

eventually present in the sample. Also, first order interference by $^{59}\text{Co}(\gamma, ^3\text{He})$ or $^{59}\text{Co}(n, \alpha)$ were reported by several authors (Hislop and Williams¹⁰²⁷, Rev.65, Kato et al.⁹¹⁹, Rev.95), but none were found significant. If ^{56}Mn is interfered uncorrectably, one has to use the other possible analysis reaction yielding ^{52}Mn . This reaction is not subject to first order interference at bremsstrahlung energies up to about 45 MeV, but the sensitivity is poor. The reaction yielding ^{53}Fe can also well be used (Meijers and Aten¹⁰⁶¹, Rev.93), but due to the short half-life of the nuclide (8.5 m) a special analysis procedure has to be undertaken. However, as also was found in the authors' laboratory, the results mostly are reliable although the sensitivity is limited.

All in all, instrumental photon activation analysis frequently is not the method of choice for trace iron determinations.

Cobalt

Cobalt is best analysed using the 811 keV gamma-ray line of ^{58}Co . This reaction is fairly sensitive and allows determinations in the submicrogram range. The first order interference from nickel, although frequently detected, normally has been found negligible due to its low activity yield. However, in matrices containing large amounts of nickel and/or copper, appreciable activity of ^{58}Co is contributed by these elements at activation energies greater than 20 MeV (Oka et al.¹¹³⁹). Chattopadhyay³³⁰ used 20 MeV bremsstrahlung for activation analysis of cobalt in sewage sludges. A gamma-ray line at 808 keV frequently overlaps the cobalt peak. Chattopadhyay assigned it to $^{106\text{m}}\text{Ag}$, but in the case of calcium present in say per cent concentrations in the sample - as was the case in the work of Chattopadhyay - 808 keV is surely predominantly emitted by ^{47}Ca . This interference can be ruled out by a long cooling time; 30 to 40 days were reported by Kato et al.⁹⁵⁶, Rev.36, or by correction routines as has been done in the authors' laboratory during routine analyses. Using modern high-resolution spectroscopy and data processing equipment the mentioned doublet can be unfolded by a computer routine (Reimers and Fusban⁶⁴⁹). Galatanu and Engelmann¹⁰⁶⁸, Rev.104, report interference by the double escape peak of the 1836 keV line from ^{88}Y (814 keV). This interference might gain particular significance if yttrium is added to the sample to serve as an internal flux monitor as has been frequently done in the authors' laboratory (Segebade et al.⁶⁰, Rev. 54). Regarding analytical sensitivity, freedom from interference, peak-to-Compton ratio and the resulting achievable accuracy and precision, thermal neutron activation analysis is surely preferable for trace cobalt determinations.

Nickel

Nickel is one of the elements which can be analysed best by instrumental photon activation analysis. The reaction producing ^{57}Ni cannot be interfered by any other photonuclear process at bremsstrahlung energies up to 45 MeV. Furthermore, ^{57}Ni emits a favourable gamma-ray spectrum and the activity yield after say hours irradiation allows the analysis of low (submicrogram) traces of nickel. Gamma spectroscopy can be used as well as low energy photon spectroscopy. In the latter case, the (γ, p) reaction yielding ^{57}Co is exploited. The first order interference due to $^{59}\text{Co}(\gamma, 2n)$ normally is negligible and the 122 keV gamma-ray line does not suffer from significant interference by peak overlap in normal cases. The 127 keV line of ^{57}Ni can also well be measured (Segebade et al.¹⁵⁷, Weise and Segebade¹⁵⁴).

Using 1379 keV for analysis, however, the close neighbourhood of the 1368 keV gamma-ray line of ^{24}Na has been complained frequently (Sato et al.¹⁰⁵², Rev.86 and others). Schmitt et al.¹⁰⁴⁹, Rev.82, therefore used the 1919 keV line of ^{57}Ni although being less abundant. In several cases this line was used also in the authors' laboratory because of more favourable peak-to-background ratio in the higher energy region (Neider et al.⁹⁵⁰, Rev.37). However, equipped with modern gamma spectrometry devices, the 1379 keV line is not seriously swamped by ^{24}Na and normally can well be used for nickel analysis.

If nickel is present in large concentrations as e.g. in highly alloyed steels, it produces an intense, possibly interfering background radiation, and it might be necessary to allow the sample to cool for a long - say weeks - period before activity measurement.

Copper

The integrated photoneutron cross sections of copper are large and thus high activities are yielded by bremsstrahlung bombardment (see Ch.2), but the most abundant product nuclides have unfavourable data for analytical purpose (short half-lives, low abundant gamma-ray lines). Fairly sufficient sensitivity can be achieved by low energy photon spectroscopy measuring the kX-rays of nickel produced by ^{64}Cu (Weise and Segebade¹⁵⁴, Segebade et al.¹⁵⁷). However, due to its low energy, this radiation may be subject to strong self-absorption within the sample matrix and special precautions are necessary during preparation for measurement (e.g. preparing a thin sample pellet). If copper is analysed as a major component, the annihilation quanta emitted by ^{62}Cu sometimes can be used;

this was done by Pradzynski¹⁰⁶⁶; Rev.100, Janiczek et al.²⁵⁶, Pradzynski et al.^{1140,1141} and many others. Galatanu and Grecescu²⁵⁹ utilised ^{61}Cu produced through $(\gamma,2n)$ for copper analysis in ores and concentrates. The annihilation quanta due to ^{64}Cu , after a radiochemical separation, were used by Williams and Hislop¹⁰³⁸, Rev.69, for copper analysis in bone ash. They found the first order interference by $^{66}\text{Zn}(\gamma,np)$ significant and applied a correction routine during data evaluation.

However, instrumental photon activation analysis (and also other activation methods) are not very favourable for routine trace analysis of copper and one would normally select another technique.

The (γ,an) -reaction yielding ^{58}Co was used as an internal flux monitor during analysis of noble metals in high purity copper (Segebade et al.¹⁰⁷¹, Rev.109)

Copper as a major matrix component produces an intense background radiation which is rather short-lived (maximum half-life: 12.7 h of ^{64}Cu). Samples normally can be measured after several days cooling period (Carter et al.¹⁰⁹¹, Rev.120, Segebade et al.¹⁰⁹⁴, Rev.121).

Zinc

If zinc is to be analysed as a minor component, ^{63}Zn is most favourable because only short irradiation periods are required and the nuclide emits a very convenient gamma spectrum. For trace quantity determinations either ^{65}Zn or ^{67}Cu can be used. The 185 keV gamma-ray line of the latter can be well measured both by conventional gamma-ray spectroscopy and - along with the 93 keV line - with a low energy photon diode. Due to the low natural abundance of ^{70}Zn the use of the 439 keV gamma-ray line of ^{69m}Zn is not recommendable.

Frequently, the 1116 keV gamma-ray energy of ^{65}Zn has not been used for its close neighbourhood to 1121 keV emitted by ^{46}Sc produced through $^{47}\text{Ti}(\gamma,p)$ (Kato et al.⁹⁵⁶, Rev.36). Aras et al.⁹⁴⁹ report greater accuracy using 185 keV. Williams and Hislop¹⁰³⁸ used the same line for its greater count rate yield. Other authors (Kato et al.⁹¹⁹, Rev.20, Galatanu and Engelmann¹⁰⁶⁸, Rev.104) preferred 1116 keV from ^{65}Zn because of its more favourable peak-to-Compton ratio and relative freedom from interference (with a modern high-performance spectrometer 1116 keV can well be separated from the adjacent ^{46}Sc line). Chattopadhyay³³⁰ reported spectral interference through 1115 keV emitted by ^{120m}Sb but found it negligible.

Zinc produces long-lived background activities if present as a major component of a sample matrix irradiated for long - say hours - time.

Gallium

The photon reaction of gallium with the highest activity yield is $^{69}\text{Ga}(\gamma, n)$ ^{68}Ga . However, this reaction can be used for trace analysis in exceptional cases only since due to the short half-life of ^{68}Ga (68.3 m) its gamma radiation mostly is swamped by short-lived activities of matrix components. Oka and Kato¹¹⁴² used the annihilation quanta effected by this isotope for gallium analyses after 15 MeV bremsstrahlung activation; see also Ref.¹¹⁴³. Gedeonov and Kusnetzov²⁵⁴ used ^{68}Ga for gallium determinations in gallium-niobium alloys.

The $(\gamma, 2n)$ reaction yielding ^{67}Ga is usable and fairly sensitive but the gamma spectrum is interfered by ^{67}Cu produced through zinc activation (Segebade et al.^{60,158,159}, Rev.54, Schmitt et al.⁹⁸⁴, Rev.50, Fusban et al.⁹⁸², Rev.44). In these works correction routines were used to account for the named interference.

If gallium is present in high concentrations, e.g. in semiconductor material, a source of multiple interference might be ^{72}Ga produced through activation with photoneutrons. This nuclide emits a very complex gamma-ray spectrum. However, this interference can be ruled out by cadmium shielding.

Germanium

The analysis of germanium using 1107 keV from ^{69}Ge frequently suffers from the close neighbourhood of the 1116 keV peak from ^{65}Zn produced by zinc. The sensitivity achievable using the Ga kX-ray emission measured with a low energy photon diode is fairly good but the evaluation is somewhat problematic since the radiation is emitted both by ^{69}Ge and by ^{71}Ge and therefore, the decay function of the common X-ray line is complex.

Oka et al.⁹⁰⁷, Rev.5, proposed to use $^{75\text{m}}\text{Ge}$ (half-life: 48 s) after short irradiation periods. Abe¹¹⁴⁴ analysed germanium in germanium-titanium oxide mixtures using the 511 keV annihilation radiation due to ^{69}Ge after sufficiently long cooling periods so that virtually all possibly interfering activities had decayed to negligible level.

Germanium, if present in large amounts, e.g. in semiconductor material, pro-

duces an extremely complex gamma-ray background spectrum and thus might interfere with the signals of many trace components to be analysed. In this case the use of low energy photon spectrometry is recommendable.

Arsenic

Arsenic can well be analysed by the 596 keV gamma-ray line of ^{75}As . Frequently this line is partly overlapped by 593 keV of ^{43}K produced by calcium. In the authors' laboratory, a correction routine using other gamma energies of ^{43}K has been successfully applied. The next abundant gamma-ray line of ^{75}As (635 keV) normally is not seriously interfered, but is much less intense than the 596 keV line, so that the achievable sensitivity might be insufficient.

Chattopadhyay and Jervis⁸⁸³, Rev.40, reported interference from $^{76}\text{Se}(\gamma, np)$ and $\text{Se}77(\gamma, nt)$ but found it negligible. Chattopadhyay³³⁰ ruled out the interference due to ^{43}K by allowing this nuclide to cool to quasi-zero activity (decay period: 14 d). Galatanu and Engelmann¹⁰⁶⁸, Rev.104, found first order interference by $^{79}\text{Br}(\gamma, \alpha n)$. This might gain importance in the analysis of air dust because of the automotive bromine exhaust (Aras et al.⁹⁴⁹, Rev.31). Aras et al. also reported interference by the 597 keV-line of ^{62}Zn produced by $^{64}\text{Zn}(\gamma, 2n)$. Since in airdust zinc usually is one of the major constituents this interference has to be paid attention to. Aras et al. proposed a long decay period to avoid the mentioned peak overlap.

