

multielement reference material. Samples and several batches of the reference material were packed into the irradiation vessel; Copper foil flux monitors were placed at the front and rear ends of each sample to trace the flux gradient relevant for the activation. The irradiation container, an aluminium can of one inch outer diameter, was placed in the bremsstrahlung beam axis, at a distance of about 25 cm between its front face and the bremsstrahlung converter. 2.5 mm tungsten was used as converter material. A steel sheet of 8 mm thickness was used as absorber for unconverted electrons. Irradiations were conducted at 28 MeV electron energy for the analysis of Ca, Ti and Ni. Another set of the mentioned samples was irradiated at 23 MeV for the determination of magnesium. There is no information about the electron beam current available. Measurements were performed with a 30 cm<sup>3</sup> Ge(Li)-detector. The copper monitors were measured with a scintillation detector. The results were in agreement within  $\pm 3\%$  to  $\pm 5\%$  compared with reliable literature data. It was found (as also by many other groups working on instrumental photon activation analysis) that an energy of about 30 MeV is optimal for instrumental analysis. The individual irradiation at 23 MeV for magnesium was performed to avoid eventual first order interference by other elements. The interference of the magnesium determination by thermal neutron reaction of sodium leading to the common <sup>24</sup>Na was checked experimentally and was found negligible under the described experimental conditions. For the analysis of calcium, <sup>47</sup>Ca was selected for evaluation although less sensitive than <sup>43</sup>K by an experimentally determined factor of 1/55. However, <sup>47</sup>Ca provided more accurate results. This has been found also by other working groups including the authors of this book, but it was discussed controversially in the literature. This problem is discussed further in paragraph 6.2.4.8 below.

83) The instrumental photon activation analysis of Mg, Ca, Ti and Sr in rock material was described by Das and Zonderhuis<sup>1050</sup>. This analysis was performed within a sequential analysis system using fast and thermal neutron and high energy photon activation analysis as in the work described above. 100-200 mg of powdered rock material were packed in polyethylene vials and irradiated with 45 MeV bremsstrahlung (mean electron beam current = 50 microamperes) of an electron linear accelerator. Exposure times were typically about one hour. After a first cooling period of about five hours samples were measured with a NaI spectrometer. During this counting period, <sup>47</sup>Sc (from Ti), <sup>24</sup>Na (from Mg) and <sup>87m</sup>Sr (from Sr) were measured. After another decay period of about 40 hours, another measurement was carried out using the same spectrometer. <sup>47</sup>Sc (this time from both Ca and Ti), and <sup>43</sup>K (from Ca) were counted. No information was given the obtained concentration data, their quality, and the reference material which

was used. Therefore, there is no information about the reliability of the method, as far as instrumental photon activation analysis is concerned.

84) The capability of instrumental photon activation analysis of geological and ore sample using a 25 MeV betatron was investigated by Galatanu et al.<sup>257</sup>. In this study elements were considered which on the one hand are of geological interest and on the other hand groups of them have very similar chemical properties so that their separation by conventional methods is difficult. These elements are Rb, Sr, Zr, Nb, Sn, Cs and Ta. Irradiations were conducted at 25 cm distance from the bremsstrahlung converter, measurements were performed with small volume Ge(Li)-detectors. The suitability of this method was limited by several parameters: a) the maximum electron beam current of a betatron and therewith the analytical sensitivity is lower than that achievable with a linear accelerator by two orders of magnitude. b) Since only small volume detectors (4 and 11 cm<sup>3</sup>) were available, the counting efficiency particularly in the high energy regions, was poor. c) Since only comparatively low photon fluxes could be achieved, one strived to analyse relatively short-lived product nuclides. This might lead to difficulties in terms of short-lived background activities. Exposure periods varied between 40 minutes and 2 hours, cooling times were between 1 and 70 minutes and spectra collecting periods were between 8 minutes and 1 hour. A very extended investigation of possible interferences was carried out.

85) USGS standard rock samples were analysed by Hislop and Williams<sup>1027</sup>, see also Rev.65. 50 mg batches were irradiated for 0.5 hours with bremsstrahlung from 35-40 MeV electrons. Measurements were performed using a 40 cm<sup>3</sup> Ge(Li) detector. The following elements were identified and determined: Na, Mg, Ca, Sc, Ti, Cr, Mn, Fe, Sr and Zr. Comparison with the results of conventional methods applied to the analysis of the same material yielded generally satisfactory agreement. The reference material used in this work is worthwhile discussing. It was a synthetic mixture of the oxides of 39 elements present at a concentration of 1% each in an ammonium sulphate matrix. For rock analysis application, a batch of this material was mixed homogeneously with an artificial average rock matrix. This is useful since it provides similar signal-to-background ratios during photon spectroscopy. However, the uniform quantitative composition leads to an extremely inhomogeneous intensity distribution among the gamma-ray lines, hence several elements will dominate in the spectrum and others will be swamped. Elements were included which do not undergo usable photonuclear reactions under the described experimental conditions (B, Li). Finally, several

elements are unlikely to be detectable in rock material (Ga, In, Platinum Group Metals). See also Rev. 65.

