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A critical review of

## NUCLEAR ACTIVATION TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN ATMOSPHERIC AEROSOLS, PARTICULATES AND SLUDGE SAMPLES

(Technical Report)

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# **A critical review of nuclear activation techniques for the determination of trace elements in atmospheric aerosols, particulates and sludge samples (Technical Report)**

## **ABSTRACT**

Activation analysis is one of the major techniques for the determination of many minor and trace elements in a large variety of solid environmental and pollution samples, such as atmospheric aerosols, particulate emissions, fly ash, coal, incineration ash and sewage sludge, etc. Neutron activation analysis of total, inhalable or respirable airborne particulate matter collected on a filter or in a cascade impactor on some substrate, is very popular. By Instrumental Neutron Activation Analysis (INAA) up to 45 elements can be determined. The irradiation and counting procedures can be adapted to optimize the sensitivity for particular elements. The precision is largely governed by counting statistics and a high accuracy can be obtained after calibration with multi-elemental standards. Radiochemical Neutron Activation Analysis (RNAA) is applied only when extremely low limits of determination are required. Instrumental Photon Activation Analysis (IPAA) is complementary to INAA, since some elements of environmental interest can be determined which do not produce appropriate radionuclides by neutron irradiation. Charged Particle Activation Analysis (CPAA) is used in particular circumstances such as for certification purposes or coupled to radiochemical separations for extremely low concentrations.

## **1. INTRODUCTION**

Fine dust and fly ash emitted in the atmosphere or in workrooms can have long residence times in the air and as such be potential hazards for human health and for the environment. Ash, slag and sludge are disposed of by dumping at sea or as landfill materials, are used as filling material in concrete or may be applied as a manure to agricultural land. These procedures may give rise to contamination of the environment, by various substances such as heavy metals, excess of nutrients, carcinogenics, etc. Before actions for environmental sanitation can be undertaken, one needs an accurate knowledge of the nature of the pollutants and their concentrations and above all their major sources and their pathways through the environment. Therefore all kinds of emission sources, wastes and various environmental samples must be investigated starting with an elemental analysis.

An important question concerns which elements should be determined and which need not be. At the present state of knowledge it is a very difficult task to rank pollutants according to their importance. Most elements in environmental samples are in some sense more or less important either as nutrients, as elements of environmental interest, as elements of toxicological importance, or as indicators of the origin and pathways of pollution. Table 1, compiled for atmospheric aerosols (ref. 1 updated), illustrates this point. From this table it is obvious that the safest approach is not to limit the scope of the analysis, but to analyze for as many elements as possible, preferably with a multielement technique. This technique should allow sensitive, specific and accurate

**Table 1:** Elements of Interest in Environmental Studies (ref. 1 updated)

Interest <sup>a</sup>						Interest <sup>a</sup>					
Element	Env.	Indic.	Tox.	INAA <sup>b</sup>	IPAA <sup>b</sup>	Element	Env.	Indic.	Tox.	INAA <sup>b</sup>	IPAA <sup>b</sup>
Al	X	X	X	+	-	K		X		+	+
Ag		X		+	+	Mg		X		+	+
As	X	X	X	+	+	Mn	X	X		+	+
B	X			-	-	Na		X		+	+
Ba		X	X	+	+	Ni	X	X	X	+	+
Be			X	-	-	Pb	X	X	X	-	+
Br		X		+	-	Rb		X		+	+
C		X		-	-	S	X	X		+	-
Ca		X		+	+	Sb	X	X	X	+	+
Cd	X		X	+	+	Sc		X		+	+
Cl	X	X		+	+	Se	X		X	+	+
Co	X			+	+	Si		X		+	+
Cr	X		X	+	+	Sn	X	X	X	-	+
F	X	X	X	+	-	Tl	X		X	-	+
Fe		X		+	+	U	X			+	+
Hg	X	X	X	+	+	V	X	X	X	+	+
I	X	X		+	-	Zn		X	X	+	+

<sup>a</sup> Env., of environmental interest; Indic., indicator of pollution pathway; Tox., of toxicological interest

<sup>b</sup> determination (+) feasible (-) not feasible by purely instrumental approach

determinations of major, minor and trace elements. Because a large number of analytical data is required before meaningful conclusions can be drawn on pathways and environmental impact an easily automated instrumental technique is highly desirable.

Most analytical techniques routinely used for this purpose (AAS, AFS, Spect-Phot., ICP-AES, ICP-MS, ASV, EDXRF, PIXE, PIGE, EMPA, etc.) only partly meet these requirements. When solid samples, such as dust, ash or sludge are to be investigated most techniques involve a dissolution of the sample and possibly subsequent chemical separation or preconcentration steps with the inherent danger of analyte loss or contamination. The microchemical methods on the other hand are faced with the inherent inhomogeneity of most environmental samples and with the difficulty of calibration. Standards almost identical to the samples are often needed for an accurate calibration. This is not the case with several nuclear activation techniques of analysis. Instrumental Neutron or Photon Activation Analysis (INAA or IPAA) allow, as shown in Table 1, the detection of the large majority of elements with atomic number > 8 in many solid environmental matrices. For the detection of particular elements, with less favorable sensitivity or present in extremely low concentrations radiochemical separations can be performed after irradiation, or special irradiation and counting systems can be applied. While both techniques are quite complementary, in some cases, Charged Particle Activation Analysis (CPAA) can enable even more elements to be determined. As well as the intrinsic sensitivity, precision and freedom of contamination after activation, these purely instrumental techniques can easily be automated and leave the sample although slightly radioactive available for other analyses. Since the methods are based solely on

nuclear properties the results are independent of the chemical form of the element and there are essentially no large matrix effects and minimal interferences. This makes calibration straightforward and can mean that the results are free of systematic errors, and have precisions and accuracies adequate for almost all environmental samples. Corrections for shadowing effects during activation, nuclear interferences, spectrometric interferences,  $\gamma$ -attenuation, dead-time losses during counting, etc. can generally easily be assessed, overcome or corrected for by some appropriate measures. Due to the theoretical foundation whereon the techniques are based all sources of systematic or random variation are identifiable. The accuracy of the results is therefore often not limited by the analytical measurement but rather by the sampling technique used for atmospheric aerosols, workroom dust or fly ash or by the homogeneity of the ash or sludge.

## 2. SAMPLING OF AEROSOLS OR DUST FOR ACTIVATION ANALYSIS

Suspended atmospheric particulate matter can be sampled in urban, industrial, rural, marine and remote areas. Also airborne emissions from industrial processes, power plants, incineration plants, combustion facilities and all types of mobile sources can be sampled. Such sampling procedures require however specialized techniques, adapted for the high temperature and water and dust concentrations found in these samples.