Arsenic, if present in larger concentrations, produces an intense long-lived background activity.

Selenium

Either ^{75}Se produced through photoneutron reaction or ^{77m}Se produced through isomeric state photoexcitation has been used mostly for selenium analysis. The analytical sensitivity is fairly good but the most abundant gamma-ray energy of ^{75}Se (265 keV) is interfered by several other radionuclides. Galatanu and Engelmann^{1068, 1073}, Rev's.104, 110, respectively) therefore measured this nuclide after a long (up to 60 d) cooling period. In the authors' laboratory, 136 keV emitted by ^{75}Se has been used for analysis. Low energy photon spectroscopy has been applied. In the case of excessive nickel concentrations present in the samples the gamma-ray overlap from ^{57}Co has to be considered and accounted for (Segebade et al.¹⁵⁹). Chattopadhyay and Jervis^{330, 883}, Rev.40, used 103 keV emitted by ^{81m}Se and did not detect any interference. Using short irradiation

periods, ^{77m}Se has frequently been utilised for analysis. This nuclide has been produced either by photoneutron reaction (Oka et al.⁹⁰⁷, Rev.5) or by isomeric state photoexcitation using either radionuclide sources, especially ^{60}Co (Veres¹⁹⁰, Rev.78, Veres and Pavlicsek¹⁸⁸) or accelerator bremsstrahlung (Boivin et al.¹¹⁶, Lukens et al.^{121,124}, Rev.s.23 and 24, respectively, and many others). The high energy (6.14 and 7.11 MeV) gamma radiation of reactor-produced ^{16}N has been used for isomeric state formation by Akbarov et al.¹⁹⁵. This method is interesting since higher activity yields can be expected due to the higher exciting energy, but because of the short half-life of ^{16}N (7.4 s) experimental difficulties have to be taken into account. However, it may be possible to perform an in-situ activation through a suitable secondary target (e.g. oxygen) with help of accelerator-generated fast neutrons. As yet no report about such an application has been available to the authors.

If the photoexcitation method is used the analysis is free from interference but - due to the short half-life of the activation product (17.5 s) - requires a special analysis procedure. Dams⁹²⁴, Rev.29) reported the use of ^{79m}Se for analysis after activation with 25 MeV bremsstrahlung.

Selenium, if present as a major or minor component, emits a very complex gamma-ray spectrum after high energy activation and thus may cause interference during analysis of other elements, especially traces.

Selenium might be subject to volatilisation losses, particularly if organically bound (see above, 6.2.4.3). Chattopadhyay¹⁰¹⁵, Rev.62, stated selenium losses of up to 30% during lyophilisation of fish samples.

Bromine

In exceptionally favourable cases, bromine can be analysed most sensitively using the short-lived product nuclides ^{78}Br or ^{80}Br (half-lives 6.5 m and 17.6 m, respectively). However, particularly in multicomponent samples, mostly the gamma radiation of these nuclides is swamped by an intense, short-lived matrix background radiation. Therefore, ^{77}Br produced through $^{79}\text{Br}(\gamma, 2n)$ has to be used. This reaction is fairly sensitive too, and the product nuclide is conveniently measurable after about 1 d cooling period (Aras et al.⁹⁴⁹, Rev.31, Neider et al.⁹⁵⁰, Rev.37). A theoretically possible first order interference by krypton (Kato et al.⁹¹⁹, Rev.20) can be neglected.

Abe¹¹⁴⁵ used ^{80}Br and ^{80m}Br for bromine analysis in halide mixtures. Isomeric

state photoexcitation yielding ^{79m}Br has also been used (Dams⁹²⁴, Rev.29, Engelmann and Jerome¹²², Breban et al.⁹²¹, Rev.102). Veres and Pavlicsek¹⁸⁸ used a ^{60}Co source for excitation. However, experimental difficulties arise due to the extremely short half-life of the measured nuclide (4.9 s). The formation of ^{79m}Br by irradiation with gamma radiation from ^{16}N was reported by Akbarov et al.¹⁹⁵. This method was also used for selenium activation (see there).

Many bromine compounds are volatilised under heat and radiation attack; one should therefore carefully check for possible losses during bremsstrahlung exposure.

Rubidium

Among the photonucleide reactions usable for rubidium analysis $^{85}\text{Rb}(\gamma, n)^{84}\text{Rb}$ is most frequently used for its sensitivity and convenience regarding both half-life (34.5 d) and gamma energy (881 keV). ^{86}Rb can also be used but is much less favourable (Ölmez et al.⁹⁵³, Rev.33) due to poor sensitivity. First order interference from strontium was found negligible at comparable concentration of both target elements (Ölmez et al., see above, Kato et al.⁹¹⁹, Rev.20) Hislop and Williams¹⁰³⁷, Rev.65, found that at bremsstrahlung energies up to 40 MeV interference due to strontium and $^{89}\text{Y}(\gamma, \alpha n)$ are negligible if the corresponding target elements lie before in comparable concentrations. Chattopadhyay³³⁰ and Hui-Tu Tsai et al.¹¹⁴⁶ suggest the selection of 20 MeV bremsstrahlung for activation. Thereby all competing reactions are ruled out although the threshold energy of $^{86}\text{Sr}(\gamma, np)$ is somewhat lower (17.8 MeV). Galatanu and Gresescu²⁵⁷, Rev.84, and Dams⁹²⁴, Rev.29, reported the use of ^{84m}Rb with a half-life of 21 m, and Dams (see above) also reported ^{86m}Rb (half-life = 1.02 m) as usable for analysis evaluation. Hui-Tu Tsai¹¹⁴⁷ used both ^{84}Rb and ^{86}Rb for evaluation of rubidium analysis.

Strontium

The reaction mostly used for strontium analysis, namely $^{88}\text{Sr}(\gamma, n)^{87m}\text{Sr}$, yields one of the highest specific product activities encountered in all analytically usable photon reactions. A disadvantage is the relatively short half-life (2.81 h) of ^{87m}Sr . However, in the literature reviewed by the authors, essentially different findings were reported. Most of the workers did not detect any interference of ^{87m}Sr or found it negligible if the concerned elements were present in comparable amounts (Sato et al.¹⁰⁵², Rev.86, Kato et al.¹⁰⁵⁸, Rev.91, Hislop and Williams¹⁰²⁷, Rev.65, Kato et al.⁹¹⁹, Rev.20). Galatanu and Gresescu²⁵⁷,

Rev. 84, mentioned several gamma-ray line overlaps, most of them usually irrelevant. One of them, namely the spectral interference due to 388 keV from ^{126}I produced through $^{127}\text{I}(\gamma, n)$ might gain importance in certain matrices, but mostly this interference can be ruled out by short cooling periods. Hislop and Williams¹⁰²⁷, Rev.65, reported distortion of the 388 keV peak by the huge neighbouring 372 keV line from ^{43}K produced by calcium. Complete overlap of both lines were found by Das et al.^{51,1053}, Rev.87, but in this case scintillation spectrometry was used.

However, other authors recommended the use of the 232 keV line from $^{85\text{m}}\text{Sr}$ since they found significant interference by competing reactions due to yttrium and zirconium, or gamma-ray line overlap (Galatanu and Engelmann^{1068,1073}, Rev.s. 104,110, respectively, Chattopadhyay and Jervis⁸⁸³, Rev.40). Chattopadhyay³³⁰ recommended 20 MeV as bremsstrahlung energy to exclude first order interference by $^{90}\text{Zr}(\gamma, \alpha n)$. Isomeric state photoexcitation was used by many workers but trace determinations are hardly possible because of low intrinsic sensitivity due to small cross section values.

The (γ, p) reaction of strontium yielding ^{83}Rb was used for internal flux monitoring by Hui-Tu Tsai et al.¹¹⁴⁶.

In large concentrations strontium can produce a complex background but normally with moderate specific activities.

Yttrium

Yttrium can be well analysed using ^{88}Y . Its most prominent gamma-ray energy (1836 keV) usually offers an excellent peak-to-background ratio. At bremsstrahlung energies normally used for photon activation analysis, only zirconium interferes by $^{90}\text{Zr}(\gamma, np)$ or $^{90}\text{Zr}(\gamma, 2n, \beta^+)$. Particularly after long, say weeks, cooling periods this interference can cause difficulties since, due to both modes of its production, ^{88}Y decays along a complex function and corrective calculations become complicated. However, due to the very small apparent cross section of the interfering reactions the contribution of zirconium to the total ^{88}Y yield is small at Zr/Y concentration ratios which are comparable to the average natural distribution (Ölmez et al.⁹⁵³, Rev.33, Kato et al.¹⁰⁵⁸, Rev. 91). Interference by $^{93}\text{Nb}(\gamma, \alpha n)$ is theoretically possible, but normally not detectable after 30 MeV bremsstrahlung irradiations (Kato et al.⁹¹⁹, Rev.20). Lutz and LaFleur¹¹⁴⁸ achieved optimal sensitivity (about $1\mu\text{g}$) by coincidence counting of ^{88}Y with two NaI-crystals.

Photon activation analysis of yttrium by isomeric state excitation has been used frequently (Lukens et al.^{121,124}, Rev's.23,24, respectively, Engelmann and Jerome¹²² and many others) with fairly good sensitivity. ^{89m}Y was formed by radionuclide gamma excitation by Akbarov et al.¹⁹⁵ using gamma radiation from ^{16}N . Further information about this application can be found in the subparagraph on selenium.

Yttrium emits a quite simple gamma-ray spectrum after activation with 30 MeV bremsstrahlung. Therefore it has been used as an additive internal photon flux monitor (Segebade et al.⁶⁰, Rev.54).

Zirconium

Zirconium has very favourable properties for instrumental photon activation analysis determination regarding effective activation cross section, gamma-ray data and half-life of the major product nuclide (^{89}Zr , half-life = 78 h). Zirconium undergoes many photonuclear reactions, but only three of them have been used for analysis, namely those yielding ^{89}Zr , ^{89m}Zr and ^{95}Zr . The latter is less sensitive and normally cannot be used if zirconium is present as a trace component but the nuclide has the advantage of a longer half-life (64 d). ^{95}Zr is also produced through photofission if appreciable amounts of fissile material are present in the sample. However, in almost all cases 909 keV of ^{89}Zr has been used for analysis as yet. Tong et al.¹¹⁴⁹ recommended to use 20 MeV bremsstrahlung energy for activation to exclude all possible interferences from adjacent elements. Aras et al.⁹⁴⁹, Rev.31, found ^{89}Zr free from interference by niobium and molybdenum at 35 MeV bremsstrahlung energy. Chattopadhyay et al., Ref's. 330,883, Rev.40, found negligible contribution of niobium and molybdenum at 22 MeV activating bremsstrahlung energy and an overlapping gamma-ray peak from ^{204m}Pb (911 keV) which could be discarded by allowing the nuclide to decay out (half-life = 66.9 m). Kato et al.^{919,1058}, Rev's.91,95, respectively, found first order interference by molybdenum detectable but negligible at 30 MeV bremsstrahlung activation. Hislop and Williams¹⁰²⁷, Rev.65, irradiating with 30 MeV bremsstrahlung, found no detectable contribution from molybdenum but minor interference from niobium.

