pm 0.5	6.9 \pm 0.5	--
Te	--	2.32 \pm 0.2	--	--	2.3 \pm 0.3	--	--
I	--	--	2.9 \pm 1.2	--	2.8 \pm 1.0	3.0 \pm 1.0	--
Cs	--	0.63 \pm 0.06	--	--	8.0 \pm 1	8.3 \pm 1.0	--
Ba	--	2610 \pm 210	--	--	2600 \pm 160	2710 \pm 190	--
Ce	--	--	--	153 \pm 1	152 \pm 10	140 \pm 10	--
Hg	0.14 \pm 0.01	0.135 \pm 0.01	--	--	0.13 \pm 0.03	0.16 \pm 0.04	0.20 \pm 0.02
Tl	(4)	3.64 \pm 0.34	--	--	3.7 \pm 0.4	--	3.5 \pm 0.5

Tab.6.2-10, continued

El.	a	b, c, d, e	f	g, h	i, j, l	k	m
Pb	70±4	70.7±2.6	75±5	--	71±3	--	68±4
Bi	--	(1.08)	--	--	41	--	--
U	11.6±0.2	--	--	--	--	--	11.9±0.6
	12.1±0.8(n)						
	12.2±1.0(n)						

- Analysis of waste incineration fly ash (Schmitt et al.⁹⁸⁴)

Explanations to Tab.6.2-11

- a - Schmitt et al., photon activation⁹⁸⁴
- b - Hancock¹¹⁰⁹
- c - Schmitt et al., neutron activation⁹⁸⁴
- d - Schneider¹¹⁰⁸

Neutron activation analysis was performed with different procedures; the values marked with an asterisk were obtained by 14 MeV neutron activation. Several of the photon activation values do not agree with those presented in⁹⁸⁴; they have been updated on grounds of more recent results. The relative standard deviations of the X-ray fluorescence results range between 5 and 10 %. Values in brackets are not certain.

A batch of very similar material (BCR No.176) has recently passed the certification procedure of the European Community Reference Bureau (BCR). The results including those obtained by instrumental photon activation analysis can be found in Ref's. 1110,1205.

Tab.6.2-11; values given in $\mu\text{g/g}$ unless stated

El.	a	b	c	d
C%	2.5 ± 0.1	--	--	--
F%	0.15 ± 0.03	--	--	--
Na%	1.66 ± 0.04	1.51 ± 0.02	1.64 ± 0.05	1.71
Mg%	1.80 ± 0.07	1.67 ± 0.25	$1.54 \pm 0.04^*$	1.64
Al%	--	6.92 ± 0.12	$8.28 \pm 0.07^*$	7.63
Si%	14.00 ± 0.07	--	$14.2 \pm 0.3^*$	14.0
P%	0.3 ± 0.1	--	--	0.37
Cl%	1.28 ± 0.02	1.32 ± 0.02	--	--
K%	3.37 ± 0.09	3.03 ± 0.06	$2.26 \pm 0.15; 3.3 \pm 0.1^*$	2.71
Ca%	10.16 ± 0.18	9.87 ± 0.27	$10 \pm 1^*$	9.70
Sc	16 ± 6	9.71 ± 0.27	20 ± 2	--
Ti	7100 ± 10	6420 ± 280		6114
Cr	410 ± 13	463 ± 20	456 ± 33	436
Mn	1560 ± 50	1590 ± 30	1012 ± 70	1425
Fe%	7.89 ± 0.16	6.99 ± 0.25	$7.55 \pm 0.1; 7.6 \pm 0.1^*$	7.18
Co	31 ± 2	36.4 ± 1.8	38 ± 1	(36)
Ni	126 ± 4	--	--	128
Cu	727 ± 30	--	769 ± 69	(707)
Zn%	1.24 ± 0.05	--	$1.12 \pm 0.06; 1.2 \pm 0.1^*$	(1.6)
Ga	261 ± 28	--	--	--
Ge	16.4 ± 0.4	--	--	--
As	93 ± 3	61.7 ± 3.7	82 ± 7	--
Se	25 ± 6	--	20 ± 3	--
Br	145 ± 18	80.9 ± 2.8	136 ± 12	--
Rb	140 ± 2	135 ± 6	138 ± 5	136
Sr	778 ± 38	750 ± 230	--	774
Y	34 ± 1	--	--	(50)
Zr	154 ± 3	--	151 ± 21	154
Nb	15.9 ± 0.7	--	--	(24)
Mo	20 ± 2	--	28 ± 2	--
Ag	42 ± 2	--	41 ± 2	--
Cd	273 ± 9	--	229 ± 60	--
Sn	3240 ± 150	--	3900 ± 600	(3400)
Sb	228 ± 12	155 ± 7	212 ± 12	--
I	24 ± 1	--	--	--
Cs	19 ± 1	13.7 ± 0.3	14 ± 1	--
Ba	4410 ± 80	4520 ± 100	4010 ± 140	(4850)

Tab.6.2-11, continued

El.	a	b	c	d
Ce	53 ± 2	70.7 ± 2.5	61 ± 5	61
Nd	32 ± 2	27 ± 3	56 ± 9	--
Sm	6 ± 1	4.92 ± 0.15	--	--
Hg	0.3 ± 0.1	--	0.27 ± 0.01	--
Tl	3.91 ± 0.3	--	--	--
Pb	6350 ± 180	--	--	6400
U	4.3 ± 0.2	8.28 ± 0.78	4.1 ± 0.2	--

- Analysis of air particulate⁹⁵⁰

Explanations to Tab.6.2-12:

a - consensus mean value

b - Neider et al.⁹⁵⁰

This large-scale investigation work was reviewed in the subparagraph on air particulate analysis. Altogether, about 30,000 single analysis data were obtained by many laboratories using a large variety of analytical methods. The results of one specimen are presented in the following table. All values are given in nanograms per cubic meter of air. The following techniques were applied: instrumental photon activation analysis, thermal and epithermal neutron activation analysis, atomic absorption spectrometry, inductively coupled plasma excited atomic emission spectrometry, proton induced X-ray emission spectrometry and X-ray fluorescence analysis methods, among them one using multiple total reflection of the exciting beam (Schwenke and Knoth¹¹¹¹).

Tab.6.2-12; values given in $\mu\text{g/g}$

El.	a	b
Ca	5660 \pm 400	5925 \pm 484
Cr	54 \pm 4	44.5 \pm 8.7
Mn	208 \pm 20	202 \pm 10
Co	5 \pm 1	3.9 \pm 0.7
Ni	44 \pm 3	48 \pm 6.9
Zn	897 \pm 70	1004 \pm 80
As	89 \pm 5	60.3 \pm 19.8
Br	245 \pm 15	259 \pm 21
Cd	14 \pm 3	10.7 \pm 2.9
Sn	71 \pm 6	73.7 \pm 4.6
Sb	30 \pm 4	25.1 \pm 3.6
Pb	923 \pm 70	991 \pm 80

- Analysis of U.S.G.S. standard rocks

Explanations to Tab.6.2-13 (AGV-1) and Tab.6.2-14 (BCR-1)

In the analysis of rock matrix there is a standard material - more exactly, a set of standards - which is referred to most, as to the above discussed NBS fly ash in the environmental analysis, namely the U.S.G.S. standard rocks (Flanagan¹¹¹²). In the following, photoactivation analysis results of some of these specimens are compared with other results. Out of the large number of comparative data, the analytical results of two rock samples are presented here, namely the samples AGV-1 and BCR-1; apparently, these two materials have been used most in geochemical photon activation analysis.