86) A somewhat similar procedure was applied for the analysis of rock material by Sato et al.<sup>1051,1052</sup>. The following elements were analysed: Na, Mg, Ca, Ti, Mn, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba and Ce. Several standard rock were examined. Synthetic mixtures of the elements to be determined in a synthetic rock matrix were prepared to serve as reference materials. In this work, other than the above reviewed one, element concentrations were adjusted according to the expected product activities. Four different reference materials were synthesised, each containing different minor and trace elements. Magnesium was analysed individually to check for interference by Na and Al present in the samples. About 400 mg batches of each sample plus a set of the mentioned reference materials were irradiated with 30 MeV bremsstrahlung of an electron linear accelerator (mean electron beam current = 70 microamperes). Bremsstrahlung was produced in a 3 mm platinum converter. The bremsstrahlung intensity was monitored by copper discs irradiated simultaneously with the samples. It was found that the flux gradient along the sample length was less than 10%, but the FWHM of the photon beam intensity perpendicular to the beam axis was about 12 mm. Exposure times did not exceed 4 hours. Gamma spectrometry was performed with a 24 cm<sup>3</sup> Ge(Li)-detector. Eventual interference from overlapping peaks were corrected by decay-curve analysis. Major first order interference yields were found in the analysis of magnesium (through <sup>24</sup>Na) by <sup>27</sup>Al(n,α) and, most significant, in the determination of manganese (through <sup>54</sup>Mn) by <sup>56</sup>Fe (γ,np). The analysis of nickel was difficult because of the close neighbourhood of the main gamma-ray line of <sup>24</sup>Na to the most prominent <sup>57</sup>Ni-peak. The second <sup>57</sup>Ni-line (E<sub>γ</sub>=1919 keV) could not be used because of its low emission probability. Sensitivity data were given in terms of photopeak count rates achieved under the named conditions; they ranged from 28 min<sup>-1</sup>mg<sup>-1</sup> (for <sup>22</sup>Na from Na) to 2.6 million min<sup>-1</sup>mg<sup>-1</sup> (for <sup>87m</sup>Sr from Sr).

As a result, the obtained values were in good agreement with the certified or recommended consensus literature values cited for the analysed specimens. Several elements could be analysed whose determination is difficult or not possible with thermal neutron activation analysis. These were Ca, Ti, Ni, Y and Nb.

87) Standard rock material was analysed by Das et al.<sup>1053</sup> using instrumental photon activation analysis. Samples were packed in polyethylene vials which were then placed on an aluminium wheel which served as a rotating irradiation

position. It was rotated by motor-drive and cooled during irradiation with an electric fan. Obviously, there was no pneumatic sample transfer system available. Samples were irradiated for 90 minutes with bremsstrahlung of an electron linear accelerator. Samples were measured with a NaI-crystal and a 45 cm<sup>3</sup> Ge(Li)-detector. Several first order interference cases were discussed and evaluated quantitatively. The results showed satisfactory agreement with the consensus values taken out of the literature.

One of the elements which can be analysed more conveniently by photon activation analysis than by other activation techniques is nickel. The most prominent reaction, namely  $^{58}\text{Ni}(\gamma, n)^{57}\text{Ni}$  is practically free from any interference by eventual competing reactions. Moreover, the gamma spectrum of  $^{57}\text{Ni}$  contains lines which can be measured without serious interference, at least with modern high-performance semiconductor detectors. Earlier, when Ge(Li)-detectors did not yet offer energy resolution capabilities as usual nowadays, the most prominent gamma-ray line in the spectrum (1379 keV) was somewhat disturbed by the nearby  $^{24}\text{Na}$  gamma energy at 1369 keV which is mostly more intense as already noted. The gamma energy of  $^{57}\text{Ni}$  which is the next intense one is located in an unfavourable energy region (127 keV), and all other emission energies are of poor intensity.

88) Therefore, Kato et al.<sup>1054</sup>, in order to achieve maximum sensitivity, carried out a radiochemical separation of nickel after bremsstrahlung exposure of several standard rocks and glasses. 400 mg batches of rock powder were made into discs of 9 mm diameter; the glass material was supplied as thin wafers. Reference materials were prepared by pipetting aliquots of a calibrated nickel solution onto sheets of glass fibre so as to obtain a similar matrix. Samples and reference materials were sealed in a silica tube which was then placed into a water-cooled sample holder for bremsstrahlung irradiation located immediately behind the electron converter of an electron linear accelerator. Samples were irradiated for two hours with 30 MeV bremsstrahlung at an average electron beam current of about 70 microamperes. After the radiochemical separation step samples and reference materials were counted with a standard Ge(Li) spectrometer. The obtained concentration data were in satisfactory agreement with the comparative data of other analysts or recommended or certified values respectively. Only in one case, significant disagreement was stated which could not be readily explained.

89) In a paper presented at the 6th Modern Trends in Activation Analysis Conference, Ivanov et al.<sup>1055</sup> pointed out the possibility of quasi-selective ana-

lysis using the different photonuclear reaction thresholds. The components in rock and ore material were differentiated into rock-forming elements (C, O, Na, Mg, Al, Si, K, Ca and Fe) and ore-forming ones (heavier elements). Going out from the fact that most of the rock-forming elements have high photonuclear activation thresholds whereas heavier elements have lower ones, it was found that using 8 MeV bremsstrahlung these components can be activated quasi-selectively, mostly by isomeric state photoexcitation. Interference activities due to fissile elements were examined by experiment. Using about one milliampere electron beam current irradiating several hundreds of grams ore material and subsequent scintillation counting determination limits ranging from 400 ng/g (for gold) to about 0.003% (for tungsten) were found. Another special advantage of the described procedure is its simplicity and rapidity; more than 300,000 gold analyses were reported as having been performed per year.