Several workers used short-lived (half-life = 4.16 m) ^{89m}Zr for analysis evaluation (Galatanu and Grecescu²⁵⁷, Rev.84, Dams⁹²⁴, Rev.29, Oka et al.¹¹⁵⁰). In this case, the interference problems and their handling are virtually the same as if ^{89}Zr was used.

If zirconium is present in large concentrations (e.g. in zircaloy or certain minerals) one has to take into account an intense and long-lived background activity.

Niobium

Niobium can be analysed very sensitively using the 934 keV line of ^{92m}Nb . The half-life is convenient (10.15 d) for relatively interference-free measurement. It is the only analytically usable gamma-ray line for niobium analysis by photon activation. In an early work another isomeric state of ^{92}Nb was reported (James¹¹⁵¹) but has not been verified using photonuclear reaction of the stable isotope (Silva et al.¹¹² and many others). The only relevant possible interference is caused by gamma-ray peak overlap of 934 keV emitted by ^{52}Mn due to iron in the sample. This interference, because of poor specific activity yield, frequently can be neglected or easily be accounted for (Kato et al.⁹¹⁹, Rev.20, Galatanu and Engelmann¹⁰⁶⁸, Rev.104). Only in the case of niobium analyses in steel matrix is it necessary to discard the interfering iron reaction by irradiating at lower (about 18 MeV) bremsstrahlung energy. First order interference by molybdenum could not be detected during analysis work in the authors' laboratory but was found by Kato et al.¹⁰⁵⁸, Rev.91, under similar experimental conditions.

Galatanu et al.^{257,258}, Rev's.84,101, respectively, irradiating with 25 MeV bremsstrahlung of a betatron, obviously did not detect any significant interference.

Abe¹¹⁹⁵ analysed niobium and tantalum synchronously using an NaI(Tl)-detector.

Molybdenum

140 keV from ^{99m}Tc is mostly used for molybdenum analysis. The sensitivity is fairly good. However, since ^{99m}Tc is a secondary decay product, a minimum decay period of 30 h is required, until the radioactive equilibrium is established and the apparent half-life is defined (Ratynski et al.¹⁰⁶⁴, Rev.97). Moreover, the gamma-ray peak is located in an unfavourable region of a normal gamma spectrum. Therefore it is of advantage to use low energy photon spectrometry for activity measurements. Using bremsstrahlung energies up to 40 MeV, first order interference is possible only by ruthenium or rhodium, but these were normally found negligible (Chattopadhyay et al.^{330,883}, Rev.40, Galatanu and Engelmann, Ref's.^{1068,1073}, Rev's.104,110, respectively). The most intense possible inter-

fering reaction of ruthenium, namely $^{100}\text{Ru}(\gamma, p)$, was only mentioned by Chattopadhyay and Jervis⁸⁸³, Rev.40; this interference can be discarded by long (about 4-5 d) cooling period; after this time, $^{99\text{m}}\text{Tc}$ is only due to beta-decay of ^{99}Mo . Using $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ for analysis one has first to check for interference by photofission of fissile material possibly present in the sample. Using short-time (minutes) irradiation $^{91\text{m}}\text{Mo}$ (half-life = 65 s) has been used for analysis (Oka et al.⁹⁰⁷, Rev.26, Dams⁹²⁴, Rev.29). Tong et al.¹¹⁴⁹ used molybdenum as an internal standard in the analysis of zirconium in Zr/Mo mixtures. After irradiation with 20 MeV bremsstrahlung, ^{88}Zr was used for flux monitoring. It was found that at this energy no appreciable activity of ^{89}Zr (used for zirconium analysis) was produced by molybdenum.

Ruthenium

According to the literature accessible to the authors, ruthenium was analysed but twice by photon activation as yet (Weise and Segebade¹⁵⁵, Rev.109, Oka et al.¹¹⁵²). Both ^{95}Ru and ^{97}Ru measured by gamma spectrometry, and ^{95}Tc measured by low energy photon spectrometry or gamma spectrometry were used for analysis evaluation. The achievable sensitivity is fairly good, but surely insufficient in the most cases, regarding the extremely small natural abundance of the element.

Interference by photofission products have to be considered if ^{103}Ru is used for analysis.

Rhodium

The analysis of rhodium in trace quantities entails difficulties in many instrumental methods including photon activation. The photoreaction product best suitable for analytical purpose is $^{101\text{m}}\text{Rh}$ (half-life: 4.4 d; see Weise and Segebade¹⁵⁵, Rev.109). However, this reaction is of relatively poor sensitivity and the major gamma-ray energies are located in unfavourable regions. Therefore, trace analyses mostly are not possible under reasonable experimental conditions (Ratynski et al.¹⁰⁶⁴, Rev.97). Moreover, the product nuclide is strongly interfered by $^{102}\text{Pd}(\gamma, p)$. Breban et al.¹⁰⁶⁵, Rev.99, used the (γ, n) products for analysis of rhodium in Black Concentrates; they claimed a detection limit of 1.5 micrograms.

^{102}Rh was used as an internal flux monitor in the analysis of ruthenium in rhodium as reported by Oka et al.¹¹⁵². They also performed rhodium analyses using

^{102}Rh after activation with 20 MeV bremsstrahlung¹¹⁵³.

Isomeric state photoexcitation was also proposed for rhodium analysis (Otvos et al.²¹¹, Boivin et al.¹¹⁴, Breban et al.⁹²¹, Rev.102 and many others). However, only low energy, photons, primarily the characteristic Rh X-rays, are emitted by $^{103\text{m}}\text{Rh}$, so that low energy photon spectrometry can be used only; moreover, the activity yield is relatively poor, and trace analyses are barely possible.

Palladium

Palladium can be analysed very sensitively by the 296 keV-line of ^{101}Pd using gamma spectrometry, and yet more sensitively by measuring 88 keV of ^{109}Pd using low energy photon spectrometry (Weise and Segebade¹⁵⁵, Rev.109). ^{103}Pd was also used for analysis (Segebade et al.^{1071,1072}, Rev.109). The latter nuclide offers somewhat less sensitivity, but is more conveniently measurable because of its longer half-life (17 d). Breban et al.¹⁰⁶⁵, Rev.99, found 1289 keV of ^{101}Pd most favourable because of its freedom from any interference.

Normally, activating with bremsstrahlung up to 40 MeV, all the mentioned reactions are relatively free from first order interference and gamma-ray line overlap. Difficulties usually arise predominantly from peak-to-Compton ratio deterioration due to eventual intense background as was found in the authors' laboratory.

If palladium lies before in higher amounts (e.g. in Noble Metals processing concentrates) it might interfere with the determination of many elements by an intense and very complex background gamma spectrum; the application of low energy photon spectrometry is recommendable in this case.

Silver

Silver has been analysed with good sensitivity using $^{106\text{m}}\text{Ag}$ and ^{105}Ag . The former offers better peak-to-background ratio if the higher gamma energies of the nuclide (e.g. 1527 keV) are used. The latter, using the 344 keV-line has a higher count rate yield. The short-lived isotopes (^{106}Ag and ^{108}Ag) have been used in exceptional cases only; they are produced with great activity yields but emit unfavourable gamma-ray spectra. The analytical use of $^{108\text{m}}\text{Ag}$ (half-life: 127 a) has not been reported in the literature inspected by the authors.

Weise and Segebade¹⁵⁵, Rev.109, used low energy photon spectrometry measuring

the kX-emission of palladium during analysis of silver in metals and ores. A comparison of the analytical results of silver obtained by ^{106m}Ag and ^{105}Ag yielded excellent agreement (see also Segebade et al.^{1071,1072}, Rev.109). Breban et al.¹⁰⁶⁵, Rev.99, used the 280 keV gamma-ray line of ^{105}Ag for analysis evaluation. This line is somewhat more sensitive than the 344 keV peak, but in the most cases is subject to strong overlap interference by the 279 keV-line of ^{203}Pb produced by lead possibly present in the sample. However, this interference can be discarded by long decay periods (half-life of ^{203}Pb : 51.9 h, compared with 41.3 d of ^{105}Ag). Chattopahyay et al.^{330,883}, Rev.40, reported possible first order interference of ^{106m}Ag by $^{108}\text{Cd}(\gamma, np)$. In the case of excessive amounts of cadmium present they recommended to minimise its contribution to the common product activity by activation at 20 MeV electron energy. Dams⁹²⁴, Rev.29, reported analyses using both the short-lived photoneutron products of silver (^{106}Ag , ^{108}Ag), and also ^{107m}Ag and ^{109m}Ag produced by isomeric state photoexcitation. The latter method has been recommended and applied by many workers. As early as 1942 the mentioned nuclear levels were detected using photoexcitation (Feldmeier and Collins¹⁰³); the two isomeres could be identified separately by Wolicki et al.¹¹⁷ in 1951. Most workers used accelerator bremsstrahlung for excitation, but also isotope sources, ^{60}Co in particular were applied for photon activation analysis of silver (Law and Iddings¹⁸⁹, Veres and Pawliczek¹⁸⁸). Gamma radiation from ^{16}N was also applied for excitation (Akbarov et al.¹⁹⁵, see also selenium).

Apparently, the first analytical applications of photoexcitation analysis of silver were made in the beginning of the 1960's (Lukens et al.¹²¹, Rev.23, Otvos et al.²¹¹, Bilefeld¹¹⁵⁴).

Silver, if present in large concentrations, produces a very intense and complex background after high energy photon activation. This is also true in all other activation techniques. Therefore, trace activation analyses in matrices bearing silver as a major component are mostly not possible without chemical separation. In some cases it is possible to circumvent interference through complex matrix spectrum by using low energy photon measurement; these spectra usually are much less complex than gamma-ray spectra (Weise and Segebade¹⁵⁵, Rev.109).

Cadmium

Among the numerous photonuclear reactions which cadmium undergoes during irradiation with high energy bremsstrahlung only two are analytically usable if trace cadmium determinations are required, namely $^{112}\text{Cd}(\gamma, n)^{111m}\text{Cd}$ and ^{116}Cd

$(\gamma, n, \beta^-)^{115m}\text{In}$. Mostly the latter is used although the other yields greater specific activity. However, the use of ^{111m}Cd is hampered by several interferences and its relatively short half-life (49 m; Baciu et al.²⁸², Aras et al., Ref.⁹⁴⁹, Rev.31).

Ricci⁹¹⁵, Rev.18, see also Ref.⁹⁷⁴, studied the analytically useful cadmium reactions with bremsstrahlung energies up to 140 MeV and found a sensitivity ratio (100 being the greatest) of $^{111m}\text{Cd}:^{105}\text{Cd}:^{115}\text{Cd}:^{115m}\text{In}:^{112}\text{Ag} = 100:8.2:1.2:2:0.6$. Jervis et al.¹⁰⁴¹, Rev.74 (see also Chattopadhyay and Jervis⁸⁸³, Rev.40, Chattopadhyay^{330,990}), studied all detectable photonuclear cadmium reactions after irradiation with bremsstrahlung from 8 to 40 MeV in small increments. They suggest the use of ^{111m}Cd after 15 MeV bremsstrahlung activation. They also report significant interference of ^{115m}In produced by indium and tin. During experimental work, these interferences were not found significant by the authors of this book, and if they eventually occur, their contribution to the common product nuclide can be easily discarded by allowing it to decay to negligible activity (see above, paragraph 6.2.3.4).

