

the nuclides of interest in this spectrum were the first three named above. After one day cooling period nuclides of interest (target nuclides) were: ^{43}K (^{44}Ca), ^{47}Ca (^{48}Ca), ^{48}Sc (^{49}Ti), ^{57}Ni (^{58}Ni), ^{67}Cu (^{68}Zn), ^{77}Br (^{79}Br), ^{122}Sb (^{123}Sb), ^{203}Pb (^{204}Pb). Apparent half-lives of unidentified gamma-ray lines were given. Another spectrum was taken after 11 days decay time, and the following nuclides were identified: ^{47}Sc (^{48}Ti ; $^{47}\text{Ca}, \beta^-$), ^{203}Pb (see above), ^7Be (^{12}C), the latter produced by the $(\gamma, \alpha n)$ reaction in the organic filter matrix. Individual elements detected during the measurements were discussed and the conditions of their determinability were evaluated. It was found that the following elements could be analysed without severe interference to be taken into account: Na, Cl, Ca, Ti, Cr, Ni, Zn, As, Br, Zr, Sb, I, Ce and Pb. Under proper conditions also the following elements were found to be possibly determinable: C, Mg, Fe, Se, Rb, Y. Possible interference by neighbouring elements was checked by irradiating and measuring several individual pure elements. The accuracy of the method was assessed by analysing a certified reference material (NBS-SRM 1571, orchard leaves), whereby an excellent agreement was found between the obtained concentrations and the certified values. The integral reproducibility was tested by replicate analysis of different sections of a dust filter. 5 to 10% standard deviation of the mean values of most elements were stated; for many elements the concentrations in one of the analysed filter sections was significantly lower than in the others, suggesting that the particulate may not have been deposited uniformly over the filter. It was estimated that the accuracy of the analytical procedure (i.e. the analysis of the filter plus particulate) was within $\pm 5\%$. The overall accuracy, taking into account also sampling parameters, was estimated around 10 to 15%. An absolute accuracy value for the analysis results could not be given; This is only possible by an interlaboratory Round Robin analysis evaluation. Later on in this paragraph, intercomparison results of air particulate analyses are reviewed and discussed. Sensitivities under the quoted conditions were found between 0.05 (for Ni) and 30 (for Ca) nanograms per cubic meter of air volume. These were compared with the detection limits of other instrumental methods, particularly instrumental neutron activation analysis. It was found that, in terms of sensitivity, photon activation analysis is superior for Ti, Ni, As, Zr and I. Moreover, in the given task several elements analysed cannot be determined with instrumental neutron activation analysis which generally is of greater intrinsic sensitivity; these are: Ca, Ti, Ni, As (the latter because of severe interference by bromine), Sr, I, Pb. Moreover, the samples did not undergo significant heating during irradiation - less than 25°C increase were reported - so that there was no concern about loss of volatile components as frequently is to be considered in activation in a nuclear reactor.

The behaviour of the filter material was satisfactory; the polystyrene matrix is quite inert against radiation exposure. Significant contaminations of chlorine and zinc were observed and - through comparison with investigations of other laboratories - severe inhomogeneities for many trace elements were stated so that frequent blank runs were necessary.

As a result, instrumental photon activation analysis was found to be especially useful in the systematic study of automobile emissions because Pb, Br, and Cl present in gasolines can be observed within routine analysis (in later investigations it was found that some other atmospheric dust components are primarily of automotive origin, e.g. Zn and Sb (see Ref's. ^{950,951}), which also can be easily determined by instrumental photon activation analysis). Finally, the advantages and drawbacks of the method compared with instrumental non-radioactive analytical methods were outlined, regarding air particulate analysis.

32) In the same year, the analysis of air particulate from an urban environment was reported by Hislop and Williams⁹⁵². This work was performed within a large-scale investigation about the applicability of instrumental photon activation analysis for trace element survey analysis. In this paper, the filter material selected was not given (it was only said that paper was used). The filter was folded into a suitable size. Since the number of replicate analysis was not mentioned, the basis of the quoted deviation values of the results is not clear. As in the paper discussed above, synthetic reference materials were used for activity comparison. 39 elements were present in a cellulose powder matrix. Samples and reference materials were irradiated in sandwich geometry at an electron energy of about 40 MeV. The exposure period was 30 minutes. After a cooling time of 5.5 hours one reference sample was measured for about 1000 seconds, immediately thereafter one filter sample was counted for about 4100 seconds. After another cooling period of 270 hours the filter sample was counted for 36.4 hours and after a decay time of 308 hours the reference material was counted again for 18.3 hours. A 50 cm³ Ge(Li) detector was used for spectra collection, and the data were processed by computer. Thirteen elements were detected and analysed in the air dust filter, namely: Na, Mg, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Sr, Sb and Pb. Several additional ones were detected in the reference material spectra, namely, Rb, Zr, Mo, Cd, Cs, Tl and Bi. No information was given about a matrix blank. Detection limits were found to range from 0.02 (for Sr) to 12 (for Ca) micrograms. These values cannot be compared with those quoted by Aras et al.⁹⁴⁹ cited above (Rev.31), since they gave detection limits in terms of concentration in air volume and not absolute masses of elements as given by Hislop and Williams.

33) Ölmez et al.⁹⁵³ reported the extension of photon activation analysis as applied by Aras et al. cited above⁹⁴⁹ (Rev.31) to the analysis of Si, Rb and Y. Except silicon (as a major component of asbestos) these elements generally are not of particular environmental concern in terms of toxicity, but the knowledge of their concentrations can be helpful in the determination of the origin of the particulate.

Sample preparation and irradiation parameters were the same as used by Aras et al.⁹⁴⁹ (Rev.31), but due to the very different half-lives of the product nuclides (2.25 m of ^{28}Al , 6.6 m of ^{29}Al , 33 days of ^{84}Rb , 18.7 days of ^{86}Rb and 108 days of ^{88}Y , respectively) samples had to be irradiated with different exposure periods. For the analysis of silicon, the samples were irradiated for 1 m. After 2 m cooling time the spectrum was taken for 10 m. The reaction producing ^{29}Al is free from any interference at the named irradiation energy. The potential interference in the production of ^{28}Al is the neutron reaction of ^{27}Al with photoneutrons; however, it was shown that this interference was negligible in the present case; the result of both reactions used for analysis were in excellent agreement. The sample batches for the analysis of rubidium and yttrium were irradiated several hours. It was found that a cooling period of three weeks or more was optimal (in terms of spectral interference) for the analysis of the mentioned elements. ^{84}Rb was superior for the analysis of rubidium; it was found that the only possible interference due to strontium in the sample could be neglected. The analysis of yttrium was interfered by different reactions of zirconium (see also paragraph 6.2.3.4 and chapter 5), but in the analysis reported here the total error did not exceed 4% relative to the yttrium content as found by experiment. It was concluded that especially silicon can be analysed by instrumental photon activation analysis very quickly in small amounts as present in air particulate filters.

34) A very interesting Round Robin program of air particulate analysis was reported by Cawse⁹⁵⁴. Air particulate was collected on cellulose air dust filters in an industrial town and in a non-urban site. Analyses of the deposits were carried out using instrumental neutron activation analysis with both thermal and fast reactor neutrons, wavelength-dispersive X-ray fluorescence spectrometry, flame atomic absorption analysis, colorimetry and instrumental photon activation analysis. Within the program 38 elements were analysed, among them the following ones by photon activation: Na, Mg, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Rb, Sr, Zr, Nb, Mo, Cd, Sn, Sb, Tl and Pb. The filters were divided into 24 disc-shaped subsamples of 7.55 cm^2 each. For photon activation these subsamples were pressed into pellets of 5 mm diameter. A sythetic mixture of simple com-

pounds of all elements detected in a preliminary qualitative filter analysis served as multi-element reference material. The components were so quantised that no gamma-ray energy in the resulting spectrum dominated and all peaks could be measured with satisfactory precision. Additionally, individual primary standards consisting of the pure elements were also included as reference materials for Cr, Mn, Fe, Ni, Zn, As, Cd and Sb since these were elements of special interest within the investigation program. Moreover, certain first order interferences could thereby be quantified. About 5 mg of the multi-element reference material were mixed with cellulose powder and pelletised similar to the filter samples. The pellets, multi-element reference samples and primary standards were irradiated simultaneously in a rotating device for 10 hours. Bremsstrahlung of about 40 MeV at a mean electron beam current of 40 microamperes was used for activation. A 2 mm thick gold target was taken as a bremsstrahlung converter. This is not a "thick" target to absorb all electrons. Therefore, unconverted electrons were caught with an air-cooled aluminium block (4 cm thick) to prevent damage of the sample. The samples were measured triply with a Ge(Li)-spectrometer after cooling periods of 6, 120 and 240 hours to ensure the detection of both short and long-lived product nuclides. The overall uncertainty of the technique was estimated ± 10 relative per cent for each element determined. First order interference was accounted for by calculating interfering contributions from neighbouring elements using the spectra of the pure single element standards. In order to assess the accuracy of the method, a certified multi-element reference material (NBS-SRM 1571, orchard leaves) was analysed separately. Concerning instrumental photon activation analysis, the result of the intercomparison study indicated that this method outstands other instrumental techniques in the analysis of Ni, Sb, and Pb. Less satisfactory accuracy and precision was observed for Fe, Cd, and Zn. It was noted that the accuracy of instrumental photon activation analysis and the neutron activation techniques used have been shown to be satisfactory for the majority of the elements.

35) Whilst integral studies of air filter deposits were carried out in the investigations cited above, elemental concentrations were analysed regarding different particle size fractions by Jervis et al.⁹⁵⁵. By a multiple-step fractionated sampling method the collected aerosols could be differentiated into several size ranges. Whatman 41 cellulose filters were used for their relative freedom of contaminants and thus low blank concentration values. For comparison purpose at the sampling site batches of soil material were taken, and also scalp hair samples from residents in the area of interest were analysed. The sampling areas were rural and urban, residential and industrial sites (adjacent

to metal refineries) and areas of enhanced automotive traffic activity. Analyses were performed using instrumental neutron activation, atomic absorption spectrometry and instrumental photon activation. The following elements were analysed: Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Zr, Sb, I, La, Sm, Hg and Pb. The instrumental photon activation analysis was carried out using the following parameters: 2 hours exposure to 35 MeV bremsstrahlung at an average electron beam current of 200 microamperes; decay time: 12 hours, counting time: 1000 seconds using high-resolution gamma spectrometry. The obtained concentration values were evaluated very extensively from various points of view, e.g.: the problem of particle behaviour on the filter material was discussed as well as correlations to meteorological data. Provenience studies were carried out and - among many other results - it was found that the elements enriched in the smaller particle fractions (less than one micron) were likely to be emitted from combustion and other high temperature sources (metal casting, incineration etc.) and the larger particles (greater than 10 microns) probably were wind-transported soil material, deposited dusts or emissions from any dust producing activities; lead and bromine were primarily due to automobile exhaust and strongly correlated, so that the bromine values can provide a good indicator for automotive exhaust quantification also in eventual close vicinity to other lead-emitting sources. Within extended epidemiological studies the concentrations of airborne pollutants were analysed in hair and blood samples of persons exposed to relatively high particulate emissions and of urban control groups. In this study, especially lead was focussed, being one of the most prominent pollutants in high abundance in special regions of anthropogenic emission source concentration, e.g. roads or smelters. Finally, concerning the analytical methods applied, a comparison of the obtained concentration values of commonly determinable elements would have been interesting but was not given since obviously the purely analytical part was of minor concern. See also Ref's. ^{975,976}.

36) The analytical methodology was more emphasised in the paper of Kato et al. ⁹⁵⁶. Millipore AA membrane filters were used for atmospheric particulate collection and then pressed into pellets of 13 mm diameter and 5 mm thickness. Unused filters were also pelletised to provide blank values. Synthetic mixtures of the elements of interest were used as reference materials. These elements were: Na, Mg, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, As, Rb, Sr, Y, Zr, Sb, I, Ce and Pb. Oxides of these elements were distributed homogeneously in a boric acid matrix. Another dozen of elements were also included in the reference material but obviously were not detected in the filter samples. A certified reference material (NBS-SRM 1633) was also analysed for interlab comparison pur-

pose and additional accuracy check for the obtained concentration data. Samples and reference materials were placed in a silica tube in a sandwich order for simultaneous irradiation. Irradiations were carried out with 30 MeV bremsstrahlung of a linear accelerator using 70 microamperes mean electron beam current. The irradiation period for the filter samples was six hours. No chemical decomposition of the filter matrix was observed. The samples were counted with a 33 cm³ Ge(Li) detector. Counting was performed multiply over a period of a month or longer. Counting periods varied from a few minutes for short-lived nuclides to about one day for extremely long-lived ones. In some questionable cases, decay function analyses were used to check for interference by other nuclides. It was found that errors due to interference mostly could be avoided by either allowing the interfering nuclide to decay to insignificant activity or by selection of another gamma-ray energy for evaluation. Detection limits were reported to range from 0.3 (for Y) 280 (for K) ng per cubic meter of air. Concerning the filter material used, contaminations were found to be satisfactorily low in the most cases, but analysing several blank samples and comparison with other analyses of the same material performed by other laboratories yielded considerable inhomogeneities between different filter lots and also in the areal distribution of one filter. The only element present in significantly large contamination level was chlorine as also reported for other filter matrices.