- Water-related material

Only very few reports about water investigations using photon activation analysis can be found in the literature, although this method offers several advantages in water analysis compared with other instrumental techniques, particularly neutron activation. The inconveniences associated with high sodium and chlorine concentration in water are significantly reduced using photon activation. Moreover, as stated in paragraphs 6.2.3.1 and 6.2.4.2, also comparatively large liquid volumes can be irradiated with usual bremsstrahlung sources. A comparison of the results of a water sample analysed by several methods including photon activation analysis can be found in Ref.<sup>1056</sup>.

90) Strontium in sea water samples was analysed by Gordon and Larson<sup>1057</sup> using photon activation with a simple radiochemical separation procedure after bremsstrahlung exposure. 2 ml batches of deep sea water from different locations were lyophilised and wrapped in polyethylene and aluminium foil. Known amounts of strontium in a NaCl solution served as reference material which was pretreated in the same manner. Irradiations were conducted with 30 MeV bremsstrahlung of an electron linear accelerator, at a mean electron beam current of 30 microamperes. The typical exposure period was 0.5 h. After the separation, samples and reference materials were measured with a 40 cm<sup>3</sup> Ge(Li) spectrometer. The 388 keV gamma-ray line of <sup>87m</sup>Sr was selected for analytical evaluation, being the most intense line after relatively short cooling periods. The comparison with literature data yielded satisfactory agreement, but the obtained precision (about ±5%) was poorer than achievable with conventional methods.

91) The Tohoku University photon activation analysis research group reported the instrumental photon activation analysis of deep sea sediments (Kato et al.<sup>1058</sup>). The sediments were sampled in the Western Equatorial Pacific region from depths ranging from 4000 to 6500 m. Single samples as well as bore-cores were taken. The cores were cut into 1 cm segments. 300 mg batches were taken and subjected to analysis. The samples were wrapped in aluminium foil and made into small discs. A standard rock powder was used as multielement reference material. Iron foil discs were also irradiated to check the Fe/Mn interference yield. Samples, reference materials and monitors were sandwiched and stacked into silica tubes which served as irradiation vessels. The photon flux gradient within the sample area along the beam axis was found not to exceed 10%. Irradiations were carried out using bremsstrahlung from electrons with a mean current of 70 microamperes and an energy of 30 MeV impinging on a platinum converter. Irradiations lasted 4-5 hours. After bremsstrahlung exposure samples were repacked into counting vials and measured with a large Ge(Li)-detector. The following elements were determined: Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Rb, Sr, Y, Sr, Nb, Ba and Ce. Interfering reactions were evaluated quantitatively. Detection limits (the criteria used were not specified) were between 0.47 mg (for Ca) and 500 ng (for Nb).

92) In the same institute, analyses of sea sediments were performed as reported by Masumoto and Suzuki<sup>1059</sup>. Major attention was directed to the analysis of nickel. A special background suppressing method was developed using a gamma-gamma coincidence configuration with help of a Ge(Li)- and a NaI-detector. Two gates were set: one for the annihilation photopeak region and another for the higher Compton plateau region. Thereby interfering activities, not emitting annihilation radiation (e.g.  $^{24}\text{Na}$ ) could be gated off. The practical detection limits in instrumental photon activation analysis using this configuration were determined for the following elements: Na (using  $^{22}\text{Na}$ ), Sc ( $^{44\text{m}}\text{Sc}$ ), Co ( $^{58}\text{Co}$ ), Ni ( $^{57}\text{Ni}$ ), As ( $^{74}\text{As}$ ) and Rb ( $^{84}\text{Rb}$ ). The detection limits were found between 1.2 micrograms (for As) and 110 micrograms (for Na). Using the described coincidence spectrometer, nickel was analysed in off-shore sea sediments, sampled from depths between 90 and 900 m, and several certified reference materials. Irradiations were conducted with an electron linear accelerator using 30 MeV bremsstrahlung. Samples were irradiated for five hours. A standard rock material was used as comparative material. Comparison of the concentration data obtained for the standard rock materials with literature data yielded satisfactory agreement in the most cases. The described method is particularly useful if material has to be analysed which contains elements in large concentrations whose reaction

products with high energy bremsstrahlung are  $\beta^-$ -emitters, e.g. Mg ( $^{24}\text{Na}$ ), Ca ( $^{43}\text{K}$ ,  $^{47}\text{Ca}$ ) and Ti ( $^{46,47,48}\text{Sc}$ ). A similar material was also analysed by Marshall<sup>1060</sup>.

- Cosmogenic material

As is also true for water-related material, photon activation analysis has been applied for cosmochemical analyses in a few exceptional cases only. Mostly meteorites have been studied and there is only one report known by the authors in which instrumental multielement photon activation analysis of lunar material is described (Hislop and Williams<sup>1027</sup>; see also Rev.65,85).