While the concentrations of atmospheric aerosols may vary from a few  $\mu\text{g m}^{-3}$  up to nearly  $1 \text{ mg m}^{-3}$  the proportional composition is relatively stable. About 10-30 % of the mass of the aerosol is organic, 30 to 70 % inorganic and up to 40 % amorphous carbon can be present. Workroom dusts and exhausted particles can be present in much higher concentrations ( $1$  to  $100 \text{ mg m}^{-3}$ ) than atmospheric aerosols and their composition depends strongly on the nature of the source producing them. In studies of air pollution not only the total mass of suspended particulate and its composition must be determined, but so must the distribution of the mass as a function of the aerodynamic particle size. Samplers have been designed to separate inhalable and non-inhalable ( $> 10 \mu\text{m}$ ) particles or coarse inhalable particles ( $2.5 - 10 \mu\text{m}$ ) from fine inhalable or respirable particles ( $< 2.5 \mu\text{m}$ ). Studies of atmospheric behaviour or source attribution even require a more detailed classification as a function of particle size.

The sample to be analysed can therefore be in different physical forms or collected on different substrates. This has a strong impact on the purely instrumental techniques which do not require a removal of the dust from the collecting substrate. In principle, several techniques can be used to sample airborne particulate matter: wet and dry impaction, thermal and electrostatic precipitation, centrifugation, and filtration (refs. 2-6). Not all these techniques are, however, suited for subsequent activation analysis. The most direct way to collect a sufficient mass for weighing and analysis is by filtration of a known volume of air through a fibrous or membrane-type filter.

### Sampling total suspended particulate matter (TSPM)

If the total concentration of the elements is to be determined the particulate matter is generally collected by filtration. When high volume sampling is applied up to  $1000 \text{ m}^3$  of air can be sampled and thus 10 to 1000 mg of dust is collected on a large filter. Low volume samplers collect only a few mg of dust on 25 or 47 mm diameter filters. In order to be useful for the sampling of aerosols and subsequent elemental analysis the filters

should meet a number of requirements. These are (a) high efficiency (which is a function of particle size and face velocity), (b) a low pressure drop across the filter, (c) a low reduction of flow rate by dust loading in order to guarantee a fairly constant airflow and (d) small and reproducible blank values. Of secondary importance are hygroscopicity, ease of handling, tensile strength, thickness and finally cost. From all this it will be clear that it is difficult to find one type of filter which fulfils all these criteria. The selection of the optimum filter requires simultaneous consideration of physical and chemical properties. Because of the diversity of filter types available, the choice is not obvious, and generally the best compromise between physical and chemical merits should be sought.

The important physical properties of the commonly used filter materials and the filter efficiencies can be found in manufacturers' documentation sheets, in text books and in a number of reports or research papers (refs. 2, 6-9). Fibrous filters are made of glass fibers, cellulose, quartz, polystyrene, etc. Membrane filters are made of cellulose esters, polytetrafluoroethylene (PTFE), polyethylene, polycarbonate, silver, etc. Solely on the basis of physical properties, glass fiber filters should be used. Unfortunately, due to their inorganic nature they become highly radioactive and are therefore hardly usable when a nondestructive activation technique is applied. For subsequent elemental analysis the blank value is of course a major parameter. Therefore, extensive analyses to determine the blank values of various materials have been performed, mostly by INAA. Table 2 lists some of the obtained blank values for fibrous and membrane filters. These

**Table 2:** Impurity levels (ng cm<sup>-2</sup>) in various filter materials (refs. 9, 11, 12)

Element	W 41	W 541	MFHA + W 41	MFAA + W 41	Nucl.	QM-A
Na	150	100	800	740	45	58000
Mg	< 80	< 60	< 400	< 370	< 5	-
Al	12	11	30	17	4	-
Cl	100	400	1200	1400	-	2900
K	15	12	145	62	2	6700
Ca	140	35	810	560	3	-
Sc	< 0.005	0.004	0.006	0.008	0.0003	0.12
Ti	10	2	25	< 30	1.4	-
V	< 0.03	0.03	< 0.10	< 0.21	0.01	-
Cr	3	2	25	36	1	24
Mn	0.5	0.5	8	2.1	< 0.2	3.9
Fe	40	30	80	100	12	580
Co	0.1	0.04	0.3	0.25	0.01	9.3
Cu	< 4	2	24	17	1.2	29
Zn	< 25	3	50	< 180	0.7	880
As	< 0.1	0.04	< 0.4	0.13	0.04	-
Se	< 0.3	0.2	-	1.0	6.2	-
Br	5	2	9	7.7	2	-
Sb	0.15	0.07	0.8	0.23	0.006	4.1
La	< 0.2	0.04	< 0.6	< 0.5	< 0.003	-

W 41: Whatman 41, cellulose fiber

W 541: Whatman 541, cellulose fiber

MFHA: Millipore cellulose ester membrane (pore size 0.45 μm)

MFAA: Millipore cellulose ester membrane (pore size 0.8 μm)

Nucl.: Nuclepore membrane (pore size 0.4 μm)

QM-A: Whatman QM-A, quartz micro-fiber filter

should however be treated as merely illustrative because each lot of filters has different blanks and even within one lot significant differences of 10 to 50 % may occur. A primary prerequisite for obtaining reliable atmospheric concentration data is therefore a careful analysis of the filters to establish the filter blanks. Especially when less than 0.3 m<sup>3</sup> of air per cm<sup>2</sup> of filter material is sampled or when sampling is performed in clean areas stringent requirements are to be set for the blank determinations. The most critical elements are often Ca, Cl, Na, Cr, Al and sometimes Cu or Zn.

The best choices for high volume sampling cellulose or quartz fiber filters are probably owing to their purity, low pressure drop, low cost and ease of handling. For low volume sampling 0.45 or 3.0 µm pore size membrane filters. These filters have excellent particle retention efficiency but induce high flow resistance and therefore greatly reduce the obtainable flow rates and they become brittle and electrostatically charged. Nuclepore polycarbonate filters lack most of these disadvantages and are therefore increasingly being used.

#### **Sampling inhalable and respirable particles**

The German Technische Anleitung der Reinhaltung der Luft (ref.13) has since 1974 prescribed sampling of particles only with an aerodynamic diameter  $\leq 10$  µm. Including recommendations by an ad hoc group of the International Standards Organization (ref. 14), the EPA (Environmental Protection Agency, USA) now considers that a sampling inlet with a 10 µm cutpoint will mimic deposition in the extrathoracic regions of the human respiratory system. The fraction that penetrates into the human thorax is also called the inhalable fraction and defined as the airborne particles with diameter less than or equal to a nominal 10 µm (PM<sub>10</sub>). Size selective inlets were developed for the classical high-volume samplers and evaluated. Also cyclone pre-separators are often employed to collect the larger particles as a separate fraction, for example during emission measurements or incorporated in a personal sampler (refs. 15-18). Typical TSP/PM<sub>10</sub> ratios vary from 1.5 to 2.5. For more than 10 years the virtual or dichotomous sampler has been in operation (ref. 19). Based on impaction into a void the particles are separated into a fine or respirable fraction (0 - 2.5 µm) and a coarse fraction (2.5 - 10 µm) and subsequently collected using two 37 mm PTFE or Nuclepore (polycarbonate) filters. Ratios of coarse to fine particulate matter vary from 0.7 to 2.5 in highly industrialized areas. Since most of the elements are preferentially linked to large or to small particles this ratio can easily be as low as 0.1 and as high as 10 for particular elements.