Sulin²⁵¹, Galatanu and Engelmann^{1068,1073}, Rev's.104,110, respectively, and Berthelot and Carraro⁹⁹⁹ used both ^{115}Cd and ^{115m}In . The latter authors reported excellent agreement between the results obtained by both reactions. However, the 527 keV line of ^{115}Cd might be overlapped by several other emissions (e.g. 528 keV from ^{147}Nd produced by neodymium) and the error thereby induced might become significant if cadmium is present in trace concentrations.

The isomeric state photoexcitation of ^{111m}Cd using either accelerator bremsstrahlung or radioisotope gamma radiation was proposed by many authors, but the achievable sensitivity is limited so that trace analyses are mostly not possible.

Indium

Assuming that indium mostly is present in small trace quantities in samples to be analysed, its determination by photon activation is accompanied by several severe difficulties. On the one hand, many photon reactions of indium yield large product activities. On the other hand, the product nuclides either have inconveniently short half-lives (^{112}In , ^{112m}In , ^{111m}In , ^{114}In) and/or emit gamma-rays with unfavourable energies (^{112m}In , ^{113m}In , ^{114m}In) or the gamma-rays are emitted with poor abundances (^{112}In , ^{114}In). The nuclide produced during high energy accelerator irradiation which is most suitable for analysis

(^{116m}In) is produced by reaction with photoneutrons and thus of limited usability. Moreover, all reactions are possibly subject to first order interference by tin and cadmium.

Kuttemperoor and Kubiske²⁴⁴ studied the photonuclear reactions of indium at bremsstrahlung energies up to 25 MeV generated by a betatron. Oka and Kato¹¹⁴² used ^{114m}In as an internal monitor in the analysis of gallium/indium/thallium mixtures. However, a relatively interference-free photon activation analysis with fairly good sensitivity is only achievable by irradiating at low bremsstrahlung energies to exclude competing reactions (Chattopadhyay et al.^{330,883}, Rev.40) exploiting the isomeric state photoexcitation. ^{115m}In was first produced by photoexcitation as early as 1939 (Waldman et al.¹⁰²). The first analytical application was reported by Harbottle¹⁸⁵. (Besides, this was the first application of isomeric state photoexcitation to analysis at all). Many authors used this method with surprisingly good sensitivity; Veres and Pavliczek¹⁸⁸ claimed a detection limit of 20 $\mu\text{g/g}$ of indium in a 50 g metal alloy sample using a ^{60}Co gamma-ray source for photoexcitation. The same detection limit was achieved by Breban et al.⁹²¹, Rev.102, using 6-8 MeV bremsstrahlung of a linear accelerator.

However, in the "normal" analytical case, i.e. traces (micrograms per gram and less) determinations in small, say tens of milligrams, sample masses required, instrumental photon activation analysis will surely not be the method of the choice.

Tin

The most sensitive reaction of tin is $^{118}\text{Sn}(\gamma, n)^{117m}\text{Sn}$. ^{117m}Sn has a conveniently long half-life (14 d) but emits only one single gamma-ray line, namely the isomeric conversion energy of 158 keV. In gamma-ray spectra, this is located very unfavourably; many photonuclear reaction products emit gamma-rays in this energy region, and mostly the 159 keV line of ^{47}Sc produced by titanium and/or calcium dominates. Therefore, ^{111}In is best used in gamma-ray spectrometry. Its major gamma emission energy (245 keV), although not appreciably high, is relatively free from interference and the achievable sensitivity is satisfactory in the most cases, although ^{117m}Sn excels. However, the latter can well be exploited using low energy photon spectrometry. Modern planar low energy photon diodes have sufficient resolution capability to enable a spectral separation of the gamma energies from ^{47}Sc and ^{117m}Sn (159.4 keV and 158.4 keV, respectively). Moreover, the low gamma-ray energy of ^{111}In ($E=171$ keV) can be

measured simultaneously for verification of the results. This line, as also gamma-ray line of ^{117m}Sn , cannot be resolved rigorously from eventually occurring neighbouring gamma-ray energies in normal gamma-ray spectrometry (e. g. 166 keV from ^{139}Ce , 175 keV from ^{48}Sc etc.).

At irradiation energies up to about 40 MeV, significant first order interference has not been observed, and ^{111}In can only be interfered by appreciable concentrations of indium in the sample. Chattopadhyay³³⁰ used ^{117m}Sn measuring with a coaxial Ge(Li)-detector after long (more than 3 weeks) decay periods. ^{47}Sc had then decayed to quasi-zero activity and all other possible sources of interference were assumed negligible. Galatanu et al.²⁵⁷, Rev.84, used 160 keV emitted by ^{123m}Sn . They mentioned many sources of interference, particularly in the case of rock and ore matrix analysed, but there was no information given about the management of the interferences. However, this problem was discussed in detail in a later publication of the same authors²⁶⁰. The same reaction was also used by Nguyen et al.^{1201,1202}.

Very high activity yield of ^{117}In was obtained after activation with 110 MeV bremsstrahlung as reported by Ricci⁹¹⁵, Rev.18. However, multiple interference by competing reactions and gamma-ray overlap has to be taken into account in this case, particularly during analysis of multicomponent samples.

Several workers also proposed isomeric state photoexcitation with accelerator bremsstrahlung, but the activity yield of ^{117m}Sn is extremely small and hence the analytical sensitivity is mostly insufficient (Otvos et al.²¹¹, Breban et al.⁹²¹, Rev.102).

If tin is present in larger amounts it emits an intense, complex gamma-ray background after high energy photon exposure, and thus trace quantities of other components might not be detectable.

Antimony

Antimony can be analysed quasi-selectively with excellent sensitivity by ^{122}Sb produced through $^{123}\text{Sb}(\gamma, n)$. Half-life and major gamma energy are favourable. Theoretically possible interference by competing reactions of tellurium normally are unlikely to occur because of the low natural abundance of the element and the small concentration of the possibly interfering isotope (^{123}Te) in the natural mixture (0.87%).

Hislop and Williams¹⁰²⁷, Rev.65, reported interference from tellurium, but in this special case antimony and tellurium were present in equal amounts. Aras et al.⁹⁴⁹, Rev.31, however, reported no detectable interference under comparable conditions. Hislop and Williams (see above) and Carter et al.¹⁰⁹¹, Rev.120, also used ^{120m}Sb for confirmation of the obtained values. ^{120m}Sb offers less sensitivity but has a longer half-life. No interference was reported for this nuclide. Chattopadhyay³³⁰ irradiated at 15 MeV to discard interference from tellurium.

The use of ^{120}Sb (half-life = 15.9 m) was mentioned only once in the literature accessible to the authors (Dams⁹²⁴, Rev.29).

Antimony, if present at higher concentrations, may cause interference by creating an intense background activity; the gamma-ray spectrum is not too complex, but peak-to-background ratios might be degraded by activities due to antimony in the matrix.

Tellurium

There are very few reports about tellurium analyses using photon activation; among the literature inspected by the authors, not more than three papers report tellurium analysis. ^{121}Te was found suitable for analysis during studies in the authors' laboratory. Campbell and Steele¹⁰⁰⁰, Rev.47, also used this isotope. It offers fairly good sensitivity and is free from first order interference by neighbouring elements at bremsstrahlung energies up to 40 MeV. Campbell and Steele report possible overlap interference of the major gamma-ray line by ^{69}Ge (half-life = 39 h, E=574 keV), but this can be ruled out by a minimum cooling period of three weeks. A special advantage of photon activation used for tellurium analysis as compared with neutron activation is its freedom from first order interference by fission products from thorium and uranium possibly present in the matrix. Chattopadhyay et al.^{330,883}, Rev.40, used ^{129}Te and found that at an irradiation energy of 20 MeV it was not interfered. However, ^{129}Te is a fairly abundant fission product, and therefore, using this isotope, one has to check for larger concentrations of fissile material in the sample prior to analysis.

Iodine

Iodine can be analysed conveniently with excellent sensitivity by instrumental photon activation analysis. ^{126}I has been used almost exclusively. This isotope

is free from interference by competing reactions. However, the gamma-ray energies (388 and 666 keV) frequently are overlapped by gamma-ray lines from ^{87m}Sr (388 keV) and/or ^{132}Cs (668 keV), respectively. The former interference mostly can be avoided by longer cooling periods or, if ^{87m}Sr is a decay product of ^{87}Y produced by $^{89}\text{Y}(\gamma, 2n)$, by use of low bremsstrahlung energies (up to 20 MeV). The overlap by 668 keV from ^{132}Cs cannot be circumvented. However, using modern, ultra-high resolution germanium detectors, it should be possible to separate both lines insofar as they can be unfolded mathematically with help of appropriate computer routines during spectra processing (Reimers and Fusban, Ref.⁶⁹⁴). Another way out is the application of low energy photon spectrometry measuring the kX-ray line of tellurium emitted by ^{126}I which is not interfered. Both spectroscopy methods yield comparable sensitivities.

Hui-Tu Tsai et al.¹¹⁵⁵ used ^{126}I , ^{124}I and ^{123}I for analysis of caesium/iodine mixtures after activation with bremsstrahlung energies up to 65 MeV. ^{130}I , produced by caesium, served as an internal photon flux monitor. Several authors (Kato et al.^{919,956}, Rev's.20,36, respectively, Galatanu and Engelmann¹⁰⁶⁸, Rev.104) report possible first order interference by xenon. However, in nearly all cases this source of error surely can be neglected. Aras et al.⁹⁴⁹, Rev.31, recommended a cooling time of about 10 days to exclude overlap interference from ^{80}Br and ^{132}Cs . It remains unclear why in this case the interference due to caesium was negligible (half-life of $^{132}\text{Cs} = 6.47$ d).

A common problem in the different activation analysis techniques as applied to iodine determinations is the volatility of this element and many of its compounds. Williams and Hislop⁹⁷⁹, Rev.77, undertook a thorough study about photon activation analysis of iodine, focussing its behaviour under bremsstrahlung bombardment and heat attack. In particular they studied iodine as encountered in soil environment. Significant losses of iodine during heating were stated but no detectable changes of concentration during multiple long-time exposure to high-energy bremsstrahlung, although most of the iodine content in soils is probably bound organically and thus rather volatile (Whitehead¹¹⁵⁶). Nonetheless, particularly in organic matrix, it is recommendable to provide precautions against loss of volatile iodine prior to or during bremsstrahlung irradiation, e.g. by cooling during activation or sealing of the sample in appropriate containments.

Caesium

With help of ^{132}Cs , caesium can be analysed with excellent sensitivity. Using

bremsstrahlung energies of up to 35 MeV, competing reactions are unlikely to interfere. However, the only usable gamma-ray line ($E=668$ keV) partly coincides with the 666 keV line from ^{126}I as mentioned in the preceding subparagraph. Since the other gamma energy of ^{126}I might also be interfered (see above) it is of limited use as a reference line for an eventual interference computing routine. Therefore, the only way out in the case of significant overlap interference is to use low energy photon spectrometry measuring the very intense xenon kX-radiation effected by the electron capture decay of ^{132}Cs . Chattopadhyay³³⁰ found the 668 keV line of ^{132}Cs free from interference if measured at least three days after irradiation with 15 MeV bremsstrahlung. The above discussed interference by iodine was not mentioned although in the analysed samples (sewage sludges) iodine is not unlikely to be present in measurable amounts.