93) The earliest reports on multielement photon activation analysis of cosmogenic matter - as far as the the authors know - were published by Meijers (see Ref's. 787,1061,1062). Since the ratios of Fe/Ni and Ni/Co reflect age and provenience of meteorites the analysis of these elements are of cosmochemical interest. In the mentioned thesis, an instrumental photon activation analysis method is presented which enables fast and accurate determinations of these elements. Pieces of meteorites were irradiated together with discs of iron, cobalt and nickel and of an alloy containing large concentrations of these elements. the electron energy was 23 MeV at a mean beam current of 5 microamperes. The first measurment was made 10 minutes after irradiation with a NaI crystal to analyse the decay curve of  $^{53}\text{Fe}$  using the 511 keV annihilation photopeak. Several subsequent measurements were then carried out after different decay periods using a small Ge(Li)-detector. The decay curves of longer-lived  $\beta^+$ -emitters were also analysed using the mentioned spectrometer. Several first order interferences were quantified using the pure element samples which had been irradiated together with the analytical samples.  $^{56}\text{Mn}$  was attributed to the reaction  $^{58}\text{Fe}(\gamma, np)$  which is unlikely; under the described irradiation conditions  $^{56}\text{Mn}$  is mainly due to  $^{57}\text{Fe}(\gamma, p)$  and  $^{55}\text{Mn}(n, \gamma)$ , the latter induced by photon neutrons. A careful accuracy assessment was made. The angular energy gradient and the gamma-ray counting statistical error were estimated as major sources of deviations of the results from the accurate values. However, comparison of the obtained data with literature values showed partly significant disagreement.

94) Meteorite material and several standard rocks were analysed using instrumental photon activation analysis by van Zelst<sup>1063</sup>. Samples of powdered meteorites, standard rock powders and a synthetic oxide mixture containing the elements of interest were irradiated at two different bremsstrahlung energies, namely 40 and 20 MeV using 40 microamperes mean electron beam current. The

high energy irradiation lasted 1.5 hours and the other one 2 hours. Ca, Cr, Fe and Ni were analysed. Three hours after the 40 MeV bremsstrahlung exposure the  $^{56}\text{Mn}$  activity due to iron was measured with a scintillation crystal. After another decay period of one day, the activity of  $^{43}\text{K}$  originating from calcium was determined using a  $38\text{ cm}^3$  Ge(Li)-detector. After a third cooling period of about three days, the gamma radiation of  $^{57}\text{Ni}$  (from Ni) was measured with the Ge(Li) spectrometer. Interference due to the  $^{24}\text{Na}$  activity resulting from magnesium and aluminium in the samples was accounted for using a correction calculation with help of the other gamma-ray energy of  $^{24}\text{Na}$  (2754 keV). The 20 MeV bremsstrahlung activation was carried out for chromium analysis to avoid first order interference due to  $^{56}\text{Fe}(\gamma, \alpha n)$  which has a high threshold energy. The 320 keV gamma-ray line of  $^{51}\text{Cr}$  was measured about three weeks after bremsstrahlung exposure with a NaI-crystal. Parallel analyses of these elements plus titanium were carried out with proton activation analysis using a synchrocyclotron providing maximum proton energies of 52 MeV. Comparison of all obtained values for the standard rocks with literature values yielded satisfactory agreement except for a few cases. It is interesting to note that photon activation analysis results on the average are somewhat higher than those obtained by proton activation analysis for iron and nickel whereas the results for the other elements do not tend to show a systematical disagreement.

95) A meteorite sample was analysed using instrumental photon activation analysis within a largescale systematic investigation about photonuclear reaction yields (Kato et al.<sup>919</sup>; see also Rev.20). Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Rb, Y, Sr, Zr, Nb, Ba and Ce were analysed with 30 MeV bremsstrahlung activation. Samples were irradiated for 1-6 hours at an average electron beam current of about 70 microamperes. Measurements were carried out with a  $33\text{ cm}^3$  Ge(Li)-detector. An extended quantitative evaluation of first order interferences was presented. In the case of niobium analysis in the meteorite material severe interference due to  $^{52}\text{Mn}$  produced through  $^{54}\text{Fe}(\gamma, np)$  was necessary; about 50% of the total net area of the 935 keV gamma-ray line was found to be due to  $^{52}\text{Mn}$ .

In the following table, various applications of photon activation to the analysis in the field of geo- and cosmochemistry are summarised.



Tab.6.2-7: Application of instrumental photon activation analysis  
in geochemistry

Material analysed	Bremsstr. energy, MeV ( $I_e, \mu A$ )	Elements determined	Ref.	Rev. no.
Rock samples	variable	Zr	705	80
Meteorites	23 (5)	Fe, Ni, Co	787, 1061, 1062	93
Rock samples	23, 28 (not given)	Mg, Ca, Ti, Ni	1049	82
Rock samples, sediments	45 (not given)	Mg, Ca, Ti, Sr	1050	83
Sea water	30 (30)	Sr	1057	90
Meteorites	40 (40)	Ca, Cr, Fe, Ni	1063	94
Ores, various geol. material	25 (not given)	Rb, Sr, Zr, Nb, Sn, Cs, Ta	257	84
Lunar rocks	35-40 (4-8)	Ca, Ti, Cr, Fe, Sr, Zr, Sb, Cs, Tl	1027	85
Rock samples	30 (600 mA max.)	Te	1000	47
Rock samples	30 (90)	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, Ce	1051, 1052	86
Minerals	12-30 (variable)	F, Na, Mg, Al, Ca, Ti, Mn, Fe, Cu, Zn, As, Sr, Zr, Nb, Mo, As, Cd, Sb, Ba, W, Au, Pb	251	
Various geol. material	25 (not given)	F, Cl, Ti, Cu, Se, Rb, Sr, Zr, Cd, Sn, Ba, Ta	261	