37) Recently⁹⁵⁰, a large-scale investigation work on the concentration and composition of air dusts has been completed. In several locations of the Federal Republic of Germany air particulate samples were taken. Rural and urban, industrial and residential sites were included. The particulate was collected on cellulose nitrate membrane filters. This material has several advantages: (a) It has an extremely low contamination level, (b) it is fairly resistant against ionising radiation, (c) it is soluble in several organic solvents, e.g. acetone. This latter property has proven to be helpful in the sample preparation for photon activation analysis. Samples were taken every week over a year's period. Eighteen subsamples were cut out of each filter. These subsamples were then analysed by eleven laboratories using seven different analytical methods; several laboratories performed multiple determinations using different techniques so that for each filter a total of seventeen comparative analytical results lay before. The analytical methods used were: X-ray fluorescence spectrometry, atomic absorption spectrometry, instrumental neutron activation analysis, total reflection X-ray fluorescence, inductively coupled plasma emission spectroscopy, proton-induced X-ray emission and instrumental photon activation analysis. The following elements were analysed: S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Cd, Sn, Sb, Ba, Hg and Pb, among these the

following ones by photon activation analysis: Ca, Cr, Mn, Co, Ni, Zn, As, Br, Cd, Sn, Sb and Pb. In this analysis the internal standard technique was applied as described above in paragraph 6.2.2. The samples were impregnated with an aliquot of a calibrated scandium solution. Then they were dried and dissolved in acetone, stirred at room temperature to dryness, powdered and pressed into pellets. Fly ash of a waste incineration facility was used as a reference material, but also a mixture of oxides or other convenient compounds of the elements of interest, distributed evenly in cellulose powder to provide a similar matrix as the sample pellets. The pellets had 13 mm diameter and only less than 1 mm thickness; this was done for interference-free low energy photon spectroscopy performed after bremsstrahlung irradiation besides conventional gamma spectrometry; using a thin pellet with a low average atomic number matrix one avoids - in certain limits - miscalculations due to matrix absorption of soft photon energies measured (see 6.2.3.4). 30 MeV bremsstrahlung of an electron linear accelerator was used for activation. The exposure time was four to five hours. After one day cooling period gamma spectra were measured for 24 hours and low energy photon spectra for 12 to 24 hours. Five coaxial detectors and three low energy photon diodes were used simultaneously so that considerably large sample numbers could be analysed within reasonably short time. Since many samples had to be analysed, special interference calculation routines had to be run during data evaluation by computer; it was not possible to avoid every interference by allowing the interfering nuclide to decay to zero activity level or perform multiple measurements after several decay periods as done in most of the above discussed works. Keeping the time schedule of the entire project, there was time enough for one activation and one measuring cycle each for both spectroscopy systems. After complete evaluation of all collected data, very interesting conclusions could be drawn concerning regional, seasonal, meteorological and other influence parameters. The comparison of the different techniques used generally yielded satisfactory agreement between the photon activation analysis data and the consensus mean values of all methods; in many cases, the photon activation analysis chromium values tended to be high in comparison to the average. The precision of the photon activation analysis values of cobalt and cadmium suffered from comparatively poor precision due to the extremely low amounts of these elements present in the samples and, in the case of cobalt, comparatively unfavourable nuclear data of their photon reactions used for analysis; for the analysis of these elements, if present in nanogram amounts, instrumental photon activation analysis probably would not be the method of choice.

In the following table, the applications of photon activation analysis to the

analysis of air particulate filters are summarised including the most relevant literature data accessible to the authors. Other publications on air particulate photon activation analysis can be found in Ref's. 178,957-972.

Tab.6.2-3: Application of instrumental photon activation analysis to the investigation of atmospheric particulate

Bremsstr. energy, MeV (I_e , μ A)	Filter material	Elements determined	Ref.	Rev. no.
35 (50)	Polystyrene	Na, Cl, Ca, Ti, Cr, Ni, Zn, As, Br, Zr, Sb, I, Ce, Pb (Fe, Se, Rb, Y) ¹	949	31
35-45 (5-10)	Paper ²	Mg, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Sr, Zr, Sb, Pb	952	32
35 (225)	Whatman 41 paper	Pb	975,976	
30 (70)	Millipore AA membrane filter	Na, Mg, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, As, Rb, Sr, Y, Zr, Sb, I, Ce, Pb	956	36
40-44 (40)	Whatman 41 paper	Na, Mg, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Rb, Sr, Zr, Nb, Mo, Cd, Sn, Sb, Tl, Pb	954	34
35 (200)	Whatman 41 paper	Ni, Zr, Pb	955	35
30 (150)	Cellulose nitrate	Ca, Cr, Mn, Co, Ni, Zn, As, Br, Cd, Sn, Sb, Pb (Na, Mg, Si, Cl, K, Ti, V, Fe, Se, Rb, Sr, Y, Zr, Nb, Mo, I, Cs, Ba, Ce, Nd, Sm, Tl, U) ¹	950	37
35-40 (50)	polystyrene	Si, Rb, Y	953	33

¹Elements detected and recognised as determinable, but not analysed in the cited work; ²Material not specified in the cited paper

- The analysis of soil samples

The problems which arise during instrumental photon activation analysis of soil material are somewhat different compared with those in air dust analysis discussed above. On the one hand, usually much more sample material is available for analysis, mostly quasi-unlimited amount per sample. However, frequently the components to be analysed lie before in considerably low concentrations in a matrix which sometimes contains elements as minor or major constituents which produce an intense interfering background activity after bremsstrahlung exposure, e.g. Mg, Ca or Ti. Moreover, the pretreatment of soil samples prior to activation requires considerable effort, whereas dust filters usually can be analysed readily without much pretreatment. Therefore, in photon activation analysis, the overall sensitivity of trace component determination is about equal in both application cases. One advantage of photon activation analysis as compared to other activation analysis techniques is particularly inherent in soil analysis, namely the comparatively low background activity due to sodium which normally is one of the major soil components. However, according to the literature reviewed by the authors, surprisingly photon activation was applied to soil analysis in comparatively few cases only as yet. Frequently, soil analyses are associated with air dust analyses, e.g. in large area dustfall investigations. This is discussed further in the following review of the most relevant literature about photon activation analysis of soils.

38) One of the first papers about photon activation analysis of soil samples was published by Lutz⁹⁷⁷. It deals with the analysis of lead in various matrices, as a complement to neutron activation with help of which lead analyses are possible but unfavourable. Samples were activated in polyethylene vials in a rotating irradiation position. Relative photon flux data were obtained by measuring the 478 keV gamma-ray line of ⁷Be produced by ¹²C($\gamma, \alpha n$) in the polyethylene matrix-inherent carbon of the irradiation vessel. Bremsstrahlung energies from 20 to 45 MeV were used for preliminary yield determinations of the most prominent lead reaction yielding ²⁰³Pb. This reaction was found most suitable for analysis (in contrast to Chattopadhyay⁹⁷⁸; see also Rev.39). Beam currents were typically about 50 microamperes. The sample transportation was conducted by a pneumatic tube system. Samples were either counted with a Ge(Li) spectrometer or - if very sensitive analyses were required - with a NaI crystal counter after radiochemical separation. Detection limits of about 500 and 10 ng of Pb were stated for instrumental and radiochemical analysis, respectively. There was no evidence of severe interference under these conditions, neither by competing reactions of neighbouring elements nor by overlap of gamma-ray lines

from other nuclides. The various sources of error in the present case were discussed in more detail by Chattopadhyay⁸⁸³. The accuracy of the obtained data was checked by analysis of the samples with other methods, and the results were found to be in satisfactory agreement.

39) Another early report on instrumental photon activation analysis of soil material was given by Chattopadhyay et al.⁹⁷⁹. Zn, As, Cd and Hg were determined by radiochemical neutron activation analysis and Pb by photon activation analysis using high resolution gamma spectrometry. The soil samples, together with a lead standard (which was not furtherly specified) were placed in glass vials and irradiated for one hour with 35 MeV bremsstrahlung of an electron linear accelerator. The electron beam output power was 8 kW. A 40 cm³ Ge(Li)-detector was used for gamma spectrometry. Both the activities of ^{204m}Pb and ²⁰³Pb from (γ, γ') or ($\gamma, 2n$) and (γ, n) reactions, respectively, were used for analysis evaluation in this case; for routine analysis of larger sample numbers, ²⁰³Pb was recommended due to its more convenient half-life. Under the above named conditions, an overall sensitivity of 0.1 micrograms of lead was stated.

40) The paper discussed in the following review is one of the most relevant publications in instrumental photon activation analysis of soil material and also of multi-element photon activation analysis in general (Chattopadhyay and Jervis⁸⁸³). Virtually all aspects of the technique are evaluated and discussed in a clear and comprehensive manner. Emphasis is placed upon the methodological part of the work to outline the suitability of instrumental photon activation analysis to multi-element determinations in soils and other matrices. It is interesting to note that the above complaint about obvious poor interest of analysts in photon activation analysis of soils is already expressed in this early paper. Obviously, over the period of about a decade between the publication of Chattopadhyay et al. and of this book the interest in photon activation analysis of soils did not rise, regarding the photon activation literature. It is clearly shown that this lack of interest is not justified and particularly for soil material analysis, photon activation offers several advantages compared with its sister method, namely instrumental neutron activation analysis. Consequently, the paper of Chattopadhyay et al. is discussed in somewhat more detail than the other ones about soil analysis reviewed here.

Soil samples were taken from the close vicinity of particular plants which were also analysed to detect eventual correlations between the concerning trace component contents. A soil pit was then dug at the plant sampling site and soil batches were taken from the surface down to a depth of 45 cm in steps of 7.5

cm. The material was air-dried, presumably to avoid loss of any volatile components of interest. One-gram subsample batches were sealed in polyethylene bags which were then placed in cylindrical polyethylene irradiation containers. A synthetic standard was used as multi-element reference material. A synthetic soil matrix was formed using high purity starch powder as a main component. This was done because about 90% of the soil material considered consisted of organic compounds. Thereby similar integral gamma spectrum shapes were provided for both analysis samples and reference materials which is of some importance for the accuracy of the final results (see above paragraph 6.2.3.4). The trace elements to be analysed were added in microgram amounts to give trace component concentrations in the microgram per gram region as was expected to be determined in the analysed samples. The following elements were analysed: Na, Mg, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Sr, Zr, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Hg, Tl, Pb and Bi. These elements were added to the reference matrix and the mixture was rotated in a mixer. The homogeneity and the accuracy of the composition was examined by comparison with certified reference materials and also by analysis with alternative methods. The irradiations were carried out with an electron linear accelerator using 15 to 44 MeV bremsstrahlung in several steps for each sample to avoid first order interference by preselection of the exciting energy with regard to the different reaction thresholds. The electron beam current was 80 to 225 microamperes, depending upon the electron energy. In order to avoid interference by thermal neutron reactions samples, reference materials and empty polyethylene bags (to obtain a blank value) were wrapped in cadmium foils. The photon and thermal neutron fluxes were monitored with copper and cobalt wires, respectively. The samples were irradiated in a slowly rotating Lazy Susan at 1cm distance from the rear face of the tungsten bremsstrahlung converter. To avoid excessive heating-up of the samples they were cooled by an air jet. Typical exposure time was one hour. The samples were measured without rupturing the polyethylene bags, again to avoid any losses of material eventually volatilised by radiolysis during irradiation. After a cooling period of about one hour measurements were carried out using a 60 cm³ and a 40 cm³ Ge(Li) detector. At an early stage of this work, frequent interference of different types had been recognised. Due to the lack of reliable experimental photonuclear data at that time, thirty selected elements had been irradiated at twelve different bremsstrahlung energies ranging from 8 to 46 MeV to assess interference yields and provide an experimental data collection with help of which some preliminary work in multi-element instrumental photon activation analysis could be performed, e.g. peak assignment, sensitivity estimation etc.. Several types of interference were discussed in detail, namely the partial or complete overlap of gamma-ray lines by emissions of other nuclides, the compet-

ing reactions and the masking of softer radiation signals by excessive annihilation radiation almost always dominant in the gamma spectra of photon-activated samples. Also interference due to thermal neutron reactions are mentioned but found negligible in the case of sample shielding by cadmium during irradiation as mentioned above. The interference by secondary decay was not considered. The first two types of interference were handled as described above in paragraph 6.2.3.4. The masking of radiation softer than 511 keV is due to the high Compton background which might degrade the peak-to-background ratio; in unfavourable cases the peak to be analysed renders insignificant. In the described case this interference was particularly disturbing since the major source of annihilation radiation was ^{11}C produced in the organic matrix component which made - as mentioned above - 80 to 90% of the total sample. Hence, if product nuclides with gamma energies less than 511 keV and say hours of half-lives were to be measured (e.g. ^{129}Te with 69 minutes half-life and 459 keV gamma energy) the electron energy of the accelerator was adjusted below 20 MeV and thereby the threshold energy of the carbon reaction but well above the giant resonance maximum of the analytical reaction. To ascertain the accuracy of the concentration data of the synthetic multi-element reference material used, it was analysed by methods other than photon activation analysis and most values were found in excellent agreement for each technique. Another accuracy check was performed analysing several certified or candidate multi-element reference materials. Also here, good agreement was stated with certified concentrations or recommended orientation values. Potential sources of error were discussed, such as bremsstrahlung flux gradients, uncontrolled shift of the electron beam energy and others. A total error of 7 to 8% (unfortunately, this number was not specified further) was claimed and proved by the above mentioned intercomparison check. Detection limits between 10 (for Sr) and a 1000 (for Sn) nanogramms were reported. It was concluded that the accuracy of the obtained data are comparable to that of other sensitive instrumental methods. However, careful selection of the bremsstrahlung energy is essential.