- a - Certified or recommended value (Flanagan¹¹¹²) or mean value of the given range (Kato et al.¹⁰⁵²)
- b - Kato et al.¹⁰⁵²
- c - Das et al.¹⁰⁵³
- d - Segebade¹¹¹³
- e - Hislop and Williams¹⁰²⁷
- f - Schmitt et al.¹⁰⁴⁹
- g - van Zelst¹⁰⁶³
- h - Segebade and Fusban⁶⁸⁸
- i - Masumoto and Suzuki¹⁰⁵⁹
- j - Kato et al.¹⁰⁵⁴

No uncertainty data were given by Flanagan (a) and van Zelst (g).

Tab.6.2-13; values given in $\mu\text{g/g}$ unless stated

El.	a	b	c	d	other
Na%	3.21	3.07 ± 0.1	--	3.21 ± 0.1	--
Mg%	0.90	0.93 ± 0.008	0.94 ± 0.04	0.94 ± 0.05	0.92 ± 0.02 (f)
Ca%	3.56	3.42 ± 0.01	3.40 ± 0.04	3.50 ± 0.05	4.02 ± 0.08 (f); 3.43 (g)
Sc	13.4	--	--	12 ± 2	--
Ti%	0.65	0.69 ± 0.006	0.60 ± 0.03	0.61 ± 0.02	0.73 ± 0.014 (f)
Cr	12.2	--	--	12 ± 1	--
Mn	728	600 ± 24	670 ± 18	850 ± 100	--
Fe%	4.76	4.95 ± 0.18	--	4.76 ± 0.2	4.8 (g)
Co	15.5	19.6 ± 2.6	--	16 ± 4	--
Ni	17.8	13.1 ± 0.9	--	20 ± 4	24 ± 3 (f); 16.2 ± 2.2 (i); 27.7 (j)
Zn	84	--	--	90 ± 5	--
As	0.8	--	--	≤ 1	--
Rb	89.4	91.6 ± 7.0	--	70 ± 8	--
Sr	657	742 ± 6	626 ± 18	662 ± 20	--
Y	25.3	26.0 ± 1.6	--	25 ± 2	--
Zr	227	219 ± 12	220 ± 20	231 ± 14	--
Nb	21.7	18.8 ± 0.6	29 ± 10	14 ± 4	--
Sn	4.2	--	--	≤ 20	--
Sb	4.5	--	--	4.3 ± 0.5	--
Cs	1	--	--	≤ 1	--
Ba	1410	1326 ± 10	--	1215 ± 30	--
Ce	76	73.2 ± 4	--	60 ± 2	--
Nd	39	--	--	42 ± 4	--
Sm	5.9	--	--	≤ 5	--
Tl	1	--	--	1 ± 0.3	--
Pb	35.1	--	--	37 ± 3	--
U	1.88	--	--	--	2.4 ± 0.1 (h)

Tab.6.2-14; values given in $\mu\text{g/g}$ unless stated

El.	a	b	c	d	other
Na%	2.46	2.40 ± 0.08	--	--	--
Mg%	1.98	2.10 ± 0.01	2.0 ± 0.1	--	1.9 ± 0.04 (f)
Ca%	4.97	4.82 ± 0.08	4.62 ± 0.08	4.93 ± 0.1	5.09 ± 0.12 (f); 4.91 (g)
Ti%	1.34	1.25 ± 0.005	1.32 ± 0.02	1.37 ± 0.03	1.30 ± 0.03 (f)
Mn	1350	1301 ± 3	1476 ± 28	--	--
Fe%	9.45	9.48 ± 0.03	--	9.51 ± 0.2	9.2 (g)
Co	35.5	32.6 ± 3.8	--	--	--
Ni	15.0	14.5 ± 4.0	--	--	10 ± 3 (f)
Rb	72.8	43.3 ± 5.0	--	--	--
Sr	345	346 ± 5	297 ± 8	310 ± 15	--
Y	46.2	45.6 ± 4.1	--	--	--
Zr	185	171 ± 2	200 ± 25	180 ± 10	--
Nb	34.1	27.3 ± 2.3	44 ± 15	--	--
Sb	0.7	--	--	≤ 10	--
Cs	12.5	--	--	≤ 10	--
Ba	790	1404 ± 59	--	--	--
Ce	49	47.8 ± 4.3	--	--	--
Tl	0.4	--	--	≤ 10	--

- Analysis of ancient Roman pottery (Neider et al.⁵⁸)

Explanations to Tab.6.2-15:

The results were obtained by instrumental photon activation analysis, thermal neutron activation analysis and wavelength-dispersive X-ray fluorescence analysis. Uncertainty values were not given in the quoted paper; in photon activation analysis they varied between 2 rel.% (for Ti) and 25 rel.% (for Eu). The X-ray fluorescence values have standard deviations between 3 and 5 rel.%, and in thermal neutron activation analysis they were found between 3 rel.% (for Rb) and 20 rel.% (for Se).

For this intercomparison study, a standard pottery powder was prepared and spiked with several trace elements, e.g. Cr, Ni, Cs.

Tab.6.2-15; values given in $\mu\text{g/g}$ unless stated

El.	IPAA	XRF	therm. NAA
Na%	0.43	0.45	--
Mg%	1.17	1.15	--
Si%	29.0	30.0	--
K%	2.49	2.08	2.16
Ca%	5.0	4.5	--
Sc	14.1	--	16.7
Ti%	0.44	0.46	--
Cr	220	182	215
Fe%	2.94	3.01	2.9
Co	16.0	--	14.7
Ni	266	262	--
Zn	280	292	--
Se	0.4	--	0.3
Rb	140	152	131
Sr	200	184	--
Zr	250	252	--
Cs	110	--	122
Ba	660	603	659
Ce	223	--	217
Eu	1	--	1.4
W	1.1	--	2.4

- Analysis of NBS-SRM 1645 (River Sediment)

Explanations to Tab.6.2-16:

a - Certified or recommended value

b - Berthelot et al.¹⁰⁰⁵

c - Kato and Kato¹¹¹⁴

Standard deviation values were not given by Berthelot et al. (b); the quality of the values is specified thus: "...depending on the concentration, the specific activity and the half-life of the radionuclide, the accuracy is of the order of 2% to 30%." It remains unclear if this value is established theoretically or by experiment, and what is the precision of the data.