Tab.6.2-7, continued

Material analysed	Bremsstr. energy, MeV ( $I_e, \mu A$ )	Elements determined	Ref.	Rev. no.
Rock samples	not given	Mg, Ca, Ti, Cr, Mn, Ni, Sr, Zr, Nb	1053	87
Minerals	8, 14 (700)	Ta, Au	1160	
Rock samples, glass	30 (70)	Ni	1054	88
Meteorites	30 (70)	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, Ce	919	95
Marine sedim.	30 (70)	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, Ce	1058, 1114	91
Suspended matter	35 (110)	Si, Ni, Y, Zr, Sb, Tl, Pb, Bi	1006	55
Various geol. material	30 (not given)	Na, Sc, Co, Ni, As, Rb	1059	92
Rock samples	8 (500-1000)	Se, Br, Y, Ag, Ba, Er, Hf, W, Au	1055	89

#### 6.2.4.5 Analysis of raw materials and industrial products

This paragraph is divided into four sections. In the first, works about analyses of ores and ore-related products are reviewed. In the second section, papers about analyses of metal matrices are discussed, in the third, analyses of fuel materials and in the last section analyses of miscellaneous matrices are presented.

##### - Ores and ore-products

In reviewing the literature about instrumental photon activation analysis of raw products, ore analyses were found to dominate. Frequently, as already noted in the preceding paragraph, ore analyses are combined with analyses of other geological material because both materials are of similar provenience and thus have a similar matrix. Hence relevant factors like shape of the resulting photon spectra after activation, signal-to-Compton ratios etc. are of similar quality. Normally, equal reference materials can be used in the instrumental photon activation analysis of both species. Therefore, analyses of ores and related materials were frequently reported in papers reviewed in the preceding paragraph.

Frequently, Noble Metals are of major interest in the analysis of ores. Therefore, many works in this field have been concerned with the determination of gold, silver and the platinum group metals.

96) In the work of Kapitsa et al.<sup>283</sup>, an electron cyclotron was used as a bremsstrahlung source. Unfortunately, no description of this accelerator was given so that it is not known if it was a microtron or a different machine type. Gold was analysed using the production of  $^{197m}\text{Au}$  by isomeric photoexcitation. 100-200 g of powdered gold ore material was packed in a plexiglass container and located in front of the tungsten converter target at a distance of 10 cm. A monorail carriage transport system was used for sample transfer. Samples were then irradiated with 9 MeV bremsstrahlung at an average electron beam current of 30 microamperes. The exposure time was 18 seconds which means that the induced activity yield function nearly reached its saturation range (the half-life of  $^{197m}\text{Au}$  is 7.3 s). The sample container was then transported to the detector. Since the transfer line terminated directly at the detector (NaI well-type crystal connected to a single channel analyser and a scaler) the induced activity could be measured without any further delay; the total cooling period was as small as 3 s. Samples were measured for 18 s. Analysing the re-

sulting spectrum, it had previously been found that under the described conditions the photopeak which was located closest to the 279 keV line of  $^{197m}\text{Au}$  was the 217 keV gamma-ray line of  $^{179m}\text{Hf}$  originating from hafnium sometimes present in the ore samples. However, the resolution capability allowed a complete separation of the analysed photopeak from any signal in the neighbourhood. Three micrograms per gram were found to be the detection limit of the method. The most evident advantage of the method is its rapidity; large numbers of analyses, several tens of thousands per year, could be performed.

97) A compilation of photonuclear data of several selected elements frequently encountered in copper mining products was presented by Ratynski et al.<sup>1064</sup>. Elements were included which either were analysed in the material or contributed to the interfering background radiation. The authors underlined the urgent need of systematic photonuclear data compilations, preferably based upon experimentally obtained results, to serve as a reference during practical analysis work. The above listed elements were irradiated as such with a 30 MeV betatron at different electron energies ranging from 15-30 MeV. Then they were measured with a 20 cm<sup>3</sup> Ge(Li)-detector after different cooling periods. The reactions of Ti, Cu, Mo and Rh were evaluated and discussed in detail.

98) The analysis of gold and silver in rocks and ores was reported by Kapitsa et al.<sup>291</sup>. A microtron was used for irradiation at different energies, namely 9 MeV (average electron beam current: 30 microamperes) and 14 MeV (20 microamperes). With help of the lower energy, activities due to isomeric state photoexcitation were included ( $^{107m}\text{Ag}$ ,  $^{109m}\text{Ag}$ ,  $^{197m}\text{Au}$ ) and by irradiation at the higher energy, ( $\gamma, n$ )-reactions were effected. The isomers could be measured fairly interference-free with a NaI spectrometer whereas the photonuclear products had to be counted with a semiconductor detector because of the somewhat more complex gamma-ray spectra due to reaction products of other elements present in the sample (Ba, Pb).

99) The photon activation analysis of Rh, Pd, Ag, Ir, Pt and Au in Black Concentrates (residues of ore-processing steps which are rich in precious metals, e.g. copper ore residues) was reported by Breban et al.<sup>1065</sup>. About 20 mg of sample material were mixed with cellulose powder and pressed to a 1 mm thick pellet with 1 cm diameter. This was done to avoid errors by self-absorption of soft gamma-rays within the matrix during activity counting. Pure element discs having the same shapes as the samples were used as reference materials. Samples and element standards were sandwiched and then irradiated with 35 MeV bremsstrahlung (average electron beam current = 66 microamperes) of an electron

linear accelerator. Gamma activity measurements were performed with Ge(Li)-detectors. Possible interferences were studied in detail, using the pure element spectra and also literature data. Detection limits were found between 20 ng (for Au) and 6 micrograms (for Ag). The reproducibility of the obtained results varied from 1 to 7%. Comparison with the results of classical methods yielded excellent agreement in the most cases.