An alternative way to separate respirable and non-respirable particles is by sequential filtration. The literature contains ample information on the use of Nuclepore filter for this purpose, and was critically reviewed by Heidam (ref. 20). A stacked filter unit (SFU) equipped with 8 µm and 0.4 µm Nuclepore filters can at a face velocity of 5 cm.s<sup>-1</sup> sample the fraction collected in the upper - and lower - respiratory tracts respectively.

#### **Measurement of mass-size functions**

More detailed information on particle size distribution can be obtained by sampling with inertial cascade impactors. Considering the fundamental role played by aerodynamic particle size in the atmospheric behaviour of aerosols, their physicochemical

properties and their toxicological effects, a study of the mass versus size dependence of the elements in the aerosol is highly desirable. In cascade impactors particles are classified on the basis of their inertia. A typical cascade impactor is made up of a number of stages consisting of a nozzle and an impaction plate. The stages can have single or multiple nozzles, consisting of circular or rectangular slots. For sampling, the impaction surfaces will generally be covered with a thin film of a pure material, such as polyethylene, Mylar, teflon, Nuclepore or cellulose. For high temperature emission measurements quartz must be used. When the blanks of these impaction surfaces are low enough a purely instrumental activation technique can again be applied, without removing the dust from the substrate. The blank values of organic polymers have been investigated by INAA and PIXE (refs. 11, 21). The use of Mylar is limited, owing to its high Mn and Sb content. The impurities seem to be present in the bulk of the material rather than the surface, making the thinnest sheeting the best.

The collection efficiencies for unit density spheres expressed as the 50 % equivalent aerodynamic cut-off diameter of the different stages vary from 15 down to 0.2  $\mu\text{m}$ , or even lower with low pressure impactors (ref. 22). Many types of cascade impactors are commercially available. An excellent discussion of the design and performances of impactors has been given by Marple and Willeke (ref. 23) and Bauman et al. (ref. 24).

#### **Preparation of samples for activation analysis**

Precautions in handling and storing the filters or impaction surfaces are basically those dictated by good analytical laboratory practice. Generally a representative fraction of the filter is cut off before irradiation. The fractionation of the filter implies the need for homogeneity of the filter or the impaction surface. If at least one fourth of the filter is analysed the uncertainty introduced by this fractionation is generally lower than 6 % (ref. 25). It should be realized that some other techniques such as Energy Dispersive X-Ray Fluorescence (EDXRF), Particle Induced X-Ray Emission (PIXE) and Electron Microprobe Particle Analysis (EMPA), etc. use a much smaller portion of the filter. In such cases large errors can be introduced. Membrane filters are quite brittle and are easily broken, which may result in loss of particulate matter. These problems can be avoided by exposing the filter to acetone, so that it can be folded into a small volume. Before irradiation it is general practice to seal the samples in precleaned polyethylene vials or polyethylene bags. In order to obtain a more reproducible sample geometry for irradiation and counting, cellulose filters and polyethylene impaction surfaces can also be wrapped in an equal amount of the same clean filter-material and pressed into a pellet (refs. 26,27). Before pressing, the polyethylene must be heated at approximately 60°C in a small die. This pelletizing procedure also assures convenience in transferring the sample from irradiation to counting vials and in storing. Also mg fractions of bulk samples of sludge, ash, etc. can be pelletized before irradiation.

### **3. NEUTRON ACTIVATION ANALYSIS**

Neutron activation analysis relies on the measurement of the radiation emitted by radioactive isotopes produced in the sample after irradiation with neutrons, mostly thermal or epithermal, in a nuclear reactor. Nowadays virtually all multielemental neutron activation procedures are based on the measurement of the  $\gamma$ -rays emitted by radio-

nuclides produced by (n, $\gamma$ ) reactions. The isotopes are identified by the energies of their  $\gamma$ -rays and quantified by the peak areas in the  $\gamma$ -spectrum. The minimum amount for detecting an element strongly depends on several factors such as the cross-section, the half-life of the isotope produced and the abundance of the gamma rays emitted. As a result the detection limits for the different elements vary over many orders of magnitude. The introduction of the high resolution Lithium-drifted Germanium [Ge(Li)] and more recently the High-Purity Germanium (HPGe)  $\gamma$ -ray detectors made a good differentiation between radioisotopes possible. The application of mini- or micro-computer assisted data reduction of the gammaspectra further opened the way to a multielemental analysis. Consequently purely Instrumental Neutron Activation Analysis (INAA) found numerous environmental applications, especially for the analysis of airborne particulate matter and fly ashes. In several text books and review articles (refs. 1, 3, 5, 28-35) on the application of neutron activation analysis to mostly solid environmental or pollution samples there is a wealth of information available. Recent and Extensive ones are those by Ehmann and Vance (ref. 34), by Das et al. (ref. 35) and by Alfassi (ref. 31). The Second Edition, Part I, Vol 14 of Treatise on Analytical Chemistry, gives a thorough treatment of the fundamentals of activation analysis and contains a chapter on environmental samples (ref. 33).

#### **Multielement instrumental neutron activation analysis**

Instrumental Neutron Activation Analysis (INAA) is feasible only when the activity induced in the matrix is not prohibitively high and no single major activity is produced that overshadows that of the other radioisotopes. Many environmental samples, such as atmospheric aerosols collected on a clean organic filter are especially well suited for such nondestructive activation analysis. The major components of such a sample - organic compounds, carbon, water, sulfate, nitrate and ammonia - do not produce significant  $\gamma$ -activities. In the organic fraction, the elemental concentrations are balanced so that most of them can be determined in the presence of each other. The most abundant elements - Si, Fe, Ca, Mg and Cl - have relatively low cross-sections or low probability for  $\gamma$ -transitions. The high Na content of marine aerosols can give rise to a troublesome  $^{24}\text{Na}$  ( $t_{1/2} = 24$  h) activity. In continental aerosols the dominant activity after a short irradiation is  $^{28}\text{Al}$  ( $t_{1/2} = 2.3$  min). After a longer irradiation and after a few days cooling time,  $^{82}\text{Br}$  ( $t_{1/2} = 36$  h) is predominant in urban aerosols. The spectral interferences caused by these radionuclides, however, by no means impede INAA. In the purely instrumental technique only rarely the extremely low detection limits of radiochemical techniques are approached, but in environmental studies this is generally not needed. More importance is attached to the multielemental character of the analysis, the relative ease with which it can be applied to a large number of samples, and the possibility of automating measurements and data reduction. After the first attempts at applying INAA to aerosols with the aid of NaI detectors for a few elements (refs. 36, 37), the major breakthrough came with the introduction of high resolution germanium detectors. When the parameters of analysis, which include irradiation, waiting and counting times, amount of sample, and counting geometry, are optimized, one can typically determine 30-40 elements in airborne particulate matter. These parameters depend not only on



nuclear characteristics, but also on the composition of the sample. With automatic data reduction of  $\gamma$ -spectra, large numbers of similar samples can be processed routinely fairly rapidly by semi-unskilled personnel if only the most intense radioisotopes are measured. With the utmost refinement of the art, that is for high neutron fluences, long counting times and the highest resolution of the spectrometer, up to 47 elements can be determined in samples of atmospheric aerosols (ref. 38), stack or exhaust emissions, dry fall-out, sewage sludge, incineration ash, etc.