41) In the framework of a large-scale investigation about the fate of toxic elements within an agricultural ecosystem (Chattopadhyay⁹⁷⁸) an instrumental multi-element photon activation analysis procedure was developed. Soil depth profiles for Na, Mg, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Sr, Zr, Mo, Ag, Cd, In, Zn, Sb, Ti, Cs, Ba, Hg, Tl, Pb and Bi were obtained. Also the uptake of these elements in some crops, depending upon its species and the element concentration level present in the soil was traced. Analyses of hair samples of residents of the investigated area were also presented. lead and cadmium, known as two of the most harmful environmental pollutants, were specially

discussed. As an accuracy check, also other analysis techniques were applied in comparison, namely instrumental neutron activation analysis and atomic absorption spectroscopy, and the concentration data were found in good agreement. Bremsstrahlung irradiations were carried out using different electron energies as already reported in the paper reviewed previously. Measurements were performed using several high resolution spectrometers with different physical parameters. The various potential sources of error as spectral interference, irradiation geometry or energy inconstancies etc. were thoroughly evaluated. It was found that lead is most favourably analysed using 30 MeV bremsstrahlung activation and measurement of the ^{204}mPb spectrum, produced by $^{204}\text{Pb}(\gamma, \gamma')$ and $^{206}\text{Pb}(\gamma, 2n)$ reactions, whereas cadmium should be determined using 15 MeV bremsstrahlung and spectroscopy of ^{111}mCd produced through $^{111}\text{Cd}(\gamma, \gamma')$ and $^{112}\text{Cd}(\gamma, n)$. The only disadvantage of these product nuclides are their relatively short half-lives (67 and 49 minutes, respectively).

42) Again by the Toronto group, the lead distribution in soils adjacent to two lead refineries was analysed using instrumental photon activation analysis (Roberts et al.⁹⁷⁵). This paper was already quoted in the air pollution context in the preceding paragraph (Jervis et al.⁹⁵⁵, Rev.35).

43) In 1976, Williams and Hislop⁹⁷⁹ presented a paper at the 1976 Activation Analysis Conference in Munich, which dealt with the analysis of iodine in soils and other materials by photon activation. Iodine, playing an important role in the physiology of plants and animals, can hardly be analysed in soils using neutron activation or other instrumental methods (excessive ^{24}Na background activity, lack of sensitivity etc.). By photon activation analysis, however, it can be determined conveniently with appreciable sensitivity; the product nuclide has a long half-life (13 days), whereas the (n, γ) -product of thermal neutron activation (^{128}I) has only 25 minutes half-life. The gamma-rays of ^{126}I can be easily measured by standard gamma spectrometry. 250 to 400 mg of soil material were irradiated with 40 to 44 MeV bremsstrahlung at 40 microamperes mean electron beam current for 6 to 10 hours. Measurements were made with a 40 cm^3 Ge(Li) detector. Replicate measurements were carried out to confirm the half-lives of both gamma-ray peaks (388 and 666 keV) and to check for eventual spectral interference. Various sources of error were investigated, namely:

- chemical decomposition and volatilisation of iodine components during irradiation

- thermal instability of the present iodine compounds
- interference by competing nuclear reactions
- spectral interference by gamma-ray overlap from activities other than ^{126}I

The obtained concentration data were in satisfactory agreement with those of colorimetric analyses performed comparatively. As a result of the error source assessment it was found that errors due to volatilisation during activation could be neglected. During heating experiments the total iodine in soils showed and appreciably good thermal stability so that the samples did not have to be cooled during long-time bremsstrahlung exposures. No significant first order interference could be detected since the only thinkable sources of competing reactions (Xe, Sb, Te) either were present in negligible concentrations or their nuclear reactions giving rise to ^{126}I have extremely low effective cross sections.

44) Concentration profiles were analysed by instrumental photon activation analysis more recently by Fusban et al.⁹⁸² and by Segebade et al.⁹⁸³. These papers are discussed jointly since their methodological parts are quite similar (both works were carried out in the authors' laboratory).

Soil samples of a sewage farm were analysed using different methods. 43 elements were determined, among them the following ones by instrumental photon activation analysis: Na, Mg, Si, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, Ce, Nd, Sm, Hg, Tl, Pb and U. Samples were taken from bore cores following both a course scale (15 meters total length, samples taken at visible layer changes, roughly one each meter) and a fine scale (1.5 meter total length, samples taken in distances of about 6 cm). Bore cores were also taken from adjacent virgin soils and samples of according depth levels were analysed to obtain comparative concentration values for both soil qualities. The dried samples, (about ten grams each) were ground in a ball mill and one-gram batches of each were taken and impregnated with a standard scandium solution to obtain an additive internal flux monitor. Subsamples of about 200 mg each were taken and irradiated. Fly ash of a waste incineration facility was used as a multi-element reference material (this reference material is described further in the paragraph on reference materials, 6.2.4.7, and was also described by Schmitt et al.⁹⁸⁴⁻⁹⁸⁶). 30 MeV bremsstrahlung at an average electron beam current of 150 microamperes was used for activation. Different irradiation periods were used to enable the

analysis of product nuclides with short half-lives (several minutes, e.g. ^{28}Al , ^{29}Al , ^{38}K), medium (several hours, e.g. ^{56}Mn , $^{87\text{m}}\text{Sr}$) and long ones. In this case, the scandium monitor is suitable for every irradiation period used (see above, paragraph 6.2.2). After irradiation, samples were mixed with cellulose powder (which served as a binder material) and pressed to pellets of 20 mm diameter and less than 1mm thickness. Measurements were conducted with both a coaxial Ge(Li) detector and a planar intrinsic germanium diode. Spectra were stored in a multichannel pulse-height analyser, using 2048 channels for each individual spectrum. Spectra were processed by standard computer programs. It was shown that Na, Mg, Si, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Ga, Ge, As, Br, Rb, Sr, Y, Zr, Nb, Ag, Cd, Sb and Cs are suitably determinable using conventional gamma-ray spectrometry whereas Zn, Se, Mo, Sn, I, Ba, Ce, Nd, Sm, Hg, Tl, Pb and U are analysed more advantageously by low energy photon spectroscopy. Detection limits were found to range between 10 ng and 20 mg. As a result of the comparison of both soil qualities investigated, it was found that the adsorption of pollutants, especially the heavy metals, primarily occurs in the upper few centimeter soil layers. This is particularly true if this layer contains a significantly high percentage of organic material. The mentioned heavy metal distribution had also been observed by other investigators (Chattopadhyay⁹⁷⁸, see Rev.41, Scheffer and Ulrich⁹⁸⁷, Schnitzer and Hoffman⁹⁸⁸, Mitchell⁹⁸⁹).

In the following table, the most relevant literature data of instrumental photon activation analysis of soils are summarised; more about soil analysis by photon activation can be found in Ref's. 60,958,979,990-997.

Tab.6.2-4: Application of instrumental photon activation analysis to the investigation of soil material

Bremsstr. energy, MeV ($I_e, \mu\text{A}$)	Detector	Elements determined	Ref.	Rev. no.
20-50 (50)	NaI(Tl); Ge(Li)	Pb	977, 1121	38
35 (220)	Ge(Li)	Pb	979	
35 (225)	NaI(Tl); Ge(Li)	Pb	991, 1182, 1183	
not given; probably 15-20	Ge(Li)	Cd	990	

Tab. 6.2-4, continued

Bremsstr.				
energy, MeV				
(I_e , μ A)	Detector	Elements determined	Ref.	Rev. no.
15-44 (80-225)	Ge(Li)	Na, Mg, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Sr, Zr, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Hg, Tl, Pb, Bi	883	40
35 (225)	Ge(Li)	Pb	975	42
40-44 (50)	Ge(Li)	I	979	43
30 (150)	Ge(Li); planar Ge	Na, Mg, Al, Si, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, I, Cs, Ba, Ce, Sm, Hg, Tl, Pb, U	982	44
16-30 (150)	Ge(Li); planar Ge	U	688	49

- Miscellaneous applications in environmental analysis

In the following paragraph, analyses of environmental materials are discussed which are rarely analysed by photon activation due to different reasons, most likely because of experimental difficulties. These works are not reviewed in a chronological order as done in the other subparagraphs; it was rather tried to keep a certain logical order considering the scientific background of the analysed samples or the special demands of the analytical procedure.

45) The in-stack particulate of a coal-fired power station was analysed by Small et al.⁹⁷⁰. The distribution of toxic trace elements over the particle size was assessed. Particulate material was sampled from a cascade impactor. Correlating coal and fly ash batches were also taken simultaneously. Sets of these samples were taken on several different days so as to find eventual cor-

relations comparing the trace element concentrations. The sampling was performed during normal operation of the station to obtain representative analysis material. Polycarbonate filters were found suitable for particle collection, regarding filtering capacity, heat resistance and blank levels. The elements studied were analysed with thermal neutron activation and instrumental photon activation analysis. The powdered coal and fly ash samples were encapsulated in polyethylene vials and each impactor stage filter was folded and individually packed in polyethylene bags. Photon irradiations were conducted with an electron linear accelerator using 35 MeV electron energy at 50 microamperes mean electron beam current. Typical exposure periods were several hours. Gamma spectrometry was carried out with a 65 cm³ Ge(Li) detector. Several spectra were taken after different cooling periods. A synthetic multi-element reference material was prepared pipetting aliquots of calibrated solutions of the elements to be determined onto filter paper. The quality of the results was checked by analysis of certified multi-element reference materials. The obtained concentration data were found in good agreement with the certified values. The distributions of Ma, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Sb, Ba, La, Ce, Sn, Eu, Yb, Lu, Hf, Ta, Hg, Pb and Th were measured, but it was not specified, which of them by photon activation analysis. With help of literature sources cited in the paper these were probably the following elements: Na, Ca, Ti, Cr, Ni, Zn, As, Br, Rb, Zr, Sb, Ce and Pb.

As a result, the enrichment behaviour of the elements in the different particle size fractions is shown and partly interpreted. It was found that the in-stack elemental distribution obviously does not agree or correlate with that of ambient urban aerosols.

46) Berthelot and Carraro⁹⁹⁹ reported the instrumental photon activation analysis of Cd and Pb in zinc ores. These elements, being the most prominent polluting components in zinc ores, have very favourable nuclear data for photon activation analysis. Samples of about 100 mg each were encapsulated in high purity aluminium cans. A synthetic reference material containing known amounts of cadmium and lead was prepared, the matrix composition was similar to that of the analysed samples. A slowly rotating Lazy Susan was used for intermittent irradiation, so as to provide a better uniformity of the bremsstrahlung radiation dose received by the analysis samples and the reference material, respectively. A pneumatic tube system was available for sample rabbit transportation. The exposure periods were a few hours using 45 MeV bremsstrahlung at 27 microamperes mean electron beam current of an electron linear accelerator. The cooling period was about 70 hours. It was essential for the accuracy of the

cadmium analysis to provide decay of more than thirty hours because of possible interference from tin and the complex decay function of ^{115}Cd via $^{115\text{m}}\text{In}$ and ^{115}In into ^{115}Sn (see above, paragraph 6.2.3.4). Measurements were carried out with a Ge(Li) spectrometer using the built-in spectrum processing routines available through microprocessor-programmed software. A computer was also used for spectra evaluation. Excellent precision was obtained and the method was found suitable for the routine analysis of larger concentrations of the named elements; the cadmium concentrations were between 0.1 and 1.2% and the lead values ranged from 1 to 10%.

Very often analysts encounter extreme experimental difficulties when analysing special elements using a method for which this element has unfavourable properties; in activation analysis these properties are: poor resistance against radiation and heat, small effective activation cross sections, unfavourable spectral data of the product nuclides, too short half-lives etc. The three papers reviewed next deal with such elements in an environmental context.