100) Copper was analysed in ores and flotation products using instrumental photon activation analysis by Pradzynski<sup>1066</sup>. A betatron was used for activation of 100 g-batches of sample material with 13,6 MeV bremsstrahlung. Irradiation time was 10 minutes, decay period 1 minute and the samples were measured for 5 minutes with a scintillation spectrometer. The 511 keV annihilation radiation photopeak of  $^{62}\text{Cu}$  was used for analysis evaluation. It was found that the only two elements activable at this energy and present in considerable concentration in the analysed material were silver and lead. Both components did not contribute to the measured peak significantly. In the range of 0.3 to some tens of per cent of copper to be analysed, the accuracy and precision of the method were excellent. Instrumental photon activation analysis was found superior to all other methods considered in the described task (14 MeV neutron activation analysis, X-ray fluorescence spectrometry).

101) A betatron was used for instrumental photon activation analysis of niobium and tantalum in ores by Galatanu<sup>258</sup>. These elements are difficult to separate by chemical analysis, hence an instrumental method of determination was sought. 1-2 g powdered ore material was irradiated for 2 hours with 25 MeV bremsstrahlung. No information about the electron beam current was given; the integral irradiation dose rate at the irradiation site was 2600 R/min. After 10 m decay period samples were measured for the first time. Because of the complexity of the resulting gamma spectra a semiconductor detector had to be used. In the first measuring period, the energy range between 50 and 550 keV was recorded to detect the low energy  $^{180\text{m}}\text{Ta}$  gamma radiation (93 and 103 keV). After a second cooling period of 70 minutes the energy range between 500 and 1050 keV was screened with help of a biased amplifier and the 935 keV gamma energy of  $^{92\text{m}}\text{Nb}$  was measured. Possible sources of interference including natural radioactivity were studied and discussed in detail, but in the given analysis task there was no evidence of any significant interfering activity yield.

The reproducibility was checked by replicate analyses and found within  $\pm 5\%$ . Sensitivities of 0.01% for Nb and 0.001% for Ta were achievable under the described experimental conditions, with a total relative error of less than 10%.

102) Within an extended study of isomeric photoexcitation its application to the analysis of noble metals in metallurgical residues was reported by Breban et al.<sup>921</sup>. 6-8 MeV bremsstrahlung (mean electron beam current = 70 microamperes at 7 MeV) of an electron linear accelerator was used for activation of 10-20 g of powdered sample material. Because of the very short half-lives of some of the product activities a fast sample transfer had to be used. The available system permitted sample transportation time of some two seconds. For the determination of Rh, Ag, Ir, Pt and Au in several matrices, samples were irradiated for 0.5 or 1 m, total cooling time including sample transfer was about 3 seconds. The samples were then counted for 1 or 2 m. Since the gamma-ray energies of some of the activation products were very close to each other, Ge(Li) spectrometry had to be used for gamma counting. As found through replicate analyses and comparison with results of other methods, the obtained values showed satisfactory precision and accuracy, respectively. However, the values are of good quality only at rather high concentration to be determined, namely several hundreds of micrograms per gram minimally.

103) Photoexcitation of the isomeric state was used for the analysis of tungsten in ores and related material as reported by Kodiri et al.<sup>1067</sup>. 6 g of sample material were irradiated with 5 MeV bremsstrahlung of an electron linear accelerator for 15 seconds (mean electron beam current = 700 microamperes). A fast pneumatic sample transfer allowed 3 seconds total cooling period and the induced activity was then measured for 15 s. The 60 keV gamma peak of  $^{183m}\text{W}$  ( $T=5,3$  s) was measured with a scintillation spectrometer. The only possible interference was due to barium producing  $^{137m}\text{Ba}$ , but it was found that this contribution, in the case of barium concentrations comparable with those of tungsten, may be disregarded. The total experimental period amounted to about 30 s. 0.3 mg was found to be the experimental sensitivity of determination. The precision was given as maximally 5%. Comparison of the results with values of other methods yielded an accuracy of 5-10%, depending upon the concentration to be determined. The major advantage of this procedure is its relative rapidity and selectiveness.

104) The multielement instrumental photon activation analysis of a phosphate ore sample was reported by Galatanu and Engelmann<sup>1068</sup>; see also Ref.<sup>1069</sup>. 0.5 g batches were irradiated with bremsstrahlung of an electron linear accelerator. To avoid interference by unwanted reactions of some components with photoneutrons, the irradiated materials were wrapped in 0.9 mm thick cadmium foil. A synthetic multielement reference material was prepared mixing components of as many as 49 elements with calcium phosphate, so that between 0.001 and 0.1% of

each element was present. The use of this kind of reference material - as already mentioned - is somewhat problematic since frequently components are present in considerable concentrations which are not of interest in the analysed material and eventually disturb the evaluation procedure by producing interfering background radiation. As explained above in paragraph 6.2.2, the use of a reference material is recommendable which is similar to the material to be analysed with respect to the matrix composition (which was the case in the reviewed work) but also - at least to a minor extent - in the concentrations of the minor and trace components.