Tab.6.2-16; values given in $\mu\text{g/g}$ unless stated

El.	a	b	c
Na%	0.55	--	0.545 \pm 0.011
Ti%	--	825	642 \pm 13
Cr%	2.96	2.98	2.29 \pm 0.08
Mn	785	--	750 \pm 18
Fe%	11.3	--	10.51 \pm 0.18
Co	8	24	8.5 \pm 0.3
Ni	45.8	48	47 \pm 3
Cu	109	106	--
Zn	1720	1730	1540 \pm 67
Sr	--	862	851 \pm 13
Zr	--	71	55 \pm 3
Cd	10.2	11	--
Ce	--	28	20 \pm 0.6
Hg	1.1	1.3	--
Tl	1.44	1.9	--
Pb	714	724	--
Th	1.62	1.8	--
U	1.11	1.4	--

- Analysis of sewage sludge (Chattopadhyay³³⁰)

Explanations to Tab.6.2-17:

- a - Instrumental photon activation analysis
- b - instrumental thermal neutron activation analysis
- c - mean of other values obtained within a Round Robin interlaboratory test
Chawla et al.¹¹¹⁵, van Loon et al.¹¹¹⁶, van Loon¹¹¹⁷)

Tab.6.2-17; values given in $\mu\text{g/g}$ unless stated

El.	a	b	c
Na%	0.17 ± 0.02	0.18 ± 0.02	0.17 ± 0.04
Mg%	0.60 ± 0.05	0.62 ± 0.04	0.64 ± 0.10
Cl%	0.40 ± 0.03	0.44 ± 0.04	--
K%	0.20 ± 0.02	0.19 ± 0.02	0.20 ± 0.03
Ca%	4.50 ± 0.2	4.32 ± 0.2	4.53 ± 0.47
Sc	0.75 ± 0.08	0.82 ± 0.08	--
Ti%	0.16 ± 0.02	0.18 ± 0.01	--
V	26 ± 2	25 ± 2	--
Cr	390 ± 30	412 ± 24	391 ± 43
Mn	400 ± 30	385 ± 40	399 ± 30
Fe%	7.55 ± 0.65	7.70 ± 0.40	7.65 ± 1.37
Co	10.2 ± 1.1	11.1 ± 1	--
Ni	25.6 ± 2	23.2 ± 2.5	27.8 ± 3.9
Zn%	0.25 ± 0.02	0.28 ± 0.02	0.27 ± 0.01
As	10.2 ± 0.9	11.4 ± 1	--
Se	0.35 ± 0.1	0.30 ± 0.1	--
Rb	21 ± 2	19 ± 2	--
Sr	5.8 ± 0.4	6.5 ± 0.7	--
Zr	85 ± 7	94 ± 10	--
Mo	2.6 ± 0.3	3.1 ± 0.5	--
Ag	65 ± 4	68 ± 7	--
Cd	16.5 ± 1.2	--	18.7 ± 1.8
In	< 0.1	0.08 ± 0.03	--
Sn	< 8	4.2 ± 0.8	--
Sb	7.3 ± 0.62	6.8 ± 0.7	--
I	11.5 ± 1.5	10.2 ± 1.2	--
Cs	2.3 ± 0.16	2.8 ± 0.3	--
Ba	620 ± 45	710 ± 50	--
Ce	8.2 ± 0.8	7.6 ± 0.9	--
Hg	25 ± 2	31 ± 4	26.5 ± 2.1
Pb%	0.1 ± 0.005	--	0.10 ± 0.01

- Analysis of standard glass (NBS-SRM 613)

Explanations to Tab.6.2-18:

a - Certified or recommended value

b - Hislop and Williams⁹⁵², photon activation

c - Kanda et al.¹¹⁰³

d - Hislop and Williams⁹⁵², thermal neutron activation

e - Masters and Lutz¹⁰⁰¹

Tab.6.2-17; values given in $\mu\text{g/g}$

El.	a	b	c	other
Ti	50.1 \pm 0.8	--	55.2 \pm 8.3	--
Mn	39.6 \pm 0.8	--	39.0 \pm 2.6	--
Co	35.5 \pm 1.2	--	33.3 \pm 1.0	--
Ni	38.8 \pm 0.2	--	40.1 \pm 1.1	--
As	--	35 \pm 5	35.6 \pm 0.3	--
Rb	31.4 \pm 0.4	--	32.0 \pm 1.4	--
Sr	78.4 \pm 0.2	70 \pm 10	77.3 \pm 1.3	--
Zr	--	35 \pm 9	41.8 \pm 1.1	--
Sb	--	40 \pm 6	39.4 \pm 0.3	38 \pm 1 (d)
Cs	--	50 \pm 8	4.8 \pm 1.2	42 \pm 0.5 (d)
Ce	39 \pm ?	50 \pm 15	40.6 \pm 0.2	--
Tl	15.7 \pm 0.3	13 \pm 3	--	14 \pm 1 (e)

- The analysis of bismuth (Lutz and Sato¹¹¹⁸)

This short compilation was included since bismuth is one of the elements which are difficult to analyse by many methods, thermal neutron activation analysis in particular. However, it has photonuclear data which are quite favourable for photon activation analysis if the irradiation is carried out at high bremsstrahlung energies. Lutz and Sato used 45 MeV for activation. At this energy, the analytical sensitivity for bismuth is almost as good as for lead. Moreover, the the gamma-ray energies of the activation product used for analysis (²⁰⁶Bi) are located in favourable energy regions and there is no first order interference possible.

Tab.6.2-19; values given in µg/g

<u>Sample</u>	<u>PAA</u>	<u>certified or literature</u>
54-D Tin-Base Bearing Metal	485, 494, 531, 497	eight round robin values from 370 to 500; mean: 440
53-E Lead-Base Bearing Metal	525, 540, 548	520

Recently, a set of high-purity lead samples (BCR No's. 286, 287, 288) was certified for 12 trace components - including bismuth - using various techniques, among them radiochemical photon activation analysis, by the European Community Reference Bureau (BCR). The results can be taken out of Ref.¹¹¹⁹.

- Analysis of Noble Metals (Weise and Segebade¹⁵⁵)

Explanations to Tab.6.2-20 (electrolytic copper) and Tab.6.2-21 (platinum ore):

Electrolytic copper:

- a - Expected concentration
- b - Results of the round robin interlaboratory test (Pauwels et al.¹¹²⁰); the number of participating laboratories is given in parentheses.
- c - photon activation analysis using conventional gamma spectrometry
- d - photon activation analysis, using low energy photon spectrometry

Platinum ore:

- a - certified value
- b - photon activation analysis using gamma spectrometry
- c - photon activation analysis using low energy photon spectrometry

Palladium, silver, platinum and gold were added to high purity electrolytic copper and analysed by twenty laboratories using many techniques. The expected concentration (a) is based upon the amount of noble metal added to the melted matrix. The given error limit is identical to the maximum error caused by contamination of the matrix copper (Pauwels¹¹²⁰).