Hui-Tu Tsai et al.¹¹⁵⁵ used the $(\gamma, 2pn)$ -reaction of caesium as an internal flux monitor in the analysis of iodine with up to 65 MeV bremsstrahlung (see above). The photoreactions of caesium at extremely high (250 MeV) bremsstrahlung energies were investigated by Kato and Hui-Tu Tsai¹¹⁹⁴.

Barium

The most sensitive photonuclear reaction of barium yielding a long-lived (more than 1 d half-life) radionuclide is $^{136}\text{Ba}(\gamma, n)$. The reaction is fairly sensitive but the yielded spectrum is subject to overlap interference. The reaction product emits one single gamma-ray line which is located in an unfavourable energy region ($E=268$ keV). However, interference due to competing reactions were found negligible by most workers (see e.g. Kato et al.^{919, 1058}, Rev's. 91 and 95, respectively, Chattopadhyay et al.^{330, 883}, Rev. 40, and many others). In the authors' laboratory, low energy photon spectrometry has been applied successfully, measuring the very intense barium kX emission by internal conversion of the $^{135\text{m}}\text{Ba}$ level. Low energy gamma-ray lines have been used, too: 123 keV of ^{131}Ba and 66.9 keV from ^{136}Cs produced through $^{137}\text{Ba}(\gamma, p)$. These lines can be measured interference-free, but the achievable sensitivity is comparatively poor.

$^{137\text{m}}\text{Ba}$ has been used frequently (see e.g. Dams⁹²⁴, Rev. 29). Depending upon the incident photon energy, this nuclide is produced either by photoneutron reaction or by isomeric state photoexcitation. In the former case, extremely high analytical sensitivity can be achieved. Chattopadhyay³³⁰ found first order interference by lanthanum. However, during experimental work in the authors' laboratory the contribution of lanthanum to the $^{137\text{m}}\text{Ba}$ activity was found neg-

ligible.

Using accelerator bremsstrahlung, several authors reported good sensitivity for analysis through isomeric state photoexcitation (Lukens et al.¹²¹, Rev.23, Engelmann and Jerome¹²², Breban et al.⁹²¹, Rev.102). Lukens¹²⁴, Rev.24, used 15 MeV bremsstrahlung and thus probably yielded higher activity through photoneutron reaction than by photoexcitation. ^{135m}Ba produced by radionuclide gamma isomeric state excitation was also applied but with very poor sensitivity (Law and Iddings¹⁸⁹). However, in this case a ^{60}Co source was used for excitation and thus higher activity yields could not be expected.

^{136}Cs produced by $^{137}\text{Ba}(\gamma, p)$ was used as an internal flux monitor in the analysis of caesium in Ba/Cs mixtures after activation with 18 MeV bremsstrahlung (Hui-Tu Tsai¹¹⁵⁷).

The lanthanide elements

For most of the lanthanide elements, thermal neutron activation analysis is by far the most sensitive analysis technique, more sensitive than photon activation by many orders of magnitude in many cases. Moreover, for some of the elements, no analytically suitable photonuclear reaction is available using bremsstrahlung energies up to say 45 MeV. However, there are some drawbacks of neutron activation analysis as applied to the Rare Earths. First, a high sensitivity does not guarantee a high quality level of the analytical results as expressed in terms of their accuracy and precision; the extremely large neutron activation cross sections might be a source of trouble as well since they cover a large range from about one to several thousands of barns, and thereby, for instance in a multicomponent Rare Earth compound mixture, the inter-elemental distribution of the induced activity is extremely inhomogeneous. Second, if larger amounts of Rare Earth elements are present in the sample, significant matrix attenuation of the neutron beam might lead to miscalculations in the evaluation procedure. Instead, the function of the photonuclear cross section with the atomic number of the target element is fairly smooth (see chapter 2) and thus differences in the induced activities are not extremely large. Moreover, since the photoneutron cross sections of the Rare Earth elements generally are much lower than those for thermal neutrons, there is no danger of significant activating beam attenuation within the sample matrix.

Extensive studies of the analytically usable photonuclear reactions of the Rare Earth elements were published by Oka et al.⁹⁴³ who used 20 MeV bremsstrahlung,

Owlya et al.⁸³⁸ using bremsstrahlung energies from 25 through 45 MeV, Kato and Voigt³⁰⁶, Rev.30, at an activating bremsstrahlung energy of 70 MeV and several others.

However, probably because of the above mentioned sensitivity limitations, photon activation, according to the literature inspected by the authors, has been applied to Rare Earth element analyses in few cases as yet. Mostly these elements are present in small traces (except perhaps lanthanum, cerium and neodymium), and therefore thermal neutron activation excels.

Several of the lanthanides, if present in larger amounts, may cause interference in photon activation analysis (as also in neutron activation analysis) by producing a complex background gamma spectrum; frequently it is of advantage to use low energy photon spectrometry when analysing lanthanide elements; the kX-lines can be well separated and interference by spectral line overlap either is not probable or can easily be accounted for as experiments performed in the authors' laboratory have shown.

Lanthanum

Up to a bremsstrahlung energy of 40 MeV, there is no photonuclear reaction suitable for trace lanthanum analysis. As indicated in the tables in Ch.5, the highest activity yield is due to ^{140}La produced by (n, γ) -reaction with photoneutrons. As far as the authors know, no attempt has been made to analyse lanthanum by photon activation. The photonuclear reactions of lanthanum at extremely high (250 MeV) bremsstrahlung energies were investigated by Kato and Hui-Tu Tsai¹¹⁹⁴.

Cerium

Cerium can be analysed with good sensitivity by ^{139}Ce and also by ^{141}Ce , whereby the former enables greater sensitivity and more advantageous peak-to-background ratio than the latter. In normal gamma spectrometry, the major gamma-ray lines of both activation products (165 and 145 keV, respectively) suffer from the close vicinity of 159 keV emitted by several radionuclides which frequently are highly abundant in photon-activated samples (e.g. ^{47}Sc). Therefore it is recommendable to use low energy photon spectrometry. In a spectrum collected with a planar low energy photon diode both mentioned lines are clearly separated from other lines appearing in "normal" photon-activated material. Moreover, the lanthanum kX-ray lines emitted during electron capture decay of ^{139}Ce can

be measured interference-free. Extremely high analytical sensitivity for cerium was found by Oka et al.⁹⁰⁷, Rev.5, using $^{139\text{m}}\text{Ce}$ (half-life = 56.5 s, E=754 keV) produced through activation with 20 MeV bremsstrahlung; a detection limit of less than 1 microgram was stated.

Praseodymium

As also in the case of lanthanum, there is no analytically suitable photonuclear reaction for analysis of praseodymium. The highest activity level induced by accelerator irradiation is due to an (n, γ) product of a reaction with photoneutrons (^{142}Pr). Dams⁹²⁴, Rev.29, reported the use of ^{140}Pr . The achievable activity is extremely high but the nuclide does not emit an analytically usable gamma energy. Dams reported the use of the unspecific 511 keV annihilation radiation due to the positron emission of ^{140}Pr . However, it remains unclear how to overcome the unavoidable interference by many other short-lived positron emitters, among them ^{15}O being the most prominent.

Neodymium

^{147}Nd produced through $^{148}\text{Nd}(\gamma, n)$ offers fairly good analytical sensitivity and has a convenient half-life (10.98 d). However, the 531 keV line is subject to interference by other closely neighbouring gamma energies (e.g. 528 keV from ^{115}Cd produced by cadmium). Therefore it is of advantage to use low energy photon spectrometry measuring the promethium kX-ray energies and/or the 91 keV gamma-ray line, both emitted by ^{147}Nd . The latter might be overlapped by 91 keV from ^{67}Cu produced by zinc possibly present in the sample. This contribution can easily be accounted for using other gamma-ray lines emitted by ^{67}Cu as a reference. (e.g. 93 keV). During practical analysis work in the authors' laboratory it was found that negligible degradation of the quality of the analytical results was effected through the correction routine in this case.

$^{141\text{m}}\text{Nd}$ (half-life = 62 s, E=757 keV) has also been used for neodymium analyses after short-period activations (Oka et al.⁹⁰⁷, Rev.5, Dams⁹²⁴, Rev.29).

Samarium

In favourable cases, i.e. if the concentration is not below say one microgram per gram and if there is no excessive matrix background radiation, samarium can be analysed by ^{153}Sm using low energy photon spectrometry (E=103 keV and the europium X-ray series). However, the analytical sensitivity is poor, and the

application of instrumental photon activation analysis to the determination of samarium was reported in the literature accessible to the authors only once (Berthelot et al.¹¹⁵⁸). Photon activation surely is not the method of choice for trace samarium analysis, but thermal neutron activation is only superior in terms of activity yields; since the same radionuclide is produced by both techniques, the mentioned restrictions also apply to neutron activation. Samarium has been used as an additive internal flux monitor in routine multielement analyses in the authors' laboratory (Segebade et al.⁶⁰, Rev.54).

Europium

The photonuclear reaction product of europium which is most suitable for analysis is $^{152m2}\text{Eu}$. ^{150m}Eu can also be used. The half-lives of both are rather short (9.3 h and 12.8 h, respectively) which somewhat limits the detectability of the element. The intrinsic sensitivity is good but nevertheless might be insufficient since normally europium appears in very small concentrations so that thermal neutron activation analysis rather than photon activation would normally be the method chosen. Except for several systematic studies, the authors could find but two messages about photon activation analysis of europium (Korthoven et al.³⁰⁷, Rev.106, Berthelot et al.¹¹⁵⁸. The former used $^{152m1}\text{Eu}$ measured with a scintillation crystal, the latter applied high resolution spectrometry measuring both the 122 keV line and the samarium kX-ray emission of the same nuclide and found good agreement of the results obtained using both lines. The application of instrumental photon activation analysis in both cases was of particular advantage compared with neutron activation; Korthoven et al. analysed alloys containing high lanthanide metal concentrations and Berthelot and co-workers analysed boron matrix, so that in the case of thermal neutron activation both would have to face serious problems in terms of matrix absorption.

Gadolinium

There is only one photon activation product which is practically usable for gadolinium analysis, namely ^{159}Gd (half-life = 18.56 h). Since its most intense gamma-ray line ($E=364$ keV) is closely adjacent to very strong gamma emissions of nuclides which frequently are produced in multicomponent matrices during photon activation (e.g. ^{43}K , ^{87m}Sr) it is recommendable to use low energy photon spectrometry and select the kX-rays of terbium and/or the 58 keV gamma-ray line (Oka et al.⁹²⁴, Korthoven et al.³⁰⁷, Rev.106, Berthelot et al.¹¹⁵⁸). However, in the most cases the sensitivity of the method is insufficient because

of the low natural abundance of gadolinium.

Terbium

As is also true for several other Rare Earth elements, the greatest activity induced to terbium during accelerator irradiation is due to reaction with photoneutrons; the (γ, n) -product has a half-life of 150 years and therefore is produced in extremely small quantities. ^{156}Tb has a more convenient half-life (5.4 d), but, being a $(\gamma, 3n)$ product, is also produced only in small activities.

Inspecting the literature, the authors found only one paper dealing with photon activation analysis of terbium (Oka et al.⁹⁰⁷, Rev.5). They used the short-lived $^{158\text{m}}\text{Tb}$ (half-life = 10.5 s) produced by 20 MeV activation. However, for trace analyses of terbium one will normally not select photon activation.