Two different irradiation energies were used, namely 18 MeV (mean electron beam current = 60 microamperes) and 30 MeV (90 microamperes). The first electron energy was selected for the interference-free analysis of Cl, K, Sr, Cd and Pb after an exposure period of 1.5 hours. All other elements were analysed using a four hour exposure of the material to bremsstrahlung of the latter energy. The resulting gamma-ray spectra were taken with a Ge(Li) spectrometer. The following elements could be analysed in the phosphate sample: Na, Cl, K, Ti, Cr, Mn, Co, Ni, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sb, I, Cs, Ba, Ce, Pb and U. The obtained sensitivities were between 500 ng/g (for Zr, Nb and Sb) and 125 micrograms per gram (for K). The reproducibility was fairly good in the most cases. Since no comparative results from other methods were given the accuracy of the data is unknown. All kinds of possible interferences were discussed very extensively. Although interferences were included which are most unlikely to ever occur in this matrix, the given quantitative yields are valuable since they are based upon experiment and thus can be referred to by other analysts working under similar conditions.

- Metals

105) The report by Schweikert and Albert presented at the IAEA Symposium on Radiochemical Methods of Analysis<sup>903</sup> (see also Rev.1) contains one of the first applications of photon activation analysis to the determination of heavier elements in metal matrix. Zirconium was determined in hafnium using activation with 27 MeV bremsstrahlung (mean electron beam current = 50 microamperes). Exposure time was 5 minutes.  $^{89m}\text{Zr}$  was measured using NaI spectrometry. An experimental detection limit of 100 ng Zr was found. Silver was analysed in bismuth matrix using the reaction  $^{107}\text{Ag}(\gamma, n)^{106}\text{Ag}$ . After 25 m irradiation with 27 MeV bremsstrahlung the annihilation radiation peak at 511 keV was used for evaluation. Due to the lack of high resolution spectrometers a

106) The extreme difficulties of instrumental photon activation analysis at the time before the general availability of high-resolution detectors are well demonstrated in the paper of Korthoven et al.<sup>307</sup> about the analysis of gadolinium and europium in tungsten bronzes. The title of the article describes the method as "computer resolution gamma spectrometry". The bremsstrahlung radiation source used in this work was an electron synchrotron, which has been applied to photon activation analysis only in comparatively few cases hitherto. Instrumental photon activation analysis was the method of the choice in this case for two reasons. First, the analysis of tungsten bronzes by classical chemistry is severely hampered by their resistance against chemical attack; it is a long and tedious procedure to dissolve them. Second, thermal neutron activation analysis is suspect because of the significant flux gradient of the neutron beam along its path through the sample due to the extremely high thermal neutron absorption cross section, particularly of gadolinium.

Samples were irradiated with 70 MeV bremsstrahlung. There was no comment on the electron beam current. The tungsten content of the sample matrix was used as an internal standard for calculation of errors caused by the inhomogeneity of the bremsstrahlung photon beam. Mixtures of the corresponding Rare Earth oxides with  $WO_3$  as well as single samples of each matrix component were used as reference materials. Exposure periods were 5 or 20 minutes. Samples were then counted several times with a NaI spectrometer. A sophisticated computer program was used to resolve the very complex spectra. This program yielded strikingly accurate results under the following conditions: (a) well-known single component spectra, (b) equal exposure, cooling and counting periods for samples and associated reference materials.

107) Chemical separation procedures were applied in the photon activation analysis of several elements in metal matrices (Debrun and Albert<sup>843</sup>, see also Rev.8). Major attention was directed to elements which cannot readily be analysed by thermal neutron activation analysis, namely Ni, Tl and Pb. These were analysed in Co, Cu and Cr matrix. Samples were irradiated with 35 MeV bremsstrahlung (mean electron beam current = 50 microamperes) for 20 m. Measurements were performed with a NaI spectrometer. No definite results were given but experimental sensitivity data were given comparatively to values of thermal neutron activation analysis as a complementary technique.

108) A microtron was used as an activating bremsstrahlung source in the analysis of Ge, Zr and Mo in metals and alloys as described by Samosyuk et al.<sup>293</sup>. These analyses were performed within a study of the applicability of a micro-



tron for activation analysis with both high energy photons as well as with photoneutrons. (a) Analysis of 20-30% of germanium in Nb-Ge alloys; samples were irradiated with 29,2 MeV bremsstrahlung of a microtron (mean electron beam current = 10 microamperes) and counted with a  $21 \text{ cm}^3 \text{ Ge(Li)}$  detector. The results were compared with those obtained by other methods and good agreement was stated. One of these comparative methods was the activation analysis with photoneutrons from the same microtron. This comparison was not possible in another application example, namely (b) the determination of zirconium in concentrations between 0.8 and 2% in Nb-Zr alloys; both the low neutron activation cross section of zirconium and the background interference due to tantalum present in the sample did not allow a zirconium analysis by activation with either photo- or pile neutrons. In this case the matrix-inherent niobium was used as an internal monitor. (c) Analysis of molybdenum (about 2%) and zirconium (about 0.1%) in a multiphase alloy; 40-50 mg of samples were irradiated for 15 to 20 m. After a cooling period of a few minutes samples were measured with the spectrometer mentioned above. Comparative results were obtained by emission spectrometry, wet chemistry and neutron activation analysis. The comparison showed excellent agreement between the methods.

In the systematic study reported in this article analytical sensitivities were measured for nearly all elements of the Periodic Table for activation analysis with both photons and photoneutrons as supplied by the same source; the obtained sensitivity results partly were in disagreement to experimentally obtained sensitivities determined in the laboratory of the authors of this book (Segebade et al.<sup>1070</sup>).