47) Campbell and Steele¹⁰⁰⁰ reported the analysis of tellurium by photon activation. 1.5 g batches of several soil and rock samples were irradiated with 30 MeV bremsstrahlung at 600 milliamperes beam current (this value was not specified further, but it is surely the peak value) for one hour. Because of spectral interference by ^{69}Ge (half-life = 39 h) the samples were counted after a cooling period of not less than three weeks. The 575 keV gamma radiation of ^{121}Te (half-life = 17 days) was measured using a Ge(Li) spectrometer. No external reference material was used but the standard addition method spiking a set of sample batches with different known amounts of a calibrated tellurium solution along with a uranium acetate solution aliquot. This was done to check for eventual interference by higher concentrations of fissile material expected in some of the samples. A reproducibility of 20% at the quoted detection limit of 360 micrograms of Te was predicted using the criteria of Currie⁷⁸⁵ and verified during experiment. A very interesting information generally not given by any author is the quotation of the analysis financial cost; The authors claim a total amount of \$4.00 per sample (note: this paper was published in 1971). The tellurium analysis by photon activation is very useful insofar as the determination by competing instrumental neutron activation analysis, although being more sensitive by several orders of magnitude, is severely hampered by interference through fission products originating from thorium and uranium possibly present in the material analysed.

48) Another element which is very well determinable by photon activation compared with other instrumental methods, is thallium. Masters and Lutz¹⁰⁰¹ reported the analysis of thallium in glass, zinc and zinc compounds. Several severe interference sources made a radiochemical separation unavoidable. Samples were irradiated with 35 MeV bremsstrahlung at 30 microamperes average electron beam current for several hours, depending upon the expected thallium amount in the sample. Measurements were carried out with NaI crystals and Ge(Li) detectors. The chemical separation procedure is not discussed here. The accuracy of the analysis was checked by comparison of concentration data of certified reference materials (NBS Glass) obtained by photon activation with the certified values; good agreement was stated for concentrations greater than 10 micrograms per gram. Discrepancies of about 20% were found in the submicrogram per gram region. Possible interferences were studied. The most prominent source of interference was the 439 keV radiation of ^{69m}Zn from zinc present in all samples. A suspected first order interference by competing reaction of lead was not detected under the quoted conditions. In the most favourable case the minimum mass detectable (after Currie⁷⁸⁵) was found to be 0.05 micrograms.

49) Another element which involves complication during activation analysis, is uranium. Segebade and Fusban⁶⁸⁸ described particular difficulties in the photon activation analysis of uranium and in multi-element instrumental photon activation analysis of many elements in the presence of larger amounts of uranium or any other fissile material. Under high energy bremsstrahlung bombardment, photofission occurs in uranium (and in thorium as well) giving rise to extremely complex gamma-ray spectra originating from fission products. Conversely, the 208 keV gamma energy of the primary photoneutron reaction product of uranium (²³⁷U, half-life = 6.75 days) is interfered by adjacent energies emitted by photon reaction products of other elements possibly present in the sample. The different experimental measures to overcome these complications, e.g. use of lower (15 to 16 MeV) bremsstrahlung energy, application of low energy photon spectroscopy etc., were evaluated and discussed in this paper. Due to the convenient nuclear data (large effective activation cross section, suitable half-life and photon energies of the product nuclide) very good sensitivities were achieved, namely, 5 ng in multi-element photon activation analysis under the most favourable conditions.

The next works described are concerned with the analysis of reference materials used for environmental multi-element analysis. As was mentioned in paragraph 6.2.2 it is useful to provide similar gross matrix composition for both analytical sample and reference material. Therefore, a variety of reference materials

intended for use in environmental analysis, have been developed. Recently, also photon activation analysis became engaged in the certification analysis procedure. At this point, only a few examples are presented, more about the analysis of reference materials, particularly of multi-element material, can be found in paragraph 6.2.4.7 below.

50) Schmitt et al.⁹⁸⁴⁻⁹⁸⁶ reported the use of fly ash of a combined urban and industrial waste incineration facility as a multi-element reference material which can be used for the instrumental analysis of a large variety of materials, particularly environmental material. A preliminary batch of about 20 kg was prepared (ground and homogenised) for multiple analysis of all elements of interest. Different activation methods were used to analyse a total of 54 elements, among these the following by photon activation analysis, mostly purely instrumentally, but in the case of carbon and fluorine with radiochemical separation: C, F, Na, Mg, Si, P, Cl, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Lu, Hg, Tl, Pb and U. Mean values were calculated on the grounds of 3 to 50 single determinations per element. In the most cases agreements between the results obtained by the different methods used were good, but sometimes discrepancies originating from various interferences were found. These interferences were mostly due to elevated concentrations of certain elements in the material, e.g. tin which emits a very complex gamma-ray spectrum after photon activation and is present at 0.32% in the fly ash. Several toxic components were found to be highly concentrated in the material, e.g. (in micrograms per gram): F: 1500, Cr: 379, Ni: 126, Cu: 770, Zn: 12400, As: 93, Cd: 250, Sn: 3200, Tl: 4.3 and Pb: 6350.

51) A Round Robin analysis program of the NBS multi-element reference materials "coal" (NBS-SRM 1632) and "coal fly ash" (NBS-SRM 1633) was reported by Öndov et al.^{1002,1003}. Predominantly neutron activation analysis was used by the four participating laboratories, but also instrumental photon activation analysis and counting of the natural radioactivity due to K, Th and U present in the samples. Ca, Ti, As and Rb were analysed in the coal sample using photon activation, and Si, Ca, Ti, Ni, Zn, As, Rb, Y, Zr, Sb, I and Pb in the fly ash. Batches of about one gram were irradiated for a few hours with 35 MeV bremsstrahlung. Nickel monitors were used for photon flux normalisation. Larger discrepancies of the photon activation data to the mean consensus values were found in the coal analysis for Ti and As, and in the analysis of the fly ash for Ca. An overall disagreement was stated for antimony which was suspected to be distributed inhomogeneously in the materials. The comparison of the obtained

consensus values yielded certain disagreements with the data of the issuer of the material (National Bureau of Standards), namely in the concentrations of the elements Ni, Zn, As and Se in coal sample and V in the fly ash. The possible reasons of these discrepancies were discussed and in some cases could not be definitely explained. The analysis of coal fly ash by photon activation was also reported by Gladney et al.¹⁰⁰⁴.

52) The analysis of river sediments, including the NBS reference sediment sample (NBS-SRM 1645), was reported by Berthelot et al.¹⁰⁰⁵. The experimental procedure was the same as used in the work of Berthelot and Carraro reviewed above⁹⁹⁹, Rev.46. Na, Mg, Ca, Ti, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, Ce, Ta, W, Hg, Tl, Pb, Bi, Th and U were analysed. Detection limits were found between about 0.02 and 6 micrograms. Comparison with the certified NBS-values yielded good agreement with the following exceptions: Tl (1.9 micrograms per gram; NBS: 1.44) and U (1.4 micrograms per gram; NBS: 1.11). Some elements were analysed in this work which usually are not attempted to be determined by instrumental photon activation analysis, namely Cu, Ta, W and Th. For two of these, the quality of their results could be confirmed by agreement with the certified data, namely for Cu and Th, whereas no comparative values were available for Ta and W.

In the following sub-paragraph, analyses of water and water-related materials are presented. On the one hand, the instrumental photon activation analysis of water or any other liquid gives rise to very special experimental complication, particularly during bremsstrahlung exposure as was discussed above in 6.2.3.1. On the other hand, liquids can be analysed advantageously by photon activation as compared with neutron activation analysis. However, the small number of publications about photon activation analysis of liquids reflects a lack of interest in this application which is not justified, regarding the special features of the method outlined in the introductory part of this chapter. In the activation analysis of liquids, especially water samples, the nature of the sample suggests a chemical treatment before or after irradiation, be it a complete or a group separation of the components to be determined, or a pre- or post-concentration. In the reports on water analyses by photon activation accessible to the authors this was mostly done.

53) Wilkniss⁸⁶⁵ described a method with help of which all stable halogens could be analysed in a single water sample using activation with 22 MeV bremsstrahlung of an electron linear accelerator. A synthetic aqueous solution of the halogens present as sodium halides was prepared and spiked with additional salts

so as to obtain a sample whose composition is similar to that of rainwater. Batches of one milliliter each were freeze-dried. Sodium sulphate had been added to create a residual matrix of several milligrams. Thereby losses by atom recoil during activation were avoided which might occur if minute amounts of material are irradiated (Schmitt and Sharp⁷²⁰, Seitz and Hoehler⁷²¹). Samples were then irradiated with 22 MeV bremsstrahlung at 50 microamperes mean electron beam current. A pneumatic tube system was used for sample rabbit (polyethylene or aluminium) transfer, and the rabbits were rotated by air-jet during activation. In order to find the optimum counting system for each nuclide to be analysed, five different spectrometers were used for activity measurement after chemical separation. The counting of 511 keV annihilation quanta using a fast coincidence unit was found most effective for the analysis of ^{18}F (see also 6.1). This spectrometer was also used for chlorine counting. The bromine activity was counted with a thin CsI crystal since the product nuclide selected for analysis evaluation ($^{80\text{m}}\text{Br}$) does emit very soft photon radiation only. β and X-ray counting (by CsI crystal) was used for iodine determination. Interference by competing reactions was investigated. It was found that the interfering activity yields due to (γ, an) reactions were either zero or negligible when 20 MeV bremsstrahlung was used. Interference due to (γ, np) reactions of noble gases could be neglected because of their low concentrations in the samples or their easy removability, respectively. This applies also to eventual interfering reactions induced by photoneutrons. In conclusion, it was found that in some cases halogen determination by photon activation is superior to neutron activation analysis in spite of the higher intrinsic sensitivity of the latter method for Cl, Br and I. However, frequently occurring high matrix activities after neutron activation (e.g. ^{24}Na) favour the application of photon activation particularly in the case of marine water analysis.

54) The special advantages of multielement analyses of water by photon activation were pointed out by Segebade et al.⁶⁰. In this work, no chemical treatment prior to or after bremsstrahlung exposure was required. From 100 to 3000 ml of water were irradiated with 30 MeV bremsstrahlung (mean electron beam current = 150 microamperes) using a glass cylinder as irradiation vessel. This cylinder was arranged coaxially with the photon beam cone so as to provide maximum exploitation of the bremsstrahlung beam. An aliquot of a calibrated scandium solution was added to serve as an internal standard. This was necessary since using large sample volumes either a simultaneous irradiation of the analysis sample and a reference liquid was not possible or, if volumes were small enough to enable simultaneous activation, inconsistencies in the received radiation doses had to be normalised. The liquid was then transferred into a counting vessel

which surrounded the semiconductor detector housing (coaxial gamma or planar low energy photon diode) to provide an optimal counting geometry. In a river water sample of 600 ml the following elements were detected and could be determined with sensitivities between 0.1 and 20 micrograms per liter: Na, Mg, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, Ce, Nd, Hg, Tl, Pb and U.

The papers discussed next describe analyses of matter closely related to water, namely suspended particles and sewage sludges. Basically the analysis procedures are not very different from those used in the analysis of river sediments discussed above. However, the compositions of the samples to be analysed are partly significantly different and so are the problems faced by the analyst.

55) Chattopadhyay and Ellis¹⁰⁰⁶ described the analysis of suspended particles in estuarine waters by instrumental neutron and photon activation analysis. The primary difference between this problem and that in other environmental multi-element analyses is the extremely small sample mass; usually total particulate masses range between less than 1 to 10 mg. A membrane filter with a pore diameter of 0.4 micrometers were used to collect the suspended matter from the estuary. These filters were pressed to pellets of 5 mm diameter. Elemental standards, dissolved and pipetted onto a blank filter were used as multielement reference materials. Certified reference materials were also analysed to obtain accuracy data. Irradiations were conducted with 35 MeV bremsstrahlung of an electron linear accelerator at 110 microamperes average electron beam current. Samples and reference materials were irradiated in a rotating sample holder assembly. Each sample was irradiated twice; first, for one minute's period to measure short-lived (minutes half-lives, e.g. ²⁹Al from Si) product activities and another period of several hours to analyse all other product nuclides. Measurements were carried out with a 65 cm³ Ge(Li)-detector. In total, 24 elements were analysed, among them Si, Ni, Y, Zr, Sb, Tl, Pb and Bi by instrumental photon activation analysis. Investigating the homogeneity of the filter material it was found that the blank levels were much lower than that in the particulate matter and thus could be neglected, except to cobalt. Accuracy (obtained by analysis of certified reference materials) and precision (obtained by replicate determinations) studies yielded a total uncertainty of $\pm 3\%$ to $\pm 15\%$, depending upon the concentration level and the sensitivity of determination for the individual element. The method was found to meet the sensitivity requirements of the given analysis task, even at extremely small sample masses.