Dysprosium

Dysprosium can be analysed with fairly good sensitivity with help of ^{157}Dy (half-life = 8.1 h). ^{155}Dy (half-life = 9.59 h) has also been used (Berthelot et al.¹¹⁵⁸). However, the gamma-ray energies (326 keV and 227 keV, respectively) frequently are subject to overlap interference in a multi-component spectrum, assuming trace quantities of dysprosium to be analysed. The use of low energy photon spectrometry is also troublesome because the resulting terbium kX-ray lines are emitted by both mentioned product nuclides at comparable intensities. Thereby, the common decay function of these lines is complex. However, the half-lives of both nuclides are not too different (8.1 h and 9.59 h, respectively) and, depending upon the requirements concerning the quality of the analysis results, the induced error might be negligible when fitting an average half-life into the common decay function.

Holmium

Half-lives and photon energies of the (γ, n) -products of holmium are extremely inconvenient; there is no suitable reaction for trace holmium analysis.

Dams⁹²⁴, Rev.29, reported the analysis of holmium measuring the low energy photon emission of $^{164\text{m}}\text{Ho}$ after activation with 35 MeV bremsstrahlung.

Erbium

As also in the case of holmium, there is no practically usable photonuclear reaction for analysis of erbium using gamma-ray spectrometry; either the half-lives of the activation products are unsuitable (^{161}Er , ^{163}Er) and/or they do not emit a measurable gamma energy (^{163}Er , ^{165}Er). However, using low energy photon spectrometry one can exploit the very intense holmium kX-emission due to the electron capture decay of ^{165}Er , and also the thulium kX-rays due to ^{169}Er . Both nuclides can be produced with large specific activities during bremsstrahlung bombardment, but the latter might be interfered by ^{169}Yb produced through ytterbium activation. As far as the authors know, there is no reference about the analytical use of photonuclear reactions for erbium analysis. Nonetheless, frequent analytical use was made of $^{167\text{m}}\text{Er}$ produced by photoexcitation with lower incident photon energies. Excellent selectivity and fairly good sensitivity were found by many workers using accelerator bremsstrahlung (Dams⁹²⁴, Rev. 29, Lukens¹²⁴, Rev.24, Ivanov et al.¹⁰⁵⁵, Rev.89, Breban et al.⁹²¹, Rev.102, and many others) or isotope source gamma-rays (Veres¹⁹³).

Thulium

Both the (γ, n) and the $(\gamma, 2n)$ products can be applied for fairly sensitive thulium analyses. Using the latter it is recommendable to select accelerator electron energies not less than 30 MeV. However, the major gamma-ray lines of both nuclides are subject to severe overlap interference by elements occurring in many multi-component samples, e.g. 198 keV of ^{168}Tm is interfered by 197 keV from $^{120\text{m}}\text{Sb}$ produced by antimony, or 208 keV of ^{167}Tm is nearly completely overlapped by 208 keV from ^{237}U or ^{67}Ga . here again, low energy photon spectrometry might prove superior since the erbium X-ray emission can only be interfered by ^{166}Ho produced through $^{165}\text{Ho}(n, \gamma)$ by photoneutrons. This interference can be discarded by sufficiently long cooling periods (about 14 d) or neutron shielding of the sample during irradiation, e.g. with cadmium foil.

Photon activation analysis of thulium was reported by Oka et al.⁹⁴² and by Hislop and Williams⁹⁵², Rev.32. Both used the 198 keV gamma-ray line of ^{168}Tm .

Ytterbium

The most sensitive photonuclear reaction of ytterbium is $^{176}\text{Yb}(\gamma, n)^{175}\text{Yb}$. The achievable sensitivity is good and the product nuclide has a convenient half-life (4.2 d), but the gamma-ray energies with sufficient abundances are rather

low (up to 396 keV). A few other activation products can also be used for analysis (e.g. ^{173}Tm , ^{169}Yb) but enable considerably less sensitivity.

The authors found but one reference about ytterbium analysis by photon activation (Dams⁹²⁴, Rev.29). $17.7\text{ s}^{-1}\text{Yb}$ was used after short-period activation. However, in the most cases the analytical sensitivity of photon activation is insufficient for ytterbium analysis due to the poor natural abundance of the element. Surprisingly, no attempt has been made, as far as the authors know, to use isomeric state photoexcitation measuring $^{176\text{m}}\text{Yb}$.

Lutetium

The analytically most suitable photonuclear reaction of lutetium is the $(\gamma, 3n)$ process yielding ^{172}Lu . Both the (γ, n) and the $(\gamma, 2n)$ reaction yield isotopes whose half-lives are too long to produce sufficient specific activities (3.31 a and 1.37 a, respectively) for trace analysis. $^{174\text{m}}\text{Lu}$ (half-life = 142 d) does not emit a suitable photon spectrum. The authors could not find any publication in which the application of photonuclear reaction to analyses of lutetium was mentioned.

Analysis of the element using isomeric state photoexcitation is possible (Otvos et al.²¹¹, Lukens et al.¹²¹, Rev.23), but very poor sensitivities have been stated.

Law and Iddings¹⁸⁹ attempted to use a ^{60}Co gamma-ray source for excitation but could not detect any activity after irradiation except the natural radiolutetium radiation.

Hafnium

$^{176}\text{Hf}(\gamma, n)^{175}\text{Hf}$ is the most sensitive photonuclear reaction of hafnium. It has been applied in the authors' laboratory for analysis of hafnium in zirconium oxide matrix (unpublished). The major gamma energy of ^{175}Hf (344 keV) might be interfered by ^{105}Ag (E=344 keV) produced by silver and/or cadmium possibly present in the sample. As far as it is known to the authors, no application of this reaction for hafnium analyses was published.

Instead, isomeric state photoexcitation frequently has been used by many workers, mostly measuring $^{179\text{m}}\text{Hf}$ (half-life = 18.7 s). Among all elements determinable with this technique, hafnium apparently has the most advantageous proper-

ties and can be analysed with good sensitivity using accelerator bremsstrahlung (Kodiri et al.¹¹⁵⁹, Otvos et al.²¹¹, Lukens et al.¹²¹, Rev.23, Breban et al.⁹²¹, Rev.102, Ivanov et al.¹⁰⁵⁵, Rev.89, and many others). Law and Iddings¹⁸⁹ did not detect appreciable activity after irradiation of hafnium with gamma-rays of a ^{60}Co source. Akbarov et al.¹⁹⁵ used gamma-rays from ^{16}N for in-situ excitation of hafnium and yielded fairly good sensitivity. See also selenium.

Tantalum

Among the photonuclear reaction products of tantalum, $^{180\text{m}}\text{Ta}$ can be produced with the highest activity yield. However, its gamma-ray energies are low (93 and 104 keV) and have small abundances (4 and 1 emissions per one hundred disintegrations, respectively). Therefore, it is of advantage to measure the hafnium kX-ray emission due to the electron capture decay of $^{180\text{m}}\text{Ta}$ which is much more intense than its gamma radiation (Berthelot et al.¹⁰⁰⁵, Rev.52). See also Abe¹¹⁹⁵.

$^{180\text{m}}\text{Hf}$ produced through $^{181}\text{Ta}(\gamma, p)$ can also be applied. On the one hand, the activity yield is much lower than that of the above named reaction, but on the other hand, $^{180\text{m}}\text{Hf}$ emits a gamma-ray spectrum which is much more conveniently measurable.

Using the 93 keV gamma-ray line of $^{180\text{m}}\text{Ta}$ for tantalum analyses in geological material, Galatanu et al.^{257,258}, Rev.84 and 101, respectively, found spectral interference by many elements. Ricci⁹¹⁵, Rev.18, used $^{180\text{m}}\text{Hf}$ after activation with 105 MeV bremsstrahlung. However, in instrumental multielement analyses, activation with this energy entails a lot of interference problems. Nevertheless, excellent sensitivity was found.

Tungsten

During bremsstrahlung irradiation of tungsten, among the numerous photonuclear reactions the highest activity is yielded by $^{182}\text{W}(\gamma, n)^{181}\text{W}$. However, the gamma-ray lines of ^{181}W have insufficient emission probabilities, therefore low energy photon spectrometry measuring the tantalum kX-ray lines is superior to gamma spectroscopy (Berthelot et al.¹⁰⁰⁵, Rev.52). The achievable sensitivity is excellent. In gamma spectra of photon-activated tungsten taken after decay periods of not more than say a week, the most prominent lines are emitted by ^{187}W produced by photoneutrons.

^{183}Ta produced through $^{184}\text{W}(\gamma, p)$ is also well measurable, but much less sensitive than the above quoted reaction yielding ^{181}W . $^{183\text{m}}\text{W}$ produced through isomeric state photoexcitation was used for tungsten analysis by many workers. However, the achievable sensitivity is rather poor; therefore, if trace determinations are required, this technique cannot be applied.

Tungsten, if present as a major component, may be a source of spectral interference through ^{187}W . However, the associated neutron reaction can be avoided by neutron shielding, either wrapping the sample with cadmium foil or, as proposed by Berthelot et al.¹⁰⁰⁵, Rev.52, by mixing the sample with lithium salt.

Rhenium

There are two photon reactions of rhenium which enable excellent activity yields, namely those producing ^{186}Re and ^{184}Re , respectively. However, normally, due to the extremely low natural abundance of the element, the sensitivity of instrumental photon activation analysis is insufficient. ^{186}Re can be produced with one of the highest activity yields encountered in photon activation, but its gamma-ray energies are inconveniently low (123 and 137 keV) and not very abundant (1 and 12%, respectively). Moreover, both lines most probably are subject to overlap interference in multi-component spectra.

The other mentioned reaction product emits a more conveniently measurable gamma spectrum, but is produced with lower activity yield. In the case of rhenium analysis, low energy photon spectrometry does not offer any improvement; the fluorescence yields of the tungsten kX-ray lines associated with the above named product nuclides are about as low as the intensities of the gamma-ray lines. Moreover, since the X-ray lines are emitted by both nuclides at comparable emission probabilities the decay curve is complex and one would have to wait for a long (more than one month) cooling period before measurement to ascertain that ^{186}Re has decayed out.

As far as it is known to the authors, photon activation has not been applied to analysis of hafnium hitherto.

Osmium

Osmium can be analysed with fairly good sensitivity by ^{185}Os (half-life = 94 d) or $^{183\text{m}}\text{Os}$ (half-life = 10 h). ^{185}Re produced by $^{186}\text{Os}(\gamma, p)$ has also been used (Segebade et al.¹⁵⁵, Rev.109). However, regarding the low natural abundance of

osmium, the intrinsic sensitivity of instrumental photon activation analysis mostly is insufficient.

Except the above quoted paper by Segebade et al., no reference about photon activation analysis of osmium could be found by the authors. Surprisingly, photoexcitation of the two analytically usable isomeric states (^{190m}Os , ^{192m}Os) obviously was not applied to osmium analyses. Particularly the former emits a conveniently measurable gamma-ray spectrum.

Oka et al.¹¹⁵² used ^{185}Os as an internal photon flux monitor in the analysis of ruthenium in osmium-containing matrices. Several chemical compounds of osmium are easily volatilised, therefore it is recommended to cool the analysed samples during bremsstrahlung irradiation.