Tab.6.2-20; values given in $\mu\text{g/g}$

Sample#	Elem.	a	b	c	d
Pd I	Pd	1.19 ± 0.03	1.22 ± 0.10 (12)	1.20 ± 0.05	1.20 ± 0.04
Pd II	Pd	11.9 ± 0.3	12.0 ± 0.6 (17)	11.8 ± 0.2	12.1 ± 0.1
Pd III	Pd	100 ± 4	97.7 ± 3.9 (21)	95 ± 2	96.9 ± 0.4
Pt I	Pt	1.19 ± 0.06	1.19 ± 0.1 (11)	1.17 ± 0.05	1.18 ± 0.06
Pt II	Pt	11.9 ± 0.3	11.7 ± 0.4 (13)	11.7 ± 0.1	11.7 ± 0.2
Pt III	Pt	100 ± 2	98.7 ± 3.4 (20)	102 ± 2	101 ± 3
Ag/Au I	Ag	1000 ± 10	999 ± 7 (5)	999 ± 10	1005 ± 10
	Au	10.0 ± 0.1	10.0 ± 0.6 (18)	10.8 ± 0.4	10.4 ± 0.5
Ag/Au II	Ag	2500 ± 25	2490 ± 10 (7)	2478 ± 16	2491 ± 10
	Au	50.0 ± 0.5	49.1 ± 2.2 (17)	48.7 ± 0.7	49.0 ± 1
Ag/Au III	Ag	4999 ± 50	4994 ± 31 (7)	5031 ± 25	5010 ± 19
	Au	100.0 ± 1.0	101.6 ± 3.6 (17)	98.9 ± 2.1	98.0 ± 2.5

Tab.6.2-21; values given in $\mu\text{g/g}$

Elem.	a	b	c
Ru	0.43 ± 0.057	0.37 ± 0.04	--
Rh	0.24 ± 0.013	0.29 ± 0.03	--
Pd	1.53 ± 0.032	1.50 ± 0.08	1.44 ± 0.05
Ag	0.42 ± 0.040	--	0.39 ± 0.01
Os	0.063 ± 0.0068	--	≤ 1
Ir	0.074 ± 0.012	--	0.08 ± 0.01
Pt	3.74 ± 0.045	3.81 ± 0.09	3.90 ± 0.1
Au	0.31 ± 0.015	0.27 ± 0.02	0.25 ± 0.03

- Analysis of Noble Metals in Black Concentrates (Brebán et al.¹⁹⁶⁵)

Explanations to Tab.6.2-22:

a - Wet chemistry analysis

b - instrumental photon activation analysis

The chemical analyses were carried out in industrial laboratories and it was not possible for the authors of the quoted paper to get any information about the technique used and the quality of the results. Therefore, no precision data can be given for the comparative values. The results of one of many analysed samples are compiled here as representative. All values are given in weight per cent.

Tab.6.2-22; values given in $\mu\text{g/g}$

<u>Elem.</u>	<u>a</u>	<u>b</u>
Rh	31	31.16 ± 0.6
Pd	2.8	2.89 ± 0.2
Ag	1.6	1.62 ± 0.1
Ir	0.7	0.745 ± 0.01
Pt	14.7	14.69 ± 0.3
Au	2	2.08 ± 0.05

- Analysis of ancient Roman coinage; comparison of the results of seven methods (Carter et al.¹⁰⁹¹)

Explanations to Tab.6.2-23 and Tab.6.2-24:

- a - Instrumental photon activation analysis
- b - wet chemistry (gravimetry, colorimetry)
- c - X-ray fluorescence, wavelength dispersive
- d - dto., energy dispersive, radionuclide excitation
- e - dto., energy dispersive, tube excitation
- f - instrumental thermal neutron activation analysis
- g - atomic absorption spectrometry
- h - consensus mean value

Eight brass coins were analysed. The results of two of them are listed in the table below. Precision data are known for the photon activation values and the consensus mean only. Values in brackets are outliers and were discarded before determination of the consensus mean. The copper consensus value was calculated by subtracting all obtained mean values from a hundred per cent.

Tab.6.2-23; sample no. ERC4; values given in $\mu\text{g/g}$ unless stated

El.	a	b	c	d	e	f	g	h
Ni	88 \pm 4	100	20	(1000)	100	--	80	80 \pm 30
Cu%	72.6 \pm 2	72.63	72.8	72.02	70.7	--	71.3	72.8
Zn%	26.6 \pm 1	26.71	26.6	27.29	28.8	25.1	24.8	26.6 \pm 1.3
Ag	257 \pm 11	300	420	100	120	320	290	260 \pm 110
Sn	1032 \pm 82	(200)	1410	1600	860	--	960	1170 \pm 320
Sb	432 \pm 22	--	470	500	330	378	610	450 \pm 100
Pb	1095 \pm 45	1600	800	500	1100	--	820	1000 \pm 400

Tab.6.2-24; sample no. ERC6; values given in $\mu\text{g/g}$ unless stated

El.	a	b	c	d	e	f	g	h
Ni	161 \pm 8	300	240	(3000)	230	--	220	230 \pm 50
Cu%	83.6 \pm 2	83.6	83.7	81.83	83.8	--	83.2	83.2
Zn%	14.9 \pm 0.8	14.82	14.5	16.32	14.4	15.4	15.7	15.1 \pm 0.7
Ag	295 \pm 12	--0	460	(100)	240	380	400	360 \pm 90
Sn	6970 \pm 140	7000	7300	5500	6900	--	6800	6700 \pm 600
Sb	1271 \pm 72	--	1300	1200	1300	921	1300	1220 \pm 170
Pb	5250 \pm 82	5000	5800	4500	5500	--	5000	5200 \pm 400

- Analysis of NBS-SRM 1571 (Orchard Leaves)

Explanations to Tab.6.2-25:

Among all organic-based multielement reference materials the NBS orchard leaves standard was analysed most, particularly with activation methods.

- a - Certified or recommended value
- b - Jervis⁹⁹⁴
- c - Chattopadhyay and Jervis⁸⁸³
- d - Roberts et al.⁹⁷⁵
- e - Paciga et al.¹¹⁰⁴
- f - Chattopadhyay and Jervis¹¹⁰⁵
- g - Jervis et al.¹⁰¹⁸
- h - Hislop⁹⁶²
- i - Kato et al.¹⁰³⁰
- j - Kato et al.⁹¹⁹
- k - Yamashita and Suzuki¹¹²³
- l - Lutz^{1121,1122}
- m - Hislop et al.¹⁰³⁵
- n - Hislop and Williams¹⁰³⁶
- o - Jervis et al.¹⁰¹⁴
- p - Segebade and Fusban⁶⁸⁸
- q - Williams and Hislop¹⁰³⁸

Hislop (h) gave an estimated total error of ± 10 rel.% unless stated.

Tab.6.2-25; values given in $\mu\text{g/g}$ unless stated

El.	a	b,c,d,e,f,g	h	i, j	other
Na	82 \pm 6	79.3 \pm 5.0	150	87 \pm 11	--
Mg%	0.62 \pm 0.02	0.61 \pm 0.01	0.59	0.615 \pm 0.007	--
Cl	(700)	685 \pm 32	--	720 \pm 140	--
K%	1.47 \pm 0.03	--	--	1.45 \pm 0.08	--
Ca%	2.09 \pm 0.03	2.08 \pm 0.01	2.2 \pm 0.3	1.97 \pm 0.05	--
Sc	(0.205)	0.22 \pm 0.01	--	--	--
Cr	(2.3)	2.22 \pm 0.20	4.0 \pm 0.7	--	5.5 \pm 2.2(k)
Mn	91 \pm 4	88.2 \pm 3.4	89	95 \pm 4	93.8 \pm 17.2(k)
Fe	300 \pm 20	290 \pm 12	--	332 \pm 84	--
Ni	1.3 \pm 0.2	1.27 \pm 0.08	1.3	--	1.5 \pm 0.3(k)
Cu	12 \pm 2	--	--	--	12.1 \pm 1.3(q)
Zn	25 \pm 3	24.2 \pm 1.5	27 \pm 10	27 \pm 3	23.9 \pm 3.2(k); 29.3 \pm 2.5(q)
As	11 \pm 2	10.2 \pm 1.0	10.5	11 \pm 1	--
Rb	12 \pm 1	--	--	--	12.1 \pm 1.3(q)
Sr	(37)	36 \pm 2	--	37 \pm 1	--
Zr	--	0.21 \pm 0.02	1.6 \pm 0.5	--	--
Mo	\leq 5	2.26 \pm 0.21	\leq 0.7	--	--
Cd	0.11 \pm 0.02	0.11 \pm 0.01	\leq 0.2	--	0.11 \pm 0.01(o)
Sb	(3)	3.15 \pm 0.26	3.4	3.3 \pm 0.2	--
Ba	(51)	51.3 \pm 4.5	--	--	--
Hg	0.155 \pm 0.015	0.14 \pm 0.01	--	--	--
Pb	45 \pm 3	44.2 \pm 2.1	35	--	49.3 \pm 1.5(k); 45 \pm 1.5(l); 42 \pm 2(m,n)
U	0.029 \pm 0.003	--	--	--	0.030 \pm 0.005(p)
others: Ti:100(h); Co:0.2(a); Br:8(a); Nb: \leq 0.3(h); Sn: \leq 1(h); Cs: \leq 0.06(a), \leq 1(h); Ce:1.0(a), \leq 2(h); Tl:0.15 \pm 0.07(h)					