Since the publication in 1970 of the papers by Zoller et al. (ref. 39) and by Dams et al. (ref. 40) the literature now contains a large number of papers on the INAA of airborne particulates, referred to in previously mentioned textbooks (refs. 33,35) and review articles (refs. 1, 41). Fields of investigation include urban (refs. 42, 43), industrial (refs. 26, 44), rural (refs. 45, 46, 47), marine (ref. 48) and remote background aerosols (refs. 27, 49). In pollution monitoring and abatement and in understanding the atmospheric environment, where speed and reliability are vital, INAA has already played and will play an important role. To reach these goals several approaches have been used, such as areawide studies, time series analyses, and source characterization. Of very much interest, of course, are particle size analyses, to study potential toxicological effects, for source identification, and to learn about atmospheric behavior. Many of the research papers on INAA of atmospheric aerosols report particle size distributions for up to 35 elements obtained after cascade impactor sampling (ref. 50).

Because coal combustion contributes significantly to the pollution burden of the atmosphere, it was realized at an early stage that the trace element contents of coal should be measured. Since the carbon matrix does not produce  $\gamma$ -emitting isotopes, roughly the same INAA procedure as the one used for atmospheric aerosols can be applied for the determination of more than 30 trace elements. It is obviously of importance also to understand the behavior of the elements during combustion, their emission rate and their atmospheric transport. Therefore the multielement analysis of fly ash, the percentage transfer to the atmosphere, and the particle size distribution of the elements were also studied with this powerful technique at a number of coal-fired boilers and power plants (refs. 51-54). An excellent textbook has been written on the subject by Valkovic (ref. 30). Fly ash can be collected in a similar way as atmospheric particulates on filters or in cascade impactors. As for aerosols thermal and epithermal activation can be applied (ref. 55). The use of INAA allows the determination of 30 to 40 elements in the particulate emission of municipal incinerators, in collected fly ash and in bottom ash, also in sewage sludge, compost and urban road dust (refs. 56-62).

In spite of its major advantages, INAA also has some considerable drawbacks. No information is provided about the chemical state of the element, which is of vital importance in learning about the environmental behaviour and toxicological effects of the elements. Future developments should therefore encompass some pre-irradiation chemical separations, enabling the determination of trace amounts of different chemical species. Some first attempts have been made for the elements Hg, V, Cr and Se (ref. 63). However the absence of more recent work indicates the relative unsuitability of the technique for speciation work. Chromatographic separation techniques are probably least liable to introduce large contaminations or to alter the speciation significantly.

Another major disadvantage is further the lack of information on toxicologically important elements such as Be, Bi, B, P and Tl, owing to the low cross-section of these elements. Special irradiation procedures are needed for F, Pb and U. Also the sensitivity for Cd, Mo, Ni, Te, S and Sn is hardly sufficient for a purely instrumental approach by NAA owing to low cross-sections, insufficient  $\gamma$ -intensities or unfavorable half-lives. Radiochemical separations are often required. At high neutron fluxes only small samples (< 30 mg) can be used. When efficient homogenization procedures, such as the brittle fraction technique, are applied this drawback can be overcome and representative samples can be analysed (ref. 56).

#### **Irradiation-counting scheme**

Although the present germanium detectors have a high resolution, the detectability of a  $\gamma$ -ray line in the spectrum, and thus of a radionuclide, still depends on the presence of other nuclides with high intensity. In fact most interactions of the electromagnetic radiation with the detector give rise to the Compton effect, which results in a count in the Compton continuum region which extends essentially from 0 keV up to nearly the full energy peak position in the spectrum. Consequently this Compton continuum of high energy  $\gamma$ -rays forms a background which masks low intensity  $\gamma$ -rays of lower energy. Fortunately the length of the irradiation and the decay time between the end of the irradiation and the counting can be adapted to favor the detectability of short- or long-lived isotopes. The former are measured quickly after a short irradiation, while the latter are measured after longer irradiation and decay times to allow the decay of short-lived isotopes. Finally the counting time can be adapted to the intensity of the sample and the half-life of the isotopes to be measured.

In a multielement analysis it is not feasible to choose for each element the optimal irradiation, cooling and counting conditions; a compromise must be found. The balance between the working up of a reasonable number of samples and the desired quality of the analytical results will finally dictate the mode of the irradiation-counting scheme. Many examples of such schemes are to be found in the literature (refs. 9, 38, 39, 51, 56, 62, 64, 67); most, however, are quite similar to the one originally described by Dams et al. (ref. 40). This scheme consists of two irradiations and four or five  $\gamma$ -spectrometric measurements. For the determination of the elements giving rise to short-lived isotopes, a portion of each filter or 2 to 20 mg of dust, is irradiated for 5 min. After a cooling time of 3 min,  $^{28}\text{Al}$ ,  $^{37}\text{S}$ ,  $^{49}\text{Ca}$ ,  $^{51}\text{Ti}$ ,  $^{52}\text{V}$ , and  $^{66}\text{Cu}$  can be measured over 6 min period. A second measurement for 20 min follows after 15-min decay for  $^{24}\text{Na}$ ,  $^{27}\text{Mg}$ ,  $^{38}\text{Cl}$ ,  $^{56}\text{Mn}$ ,  $^{80}\text{Br}$ ,  $^{116\text{m}}\text{In}$ ,  $^{128}\text{I}$ , and, occasionally,  $^{165}\text{Dy}$  and  $^{139}\text{Ba}$ . In between, after 12 min decay, for example, a simultaneously irradiated flux monitor can be measured for 30 s to 2 min. The same or a larger portion (10 to 100 mg dust) of the filter or the impaction surface is irradiated for several hours. Up to 15 samples can be irradiated at the same time as one or two standard samples. After cooling for one day, the samples are counted over 20 to 30 min for  $^{24}\text{Na}$ ,  $^{42}\text{K}$ ,  $^{64}\text{Cu}$ ,  $^{69\text{m}}\text{Zn}$ ,  $^{76}\text{As}$ ,  $^{82}\text{Br}$ ,  $^{122}\text{Sb}$ ,  $^{135\text{m}}\text{Ba}$ ,  $^{140}\text{La}$ ,  $^{153}\text{Sm}$ , and possibly  $^{72}\text{Ga}$ ,  $^{187}\text{W}$ ,  $^{152\text{m}}\text{Eu}$ , and  $^{198}\text{Au}$ . In order to decrease the  $^{24}\text{Na}$  and  $^{82}\text{Br}$  interference, additional counting after 3-6 days is often helpful for better detection of  $^{99}\text{Mo}$ - $^{99\text{m}}\text{Tc}$ ,  $^{115}\text{Cd}$ - $^{115\text{m}}\text{In}$ ,  $^{122}\text{Sb}$ ,  $^{140}\text{La}$ ,  $^{153}\text{Sm}$ ,  $^{175}\text{Yb}$  and  $^{198}\text{Au}$ . Unfortunately, the most valuable information is obtained only after a 15-20 day cooling time when  $^{82}\text{Br}$  has