56) Sewage sludges and soil additives were analysed by Chattopadhyay¹⁰⁰⁷ using instrumental photon activation analysis at various bremsstrahlung energies. Sewage sludge-based fertilisers frequently contain significant concentrations of toxic heavy metals and therefore, this material is of environmental relevance. Sludge samples from different sites were taken, air-dried and homogenised. Samples of different commercially available soil additives were also prepared. The irradiations and measurements were conducted as described in the paper of Chattopadhyay and Jervis reviewed above⁸⁸³, Rev.40. A synthetic sludge matrix-based standard was used as a reference material. The following elements were analysed: Na, Mg, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Ce, Hg, Tl, Pb and Bi. Each element was discussed separately. The analytically most suitable photonuclear reactions were given, together with valuable information, e.g. possible interferences. It was found that all sludges examined contained high levels of toxic metals as Cr, Ni, As, Cd and others. Significant differences were found between the trace composition of materials taken from different sites; concentrations of Cd, Pb, Bi and other pollutants were concentrated higher by at least one order of magnitude in sludges from industrialised areas than in those from non-industrialised sites. According properties were found in soil additives; sludge-based fertilisers contained significantly higher concentrations of the named components than other ones. In table 6.2-5 a summary of the miscellaneous environmental applications of photon activation analysis is presented.

6.2.4.3 Analysis of biological material

Frequently, as mentioned in the preceding paragraph, analyses of biological material are performed within an environmental context. However, due to the special nature of the matrix, these analyses are discussed separately in this paragraph. Consequently, many publications are discussed in the following literature review which have already been cited above. This is the case if entire ecosystems were investigated using photon activation analysis.

Regarding biological material, components are of particular interest - and hence their analysis is demanded - which have been known as "toxic". However, even with an enormous amount of scientific research results in the background as is the case nowadays, knowledge about the effects of elements and chemical compounds upon organic life is limited due to the complex nature of interaction between a particular element (or compound) and the organism which it is part of.

Tab.6.2-5: Miscellaneous environmental application of instrumental photon activation analysis

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
in-stack particulate ¹	35 (50)	Na, Ca, Ti, Cr, Ni, Zn, As, Br, Rb, Zr, Sb, Ce, Pb	970	45
Zinc ore	45 (27)	Cd, Pb	999	46
Soil; rock mat.	30 (not given)	Te	1000	47
Zinc, zinc compounds, glass	35 (30)	Tl	1001	48
various mater.	15-30 (150)	U	688	49
Fly ash ²	30 (150)	C ³ , F ³ , Na, Mg, Al ⁴ , Si, P ³ , Cl, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Lu ⁴ , Hg, Tl, Pb, U	984,985, 986	50
Coal, coal fly ash	35 (not given)	Si, Ca, Ni, Ti, Zn, As, Rb, Y, Zr, Sb, I, Pb	1002	51
River sediment	45 (27)	Na, Mg, Ca, Ti, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, Ce, Ta, W, Hg, Pb, Bi, Th, U	1005	52
Water ³	22 (not given)	F, Cl, Br, I	865	53
Water ³	30 (30)	Sr	1057	

Tab.6.2-5, continued

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
Water	30 (150)	Na, Mg, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, Ce, Nd, Hg, Tl, Pb, U	60	54
Estuarine suspended part.	35 (110)	Si, Ni, Y, Zr, Sb, Tl, Pb, Bi	1006	55
Sewage sludge	15-44 (80-225)	Na, Mg, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Ce, Hg, Tl, Pb, Bi	1007	56
Suspended part.	30 (150)	Zn, Sr, Zr, Ba, Pb	154	
Lake sediment	15-44 (80-225)	Sc, Ti, V, Cr, Zn, As, Se, Zr, Mo, Cd, Sb, Te, Hg, Pb, Bi	994	
Water	35 (200)	Na, Mg, Cl, K, Ca, Sc, V, Mn, Fe, Co, Ni, Zn, As, Zr, Sb, Ce, Pb, Bi	1193	

¹of a coal-fired power station

²of a waste incineration facility

³radiochemically

⁴by thermal neutron activation analysis

Sometimes elements or components within a living organism are divided into three groups, namely "essential", "indifferent" and "injurious" ones¹⁰⁰⁸. Surely it is a doubtful practice to regard an element as "indifferent" a priori. The way of action of an element or component upon an organism is dependent on many parameters of which its concentration is just one, nevertheless, essential. Moreover, the picture becomes more complicated regarding synergistic effects of more than one components upon the entire organism. This problem and the toxicological significance of chemical elements are elucidated in a paper by Parizek¹⁰⁰⁹ presented at a conference on activation analysis in the Life Sciences. Parizek pointed out interrelations between trace elements in living tissue, e.g. between mercury and selenium.

Several elements are of urgent interest in biological or biomedical context. These are discussed in detail at the end of this paragraph. One of them is lead. In an account of several analytical techniques, Lisk¹⁰¹⁰ pointed out - focussing activation analysis methods - that this technique "...cannot be used to determine certain important elements such as lead...". In a comment, Kuttemperoor¹⁰¹¹ outlined the specific advantages of photon activation analysis as compared with neutron activation such as detectability of several elements of biological significance which cannot or hardly be analysed by neutron activation or the negligible background activity of most organic matrices or after photon activation, and other aspects. Moreover, the recovery of trace elements in organic and biological matrix using conventional non-instrumental techniques is troublesome in many cases, as reported in a paper about a systematic study of trace determination of elements in organic and biological matrix (Gorsuch, Ref.⁸⁹²). Instead, multielement photon activation analysis of biological material without chemical separation was first reported - according to the literature sources accessible to the authors - as early as 1967 (Cooper et al.¹⁰¹², Rev.58, Andersen et al.⁸²⁵, Rev.57, Asai¹⁰¹³, Burrows¹⁰¹⁴). All groups found instrumental photon activation analysis superior to neutron activation analysis in many cases although the latter is intrinsically more sensitive for the majority of the elements.

In the following literature review, firstly some fundamental pioneering work on photon activation analysis of biological material are discussed. Thereafter, multielement determinations in various biological matrices and finally the analyses of elements of particular biological import are reviewed.

57) The work reported by Andersen et al.⁸²⁵ was performed within a systematic study of the analytical use of photon activation. Urine, serum, hair, tooth,

tobacco, tree-bark, kale and whisky samples were analysed using different maximum bremsstrahlung energies ranging from 8 to 25 MeV. Thereby, activity was induced quasi-selectively to the components of the samples. At 8 MeV, photoexcitation of isomeric states was detected exclusively. During irradiation the beam position was monitored throughout the entire exposure period. Two machines with 17 and 45 MeV maximum electron energy, respectively, were used for experimental work. The mean electron beam currents were not explicitly given but were maximal 500 microamperes. Rotating sample positions allowed homogeneous activation of all samples. Batches of 300 to 700 mg of the biological material were irradiated for one hour at different energies. Since - with one exception - only qualitative analyses were carried out, no information about reference materials was given. Measurements were performed multiply with a standard NaI spectrometer. As a result, the following elements were detected: (urine and serum) Cl, Na, Mg; (tobacco) Na, Mg, Ca, Ni, Sr, Sn; (tree-bark) Mg, Ca, Mn, Ni, Cu, Sr, Sn; (kale) Cl, Na, Mg, Ca, Co, Ni, Sr, Sn; (hair) Cl, Na, Ni, Cu. Special attention was paid to the fluorine analysis via the reaction $^{19}\text{F}(\gamma, n)^{18}\text{F}$ since the determination of fluorine is difficult using other activation methods. The analysis of fluorine by photon activation was compared, through practical experiment, with the analysis using reactor neutrons or 14 MeV neutrons from a Cockcroft - Walton generator. Tooth samples were analysed quantitatively for fluorine and strontium, and instrumental photon activation analysis as applied for this task was found superior to the other techniques mentioned. Giving useful information and presenting a lot of experimentally obtained data this early work clearly elucidates the particular advantages of instrumental photon activation analysis as applied to the investigation of biological material.

58) In the paper of Cooper et al.¹⁰¹², a multielement analysis procedure is described using both neutron and photon activation. This is obviously the first report on the use of high-resolution gamma spectroscopy in multielement photon activation analysis of biological material. Blood and tumor tissue samples were analysed. 25 MeV bremsstrahlung of a linear accelerator was used for activation. The exposure period was several hours. Samples were rotated and cooled with dry ice to provide a uniform activation and prevent thermal destruction of the material, respectively. A Compton suppression spectrometer using a large plastic scintillator annulus surrounding the Ge(Li) crystal was applied for activity measurement. The active volume of the crystal was 35 cm³. In the range between 100 and 1500 keV (which was the region of analytical interest) the resolution (it was not specified if FWHM of any other parameter was meant) was found to be 6 to 7 keV. This value outlines the dramatic improvement of resolution capabilities of germanium photon detectors in the last fifteen years, now-

adays being less than 2 keV at about 1300 keV. In the first measurement cycle a few minutes after activation, the light elements (C,N,O) were analysed using two NaI detectors, put in coincidence to suppress background radiation of any source. The complex decay curve of the 511 keV activities from ^{11}C , ^{13}N , and ^{15}O , respectively, was measured using a 1024 channel analyser in the multi-channel scaling mode. The decay functions were then analysed by computer using a subtraction program. After a decay period of about three hours, the activity of ^{11}C had cooled down to a negligible level and the residual gamma activity was analysed with the mentioned semiconductor spectrometer. Na, Mg and I were measured in a thyroid sample, Na, Mg, Cu, Cd, Sn and Pb in a blood sample. Quantitative values were not given but a sensitivity determination yielded 0.5 micrograms minimum detectable amount for magnesium and lead. These values agreed well with theoretically calculated data using the integrated cross section data of these elements.

The applicability of instrumental photon activation analysis to biological materials using the instrumentation described in the two fundamental papers reviewed above is, of course, limited due to still unsatisfactory detector resolution capacity. Elements of urgent interest, e.g. nickel, could not be analysed reliably because of spectral interference by the neighbouring 1369 keV gamma-ray line of ^{24}Na which dominates over the nickel signal (1379 keV) in biological matrices due to the generally much higher magnesium content.

The papers on multielement photon activation analysis cited in the following subparagraph were all published at a time of more advanced maturity of semiconductor detectors so that a lot more elements could be analysed instrumentally without severe interference problems.

59) Hislop and Williams⁹⁵² reported a purely instrumental multicomponent photon activation analysis of blood, urine and bone samples. The work was carried out with the intention to assess the usability of the technique for multielement survey analyses, sensitivities for elements of interest, various kinds of interference and other important factors. The named materials were among a large variety of samples examined in this work. The liquid samples were lyophilised. The samples were packed into irradiation containers from aluminium foil. The preparation of the reference material, the irradiation, measurement and data evaluation procedure used were summarised above in the paragraph on environmental analyses (Rev.32). No trace components could be detected after short, say hours, decay periods except strontium in bone ash and urine. Activities resulting from C, Na, Mg, Cl and Ca dominated in these spectra. The other trace

elements determinable could be measured after about 4 days decay period. These were rubidium in blood and urine and zinc in bone. For these and also for Ni, As, Sr, Zr, Mo, Cd, Sb, Cs, Ce, Hg, Tl, Pb and Bi, limits of detection in biological matrix were determined.

60) In a survey article on photonuclear reactions in medicine, McNeill⁹⁴⁰, in a paragraph on photon activation analysis of organic matter, pointed out the possibility of instrumental analysis of several elements by quasi-selective activation irradiating at suitable energies. Also in-vivo analysis of calcium in humans is theoretically evaluated; the (γ, n) reaction producing ^{39}Ca is proposed. In this case, measurement has to be performed simultaneously with activation because of the short (less than one second) half-life of ^{39}Ca . Also, several interference sources to be taken into account were discussed.

61) The possibility of in-vivo photon activation analysis was also discussed by Kairento^{246, 247} in an extract paper of her PhD thesis. A betatron was used for both in-vitro analyses of blood, liver, lung, heart and thyroid tissue samples and for in-vivo studies of concentration changes of several tissue components during radiotherapy treatment of cancer patients. For both kinds of analyses 33 MeV - in several cases 18 MeV - bremsstrahlung was used for activation. No electron current data were given; the integral radiation doses received by the patients' treatment locations were, after 10 minutes exposure, about 500 rad. The above mentioned biological samples were exposed for one hour at closer distance to the converter target (50 cm compared with about 1 meter in the in-vivo case), resulting in about 1000 rad exposure dose. Measurements were performed with an 80 cm³ and a 43 cm³ Ge(Li) detector. Using pure element standards, sensitivities were measured to range between 0.6 micrograms (for Mn) to 50 micrograms (for Zn). After activation with 33 MeV bremsstrahlung, Mg, Cl, Ca, Cr, Mn, Fe, Ni, Cu, Zn, I and Pb were detected in blood, after irradiation with 18 MeV bremsstrahlung, Mg, Cl, Mn, Fe, Ni and Cu were found. Among these elements, several were also detected in the other species investigated. Mg, Cl, Ca, Cr, Fe, Ni, Zn, Sr, Sn and Pb were analysed in-vivo. No significant difference of element concentrations became apparent during the length of the treatment which lasted for several weeks. However, qualitative and quantitative differences became discernible with respect to both the kind of disease and the way of its treatment.