Iridium

Both the high energy gamma and the low energy photon spectrum of ^{190}Ir and/or ^{190m}Ir can be used for very sensitive analyses of iridium (Segebade et al.¹⁵⁵, Rev.109). The gamma-ray spectra of both activation products are conveniently measurable although some of the lines might be subject to overlap interference. The energy photon spectrum of ^{190}Ir is partly overlapped by iridium kX-rays emitted by ^{191}Pt produced through photonuclear reaction of platinum possibly present in the sample. However, these interferences easily be accounted for.

Breban et al.¹⁰⁶⁵, Rev.99, found several interferences of ^{190}Ir , most of them originating from other Noble Metals which were highly concentrated in the analysed samples.

Iridium can also be analysed with excellent sensitivity and selectivity using photoexcitation of the ^{191m}Ir level (Otvos et al.²¹¹, Lukens et al.¹²¹, Rev.23, Lukens¹²⁴, Rev.24, Engelmann and Jerome¹²² and others).

Platinum

There are several photonuclear reactions of platinum yielding fairly high activities, but their product nuclides emit gamma-ray lines which are located in inconveniently low energy regions and/or have poor intensities (^{193m}Pt , ^{195m}Pt , ^{197}Pt). Therefore, low energy photon spectrometry is recommendable, measuring the platinum kX-ray emission due to internal conversion of ^{193m}Pt and ^{195m}Pt to the ground level. Both nuclides contribute to the common signal in comparable

amounts, hence the decay function is complex. However, the half-lives are similar (4.33 d and 4.02 d, respectively), so that one can assume an average half-life without inducing excessive error. Major interference, however, is due to ^{196}Au produced by gold probably present in the sample giving also rise to platinum X-rays with extremely high fluorescence yields.

Breban et al.¹⁰⁶⁵, Rev.99, used the 99 keV gamma-ray line of $^{195\text{m}}\text{Pt}$ produced by 35 MeV bremsstrahlung activation of Black Concentrates; they found multiple interference by adjoining and overlapping gamma-ray peaks. Segebade et al., see Ref's. 155, 1071, 1072, Rev.109, used both gamma- and X-ray spectroscopy to measure the various emissions of ^{189}Pt , $^{193\text{m}}\text{Pt}$, $^{195\text{m}}\text{Pt}$ and ^{197}Pt in bremsstrahlung activated electrolytic copper.

$^{195\text{m}}\text{Pt}$ produced by photoexcitation has also been used for analysis by many workers; this method is particularly useful in the analysis of Noble Metals concentrates. By reducing the bremsstrahlung energy to say 6 MeV, one can avoid excessive background activities produced by photoneutron reactions in the matrix, particularly the above mentioned interference through gold.

Oka et al.¹¹⁵³ used the 539 keV line of ^{191}Pt as an internal flux monitor in the analysis of rhodium and rhenium in rhodium/rhenium/platinum mixtures.

If platinum is present at high concentration levels it creates a very complex and intense background gamma spectrum so that instrumental trace analyses of other components might be severely interfered. In this case it is recommended to use low energy photon spectrometry since the low energy photon spectrum of platinum after activation with bremsstrahlung is much less complex (Segebade et al.¹⁵⁵, Rev.109).

Gold

Gold can be analysed conveniently with excellent sensitivity using the gamma-ray lines of ^{196}Au (333 and 356 keV) or the platinum kX-ray emission effected by the electron capture decay of this nuclide. (Segebade et al.^{155, 1071, 1072}, Rev.109, Breban et al.¹⁰⁶⁵, Rev.99). If larger amounts of gold are present in the sample to be analysed, instrumental photon activation analysis is of particular advantage since the problem of matrix-caused attenuation of the activating beam is not as serious as in thermal neutron activation (see above, Para. 6.2.3.4). Moreover, self-absorption of the measured gamma energy mostly is negligible in instrumental photon activation analysis since ^{196}Au also emits

high energy gamma-rays (e.g. 1091 keV), whereas 411 keV is the highest of all photon energies emitted by ^{198}Au produced through thermal neutron activation (Lutz⁷¹⁷, Reimers et al.⁸⁸⁴, Rev.118). Additionally, the half-life of ^{196}Au produced through photon activation is more convenient than that of ^{198}Au (6.2 d compared with 2.7 d, respectively).

Gold can also be analysed very sensitively by isomeric state photoexcitation. This method has been frequently applied for fast routine analyses of gold in large series of ore and mineral samples in the Soviet Union (Pchelkin et al., Ref.¹¹⁶⁰, Rev.89, Kapitsa et al.²⁸³, Rev.96, Burmistenko¹¹⁹¹ and many others). Akbarow et al.¹⁹⁵ used excitation by gamma-rays from ^{16}N produced in a nuclear reactor (see also selenium).

The behaviour of thin gold layers on aluminium substrate during bombardment with 44 MeV bremsstrahlung was investigated by Eschbach et al.^{1198,1199}.

If gold is present as a major component an intense background is created through photon activation. The gamma component of this background is not very complex if the electron energy of the accelerator was set below the ($\gamma,3n$) threshold of ^{197}Au (23.2 MeV). However, experiments have shown that after irradiation of gold objects the matrix radiation emitted by ^{196}Au causes excessive dead time of the gamma counting equipment so that the results of the analysis of other components might not be reliable.

Mercury

The photonuclear data of mercury indicate excellent sensitivity for instrumental photon activation analysis. ^{203}Hg and ^{197}Hg have mostly been used for analysis evaluation. The latter is produced with higher activity than the former, but has an inconveniently short half-life; thus it might be swamped by matrix background radiation. All analytically usable gamma-ray lines emitted after high energy bremsstrahlung activation are subject to overlap interference. Some of the interference sources can be discarded by long cooling periods, for instance: 279 keV from ^{203}Hg mostly is interfered by the same gamma energy emitted by ^{203}Pb produced by lead which is frequently present in the analysed sample at considerably higher concentrations than mercury. The long half-life of ^{203}Hg (46.6 d) allows a decay time of say one month after which ^{203}Pb (half-life = 52.1 h) probably has decayed to negligible level. Another possibility to circumvent interferences is the use of low energy photon spectrometry (Raghi-Atri and Segebade⁸⁹⁶, Rev.79).

Ricci⁹⁷⁴ used the 192 keV gamma-ray line of ^{197}Hg for mercury analysis after activation with 105 MeV bremsstrahlung. Chattopadhyay et al.^{330,883}, Rev.40, found $^{199\text{m}}\text{Hg}$, being produced with the highest yield among all nuclides generated in photon activated mercury, interfered by $^{123\text{m}}\text{Sn}$ and hence not usable for analysis. They used the 134 keV conversion line of $^{197\text{m}}\text{Hg}$.

Gerstenberger¹¹⁶¹ used instrumental photon activation analysis for the determination of the abundances of several stable mercury isotopes.

However, the major problem in the analysis of mercury surely is not the lack of intrinsic sensitivity of the method; instrumental photon activation analysis and many other techniques, thermal neutron activation in particular, mostly meet the sensitivity requirements of mercury analyses. As was discussed in paragraph 6.2.4.3, major attention has to be directed to the physicochemical behaviour of this element. It is not only the overall instability of mercury compounds under heat- and radiation attack during activation which creates serious problems - although these surely are the major ones. The trouble starts with the sampling and sample storage prior to analysis. Takeuchi et al.,¹¹⁶² and¹¹⁶³, in thermal neutron activation context, recommended to store samples and - in the interest of long-term stability of the mercury concentration levels - particularly reference materials at -20°C before and after activation. At this point it is interesting to note that none of the above cited authors evaluated the volatility problem in photon activation. As far as it is known to the authors, there are but two paper dealing with this problem in bremsstrahlung activation context (Raghi-Atri and Segebade⁸⁹⁶, Rev.79, Segebade⁸⁹³).

There are several sampling techniques which prevent reliable and representative results of the analysis a priori, e.g. the sampling of mercury in air particulate on air-dust filters. Assuming that a major part of the airborne mercury lies before as pure element, this fraction whose concentration is dependent upon many parameters will be volatilised by subsequent air-flow, and finally, only very stable mercury compounds (e.g. mercury sulphide) will be collected entirely.

In the sample preparation step, mercury losses can occur during high temperature drying of the sample. This is particularly true in organic matrix. In organic environment, the mercury most likely is organically bound, e.g. as methyl mercury (Wood et al.^{1164,1165}, Ridley et al.¹¹⁶⁶, DeSimone¹¹⁶⁷) which is extremely volatile and significant losses have been stated during sample preparation techniques like drying and ashing, even at low temperatures; also during

freeze-drying it might happen that not all mercury is retained (Litman et al., Ref.¹¹⁶⁸). However, the most critical phase in this instance is the irradiation step. A systematic study of the volatility behaviour during bremsstrahlung exposure of several elements, mercury in particular, was undertaken by Segebade, Ref.⁸⁹³.

Many similar investigations were published, as touched on above, in the neutron activation context; some of these papers and the measures against mercury losses proposed therein are now summarised:

Brune et al.¹¹⁶⁹⁻¹¹⁷¹ and other workers suggest irradiation at low (-40°C) temperatures. This can be accomplished much more conveniently during accelerator activations than - as was reported in the quoted papers - in nuclear reactors. See also - in a different context - Ref.¹¹²⁵. Bate¹¹⁷² found significant losses of mercury from sealed plastic irradiation containers and recommended sealing the samples in quartz vials. This was reported also by many other authors (e.g. Rook et al.¹¹⁷³, Sjöstrand¹¹⁷⁴).

The addition of strong inorganic acids or oxidising agents minimises loss of mercury from plastic irradiation containments as found by McFarland¹¹⁷⁵.

However, all these methods are associated with considerable procedural effort. A more elegant way is to "trap" the mercury chemically with help of appropriate compounds. Takeuchi et al.^{1162,1163} mixed sulfur compounds like thiourea, L-cystein, thioacetamide and ammonium sulphide with the sample prior to irradiation. By these chemicals, mercury which is set free by heat and radiation energy, is caught and transferred into heat- and radiation-resistant HgS. Ragh-Atri and Segebade⁸⁹⁶, Rev.79, used LiHS for mercury fixation during photon activation. Experiments of both groups have indicated stability of the mercury contents both during and after (by eventual radiolytic reactions) activation.

Particularly in photon activation analysis this method is suitable since no additional background radiation is created by lithium sulphide. However, the described trapping method bears the danger of contamination; therefore it is recommendable to run chemicals blanks along with the samples to be analysed.

Thallium

Thallium is one of the elements which are very well determinable by instrumental photon activation analysis compared with other instrumental techniques. Un-

like thermal neutron activation, high-energy photon irradiation gives rise to a conveniently measurable product nuclide (^{202}Tl) produced with high specific activity. The 440 keV gamma-ray line most likely is interfered by 439 keV from $^{69\text{m}}\text{Zn}$ produced by zinc, but after a cooling period of say one week, this nuclide (half-life = 13.9 h) will have decayed to negligible activity and ^{202}Tl (half-life = 12.2 d) can be measured interference-free. If, for any reason, a long cooling period is not allowed, thallium can be analysed with quasi-equal sensitivity by the mercury kX-ray lines due to ^{202}Tl (Berthelot et al.¹⁰⁰⁵, Rev.52). These are partly overlapped by thallium kX-ray signals, but this interference can easily be accounted for. A theoretically possible first order interference by $^{204}\text{Pb}(\gamma, \text{np})$ has been discussed; Masters and Lutz¹⁰⁰¹ and Hislop and Williams¹⁰²⁷, Rev.65, did not detect any contribution of ^{202}Tl by lead. Oka and Kato¹¹⁴² and Chattopadhyay et al.^{330,883}, Rev.40, minimised an eventual interference by irradiating at lower electron energy.