nearly completely decayed. The following isotopes can then readily be counted:  $^{46}\text{Sc}$ ,  $^{51}\text{Cr}$ ,  $^{59}\text{Fe}$ ,  $^{60}\text{Co}$ ,  $^{65}\text{Zn}$ ,  $^{75}\text{Se}$ ,  $^{124}\text{Sb}$ ,  $^{134}\text{Cs}$ ,  $^{141}\text{Ce}$ ,  $^{203}\text{Hg}$  and  $^{233}\text{Pa}$  (from  $^{233}\text{Th}$ ). In favorable cases some of the following isotopes can also be detected:  $^{58}\text{Co}$  (from Ni),  $^{86}\text{Rb}$ ,  $^{110\text{m}}\text{Ag}$ ,  $^{131}\text{Ba}$ ,  $^{152}\text{Eu}$ ,  $^{177}\text{Lu}$ ,  $^{181}\text{Hf}$ ,  $^{182}\text{Ta}$ , and  $^{192}\text{Ir}$ . Tables 3 and 4 list the nuclear reactions, the half-lives, and the main  $\gamma$ -transitions of the generally detectable isotopes. In addition realistic limits of detection, obtainable in routine conditions in urban aerosols are given. The irradiation counting scheme described above has the potential to determine 42 elements under the most favorable conditions. In general practice, however, in most environmental or pollution samples this is decreased to some 30 elements, while for the other elements only upper limits are obtained. Shorter and less complicated schemes have been used (ref. 68). The gain in counting and data-processing time per sample is achieved at the expense of precision and number of elements determined.

The multielement character of INAA, the volume of data resulting from  $\gamma$ -spectrometry and its routine application to a large number of samples have made use of a computer for data reduction a necessity. Many programmes for  $\gamma$ -ray spectra-reduction have been written and are now commercially available. Descriptions of these can be found in the literature. In a well documented chapter of the earlier mentioned book in the "Kolthoff-series" (ref. 33), Erdtmann and Petri (ref. 69) have evaluated the existing software together with fundamentals and practical details on irradiation facilities and counting equipment, including detectors and electronics. Also Bode et al. have described computerized irradiation-decay-counting systems (ref. 70).

**Table 3:** Nuclear Data of Isotopes Measured and Detection Limits in Aerosols after 5 min Irradiation (ref. 33)

Element	Isotope	Half-life	$\gamma$ -Ray used (keV)	Decay time (min)	24-h (Hi-vol) Urban sampling (ng m <sup>-3</sup> )	
					Detection limit	Typical conc.
Al	$^{28}\text{Al}$	2.31 min	1778.9	3	8	1500
S	$^{37}\text{S}$	5.05 min	3102.4	3	10,000	5000
Ca	$^{49}\text{Ca}$	8.7 min	3084.1	3 or 15	500	4000
V	$^{52}\text{V}$	3.75 min	1434.0	3	1	50
Ti	$^{51}\text{Ti}$	5.1 min	320.1	3	10	200
Cu	$^{66}\text{Cu}$	5.1 min	1039.2	3	100	100
Na	$^{24}\text{Na}$	15 h	1368.6	15	50	1500
Mg	$^{27}\text{Mg}$	9.45 min	1014.2	15	1,000	1000
Cl	$^{38}\text{Cl}$	37.3 min	1642.7;2167.4	15	100	3000
Mn	$^{56}\text{Mn}$	2.68 h	846.9;1810.7	15	0.6	200
Br	$^{80}\text{Br}$	17.4 min	616.8	15	4	200
	$^{80\text{m}}\text{Br}$	4.4 h	616.8			
In	$^{116\text{m}}\text{In}$	54 min	417.0;1097.1	15	0.1	0.3
I	$^{128}\text{I}$	25 min	442.8	15	15	10

**Table 4:** Nuclear Data of Isotopes Measured and Detection Limits in Aerosols after Several Hours Irradiation (ref. 33)

Element	Isotope	Half-life	$\gamma$ -Ray used (keV)	Decay time (min)	24-h (Hi-vol) Urban sampling (ng m <sup>-3</sup> )	
					Detection limit	Typical conc.
Na	<sup>24</sup> Na	15 h	1368.6	1	10	1500
K	<sup>42</sup> K	12.4 h	1524.7	1	50	1500
Cu	<sup>64</sup> Cu	12.7 h	511.0	1	100	100
Zn	<sup>69m</sup> Zn	13.8 h	438.6	1	300	500
As	<sup>76</sup> As	26.3 h	657.0;1215.8	1-5	4	20
Ga	<sup>72</sup> Ga	14.1 h	834.0	1	2	3
Br	<sup>82</sup> Br	35.3 h	619.1;776.5	1-5	2	700
Mo	<sup>99</sup> Mo	66.0 h	739.5	5		
	<sup>99m</sup> Tc	6.0 h	140.5	5	200	2.5
Sm	<sup>103</sup> Sm	46.5 h	103.2	1-5	0.1	0.3
Cd	<sup>115</sup> Cd	53.5 h	527.8	5	10	10
Sb	<sup>122</sup> Sb	2.7 d	564.1	1-5	1	10
La	<sup>140</sup> La	40.2 h	1596.2	1-5	0.1	2
Eu	<sup>152m</sup> Eu	9.2 h	963.5	1	0.03	0.05
Lu	<sup>177m</sup> Lu	6.7 d	208.4	5-10	0.02	0.01
W	<sup>187</sup> W	23.9 h	687.7	1-5	1	1
Au	<sup>198</sup> Au	2.7 d	411.8	5	0.01	0.03
Sc	<sup>46</sup> Sc	83.8 d	889.3;1120.5	10-20	0.01	0.3
Cr	<sup>51</sup> Cr	27.7 d	320.1	10-20	1	15
Fe	<sup>59</sup> Fe	45.1 d	1099.2;1291.6	10-20	50	2500
Ni	<sup>58</sup> Co	71.3 d	810.7	10-20	50	30
Co	<sup>60</sup> Co	5.2 y	1173.3;1132.5	10-20	0.1	2
Zn	<sup>65</sup> Zn	144 d	1115.5	10-20	5	500
Se	<sup>75</sup> Se	120 d	264.6	10-20	1	4
Rb	<sup>86</sup> Rb	18.7 d	1076.8	10-20	1	2.5
Ag	<sup>110m</sup> Ag	250 d	657.7	10-20	1	0.5
Sb	<sup>124</sup> Sb	60.2 d	1691.0	10-20	1	10
Cs	<sup>134</sup> Cs	2.1 y	795.8	10-20	0.1	1
Ba	<sup>131</sup> Ba	11.5 d	216.1	10-20	50	100
Ce	<sup>141</sup> Ce	32.5 d	145.4	10-20	0.5	3
Eu	<sup>152</sup> Eu	12 y	963.5	10-20	0.1	0.05
Hg	<sup>203</sup> Hg	46.6 d	279.2	10-20	0.5	1
Th	<sup>233</sup> Pa	27.0 d	311.8	10-20	0.1	0.3