62) The analysis of fish samples using both instrumental neutron and photon activation analysis was reported by Chattopadhyay et al.¹⁰¹⁵. Codfish samples of various age groups were collected. Muscle and liver samples were taken from

each fish, ground and homogenised while frozen. Several subsamples were freeze-dried to obtain information about losses of certain elements during freeze-drying. Typically, about 250 mg of sample material were sealed in polyethylene vials and irradiated as such. Synthetic element mixtures were used as primary reference materials; the accuracy was checked by certified organic based multi-element reference materials used as secondary standards. The samples were wrapped in cadmium foil to avoid interference through reaction with photoneutrons. Several major components of fish tissue, particularly calcium, were found to produce multiple interfering radiation through various nuclear reactions. Therefore, irradiation at different energies and several measurements were necessary. Irradiations were carried out at 15 MeV bremsstrahlung (for Cd and Sb determinations), 20 MeV (for Na, Mg, Cl, K, Ca, Mn, Co and As determinations) and 35 MeV (for Fe, Ni, Zn and Pb determinations). The mean electron beam currents varied from 90 to 240 microamperes. After 15 minutes to several hours of bremsstrahlung exposure samples were counted after different cooling periods using a 60 cm³ Ge(Li)-detector.

It was observed that up to about 30% of the total selenium content could be lost during lyophilisation, whereas no mercury losses were detected which stands in contradiction to numerous other reports; especially significant losses were observed if mercury was present as organometallic compound. However, in the work reviewed here the chemical form of the mercury present in the samples was not known. Several trace element levels were found to drop with increasing age of the fish whilst others did not appear to show any significant trend. It was also found that certain elements were deposited selectively in the different body regions whilst others were present virtually in equal concentrations throughout the whole body.

To assess the precision of the analyses, homogenised tissue samples were divided and analysed by both neutron and photon activation. The concentrations of the elements detectable by both methods (Na, Cl, Mn, Fe, Co, Zn, As, Br, Rb and Sb) agreed within the precision of the single methods (maximally $\pm 15\%$ of the mean value). The accuracy was assessed analysing certified reference materials. The obtained data agreed within the certified values within $\pm 10\%$.

In the two reports reviewed next analyses of human scalp hair is described. Hair has been recognised very early as an indicator for several parameters taking significant influence upon human life. Changes of concentrations of trace components in hair have been detected as signals for certain illnesses and diseases. In forensic science trace element contents are useful indicators to be

utilised during investigation of criminal cases, e.g. poisoning. Finally, scalp hair has been used as an indicator for the exposure of humans to environmental pollution. In comparison to other tissue matrix, e.g. blood or muscle tissue, hair offers several advantages. First, trace elements, especially heavy metals, mostly are present in higher concentrations in hair than in other tissue. Second, once accumulated in the hair body, the elements are fixed there and - with a few exceptions - do not change their concentrations significantly. Third, in the case of photon activation analysis the matrix composition of hair is more favourable than that of blood or other tissue; it mostly can be readily analysed without special pretreatment like lyophilisation or preconcentration. Moreover, and this refers to the second argument, scanning the concentration profiles of certain components over the length of a single hair strand, the investigator is enabled to trace the history of certain events in the life of the patient. However, there are certain disadvantages in the application of hair as an indicator, too. Being directly exposed to the environment of the carrier, contaminations, predominantly due to air particulate matter, are unavoidable. Washing procedures, if carried out with aggressive chemicals, may influence trace concentrations by leaching. Therefore, initialised by the IAEA, an experts committee worked out a standardised sampling, pretreatment and analytical procedure for hair analysis. The finding of a washing procedure optimising between efficient removal of external organic and inorganic contaminants and minimum leaching of internal components was of major concern (Ryabuchin^{1016,1017}). Evaluating all results obtained, mild washing using water, ethanol and diethyl ether was found not to substantially affect trace components inherent to the hair matrix. It was also found that the frequent washing of the head with cleaning substances generally used mostly has no significant effect upon the concentrations of trace components in the scalp hair.

63) Jervis et al.^{1018,1019} used scalp hair as a monitor of humans' exposure to environmental pollutants. Hair samples from several selected groups of persons exposed to different environments (rural, urban, residential and industrial regions) were taken and analysed for Zn, As, Cd, Sb, Hg and Pb by both instrumental neutron and photon activation analysis. Water and snow samples were also analysed as possible sources of toxic elements input to residents.

Prior to bremsstrahlung exposure, the hair samples were washed with doubly distilled water and organic solvents to remove organic contaminants and loosely attached dust which might falsify the obtained concentration data. The samples were dried at room temperature and sealed into polyethylene irradiation vessels to prevent any eventual losses of volatile components during sample preparation

and bremsstrahlung exposure, respectively. A separate study of the removal of the elements to be determined by the washing procedure was carried out using activation analysis and tracer methods. It was found that negligible amounts of the named elements were removed by the described washing procedure.

Bremsstrahlung irradiations were conducted at different electron energies as described above (Rev.40). The product activity measurements were carried out using standard Ge(Li)-spectrometers. As a result, no significant differences in the concentrations of the elements studied could be detected in the hair samples of rural and urban residents. However, the concentrations were found elevated significantly - in the case of lead by one order of magnitude - in samples from residents near metal refineries. The accuracy and precision of the results were confirmed by analyses of several certified reference materials.

64) The analysis of fourteen elements in hair samples was reported by Galatanu and Engelmann¹⁰²⁰. The samples were powdered and batches of 300 mg each were irradiated in polyethylene vials. Synthetic salt mixtures of 49 elements in cellulose powder which served as a carrier were used as reference materials. Selected groups of single elements were also irradiated to assess eventual nuclear or spectral interference. Samples were wrapped in cadmium foil to suppress the thermal photoneutron flux. Irradiations were conducted with an electron linear accelerator at 18 MeV (electron beam current = 60 microamperes) and 35 MeV (100 microamperes) electron energy for 90 minutes and 5 hours, respectively. After several cooling periods samples were measured multiply using a 79 cm³ Ge(Li)-detector. Counting times varied between 10 and 60 h, depending upon the half-lives of the expected product nuclides. Mg, Cl, K, Ca, Mn, Co, Ni, Zn, Rb, Sb, I, Cs, Hg and Pb were analysed. Possible sources of interference were evaluated in detail. Virtually all possible sources of interference were included. No quantitative interfering activity yield values were given, but for the competing reactions separation energies were listed.

Detection limits were found between 0.1 (for Sb) and 100 (for Cl and K) micrograms per gram. the reproducibility was obtained by five-fold replicate analysis using different single sample batches. It was found satisfactory in the most cases with respect to the fact that several elements (e.g. Sb) were present in concentrations close to the detection limit. Since no secondary standard (certified reference material) was analysed along with the hair samples and no results of other analysis techniques applied comparatively to the same material were given, there is no information available on the accuracy of the given results. However, it was shown that instrumental photon activation analysis can

well be applied to routine hair analysis.

The papers reviewed next deal with the analysis of plant material. As all other biological matrices, plant is favourable for instrumental photon activation analysis since the matrix generally does not produce background radiation of excessive half-life and intensity. The content of magnesium which is essential to all kinds of plant may be cumbersome in some cases due to the production of ^{24}Na . However, in the most cases the specific activity yield is not excessively large, and therefore, samples mostly can be counted readily without long cooling periods between irradiation and photon spectroscopy. Moreover, contamination problems specific for plant material as reported by Mitchell¹⁰²¹ are not very serious ones in the case of instrumental photon activation analysis. However, contamination by air dust particulate and soil matter might be a source of error (Thompson and Raven¹⁰²²). It depends very much upon the intention of the researcher whether these components should be included (e.g. in the case of the assessment of transfer factors of pollutants from plant via nutrition to the animal, although it is questionable if an element being present say as oxide in the outer contamination material is of equal physiological availability to the animal as if it is organically bound in the plant tissue) or washed off by any means prior to analysis (e.g. if the transfer of soil components via root resorption into the plant body is to be traced). The rinsing of outer contaminants from plant surfaces entails severe problems since one has to be aware of much more leaching activity than for instance during washing of hair discussed above (Arkley¹⁰²³, Nicholas¹⁰²⁴, Jacobson¹⁰²⁵, Jacobson and Oertli¹⁰²⁶). In this instance, other influence parameters, e.g. rainfall, might cause uncontrollable severe alteration of the trace element concentration.

65) In one of the pioneer works on intrumental photon activation analysis, Hislop and Williams¹⁰²⁷ reported the instrumental multi-element analysis of a kale sample. This work is discussed in somewhat more detail than the other biological applications since it is a fundamental work and frequently referred to in relevant publications. After a short summary of instrumental photon activation analysis in general the major purpose of this work was specified, namely to check the suitability of the method for the analysis of both rock-based and biological material. A kale sample was selected as an example for the latter. This material had been analysed also by other laboratories using different techniques (Bowen¹⁰²⁸). A synthetic mixture of elements was used as a reference material which originally was prepared for another analytical method (emission spectroscopy; see also Rev.32) and thus contained a large number of components (in total 39 elements) which were most unlikely to ever be detected after pho-

ton activation in the materials investigated, e.g. Bi, Ga, B and the platinum group metals. The elements, present as oxides, were mixed in an ammonium sulphate matrix at a concentration of 1% each. This uniform composition is favourable for other analysis methods, but normally not used for activation analysis with its different element-specific activity yields after irradiation. However, in photon activation this problem is not too serious because cross sections are not as different as for instance in thermal neutron activation.

7.4 mg of reference material were sandwiched between two 200 mg portions of cellulose powder and then pressed into a 12 mm diameter pellet. Batches of individual elements suspected to be sources of interference were irradiated separately. It was not specified which sample mass was activated; according to the average elemental concentration in this matrix it was probably a few hundred milligrams or even gram amounts. Sample and reference material pellets were wrapped in an aluminium foil and placed behind each other in an aluminium can which served as an irradiation vessel. The flux gradient along the beam axis within the sample area was monitored with lead foil discs of the pellets' diameter. A flux reduction of about 15% was found between the analytical sample and the reference material position. The irradiations were conducted with an electron linear accelerator for 30 minutes using bremsstrahlung of 35 to 40 MeV electrons absorbed in an air-cooled tungsten converter. The mean electron beam current (measured at the converter) was 4 to 8 microamperes. The total converter thickness was 3.2 mm, thus it did not absorb all electrons and a heating-up of the sample rabbit was unavoidable since no beam absorber or cleaning magnet was installed. This problem was not discussed in the paper.

The resulting activities were measured with a 40 cm³ Ge(Li)-detector. The ¹¹C activity of the kale sample was allowed to decay for more than two hours. Measurements were then carried out at increasing intervals over a period of four weeks. For several nuclides exact gamma energy data were not available at the time of the experimental work and so these nuclides had to be confirmed by irradiation and measurement of the parent elements (e.g. Ca producing ⁴³K). At times soon after the irradiations the gamma spectra were dominated by activation products of calcium (⁴³K and ⁴⁷Ca) since calcium was a major component (about 4%) of the sample. The only trace element detectable after short, say hours, cooling periods was strontium via ^{87m}Sr. In total, the following elements were detected: Na, Mg, Cl, Ca, Rb and Sr. Each element was discussed individually with special attention directed to possible interference.

The sensitivity data given in the report referred to single elements separated

from any matrix activity. Therefore, these values cannot be used for sensitivity assessments in multielement photon activation analysis. The sensitivities were found between 0.02 micrograms (for Sr) and 50 micrograms (for Ca). The precision of the results ($\pm 5\%$ on the average) based upon counting statistics, geometry factors and masses, therefore they are not comparable to those obtained by replicate analyses. The accuracy was given by comparison with literature data. In the case of kale analysis a final assessment of the accuracy is a problem since definite concentration values lay before for only two elements; for all other ones only limits of detection could be given.

66) The multielement photon activation analysis of tobacco leaves was reported by Sato et al.¹⁰²⁹. The trace composition of tobacco, being one of the most prominent sources of several diseases, is of particular interest. The incorporation of components being suspected or confirmed to be carcinogenics into the human body is effected by inhalation, and thereby their physiological effect is of different nature than that of ingested ones. Frequently the toxicological efficiency of a substance is higher if inhaled than if it was ingested (the most prominent example in this instance is plutonium). Moreover, tobacco usually is consumed daily in large amounts. Therefore, even small differences in the concentrations of toxic components might entail large differences in their biological effects.

In the reported work, three different kinds of leaves were taken from the plant, namely top, middle and low ones which reflect the age of the corresponding partition of the plant. Also, tobacco samples from cigarettes available on the open market were taken and analysed. Both a synthetic mixture of elements in a cellulose powder matrix and NBS-SRM 1571 (Orchard Leaves) were used as multielement reference materials. One-gram portions of each material to be irradiated were taken and pressed into pellets. Irradiations were conducted with an electron linear accelerator at 30 MeV electron energy and a mean electron beam current of 70 microamperes. Since a platinum converter of only 2 mm thickness was used for bremsstrahlung production and thus unconverted electrons hit the sample the irradiation position was water-cooled and the exposure period was limited to two hours maximum to avoid serious damage of the sample material during activation. Experiments indicated that the samples survived under these conditions if positioned at least 10 cm downstream from the converter.