- Analysis of NBS-SRM 1577 (Bovine Liver)

Explanations to Tab.6.2-26:

a - Certified or recommended value

b - Kato and Sato¹⁰³¹c - Kato et al.¹⁰³⁰d - Chatt et al.¹⁰¹⁵e - Williams and Hislop¹⁰³⁸f - Lutz^{1121,1122}

No standard deviation values were given by Kato and Sato (b).

Tab.6.2-26; values given in $\mu\text{g/g}$ unless stated

Elem.	a	b	c	other
Na%	0.243 \pm 0.013	0.238	0.238 \pm 0.004	--
Mg	604 \pm 9	596	596 \pm 15	--
Cl	(0.27)	0.269	0.269 \pm 0.016	--
K%	0.97 \pm 0.06	0.97	0.969 \pm 0.09	--
Ca	124 \pm 6	140	138 \pm 18	--
Mn	10.3 \pm 1.0	--	10.2 \pm 2	--
Fe	268 \pm 8	289	274 \pm 28	--
Cu	193 \pm 10	--	--	183 \pm 8(e)
Zn	130 \pm 13	138	131 \pm 13	150 \pm 10(e)
Rb	18.3 \pm 1.0	22	18.9 \pm 1.7	--
Cd	0.27 \pm 0.04	--	--	0.25 \pm 0.03(d)
Pb	0.34 \pm 0.08	--	--	0.40 \pm 0.05(d); 0.4 \pm 0.05(f)

- Analysis of Bowen's Kale (Bowen^{1028,1124})

Explanations to Tab.6.2-27:

- a - Recommended value
- b - Hislop and Williams¹⁰²⁷
- c - Kato et al.¹⁰³⁰
- d - Hislop et al.¹⁰³⁵
- e - Hislop and Williams¹⁰³⁶
- f - Lutz¹¹²¹

Bowen's comparison data (a) are the "best" consensus values out of a large number of analysis results; no standard deviations are given but the total result range for most of the elements.

Tab.6.2-27; values given in $\mu\text{g/g}$ unless stated

Elem.	a	b	c	other
Na%	0.25	--	0.199 \pm 0.015	--
Mg%	0.16	--	0.162 \pm 0.002	--
Cl%	0.34	--	0.321 \pm 0.03	--
K%	2.46	--	2.43 \pm 0.2	--
Ca%	4.01	--	4.11 \pm 0.05	--
Mn	14.7	--	14.8 \pm 4	--
Fe	118	--	124 \pm 60	--
Zn	33.2	--	34 \pm 4	--
As	0.14	\leq 3	--	--
Rb	52.2	54 \pm 4	53.2 \pm 4	--
Sr	99	83 \pm 15	90 \pm 1	--
Zr	\leq 20	\leq 2	--	--
Sb	0.07	\leq 2	--	--
Cs	0.07	\leq 2	--	--
Tl	0.2	\leq 2	--	--
Pb	3	\leq 30	--	2.7 \pm 0.4(d,e); 3.4 \pm 0.4(f)

- Analysis of NBS-SRM 1633 (Coal)

Explanations to Tab.6.2-28:

This material is one of the mostly used in multielement analyses of organic material, particularly fossile fuel material. However, in photon activation analysis it has not been applied very often as yet.

a - Certified or recommended value

b - Chattopadhyay and Jervis⁸⁸³

c - Chattopadhyay¹⁰⁰⁷

d - Öndov et al.^{1002,1003}

e - Jervis et al.¹⁰⁴¹

f - Segebade and Fusban⁶⁸⁸

Tab.6.2-27; values given in $\mu\text{g/g}$ unless stated

Elem.	a	b	c	other
Na	--	351 \pm 30	350 \pm 20	--
Mg%	--	0.160 \pm 0.015	0.16 \pm 0.02	--
Cl	--	930 \pm 48	890 \pm 100	--
Ca%	--	--	0.42 \pm 0.04	0.47 \pm 0.06(d)
Sc	--	3.58 \pm 0.35	3.6 \pm 0.3	--
Ti	(800)	973 \pm 50	900 \pm 100	890 \pm 200(d)
V	35 \pm 3	33.9 \pm 3.0	34 \pm 3	--
Cr	20.2 \pm 5	26.1 \pm 2.1	19.5 \pm 0.8	--
Mn	40 \pm 3	47.1 \pm 4.1	43 \pm 3	--
Fe%	0.87 \pm 0.03	0.869 \pm 0.041	0.87 \pm 0.04	--
Co	(6)	5.50 \pm 0.40	5.6 \pm 0.4	--
Ni	15 \pm 1	13.5 \pm 1.2	14 \pm 2	--
Zn	37 \pm 4	37.5 \pm 2.8	37 \pm 3	--
As	5.9 \pm 0.6	5.75 \pm 0.37	5.8 \pm 0.3	8 \pm 2(d)
Se	2.9 \pm 0.3	3.03 \pm 0.28	3.0 \pm 0.3	--
Rb	--	--	20 \pm 2	20 \pm 2(d)
Sr	--	133 \pm 10	140 \pm 15	--
Zr	--	15.6 \pm 1.4	16 \pm 2	--
Ag	\leq 0.1	1.05 \pm 0.1	\leq 0.4	--
Cd	0.23 \pm 0.03	0.199 \pm 0.02	0.20 \pm 0.02	0.20 \pm 0.02(e)
In	--	0.23 \pm 0.02	0.23 \pm 0.03	--
Sn	--	10.2 \pm 1.0	10 \pm 1	--
Te	(0.1)	(1.02)	\leq 1	--
Cs	--	0.35 \pm 0.04	1.3 \pm 0.1	--
Ba	--	314 \pm 20	315 \pm 20	--
Hg	(0.12)	(0.1)	(0.1)	--
Tl	0.59 \pm 0.05	0.512 \pm 0.06	0.52 \pm 0.06	--
Pb	30 \pm 9	32.1 \pm 1.8	32 \pm 2	--
U	1.4 \pm 0.02	--	--	1.55 \pm 0.1(f)
others: K%:0.27 \pm 0.01(c); Mo:0.20 \pm 0.04(c); Sb:3.09 \pm 0.26(b)				

6.2.4.8 Systematic single element study

This paragraph is intended to be used as a practical reference during analytical work. Each element considered in chapter 5, in the order of the atomic number, is studied separately. The light elements yielding pure β^+ -emitters exclusively are not included since they are discussed extensively in the preceding chapter. Interferences are mentioned and procedures to avoid or minimise them are discussed, basing upon practical laboratory experience. Furthermore, in relevant cases, the behaviour of the element during activation is discussed, regarding it as a major matrix component or as a trace to be analysed, in terms of both gained radioactivity and physico-chemical stability. Finally, papers are quoted in which the regarded element was particularly studied. If these papers were reviewed in the preceding paragraphs, the review number is also given.