### Special irradiation and counting procedures

The ultimate way to optimize the experimental conditions in NAA is to irradiate the sample with neutrons having the most appropriate energy distribution spectrum, for the most appropriate time and counting them at the most favourable moment with a selected type of detector. The reaction rate for an  $(n,\gamma)$  reaction is given by

$$R(n,\gamma) = \sigma_0 \phi_0 \left( 1 + \frac{\phi_{epi}}{\phi_{th}} \cdot \frac{I}{\sigma_0} \right)$$

where  $\phi_{th}$  and  $\phi_{epi}$  are the thermal and epithermal neutron flux respectively and  $\sigma_0$  and  $I$  are the thermal neutron cross section and the resonance integral, respectively. From this equation it is clear that the activity of radionuclides having a high  $I/\sigma_0$  ratio can be enhanced by suppressing the thermal neutron flux. This can be accomplished by irradiation under cadmium, boron carbide or nitride cover. Steinness discussed carefully the advantages and limitations of epithermal neutron activation analysis (ref. 71). It was applied to air dust samples (ref. 72) and for other solid environmental samples such as coal and fly ash (refs. 73, 74). Lower limits of determination than with thermal neutrons are obtained for elements such as U, Th, In, Au, Ta, Ag, Br, Co, Sb, etc. Short irradiation (10 to 30 s), under cadmium cover allows a better limit of determination for Se, Ag and Hf, but more important is the detection of F, which can otherwise not be detected by NAA. It can be determined with thermal neutrons by  $(n,\gamma)$  reaction producing  $^{20}F$  ( $t_{1/2} = 11.2$  s) or under cadmium cover by an  $(n,p)$  reaction producing  $^{19}O$  ( $t_{1/2} = 29$  s) (ref. 75).

Even shorter lived isotopes ( $t_{1/2} < 10$  s) can be measured after cyclic irradiation in a high-flux pulsed reactor, followed by cyclic counting (refs. 76-79). By measuring the characteristic X-ray of  $^{207m}Pb$  ( $t_{1/2} = 0.8$  s), Pb and several other elements such as Cl, Se, F, Sc, In, Hf, W and Au can be measured with a superior limit of determination.

Irradiation with 14 MeV neutrons produced by a Cockroft-Walton accelerator is only applicable for the determination of major components such as Si, O, Cl, Al, Ca, Fe, etc. owing to the limited neutron flux (refs. 80-84). Nowadays a total neutron output of  $5 \times 10^{12}$  n.s<sup>-1</sup> is obtainable. The elements Fe, Mn, Cr and Ni were determined in welding aerosols by Tölgyessy et al. (ref. 85).

The possibilities of using very thin detectors with extremely high resolution for low energy photons (Low Energy Photon Detectors, LEPD) in multielement NAA of environmental samples have been investigated (refs. 39, 72, 86). Weaver (ref. 87) listed the isotopes, which are suitable for detection with a LEPD. In general it was found that limited additional information is obtained (for example for some rare earths) and a better precision was obtained for Cu, Zn, Se or Hf determination.

The delayed neutron method can be used for the determination of U with a rather high limit of determination (ref. 78).

Radiochemical NAA has not frequently been applied to solid environmental or pollution samples. It is most useful for the detection of one or a few elements, which are not detectable in the instrumental way (ref. 89). Pietra et al. (ref. 90) have recently published a very useful review of 22 radiochemical separation procedures for environmental and biological samples.

### Calibration procedures

As explained before calibration is relatively straightforward owing to the near absence of matrix effects and to the linearity of the gamma counting. Standards can be co-irradiated and flux monitors used to correct for flux gradients in the irradiation container (ref. 91). Standards are most conveniently prepared by spotting a known amount of a standard solution on a clean filter, dried and treated in the same way as the samples. Much attention must be paid to the preparation of such standard solutions with low metal ions content, to avoid adsorption on the walls, precipitation, etc. As it is too impractical to prepare each standard separately, a general practice consists in combining several elements in proportions simulating roughly the aerosol composition into one stable solution. The amounts of elements present close to the detection limit are increased in order to obtain a larger  $\gamma$ -peak with sufficient counting statistics. Thus the shape of the standard spectrum, the dead time of the spectrometer and its decrease can be made to resemble that of the sample. When use is made of the short-lived isotopes, only very few investigators co-irradiate a standard with the sample. Large corrections for decay are needed in such procedures because the counting times are of the same order of magnitude as the half-lives of the measured isotopes. Most authors irradiate separately mixtures of the elements to be determined and monitor the flux during each irradiation. Several elements such as Ti, Al, Rb, Ni and Mn are used as flux monitors (refs. 40, 68, 92). When using Ni, three  $\gamma$ -peaks of energies varying from 365 to 1481 keV are used. This corrects largely for the slight energy dependence of the variation of the detector efficiency as a function of distance. Thus this procedure allows the measurement under different geometries for separate samples provided that the flux monitor is also measured in the same geometry as the sample. Monitors producing isotopes of sufficiently short half-life, such as  $^{51}\text{Ti}$  and  $^{28}\text{Al}$ , can be used repeatedly for a large number of analyses. Sometimes single-element standards have been used also for the calibration of the longer-lived isotope intensities (ref. 92).

To overcome the time-consuming and labor intensive work of preparing multi-element standards, single or double flux monitors with very different  $I_0/\sigma_0$  ratios such as Au and Co have been used in NAA. A much better approach is the so-called  $k_0$ -method, introduced by Simonits and De Corte (ref. 93).  $k_0$  is a "compound" nuclear constant determined for each  $\gamma$ -ray of the radionuclides used. Only an in-Al-diluted Au and Zr-monitors must be co-irradiated to determine the neutron flux and the epithermal-to-thermal flux ratio. At present little use has been made of the  $k_0$ -method in the analysis of environmental samples, but the method is quickly gaining popularity and will probably be applied more and more in the near future for routine applications.

A third alternative is the use of standard reference materials of composition similar to the sample such as standard rocks (BCR-1; W-1; G-1), coal fly ash (NBS-SRM 1633a; BCR-CRM-038) or suspended particulates (NBS-SRM-1648) (ref. 94). Since this procedure leads to a propagation of errors and only the most interesting elements are certified with high precision this approach should not be applied in accurate work. Reference materials should be used in quality assurance programmes, however.

### Accuracy and precision

INAA can be a very accurate technique for analysis of solid environmental samples provided some precautions are taken to avoid systematic errors. Errors due to neutron self-shielding are unimportant, because small amounts of material are being irradiated and because the samples consist largely of inert organic and carbonaceous material. Also, interferences due to second-order reactions can generally be neglected unless there is a matrix element in some particular sample giving rise to such interferences. Interferences due to threshold reactions are very rare under normal irradiation conditions ( $\phi_{th}/\phi_{fast} > 1$ ). Only the reactions  $^{27}\text{Al}(n,p)^{27}\text{Mg}$  and  $^{37}\text{Cl}(n,p)^{37}\text{S}$  interfere with the determination of Mg and S. Corrections are generally feasible. The low U content of environmental materials makes interferences by fission also negligible.