Lead

In reviewing the literature about photon activation analysis, one will find lead to be one of the most studied elements. Besides the general importance of this element this is due to the fact that - as in the case of thallium - lead can be readily determined during instrumental multielement photon activation analysis whereas this cannot be accomplished e.g. by thermal neutron activation. At bremsstrahlung energies up to 40 MeV two product nuclides are suitable for lead analysis, namely ^{203}Pb (which has been used the most frequently) and $^{204\text{m}}\text{Pb}$. At bremsstrahlung energies of not less than 25 MeV, both are produced with about equal activities. The gamma-ray lines of $^{204\text{m}}\text{Pb}$ are not interfered, but regarding its short half-life (66.9 m) in multi-component matrices difficulties might arise due to eventual excessive background activity. The analytical sensitivity using either product nuclide is very good and first order interference is not possible at activating bremsstrahlung energies of up to say 80 MeV. The 279 keV gamma-ray line of ^{203}Pb might be interfered by the same energy of ^{203}Hg or $^{197\text{m}}\text{Hg}$ produced by mercury, but normally this interference may be neglected. At large concentrations of barium in the sample, 276, 278 and 274 keV from $^{133\text{m}}\text{Ba}$, ^{129}Cs and ^{136}Cs , respectively, partly overlap the lead peak. Gamma-ray lines from several other activation products might also interfere, among them ^{75}Se (280 keV) produced by selenium, the same energy from ^{105}Ag , produced by silver and/or cadmium and 282 keV from ^{77}Br produced by bromine. If one or more of the named elements are present in the sample in larger concentrations, ^{203}Pb can as well be analysed by the thallium kX-ray emission using low energy photon spectrometry with about the same sensitivity

as achievable using conventional gamma spectrometry. This radiation is not seriously interfered.

Poor sensitivity for lead using instrumental photon activation analysis with a betatron was stated by Brune et al.²⁴⁰. After 140 MeV bremsstrahlung activation, Ricci⁹⁷⁴ found greater sensitivity using ^{203}Pb than by $^{204\text{m}}\text{Pb}$ by a factor of more than twenty-five. Chattopadhyay et al.^{330,883,991}, Rev.40, and many other analysts of the photon activation analysis group of the University of Toronto usually preferred $^{204\text{m}}\text{Pb}$ because of its freedom from spectral interference. However, if very small concentrations of lead had to be analysed they used ^{203}Pb , eventually after a radiochemical separation. A source of error might be the inconstant natural isotopic composition of lead (Hislop and Parker¹⁰³⁷).

The stability behaviour of lead during activation was already discussed in paragraph 6.2.4.3 (subparagraph on elements of particular biological interest at the end of the paragraph). Most lead compounds have been found relatively stable against heat and radiation during bremsstrahlung exposure. However, there are several volatile compounds of lead, in particular tetraethyl lead used as an automobile gasoline additive. This is easily volatilised during activation and hence analytical results might be erroneous. Moreover, a systematic error can also be introduced already in the sampling step, e.g. during air particulate collection on filters as has also been observed in the case of mercury (see above).

If lead is a major matrix component it creates an intense background radiation after activation and longer cooling periods might be necessary prior to measurement of other activities.

Bismuth

Bismuth can be analysed by instrumental photon activation analysis using ^{206}Bi (half-life = 6.24 d). However, the major gamma-ray lines (803 and 881 keV) frequently are subject to overlap interference by $^{106\text{m}}\text{Ag}$ (804 keV) and ^{84}Rb (881 keV). Moreover, at 30 MeV electron energy, the sensitivity is rather poor since the nuclide is produced by a $(\gamma, 3n)$ reaction which has a relatively high activation threshold (22.3 MeV) and, correspondingly, a relatively low effective activation cross section (168 MeV-mbarn, see Wyckoff¹¹⁷⁶); these data are comparable to those of the (γ, n) reaction of ^{12}C (see 6.1.4.1). Therefore, it is recommendable to use higher bremsstrahlung energies (about 40-45 MeV). No

first order interference is possible, whatsoever. Lutz and Sato¹¹¹⁸ irradiated at 50 MeV and found almost equal sensitivity for bismuth using ^{206}Bi and lead using ^{203}Pb . This is due to the low isotopic abundance of ^{204}Pb (about 1.4% compared with 100% of ^{209}Bi). Chattopadhyay³³⁰ used the 803 keV gamma-ray line; he calculated the contribution of $^{106\text{m}}\text{Ag}$ to this peak and subtracted it from the common peak integral. Chattopadhyay and Jervis⁸⁸³, Rev.40, analysed bismuth using both the corrected 803 keV line and the 881 keV peak; surprisingly they obviously did not detect any interference by ^{84}Rb . This is remarkable since rubidium usually is rather abundant in the analysed soil matrix.

Fissile elements

At this point the application of photon activation to the analysis of thorium and uranium is discussed; as far as it is known to the authors, neither other instable elements up to uranium (technetium, prometium and the elements beyond bismuth) nor the transuranium elements have been studied using photon activation as yet.

Nuclear fuel material including plutonium was analysed by bremsstrahlung-induced photofission and subsequent neutron counting (Bramblett⁶⁹, Beyster et al.¹¹⁷⁷, Franks¹¹⁷⁸). However, in this chapter, only analyses associated with photon counting are reviewed and therefore the mentioned papers are excluded from further discussion.

The analytical use of photonuclear reactions induced by high energy bremsstrahlung irradiation of thorium and uranium has not been studied very often as yet, although the analytical potential - at least for uranium - is great.

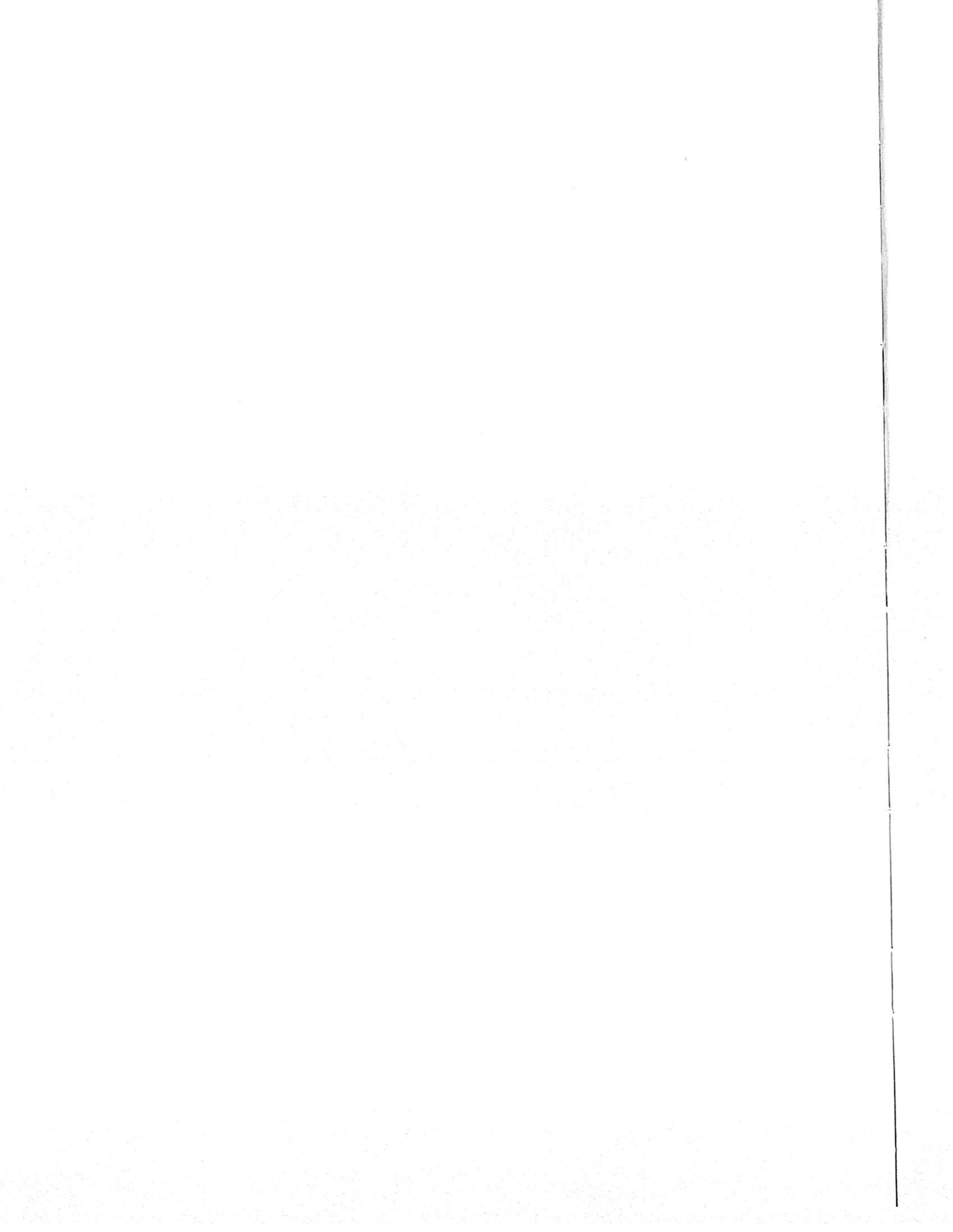
Thorium can be analysed using ^{231}Th (half-life = 25.6 h). However, this nuclide emits an unfavourable photon spectrum; the only usable lines have low energies (13, 17, 26 and 84 keV) and poor abundances. Moreover, most of them are subject to interference, mainly due to photofission products. Therefore, thorium was not included in the systematic study presented in Ch.5 of this book; it is mentioned at this point since it was analysed using photon activation by other workers.

Berthelot et al.¹⁰⁰⁵ used the 84 keV line and so did Hernandez and Belov¹¹⁷⁹ after activation with 20.5 MeV bremsstrahlung of a microtron.

Uranium can be analysed much more advantageously. The most abundant reaction with say 30 MeV bremsstrahlung, namely $^{238}\text{U}(\gamma, n)^{237}\text{U}$ allows extremely sensitive uranium determinations. The 208 keV gamma-ray line can be used for analysis evaluation. However, this line is subject to multiple interference by several nuclides (Segebade and Fusban⁶⁸⁸, Rev.49). The low energy photon emission (59.54 keV gamma-ray energy and the neptunium kX series) offer more sensitivity and is relatively free from interference. Segebade and Fusban found a detection limit of 5 ng using the 59.54 keV line measured by low energy photon spectrometry.

Berthelot et al.¹⁰⁰⁵ used the neptunium kX-ray line at 99.43 keV after activation with 40 MeV bremsstrahlung and found a detection limit of 28 ng.

Larger concentrations of fissile material in the sample can give rise to interference, by photofission, with several product nuclides used for analysis. Segebade and Fusban (see above) suggested to irradiate at 16 MeV electron energy if more than 50 micrograms per gram of total fissile material is present in the analysed sample.



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