109) The instrumental photon activation analysis of Pd, Ag, Pt and Au in high purity copper was reported by Segebade et al.<sup>155,1071,1072</sup>. This work was performed within the certification procedure of several candidate reference materials. The samples lay before as 1 g discs with 13 mm diameter or as granulate. They were synthesised by melting the mentioned elements in zone-melted ultra-purity electrolytic copper. The trace elements were present in the following concentration ranges (in micrograms per gram): Pd and Pt: 1-100, Ag: 1000-5000, and Au: 10-100.

In order to have a record of the accuracy and also to check the applicability of the method for instrumental analysis of Noble Metals in general, a reference material containing certified concentrations of all Noble Metals was also analysed. The pure elements in appropriate forms (discs or powdered, respectively) were used as reference materials. The Pd- and Pt-containing samples were also

analysed by radiochemical photon activation analysis using separation by electrolysis, ion exchange or coprecipitation. The samples and reference materials were sandwiched and exposed to 30 MeV bremsstrahlung of an electron linear accelerator (mean electron beam current = 150 microamperes) for 1-3 hours depending upon the expected concentration. In the case of radiochemical analysis, the cooling periods, including the separation step, were about six hours. These samples were measured with a well-type NaI crystal. The counting times varied between one hour and one day depending upon the induced activity levels. The other samples were allowed to cool for six days and then measured with a semiconductor detector. Both a conventional large volume coaxial Ge(Li)-detector and a planar low energy photon germanium diode were used. During practical work it has been proved that in many cases low energy photon spectroscopy is superior to classical gamma spectroscopy (see above in paragraph 6.2.3.2). One of the reasons is the fact that frequently the low energy part of the photon spectrum of photon activated specimens contains fewer energy lines than the high energy partition. This is particularly true for Pd and Ag.

The obtained results showed excellent agreement with the theoretical concentrations calculated by the element ratios of the synthetic mixture and also with the results of the other laboratories participating in the interlaboratory certification campaign. The concentration data obtained in the analysis of the certified reference material (SARM 7, Platinum ore sample, South African Bureau of Standards) agreed fairly well with the certified values; the precision of these data was somewhat poor because of the low Noble Metals concentrations (from 63 ng/g for osmium to 3.74 micrograms per gram for platinum) and the high activity background effected by the complex matrix composition. The precision achieved in the analysis of the high purity copper samples was good to excellent except for the lowest gold values (0.001%). A radiochemical separation would have been necessary to improve the precision of the data. An instrumental method required, neutron activation analysis would be the method of the choice in this case because of its better intrinsic sensitivity for gold.

- Fossile fuel material

As is the case in the instrumental photon activation analysis of biological material, the application to the analysis of fossile fuel material is of particular advantage because of the absence of components producing long-lived interfering matrix activities; the most prominent background radiation originating from the matrix is due to  $^{11}\text{C}$  with a half-life of 20 minutes. Therefore, samples can be counted a few hours after activation. If radionuclides with say min-

utes of half-lives ( $^{28}\text{Al}$ ,  $^{29}\text{Al}$ ,  $^{38}\text{K}$  etc.) have to be counted, samples must be irradiated at an electron energy lower than the  $(\gamma, n)$ -threshold of  $^{12}\text{C}$ , namely at less than 20 MeV.

110) In a paper by Galatanu and Engelmann<sup>1073</sup> the instrumental photon activation analysis of 28 trace elements in a coal sample is described. Synthetic element mixtures were used as reference materials. Different batches of samples and reference materials were irradiated at two electron energies, namely 18 MeV (mean electron beam current = 60 microamperes) and 30 MeV (mean electron beam current = 90 microamperes). The samples activated at the lower energy were counted for the first time after a few minutes after irradiation and the other ones after 15 hours. Every sample was counted several times to detect eventual spectral interferences. Gamma spectroscopy was performed with a  $79\text{ cm}^3$  Ge(Li)-detector. The following elements were analysed: 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 and U. Among these, Cl, K, Sr, Cd and Pb were analysed in the sample batches irradiated with 18 MeV bremsstrahlung. The achievable detection limits varied between 0.2 and 125 micrograms per gram. The reproducibility of the analysis data was obtained by triplicate analysis; it was fairly good for most elements. There were no comparative values from other analysis techniques available. Moreover, no certified multielement reference material was analysed along with the samples as secondary standards. Therefore, no accuracy values could be given for the described method. An extended interference assessment was included. This was already discussed in the review of another paper of the same authors<sup>1068</sup>; see also Rev.104.

111) Brown coal was analysed by Leonhardt et al.<sup>296</sup> using different techniques including instrumental photon activation analysis. A microtron was used to analyse Ca, Fe and Sr. The authors did not give any description of sample mass and its preparation. 21 MeV bremsstrahlung was used for activation (mean electron beam current = 5 microamperes). No irradiation, cooling and counting periods were mentioned and also the gamma spectrometer was not specified. Anyhow, regarding the irradiation parameters, a trace analysis was not possible (and also not required); the analysed concentrations lay between 0.04% (for strontium) and 1.5% (for calcium). The precision was 5-10%. Comparative values for iron were obtained by radionuclide excited X-ray fluorescence analysis. In some cases severe disagreement of the data was found, but in general the accuracy and precision were sufficient. The analysis of coal samples was also reported by Pringle et al.<sup>1074</sup>.