Since  $\gamma$ -rays are not strongly absorbed or scattered by matter, corrections for absorption are generally negligible when counting 1 to 100 mg samples. Even with the high energy resolution of the germanium detector, spectral interferences can make the use of prominent photopeaks of some isotopes difficult. Examples are 844.0 keV for  $^{27}\text{Mg}$  (846.8 keV of  $^{56}\text{Mn}$ ), 121.1 keV for  $^{75}\text{Se}$  (122.8 keV of  $^{152}\text{Eu}$ ), 279.1 keV for  $^{203}\text{Hg}$  (279.6 keV of  $^{75}\text{Se}$ ) and 511.0 keV for  $^{64}\text{Cu}$  (external pair production of high-energy  $\gamma$ -rays). These problems can mostly be overcome by choosing another peak or making corrections determined from pure isotope spectra.

With short-lived isotopes, corrections for count losses due to the dead time of the analyzer or pulse pile-up can be cumbersome. The application of a dead-time stabilizer or a pulse pile-up rejector may be useful.

Because the sources of random errors in NAA are generally known they can be kept under control. Therefore the reproducibility and the precision can be as good as the counting statistics, when good laboratory practice is applied. In favorable cases it can be as little as 1 to 2 %. Owing to the small amount of sample analyzed (1 to 100 mg) the largest contribution to random error is often sample inhomogeneity or variability in samples taken for the same environmental parameter, at different times or locations (refs. 25, 95, 96, 97). Continuous quality control was described by Heydorn (ref. 98).

The accuracy depends to a large extent on the composition of the standards. As described above, standards are generally prepared by carefully mixing of solutions of the elements to be determined in proportions such that the form of the spectrum and the dead-time resemble as closely as possible that of the samples. By this procedure most kinds of counting errors or uncertainties associated with peak area determination are largely avoided. To evaluate the accuracy of analyses of aerosols there is still a stringent need for developing standard reference materials certified for their trace elements content (ref. 99). Existing standard reference materials of urban dust and coal fly ash prepared by NIST and BCR are sometimes certified for only a small number of elements. The certification is often largely based on INAA results. In addition indicative values are often available for other elements and in the literature many data can be found for reference materials such as SRM 1648, SRM 1632, SRM 1633a. Inter-comparison exercises have shown the accuracy of INAA to be consistently good for analyses of solid environmental samples when appropriate precautions are taken (refs. 100, 101). As a result of this NAA plays a very important role in the certification of reference materials (ref. 102).

### Sensitivities and detection limits

The sensitivities, that is the photopeak areas per unit of mass of the elements, obtained by INAA are not immutable because they depend not only on nuclear constants but also on the neutron flux, the irradiation-counting scheme applied and the detector used. The detection limits depend on the sensitivities but also on the size and composition of the sample as well as the background of the detector. In typical environmental samples especially high Na and Br contents have deleterious effects on the detection limits. When airborne dust particles have been collected on filters or other substrates, the variability on the blanks may be the limiting factor. Detection limits (in  $\mu\text{g}$  or  $\mu\text{g}\cdot\text{g}^{-1}$ ) are therefore hardly meaningful. The detection limits given in tables 3 and 4 for urban aerosols collected during 24 hours with a high volume sampler should only be considered as illustrative. These detection limits were computed according to the  $L_Q$  criterion of Currie, and are thus quite conservative (ref. 103). When compared to other techniques, INAA is often found to be superior (refs. 104, 105). At lower air sampling rates or for shorter sampling times, longer irradiations, higher neutron fluxes, or longer counting times must be applied to larger filter fractions. In very remote places, such as the South Pole, sampling times of 1-4 weeks are needed for the detection of 30 elements at very low concentrations (ref. 12).

### 4. PHOTON ACTIVATION ANALYSIS (PAA)

Instrumental Photon Activation Analysis (IPAA) has been described for the multi-element analysis of different environmental samples (ref. 106). Using bremsstrahlung with energies varying from 10 to 45 MeV, the thresholds of  $(\gamma, n)$ ,  $(\gamma, p)$ , and  $(\gamma, 2n)$  reactions can be overcome, often producing isotopes with half-lives and  $\gamma$ -ray energies convenient for analysis. Sometimes the production of short-lived metastable isomers by a  $(\gamma, \gamma)$  reaction is also helpful. Since, as a result of the excitation functions and the shape of the bremsstrahlung spectrum, the yields of these reactions increase monotonically with increasing atomic number, the heavy metals can often be observed in the presence of much greater quantities of low atomic number material. Of the light elements abundant in environmental materials, only the activation of C introduces important interferences in  $\gamma$ -ray spectrometry. In fact, the annihilation radiation of  $^{11}\text{C}$  ( $t_{1/2} = 20$  min) dominates the spectrum shortly after irradiation. Therefore the use of isotopes with half-lives  $< 30$  min is nearly excluded. Feasibility studies on atmospheric particulates collected on filters were performed by Hislop et al. (ref. 107) and Aras et al. (ref. 108); 15 to 20 elements could be detected, of which Pb, Tl, Ni, Mo, and Zr can hardly if at all be determined by INAA. More detailed studies were described by Chattopadhyay et al. for analysis of sewage sludge, soil, suspended matter in estuarine water, coal, etc. (refs. 109-111). Thirty-four elements are determined routinely by several irradiations at 15, 20, 22, 35, and 44 MeV maximum bremsstrahlung energies for 1 h. Ge(Li)  $\gamma$ -ray spectrometry is carried after decay times varying from 20 min to 3 weeks. The precision and accuracy were found to be  $\pm 10\%$  or better. Table 5 summarizes the reactions used and the isotopes produced. Other authors have used IPAA for the analysis of atmospheric aerosols (ref. 112) and coal or fly ash (refs. 114, 115) with beams of maximum energy 30 or