Gamma spectra were taken with a 33 cm³ Ge(Li)-detector. Measurements were made consecutively in increasing intervals over a one month's period. Analyses were carried out in duplicate to obtain information about the reproducibility of the

method.

Na, Mg, Cl, K, Ca, Mn, Fe, Zn, As, Rb, Sr and Sb could be analysed with satisfactory reproducibility except for antimony whose concentration was very close to the detection limit valid for the named conditions. The accuracy obtained by parallel analyses of the certified reference material was also good with exception to arsenic which is present in the orchard leaves reference material in extremely small amounts.

It was found that the sensitivity theoretically could have been increased using higher bremsstrahlung energies for activation (e.g. for some elements by a factor of 3 using about 60 MeV electrons) but - as has settled as a consensus value during practical work of many analysts - 30 MeV was found optimal with regard to average sensitivity and nuclear interference by neighbouring elements (see also Ch.2).

67) The same group of authors¹⁰³⁰⁻¹⁰³² reported an assessment of the accuracy and precision of the method as carried out as described in the paper reviewed above (Rev.66). Several organic-based certified multielement reference materials were analysed using the above mentioned synthetic multielement reference material. The values for most of the elements included (Na, Mg, Cl, K, Ca, Mn, Fe, Zn, As, Rb, Sr and Sb were analysed) were in good agreement with the certified data and/or comparative literature values.

68) The above mentioned contamination problems which arise during plant analysis were evaluated by Beckett et al.¹⁰³³ using grasses as indicators of environmental pollution. Rye grass was selected as an indicator plant since it is widely used and easily grown. In order to assess the soil/herbage transfer, the rate of outer contamination by air dust and soil-derived components and the losses of some 18 different elements during the washing procedure and its effectiveness was studied. A very mild washing procedure using only water was selected to minimise leaching effects. Since the soil/herbage transfer is the least prominent for titanium as compared with the most of all other major or minor soil components, the soil/herbage ratio of this element was selected as an indicator for soil-derived contaminations. Different growth conditions were used in order to assess the influences of root resorption and outer contamination upon the final concentration of trace components in the plant matrix. Soil, grasses and insoluble washing residues were analysed by instrumental photon activation analysis. A synthetic multi-element reference material was used. This material has been utilised frequently by the Harwell group. Both the reference

material and the analysis procedure was described in Ref.¹⁰²⁷, Rev.65. Significant losses during the washing procedure were found for Mg, Ca, Ti, Fe, Sr, Cd and Pb. This was established in grass which had been grown apart from any contamination source, as far as this was practically possible. Therefore, to assess the hazard of grass contaminants to the health of the primary or secondary consumer, it may be analysed as harvested, but this seems unsuitable for the assessment of the uptake of plant-available pollutants from the soil.

In the following, publications are reviewed which deal with the photon activation analysis of special elements of interest in biological matrix. Since every element, depending upon its content, can be either essential or injurious, all elements should be of analytical interest in biological matrix. However, several of them have proven to be of special importance, either as nutrient or as pollutant. Hence, they have been investigated more frequently than others. Some very prominent pollutants are: Se, Cd, I, Hg and Pb. Some of these can be analysed by photon activation analysis more advantageously than by other instrumental methods, especially in trace concentrations. Particularly lead was studied extensively by many workers. Surprisingly, one element of biological importance - being an extremely toxic one - is missing in this list, namely thallium. This element cannot be analysed by routine instrumental neutron activation analysis, and also for other methods it is somewhat difficult to determine. For instrumental photon activation analysis, however, it has very favourable nuclear data and can be analysed in very small trace quantities (see chapter 5). Nonetheless, it was studied in comparatively few cases only and - inspecting the literature accessible to the authors - not as yet in biological matrix.

69) The analysis of bone matrix was described in several papers by the Harwell photon activation analyses group (Hislop and Williams¹⁰³⁴, Hislop et al.¹⁰³⁵⁻¹⁰³⁷, Williams and Hislop¹⁰³⁸). Particular attention was directed to lead. The preparation of the samples was found to be the primary problem. If wet ashing was used for removal of the organic matter and preconcentration of the elements to be determined there was the danger of contamination by impurities of the chemicals used. Instead, if dry combustion was used, no reagent blanks had to be considered but losses due to volatilisation might occur. ²⁰³Pb, produced through photon activation of untreated bone samples with 35-40 MeV bremsstrahlung was used as an inherent tracer. Activities were measured by gamma spectroscopy before and after various ashing steps. By this method one disadvantage of tracer methods - as applied to biological matrix - was somewhat reduced, namely the lack of knowledge concerning the chemical form of the elements. It

was not completely avoided since significant changes of the chemical structure of the matrix most likely also occurs during activation, so that the chemical form of the regarded element might not be the original one. Nevertheless, it was found that the lead concentration does not suffer from volatility if the combustion temperature does not exceed 600°C at one night's duration. This value does not agree with that of other researchers (see the concerning literature cited in¹⁰³⁴). This disagreement most probably reflects the complexity of the matrix (and thereby its chemical behaviour) rather than the quality standard difference between the investigating laboratories. Besides lead, also other elements were studied in the cited reports, namely Na, K, Ca, Cu and Zn.

70) The same research group (Hislop and Williams¹⁰³⁶) reported a comparative investigation of lead concentrations in different biological matrices (kale, orchard leaves, bone) using photon activation and other analytical methods. The procedure was as reported above (Rev.69). Major disagreements were found for the lead content in kale as obtained by photon activation analysis (2.7 ± 0.4 micrograms per gram) and other methods (3.2 micrograms per gram mean value). However, the values of these ranged from 1.6 to 5.4 micrograms per gram. Using radiochemical separation and scintillation counting, 0.1 micrograms were found to be the detection limit.

71) Lead was analysed in milk powder by Dutilh and Das¹⁰³⁹ using the 279 keV line of ²⁰³Pb produced through (γ, n) reaction. Milk samples were dried in a vacuum evaporator. In this case, significant losses were found at ashing temperatures exceeding 600°C, and therefore, a further preconcentration by ashing the samples was abandoned. The milk powder was pressed to pellets weighing 5 to 7 g each. These were then irradiated in PVC vials. Four samples and one reference material batch (synthetic material containing lead nitrate; no details about its preparation were given) were irradiated simultaneously in a rotating sample position. Bremsstrahlung from 40 MeV electrons at an average beam current of 30 microamperes was used for activation. Since a NaI-crystal was used for counting, a separation of the lead from the matrix had to be performed prior to the measurement. Due to the extremely low lead concentration in the samples no definite value could be given. The best estimate was that it was below 5 ng/g, calculated for the untreated material.

72) Chattopadhyay et al.¹⁰⁴⁰ reported the use of hair as a monitor of environmental lead exposure. As explained above in the subparagraph on hair analyses (see also Rev's.63 and 64), scalp hair proved to be a suitable monitoring material. More than 300 different scalp hair samples were collected from different

groups of persons. Distinguishing criteria were age, sex and residential environment. A mild washing procedure was used to remove external contaminants. An investigation of the washing effect yielded that all lead-containing external contamination was removed and no appreciable leaching of lead from the hair body occurred during washing. Samples were irradiated with 35 MeV bremsstrahlung using lead nitrate as a primary standard. Normally high resolution gamma spectrometry was used for activity counting; in the case of extremely low (less than 3 micrograms per gram) lead concentrations, a chemical separation was carried out after bremsstrahlung exposure and the counting was performed with a scintillation crystal. Both ^{204m}Pb and ^{203}Pb were measured. The accuracy of the data was checked by analysing several multielement reference materials with certified lead contents.

Interesting correlations could be found between the lead content of the hair and both age, sex and environmental exposure of the carriers. Several blood samples were analysed, too. A quasi-exponential function was found for the corresponding lead in hair versus lead in blood. However, in many cases this correlation did not hold, e.g. intermediate, unique exposure of the investigated person to elevated environmental lead concentrations. The very dynamic physiological behaviour of blood - as compared with the rather statical one of hair - does allow correlations of long-term validity only in cases of permanent exposure to a quasi-constant environment. In hair investigations, however, it is possible - in favourable cases - to trace an exposure history by element-scanning along the length of the hair strand, as was already noted above.

73) Special attention to both lead and cadmium was directed in a large-scale investigation of Chattopadhyay⁹⁷⁸, see also Rev.41. These elements were analysed in a large variety of samples from an entire agricultural ecosystem (soil, vegetation, human tissue). Various bremsstrahlung energies were used to yield maximum sensitivity and selectivity. For cadmium analysis, 15 MeV electron energy was not exceeded to avoid first order interference by tin (^{111m}Cd used for analysis evaluation, can also be produced by $^{115,116}\text{Sn}$) and excessive background activity due to ^{11}C from organic matrix components.

74) In a report by Jervis et al.¹⁰⁴¹, cadmium was studied as present in a large variety of biological material particularly nutrients. Both instrumental neutron and photon activation analysis were applied. To avoid any contamination, samples were pretreated as little as practical; after drying they were sealed in polyethylene bags and irradiated as such. Only vegetation specimens were washed prior to irradiation to remove contamination by air particulate and event-

ual soil matter. For soil analyses, a synthetic soil matrix spiked with trace amounts of cadmium, was prepared to serve as a reference material. For all other specimens to be analysed, pure cadmium oxide was used. Irradiations were conducted with a linear accelerator. 15 MeV bremsstrahlung was used for soil analyses (to avoid interference as explained above), and 35 MeV for all other samples. The activities of the product nuclides were measured by high resolution gamma spectroscopy using large volume Ge(Li)-detectors. Since no reliable photonuclear data were available, a systematic investigation about the photonuclear reactions of cadmium were carried out. Cadmium standards were irradiated at various energies ranging from 8 to 40 MeV. Product nuclides, their gamma emission energies and half-lives were then measured. Thereby, various kinds of interference were evaluated. ^{111m}Cd , produced through (γ, γ') , (γ, n) and (n, γ) -reaction of the neighbouring stable cadmium isotopes was selected as a suitable product nuclide for analysis evaluation. As a result, the cadmium content in the tissue samples was found to be extremely low compared with the concentration in soils. In animal tissue between 0.002 and 0.069 micrograms per gram were detected. Eventual higher values were found in organs such as liver or kidney. Somewhat higher concentrations were found in plants and plant-based material. Between 0.1 and 0.9 micrograms per gram were analysed. Lower contents were detected in plant seeds. In comparison, 1 to 1.7 micrograms per gram of cadmium were found in surface soil samples. The accuracy of the data was tested by analysing intercomparison standards. The agreement with the certified or consensus value was excellent. The experimental detection limit ranged between 80 and 900 ng, depending upon the irradiation parameters.

Another element of importance in biology and medicine is iodine. The analysis of iodine by instrumental neutron activation analysis if present in trace quantities is severely hampered by the short half-life of the (n, γ) -product (^{128}I , $T = 25$ m). ^{24}Na originating from sodium usually present at comparatively high concentration levels in tissue matrix, dominates in the gamma-ray spectrum shortly after activation and thereby ^{128}I might not be detectable. Instead, using photon activation, ^{126}I is produced which has a conveniently long half-life (13 days) and the matrix background activity is short-lived (^{11}C , $T = 20$ m). Therefore, instrumental photon activation analysis is very suitable for routine determinations of iodine in biological samples.

75) The earliest message about photon activation analysis of iodine in biological material originates from 1965 - as far as the authors know (Mulvey et al., Ref's. 1042, 1043). Iodine in human serum and beef thyroid samples was determined. Since no high-resolution spectrometer was applied the iodine in the

serum samples was separated prior to irradiation and preconcentrated on an ion exchange resin. The thyroid specimens were irradiated as such without any pre-treatment. The samples were then sealed in plastic vials. Irradiations were carried out with 22 MeV bremsstrahlung of an electron linear accelerator at 250 microamperes mean electron beam current. The common exposure period was 1.5 hours. Since a thin tungsten target was used as bremsstrahlung converter, the irradiation vials were either placed behind an aluminium block in which the residual electrons penetrating the converter were captured, or at greater distance to the target. This was done to avoid excessive heating of the samples and subsequent damage of their organic matrix. The gamma activity of ^{126}I was measured with a well-type scintillation detector either connected to a multi-channel analyser or two separate single channel analysers adjusted to 388 keV and 666 keV, respectively, using reference radiation sources of similar energy (^{133}Ba and $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$, respectively). Various possible sources of spectral interference were studied but it was found that these contributed negligibly to the measured iodine activity under the described conditions.