Beryllium

The analysis of beryllium using the $(\gamma,2n)$ -reaction given in 5.3.1 is not recommendable since it is very insensitive. Moreover, it is subject to first order interference by boron and carbon (Foster and Voigt¹¹²⁶, Artus¹¹²⁷, Oka et al.¹¹²⁸, Ricci⁹¹⁵).

Carbon

Carbon usually is analysed by annihilation quanta counting after activation and subsequent radiochemical separation (see chapter 6.1). However, the $(\gamma,\alpha n)$ -reaction leading to ^7Be was used as an internal flux monitor during instrumental photon activation analysis of iodine in organic matrix by Cardarelli et al.¹¹²⁹ although at the time of publication of this paper it apparently was not certain that carbon (in the organic matrix) was the target element. In one report only (Aras et al.⁹⁴⁹) this reaction was proposed (but not used) for carbon analysis. In organic matrices, carbon normally is the only significant source of disturbing background activity. However, due to the short half-life of ^{11}C (20 m) samples can be counted quasi-interference-free after relatively short cooling periods.

Sodium

Sodium can easily be analysed by the 1275 keV gamma-ray line of ^{22}Na . The half-life is conveniently long, but the sensitivity is poor. Interferences due to

gamma-ray line overlap are unlikely in many matrices, but competing reactions of magnesium and aluminium might occur and be significant if these elements are present large excess (Aras et al.⁹⁴⁹, Rev.31, Chattopadhyay and Jervis⁸⁸³, Rev.40, Chattopadhyay³³⁰). Galatanu and Engelmann¹⁰⁶⁸, Rev.104, report a secondary decay interference via: $^{24}\text{Mg}(\gamma, 2n, \beta^+)^{22}\text{Na}$. However, this interference will surely not occur since first, the threshold energy of the named reaction is too high (29,7 MeV; Galatanu and Engelmann, however, as well as the authors of this book, used 30 MeV as a maximum of the bremsstrahlung continuum). Second, the mother half-life in the secondary decay system is 3,86 s. Therefore, no detectable amounts of ^{22}Na (half-life = 2,6 years) will be generated. The first order interference reactions - if relevant - can be avoided by setting the electron energy well below the threshold energies of these reactions (in this case, to about 20 MeV), but this would degrade the integral analytical sensitivity. Sodium does not gain excessive activity during reasonable - say hours - exposure periods as is the case in thermal neutron activation. However, sodium might be a source of interference via its $(\gamma, \alpha n)$ -reaction, of photon activation analysis of fluorine (Holtzmann and Sugarman¹⁴¹, Wilkniss⁷²⁴).

Magnesium

Magnesium usually is analysed by the 1368 keV gamma-ray line of ^{24}Na . The sensitivity allows trace analyses, but this reaction is subject to first order interference by sodium and aluminium. Schmitt et al.¹⁰⁴⁹, Rev.82, Das and Zonderhuis⁵¹, Hislop and Williams¹⁰²⁷, Rev.65, Kato et al.¹⁰⁵², Rev.86, Das et al.¹⁰⁵³, Rev.87, Aras et al.⁹⁴⁹, Rev.31, Chattopadhyay and Jervis⁸⁸³, Rev.40, Chattopadhyay³³⁰, Kato et al.⁹¹⁹, Rev.20, Kato et al.⁹⁵⁶, Rev.36, Kato et al., Ref.¹⁰⁵⁸, Rev.91 and many others studied these interferences which are predominantly due to photoneutrons close to the converter target. One way to minimise these interferences is to wrap the samples in cadmium foil prior to irradiation to absorb thermal neutrons (Schmitt et al.¹⁰⁴⁹, Rev.82, Chattopadhyay and Jervis⁸⁸³, Rev.40). Another way to manage the interferences is the use of lower bremsstrahlung energies. Thereby both the neutron yield is lowered and aluminium does not undergo the $(\gamma, ^3\text{He})$ -reaction also producing ^{24}Na (Schmitt et al., Ref.¹⁰⁴⁹, Rev.82, Kato et al.⁹¹⁹, Rev.20, Chattopadhyay³³⁰). The contribution of the interfering elements to the common product nuclide can as well be obtained by simultaneous irradiation of the pure elements (Das and Zonderhuis⁵¹), but this is time-consuming and entails additional work effort.

Other nuclear reactions were proposed for magnesium analysis, e.g. (γ, n) producing ^{23}Mg (Oka et al.⁹⁰⁷, Rev.5) or (γ, p) producing ^{25}Na (Lindner et al.¹¹³⁰,

Dams⁹²⁴, Rev.29, Anon.¹¹³¹). Both product nuclides are short-lived (10 s and 1 m, respectively) and therefore, special analytical procedures are required. However, using say 30 MeV bremsstrahlung, these reactions are practically interference-free, hence precise and accurate results can be obtained.

($\gamma, 2p$) reactions yielding ^{23}Ne and ^{24}Ne (half-life = 38 s and 3,4 m, respectively) were used in connection with a separation of the produced neon isotopes from the matrix (Lindner et al.¹¹³⁰, Anon.¹¹³¹). However, by these reactions usable activities are yielded during activation with very high bremsstrahlung energies (in the quoted papers, 85 MeV endpoint energy were reported) and are then subject to first order interference. Magnesium gains high activity (^{24}Na) during normal exposure periods and causes first order interference of sodium analysis (see above).

Silicon

Silicon can be analysed fairly sensitively by the reaction yielding ^{28}Al . However, this nuclide is short-lived (2,25 m) and therefore, quasi-omnipresent oxygen is likely to interfere by its creating a high background activity. Moreover, first order interference occurs by neutron reactions of aluminium and phosphorus (Ölmez et al.⁹⁵³, Rev.33). Therefore, the use of ^{29}Al for analysis is recommendable although being less sensitive. This reaction is quasi-interference-free, but the reaction product is also rather short-lived (6.6 m) and the most prominent gamma-ray line is overlapped by the single escape line of the 1779 keV signal due to ^{28}Al . In this case, the proper selection of the irradiation and cooling periods is of importance (Dams⁹²⁴, Rev.29). Excessive sodium amounts present in the sample might eventually interfere (^{22}Na , 1275 keV) but this contribution can easily be accounted for by a second measurement of this line after the decay of ^{29}Al to quasi-zero activity (Chattopadhyay³³⁰). A possible interference due to ($\gamma, 2p$) reaction of phosphorus was reported in a paper of Chattopadhyay³³⁰ but not detected during experimental work in the authors' laboratory. Silicon does not produce longer-lived excessive activities.

Phosphorus

As far as it is known to the authors, no attempt was made as yet to use the (n, α) reaction of phosphorus (as it occurs during accelerator activation) for analytical purpose; it appears as a source of interference only.

Phosphorus was analysed using extremely high bremsstrahlung energies (110–140 MeV) via the reactions (γ, n) , $(\gamma, 2p)$ and $(\gamma, 2pn)$ (Ricci^{328, 915}, Rev. s. 8 and 18, respectively). Irradiating with these energies one has to be aware of very complex spectra due to many photon reactions in the material. However, it was claimed that no unusual interference activity was detected. In the normal case, phosphorus should be analysed with help of other techniques. As a matrix component, it normally causes no problems in terms of instability and interfering activity.

Sulfur

This element is included at this point although not considered in Ch. 5. This was done because an instrumental photon activation analysis of sulfur was reported in the inspected literature. As in the case of phosphorus, photon activation analysis normally is not the method of choice for sulfur determinations; no conveniently measurable radionuclides are produced through high energy photon bombardment. In the literature accessible to the authors there is but one message about sulfur analysis by photon activation (Dams⁹²⁴, Rev. 29). 2.6 seconds-³¹S was measured but with insufficient activity yield. Sulfur does not produce interfering activities during activation and normally its inorganic compounds are stable during irradiation.

Chlorine

Chlorine is best analysed using the 2128 keV gamma-ray line of ^{34m}Cl. The analytical sensitivity is limited by the rather short half-life of the product nuclide (32 m) and the first order interference by ³⁹K(γ, n) rather than by its activity after activation. However, by most workers the interfering contribution of potassium was found to be negligible in normal matrices (Aras et al.⁹⁴⁹, Rev. 31, Sharma et al.⁷¹⁸, Chattopadhyay³³⁰, Kato et al.⁹¹⁹, Rev. 20, Galatanu and Grecescu²⁴¹, Dams⁹²⁴, Rev. 29, Galatanu and Engelmann¹⁰⁶⁸, Rev. 104).

Normally, chlorine causes no spectral interference of other elements to be analysed.

Potassium

As in the analysis of silicon, short-lived activities only are produced by potassium when irradiated with bremsstrahlung. ³⁸K can be used for analysis; this reaction is quite sensitive and the most prominent gamma-ray line has a favour-

able energy (2167 keV), but the analytical sensitivity is limited by excessive matrix activity in many cases (Sharma et al.⁷¹⁸, Dams⁹²⁴, Rev.29). The competing reaction by calcium can be suppressed by setting the electron energy of the accelerator below the threshold of the interfering reaction (21.42 MeV; Kato et al.⁹¹⁹, Rev.20, Chattopadhyay³³⁰, Galatanu and Engelmann¹⁰⁶⁸, Rev.104).

Due to the short half-life of ^{38}K , potassium generally does not create significant interference activities during bremsstrahlung exposure; the $^{34\text{m}}\text{Cl}$ yield of the $(\gamma, \alpha n)$ reaction mostly can be neglected in the determination of chlorine (see there).

Calcium

Calcium is one of the elements which can be analysed very favourably by instrumental photon activation analysis; in almost every report about multielement photon activation analysis calcium is at least mentioned. Two reactions can be used which are both more or less interference-free; the (γ, p) reaction producing ^{43}K has a higher activity yield but the major gamma-ray line of ^{47}Ca (1297 keV) can be measured with more favourable peak-to-background ratio. In comparing the quality of the analytical results using both product nuclides many authors came to different conclusions, presumably depending very much upon the matrix analysed. Some workers - including the authors of this book - consider both reactions have roughly the same analytical quality with no systematic deviation from one another (Kato et al.⁹⁵⁶, Rev.36, Chattopadhyay³³⁰, Kato et al.⁹¹⁹, Rev.20, Kato et al.¹⁰⁵⁸, Rev.91), whereas others report systematic differences in the obtained data, in terms of both accuracy (Schmitt et al.¹⁰⁴⁹, Rev.82, Hislop and Williams¹⁰²⁷, Rev.65) and precision (see Aras et al.⁸⁴⁰, Rev.31).

Several workers report interferences by competing reactions or gamma energy overlap. Multiple spectral interference was reported by Das and Zonderhuis⁵¹ since they used scintillation spectrometry. Some authors consider the following reactions as interfering:

$^{45}\text{Sc}(\gamma, 2p)^{43}\text{K}$ (Kato et al.⁹¹⁹, Rev.20, Chattopadhyay³³⁰, Kato et al.¹⁰⁵⁸, Rev.91)

$^{46}\text{Ti}(\gamma, 3p)^{43}\text{K}$ (Kato et al.⁹¹⁹, Rev.20)

$^{49}\text{Ti}(\gamma, 2p)^{47}\text{Ca}$ (Kato et al.^{919, 1058}, Rev's.20 and 91, respectively).

Chattopadhyay³³⁰ reported gamma-ray line overlap of the 373 keV line of ^{43}K by emissions from $^{204\text{m}}\text{Pb}$ and $^{199\text{m}}\text{Hg}$. This interference can be avoided by allowing the named nuclides to decay to quasi-zero activity (half-lives = 67 m and 43 m, respectively). Aras et al.⁹⁴⁹, Rev.31, found that the 617 keV line of ^{43}K is eventually interfered by ^{82}Br . In this case (in the analysis of air particulate) it is explainable by the high bromine content due to automobile exhaust.

Possible interference by scandium and titanium was studied also by Hislop and Williams¹⁰²⁷, Rev.65, and by the authors of this book, but none was found during experiments. Both reactions mentioned above were used for the determination of the isotopical abundance of ^{48}Ca (Peisach¹¹³²).

All in all, the reaction yielding ^{47}Ca and the use of the 1297 keV gamma-ray line seems somewhat more preferable because of less interference by other gamma energies and, as touched on above, better signal-to-background ratio.

Using enriched stable calcium isotopes, various (γ, p)-products were identified and characterised after 50 MeV bremsstrahlung activation (Larson and Gordon, Ref.¹¹⁹⁷).

If calcium is a major component of the sample one has to take into account considerable matrix background activity which can cause interference of several elements to be analysed, e.g. K, Ti, V, Co, As, Hg and Pb (see there).

Scandium

Scandium has been analysed only a few times by instrumental photon activation analysis as yet, although the sensitivity is good and the main product nuclide ($^{44\text{m}}\text{Sc}$) can be measured quite conveniently (half-life = 2.44 d, gamma energy = 1157 keV). $^{44\text{m}}\text{Sc}$ is also produced by titanium. Chattopadhyay³³⁰ suggests an irradiation at 20 MeV electron energy to exclude this interference.

Scandium has been applied as an additive internal photon flux monitor in multi-element analysis because of its low natural abundance and its favourable nuclear data (Segebade⁶⁰, Rev.54).

Titanium

Titanium can be analysed by instrumental photon activation analysis very favourably compared with other instrumental methods. Various reactions can be

used for titanium determinations. Although the (γ, n) -reaction producing ^{45}Ti yields the greatest activity (Oka et al.¹¹³³) it has not been used in instrumental photon activation analysis since the 511 keV annihilation radiation is subject to serious multiple interference by other positron emitters and the other gamma radiation is very low abundant (Abe and Takano¹¹³⁴).