76) Iodine was determined in blood plasma by Brune et al.²⁴⁰ using a medical betatron. The sensitivities for the analysis of fluorine, mercury and lead were also studied. It was not specified with reference material was used for the iodine analyses. Samples were placed in a sample holder which was rotated at a velocity of one revolution per minute. The average distance between the platinum converter and the samples was 26 cm. Irradiations were carried out for 90 minutes at 35 MeV maximum bremsstrahlung energy and about one microampere mean electron beam current. This is more than two orders of magnitude less than usual in linear accelerators; Therefore, the analytical sensitivity was moderate but met the present requirements. Bremsstrahlung was produced in a platinum converter of 0.5 mm thickness. This means that penetrating electrons had to be considered. This problem was not discussed explicitly in the cited work; it was only said that - according to thermocouple measurements of the irradiation position - no considerable heating of the sample occurred which is essential for the sensitivity estimation for Hg. Using the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction the photon flux density was measured with help of polystyrene discs. The product activities were measured with a standard well-type NaI-crystal connected to a 128 channel pulse-height analyser.

The obtained concentration values for iodine agreed fairly well with the data given by the manufacturer. The sensitivities for fluorine, iodine, mercury and lead were found to be 3, 50, 15 and 400 micrograms, respectively. These are values obtained by analysis of pure elements. Therefore, they can be realised

only in the case of chemical separation in practice especially in the case of fluorine (see chapter 6.1).

77) Williams and Hislop⁹⁷⁹, Rev.43, reported the analysis of iodine in a large variety of biological materials. Samples were pressed to pellets of 5 mm diameter and then sealed in silica tubes. Potassium iodide powder, homogeneously mixed with cellulose powder, served as reference material. Several elements which possibly give rise to interference were also irradiated.

Irradiations were conducted with 40-44 MeV bremsstrahlung of a linear accelerator at 40 microamperes mean electron beam current. Gold was used as bremsstrahlung converter. Since the gold target was only 2 mm thick, residual unconverted electrons were caught by an air-cooled aluminium block to avoid sample heating. Exposure periods were 6 to 10 hours. After irradiation, the sample tubes were immersed in liquid nitrogen to avoid loss of eventually volatilised iodine from the sample. Measurements were carried out with a 40 cm³ Ge(Li) detector. The spectrometer used was claimed to provide reliable data at dead times up to 80%. After an initial decay period of about 12 days multiple measurements were made over a total period of 50 days to confirm the half-life of ¹²⁶I. The detection limits for iodine in biological material were found to range between 0.05 and 15 micrograms, depending upon the matrix; if no matrix is present (i.e. in the case of radiochemical separation after bremsstrahlung exposure) a detection limit of 5 ng was estimated.

An accuracy assessment was not given in this work. Precision values were obtained by replicate analyses; between 5 and about 20% were found. Sources of interference, either by production of ¹²⁶I by other elements or by nuclides giving rise to gamma radiation equal to or close to 388 and 666 keV, respectively, were studied. It was found that none of them had to be considered in the iodine analysis of biological material.

78) Selenium was determined in foodstuff through isomeric state excitation using a ⁶⁰Co source of some 10¹⁴ Bq (Veres¹⁹⁰). 20 g of sample material were irradiated for two minutes. The induced activity of 18 s - ^{77m}Se was measured for one minute. The detection limit was 1 mg of Se with a reproducibility of 10%. This sensitivity could be yet improved using cyclic activation.

Numerous applications of the isomeric state photoexcitation for selenium analysis are reported in the papers reviewed and cited in the section about systematic studies above and in the single element studies in 6.2.4.8 below.

A special problem for almost every analysis method is the determination of mercury because of the volatility of the majority of its compounds, in particular its organic compounds. Therefore, the difficulties of mercury analyses of organic and biological material are of very complex nature. This is discussed further in paragraph 6.2.4.9.

79) In the paper of Raghi-Atri and Segebade⁸⁹⁶ a mercury analysis in plant material is described. Prior to irradiation the powdered samples were impregnated with LiHS-solution to capture mercury which is eventually volatilised during bremsstrahlung exposure. This mercury is then converted into HgS which is fairly heat- and radiation resistant (Segebade⁸⁹³). Samples, (about 2 g each) and reference materials (HgS powder mixed with cellulose powder) were pressed into pellets of 12 mm diameter. Activation was carried out with 30 MeV bremsstrahlung at 150 microamperes mean electron beam current. Exposure periods varied from 2-6 hours, depending upon the expected mercury concentration. After one day of cooling period samples were measured for one day each with a planar germanium low energy photon diode. Characteristic gold kX-radiation emitted by ^{197}Hg produced through $^{198}\text{Hg}(\gamma, n)$ was used for analysis evaluation. This radiation is the most intense after the named decay period. The obtained concentration values were between 20 ng/g and 6 micrograms per gram. The detection limit was 20 ng/g or 0.2 micrograms, respectively. No accuracy assessment was made in this work. Several replicate analyses yielded a fairly good precision of the data (about 8-20%).

In the following table, the most relevant applications of instrumental photon activation analysis to studies of biological material are summarised as they have been accessible to the authors.

Tab.6.2-6: Instrumental photon activation analysis of biological material

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
Human blood, urine, hair; tobacco, tree-bark, kale	25 (14 kW^1)	Na, Mg, Cl, Ca, Mn, Co, Ni, Cu, Sr, Sn	825	57
Blood, thyroid	25 (5 kW^1)	Na, Mg, Cd, Sn, I, Ba, Pb	1012	58
Milk	40 (30)	Pb	1039	71
Human bone, kale, orchard leaves	35-40 (5)	Pb	1034- 1036	69
Human tissue	40 (5)	Pb	1037	69
Human bone, blood, urine	40 (10)	Na, Mg, Cl, Ca, Zn, Rb, Sr	1027	65
Liver, kidney	various	Mg, Ca, Ti, As, Mo, I, Hg	966	
Bovine liver	30 (10^6 R/min^1)	Na, Mg, Cl, K, Ca, Fe, Rb, Zn	1031	
Human bone	45 (10)	Cu, Zn	1038	69
Fish tissue	15-35 (90-240)	Na, Mg, Cl, K, Ca, Mn, Fe, Co, Ni, Zn, As, Zr, Cd, Sb Pb	1015	62
Kale	35-40 (4-8)	Ca, Rb, Sr	1027	65
Orchard leaves	20-45 (50)	Pb	1121	
Orchard leaves	40-45 (10)	Na, Mg, Cr, Zn, As, Rb, Cd, Sb, Cs, Ce	962	

Tab.6.2-6, continued

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
Edible plants	15-44 (100-200)	Na, Mg, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Sr, Zr, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Hg, Tl, Pb, Bi	994	
Various organic material	35 (225)	Cd	1041	74
Kale, tobacco, orchard leaves	30 (90)	Na, Mg, Cl, K, Ca, Mn, Fe, Zn, As, Rb, Sr, Sb	1030	67
Orchard leaves, tobacco	30 (70)	Na, Mg, Cl, K, Ca, Mn, Fe, Zn, As, Rb, Sr, Sb	1029	66
Grass	30-40 (8)	Mg, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Ce, Pb	1033	68
Orchard leaves, spinach, tea	30 (not given)	Cr, Mn, Co, Ni, Zn, Pb	1123	
Various plants, proteins	30 (150)	U	688	49
Human hair	35 (225)	Pb	958, 978, 1018, 1040	41, 63, 72, 73
Human hair	18, 35 (60, 100)	Mg, Cl, K, Ca, Mn, Co, Ni, Zn, Rb, Sb, I, Cs, Hg, Pb	1020	64
Human hair	35 (225)	Na, Ca, Fe, Co, Ni, Se, Br, Zr, Sb, Pb	1105	

Tab.6.2-6, continued

Material analysed	Bremsstr. energy, MeV ($I_e, \mu A$)	Elements determined	Ref.	Rev. no.
Human blood, thyroid	22 (250)	I	1185	75
Blood serum	35 (1) ²	I (F, Hg, Pb) ³	240	76
Various biol. material	40-44 (40)	I	979	77
Flour	⁶⁰ Co source	Se	190	78
Plant material	30 (150)	Hg	896	79
Humans in vivo, human organs	18, 33 (not given) ²	Mg, Cl, Ca, Cr, Fe, Ni, Zn, Sr, Sn, Pb	246, 247	61
Organic-based reference mat.	30 (70)	Na, Mg, Ca, Mn, Ni, Zn, As, Rb, Sr, Zr, Ba	1186	

¹electron beam current not explicitly given

²betatron was used for activation

³detected but not determined

6.2.4.4 Geochemical analysis

This paragraph is divided into three parts; in the first, works about the analysis of rock and mineral material are reviewed, in the second analyses of water and water-related material, and in the third, cosmochemical applications. Considerably fewer publications will be discussed than in the preceding paragraphs. This is done because many papers describe the analysis of many material classes of different origin. Hence, they are extensively discussed in other paragraphs. For instance, works about soil analyses have been performed mostly within an environmental context and therefore are reviewed in paragraph 6.2.4.2. Since there is no essential difference in the analytical technique as applied to equal material classes with different scientific background, there is no point in repeating the review. Therefore, papers about instrumental photon activation analysis of soil-, water- and air-related samples mostly are reviewed in 6.2.4.2. Publications about the photon activation analysis of ores and minerals are discussed either in this paragraph or in the next one on the analysis of raw products and industrial products, depending upon where major attention is directed to. Usually, the problems arising in geochemical application of photon activation analysis are somewhat different from those in the other fields of science discussed hitherto. Frequently concentration to be determined are not as small as for example in environmental or biological analyses. As outlined by Beresin et al.⁷⁰⁶ in the most cases in geology and mining industry, a sensitivity as high as one milligram in total is quite satisfactory. If a trace analysis is required, there is mostly the possibility of irradiating larger samples; as mentioned in the introductory part, using accelerators with endstanding targets, usually large volumes up to say one liter can be activated. However, in many cases, particularly during analysis of rock and ore-related material the handling of matrix component activities after irradiation might be cumbersome. Limestone matrix, if activated at higher bremsstrahlung energies (more or equal to 16 MeV electron energy) produces a very intense and complex gamma-ray background (^{42}K , ^{43}K , $^{47}\text{Ca}/^{47}\text{Sc}$). This is also true for ores, e.g. copper ore whose matrix activity after bremsstrahlung exposure does not permit measurement of product nuclides with half-lives of up to a few hours. In comparison to biological analyses, geological material normally is heat- and radiation-resistant but produces a high background activity, whereas organic based material might be damaged but usually does not contain long-lived matrix activities after activation. More general information about geochemical photon activation analysis can be found in Ref's. 1044-1047.

- Rock material

- 80) One of the first works about photon activation analysis of elements other
- than the light ones actually was concerned with geological materials. In 1965,
. Beresin et al.⁷⁰⁵ reported the analysis of rock samples by photon activation
- performed in the Soviet Union. In this paper, especially the possibility of
- selective analysis of several elements by use of a suitable bremsstrahlung
r energy is pointed out. Samples of 5 to 500 g were activated at different brems-
y strahlung energies and measured with a scintillation spectrometer. It was found
. that, for instance, zirconium in ores could be analysed without time-consuming
- chemical sample treatment. A lot of fundamental work on geochemical application
s of photon activation analysis was performed in the USSR. See also Shtan¹²⁰⁴.
1 Only a relatively small part of this literature can be presented and discussed
- here.

d 81) An extended review about nuclear, in particular photonuclear methods of
- rock and ore analysis as applied in the Soviet Union was given by the working
- group quoted above (Beresin et al.⁷⁰⁶). After a short description of the me-
e thod, a very interesting historical review on the development of photon activ-
- ation analysis especially as applied in geology and mining industries was
- given. The technological progress especially concerning the activating radiat-
g ion sources was evaluated, starting from 1950 - when photon activation analysis
- using photoneutron reactions was considered to be of doubtful use and future,
- due to the insufficiently advanced activating photon sources (Boyd¹⁰⁴⁸).

e Major attention was directed to the analysis of the light elements, but many
- application of the method to the analysis of heavier elements as well. The spe-
n cial advantage of activation at variable energies was pointed out, starting
g from photoexcitation where small accelerators can be used. Emphasis is placed
d upon the microtron and its special features. Gamma spectroscopy techniques were
t, not discussed; only a few gamma-ray scintillation spectra and several decay-
ot curves were presented as examples. All in all, this article gives a valuable
n impression about the activities in the field of nuclear analysis methods in
d geochemistry as performed in the Soviet Union.

ic 82) A procedure for the determination of several major and minor components in
ix rock material, including neutron and photon activation was developed by Schmitt
on et al.¹⁰⁴⁹. Mg, Ca, Ti and Ni were analysed in seven USGS standard rocks and
three stony meteorite sample using instrumental photon activation analysis. A
synthetic mixture of the desired elements in form of their oxides was used as

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 cm³ 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 ²⁴Na was checked experimentally and was found negligible under the described experimental conditions. For the analysis of calcium, ⁴⁷Ca was selected for evaluation although less sensitive than ⁴³K by an experimentally determined factor of 1/55. However, ⁴⁷Ca 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 Zonderhuis¹⁰⁵⁰. 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, ⁴⁷Sc (from Ti), ²⁴Na (from Mg) and ^{87m}Sr (from Sr) were measured. After another decay period of about 40 hours, another measurement was carried out using the same spectrometer. ⁴⁷Sc (this time from both Ca and Ti), and ⁴³K (from Ca) were counted. No information was given the obtained concentration data, their quality, and the reference material which