The (γ, p) -reactions producing $^{46, 47, 48}\text{Sc}$ have been all been used for analysis. Das and Zonderhuis⁵¹, Kato et al.^{1051, 1052}, Rev.86, Das et al.¹⁰⁵³, Rev.87 and Abe^{1135, 1136} preferred ^{47}Sc , mainly because of its high activity yield. Interferences due to vanadium mostly are negligible and it is possible to circumvent the interference by secondary decay of ^{47}Ca from calcium by measuring the sample before considerable contribution of ^{47}Ca -generated ^{47}Sc has grown in.

^{46}Sc has the advantage of a long half-life and a more favourable gamma-ray energy (83.3 d and 889 keV, respectively) and therefore was preferred by Galatani and Engelmann¹⁰⁶⁸, Rev.104. The contribution due to scandium reaction with photoneutrons can be suppressed with a cadmium shield if necessary and interference by (γ, α) -reaction of vanadium mostly is negligible. Many authors found that the quality of the analytical results is comparable for all of the named scandium isotopes used for analysis evaluation; the integral composition of the sample will make the choice (Schmitt et al.¹⁰⁴⁹, Rev.82, Hislop and Williams, Ref.¹⁰²⁷, Rev.65, Aras et al.⁹⁴⁹, Rev.31, Kato et al.^{919, 956, 1058}, Rev's. 20, 36 and 91, respectively .

Chattopadhyay et al.^{330, 883}, Rev.40, and the authors of this book have preferred ^{48}Sc . Although not being as sensitive as ^{47}Sc and rather short-lived ($T=43.67\text{h}$) it is not subject to serious interference and emits favourable gamma energies. Chattopadhyay³³⁰ assumed $(\gamma, 2p)$ -interference by vanadium and therefore conducted irradiations using 20 MeV bremsstrahlung, but this interference was not detected by Hislop and Williams¹⁰²⁷, Rev.65, and in the present work (see ch. 5).

Titanium produces significant integral specific activity during bremsstrahlung irradiation. Therefore, one has to consider large background activity if larger amounts of titanium are present in the sample.

Vanadium

Vanadium is one of the elements which do not have favourable properties for determination by instrumental photon activation analysis. The most intense react-

ion producing ^{47}Sc generally cannot be used for analysis - no application is reported in the literature accessible to the authors - because it is strongly interfered by titanium (see there) which yields much greater specific activity of ^{47}Sc and usually is present in samples in considerably larger concentrations. This also applies to other $(\gamma, \alpha n)$ -reactions of vanadium (Oka et al., Ref.¹¹³³). The only other usable reaction of vanadium is the $(\gamma, 2n)$ -process yielding ^{48}V . This reaction is subject to first order interference by chromium with significant yields (Chattopadhyay and Jervis⁸⁸³, Rev.40, Chattopadhyay³³⁰) and its gamma-ray spectrum coincides with that of ^{48}Sc produced by quasi-omnipresent titanium. However, the latter interference can be avoided by long cooling periods. Because of the large threshold energy (20.9 MeV) and the comparably small integral photoneutron cross section (Berman¹⁷⁴) this reaction has an insufficient activity yield at say 30 MeV bremsstrahlung used for excitation. Chattopadhyay³³⁰ therefore used 44 MeV, but small traces in the lower micrograms per gram region surely cannot be analysed within normal instrumental photon activation analytical procedures.

Chromium

Chromium can be analysed fairly well by the (γ, n) -reaction producing ^{51}Cr (27.7 d; 320 keV). The intrinsic sensitivity is good but the gamma-ray energy is located in an unfavourable region considering the fact that the peak is mostly superimposed upon a high Compton continuum caused by the quasi-omnipresent 511 keV annihilation radiation. The other possible reaction producing ^{49}Cr can hardly be exploited for analytical purpose since the gamma-ray energy is yet more unfavourable (153 keV) and due to the short half-life (42 m) is even more interfered by excessive background radiation of the sample matrix. The first order interference of ^{51}Cr due to $(\gamma, \alpha n)$ -reaction of ^{56}Fe might interfere as well as spectral overlaps by radiation due to ^{129}Cs (from barium) and ^{147}Nd (from neodymium) eventually present in considerable concentrations. Also ^{105}Ag (from silver or cadmium) can interfere, depending upon the matrix composition. The (γ, p) -reactions leading to $^{52}, ^{53}\text{V}$ have hitherto not been used for analysis, as far as the authors know. The above mentioned interference of ^{51}Cr by iron was found significant by many authors. Therefore, particularly in iron-rich matrices, other analysis methods might be preferable (Aras et al.⁹⁴⁹, Rev.31. Chattopadhyay et al.^{330, 883}, Rev.40, preferred the $(\gamma, 2n)$ -reaction producing ^{48}Cr fairly efficiently using 44 MeV bremsstrahlung. The gamma energy (308 keV) is as unfavourably located as the 320 keV line from ^{51}Cr , but it is not subject to overlaps by other gamma-ray lines and at the named bremsstrahlung energy no competing reaction can occur.

Some chromium compounds can be volatilised under radiation attack, but in the authors' laboratory no evidence of any losses have been detected and also none have been reported in the inspected literature.

Chromium, after long-time bremsstrahlung exposure, produces considerable long-lived matrix activity if present in large amounts. This can severely hamper instrumental analysis, e.g. of highly alloyed steels.

Manganese

The only photonuclear reaction usable for manganese analysis offers good sensitivity and ^{54}Mn emits a favourably measurable gamma-ray energy (835 keV) which normally is not interfered by peak overlap. However, it is recommendable either to irradiate at not more than 20 MeV electron energy or to provide a correction routine whereby the strong first order interference by $^{56}\text{Fe}(\gamma, np)$ can be avoided or accounted for, respectively. The possible interfering reaction of cobalt normally can be neglected. Das et al.¹⁰⁵³, Rev.87) report a spectral interference by 880 keV (they used scintillation spectrometry) attributed to ^{46}Sc , which seems questionable. First, in matrices as analysed in the reported work (rock material) the mentioned interference will be primarily due to 909 keV from ^{89}Zr (produced by zirconium). Second, after a longer decay period, 881 keV emitted by ^{84}Rb (from rubidium) is much more likely to dominate. The first order interference by iron (see above) which is the most probable source of error was not mentioned.

Manganese, if present in larger amounts, may cause significant interference by creating long-lived matrix background radiation. As in the case of chromium, this has been frequently encountered during analysis of iron-bearing ore and its products like steel.

Iron

The analysis of iron by photon activation is somewhat problematic. The (γ, p) -reaction yielding ^{56}Mn is sensitive but the isotope is rather short-lived (2.58 h) and therefore frequently subject to background activity interference. However, the gamma-ray energies are favourable. If large amounts of manganese are present the interference through $^{55}\text{Mn}(n, \gamma)$ might be significant. In this case, the thermal photoneutron flux has to be depressed by a cadmium shield surrounding the irradiated sample. Hislop and Williams¹⁰²⁷, Rev.65, report a possible interference by ^{134}I produced through (γ, f) reactions of fissile material