**Table 5:** Nuclear Data of Elements Determined by IPAA (ref. 110)

Element	Reaction	E <sub>sep</sub> (MeV)	t <sub>1/2</sub>	γ-energy (keV)
Ag	<sup>107</sup> Ag(γ,n) <sup>106m</sup> Ag	9.6	8.4 d	451
As	<sup>75</sup> As(γ,n) <sup>74</sup> As	10.2	17.9 d	596
Ba	<sup>136</sup> Ba(γ,n) <sup>135m</sup> Ba	9.1	28.7 h	268
Bi	<sup>209</sup> Bi(γ,3n) <sup>206</sup> Bi	22.5	6.24 d	803
Ca	<sup>44</sup> Ca(γ,p) <sup>43</sup> K	12.2	22 h	373
Cd	<sup>111</sup> Cd(γ,γ) <sup>111m</sup> Cd	-	49 min	247
Ce	<sup>140</sup> Ce(γ,n) <sup>139</sup> Ce	9.2	138 d	166
Cl	<sup>35</sup> Cl(γ,n) <sup>34m</sup> Cl	12.6	32.4 min	2128
Co	<sup>59</sup> Co(γ,n) <sup>58</sup> Co	10.5	71.3 d	811
Cr	<sup>50</sup> Cr(γ,2n) <sup>48</sup> Cr	23.3	23 h	310
Cs	<sup>133</sup> Cs(γ,n) <sup>132</sup> Cs	9.0	6.5 d	668
Fe	<sup>54</sup> Fe(γ,np) <sup>52</sup> Mn	20.9	5.6 d	1433
Hg	<sup>198</sup> Hg(γ,n) <sup>197m</sup> Hg	8.3	24 h	134
In	<sup>113</sup> In(γ,γ') <sup>113m</sup> In	-	100 min	393
K	<sup>39</sup> K(γ,n) <sup>38</sup> K	13.1	7.7 min	2170
Mg	<sup>25</sup> Mg(γ,p) <sup>24</sup> Na	12.1	15 h	1368
Mn	<sup>55</sup> Mn(γ,n) <sup>54</sup> Mn	10.2	303 d	835
Mo	<sup>100</sup> Mo(γ,n) <sup>99</sup> Mo	8.3	67 h	140
Na	<sup>23</sup> Na(γ) <sup>22</sup> Na	12.4	2.6 y	1274
Ni	<sup>58</sup> Ni(γ,n) <sup>57</sup> Ni	12.2	36 h	1378
Pb	<sup>204</sup> Pb(γ,γ') <sup>204m</sup> Pb	-	67 min	899
Rb	<sup>85</sup> Rb(γ,n) <sup>84</sup> Rb	10.5	33 d	881
Sb	<sup>123</sup> Sb(γ,n) <sup>122</sup> Sb	9.0	2.8 d	564
Sc	<sup>45</sup> Sc(γ,n) <sup>44</sup> Sc	11.3	3.92 h	1156
Se	<sup>82</sup> Se(γ,n) <sup>81m</sup> Se	9.3	57 min	103
Si	<sup>30</sup> Si(γ,p) <sup>29</sup> Al	13.5	6.5 min	1273
Sn	<sup>118</sup> Sn(γ,n) <sup>117m</sup> Sn	9.3	14 d	158
Sr	<sup>86</sup> Sr(γ,n) <sup>85m</sup> Sr	11.5	70 min	232
Te	<sup>130</sup> Te(γ,n) <sup>129</sup> Te	8.4	69 min	459
Ti	<sup>49</sup> Ti(γ,p) <sup>48</sup> Sc	11.3	1.83 d	1039
Tl	<sup>203</sup> Tl(γ,n) <sup>202</sup> Tl	7.7	12 d	440
V	<sup>50</sup> V(γ,2n) <sup>48</sup> V	20.9	16 d	983
Zn	<sup>66</sup> Zn(γ,n) <sup>65</sup> Zn	11.1	245 d	1115
Zr	<sup>90</sup> Zr(γ,n) <sup>89</sup> Zr	12.0	78.4 h	909

35 MeV. A Japanese research group has used some major and minor constituents in sediments as internal standards for IPAA (ref. 116). Accurate and precise results were obtained for 15 elements.

The application of X-ray spectrometry with an low energy photon detector was compared to γ-ray spectrometry in IPAA of water and coal samples by Weise et al. (ref. 117). The detection limits were found to be comparable for both methods for a number of elements heavier than Ti. The use of anti-Compton γ-ray spectrometry decreases the limit of detection of the IPAA of coal for some elements by up to a factor of 3 (ref. 118). Also prompt γ-activation has been applied for measuring the concentrations of a number of trace elements in various environmental samples (ref. 119).

In summary, IPAA presents an attractive alternative to INAA for the multielement analysis of environmental samples, especially because most heavy metals with potential toxicological effects such as Pb, Cd, Hg, Tl, Zn, Ni, As, Sb, Se, and Sn can be determined purely instrumentally. The major drawback is the relatively rare availability of high energy electron beams with sufficient intensity. By a combination of the complementary methods INAA and IPAA most interesting elements with atomic number above 10 can be determined in environmental samples (ref. 120).

Photon activation can also be applied for single element radiochemical determinations. An example is the determination of F in environmental samples by the reaction  $^{19}\text{F}(\gamma, n)^{18}\text{F}$  and distillation of hydrogen fluoride from a sulphuric acid medium. The annihilation radiation is counted with a fast coincidence circuit (ref. 121).

### 5. CHARGED PARTICLE ACTIVATION ANALYSIS (CPAA)

Charged particles (protons, deuterons, helium-3 and helium-4 with energies from a few MeV up to about 50 MeV), produced by a cyclotron, have been used for activation analysis of solid environmental materials. The fundamentals of CPAA and its major applications have recently been reviewed in an excellent textbook by Vandecasteele (refs. 122-123). The development and the application of this activation technique have been much slower and more limited than of NAA and PAA, for several reasons. Briefly summarized, these are the more complex nature, the limited penetration range of charged particles in matter, the limited availability of particle accelerators up to some years ago and finally the heating up of samples during irradiation. The latter reason has especially deleterious effects on the analysis of environmental samples with a low thermal conductivity. It results in volatilization of the element of interest or of part of the matrix. The problem was studied by Wauters et al. (ref. 124). For powdered environmental and rock samples irradiation under a He atmosphere with a minimum beam intensity was recommended.

The small penetration depth of the particles varies considerably with the nature of the matrix. Thus the composition of the sample and the standard must in principle be known to calculate the stopping power for standardization purposes. However matrices such as rock or fly ash are mainly composed of Mg, Al, Ca and Fe silicates for which the stopping powers vary only slightly. Problems arise, however, when organic compounds are present because C and especially H have much higher stopping powers. Two solutions have been offered for this problem; namely removal of the organic material by low-temperature ashing or use of a major component with known concentration as internal standard (refs. 116, 125).

Lead has most frequently been determined in environmental materials by CPAA (refs. 126 - 128). Irradiation with high energy protons gives rise to  $^{204}\text{Bi}$  ( $t_{1/2} = 11.2$  h) and  $^{206}\text{Bi}$  ( $t_{1/2} = 6.2$  d). The shorter-lived isotope allows rapid determinations, making the method suitable for routine determinations in airborne particulates collected on a filter. Simultaneous 30 minute irradiations and counting times varying from 5 to 50 minutes result in detection limits of  $1 \text{ ng cm}^{-2}$  (ref. 126). Also  $^3\text{He}$  activation has been applied (ref. 129) for Pb determination in airborne particulates. In coal and fly ash S has been determined by proton activation giving rise to Cl isotopes (refs. 130, 131).

Multielement instrumental CPAA is also possible. It has been applied with 30-MeV protons for airborne particulates collected on a filter and with 12 MeV protons for powdered environmental samples. In a typical urban aerosol sample 18 elements, including Cr, Mn, Ni, Cu, Zn, As, Cd, Sn, Sb and Pb, could be determined with 30 MeV protons after sampling 10 m<sup>3</sup> of air (ref. 132). While the higher energy protons give better sensitivity, the lower energetic particles reduce nuclear interferences from, for example (p,d) and (p, $\alpha$ ) reactions. Table 6 lists the nuclear reaction induced by 12 MeV protons for 12 elements which were accurately determined in a reference material (BCR-CRM 176) and in fly ash. The interferences were generally negligible (ref. 125). In both procedures 2 or 3 counting sessions after decay times varying from 4 h to 10 days were needed.

The detection limits given in Table 6 for incineration ash are largely determined by the complex nature of the material, which had extremely high concentrations of many heavy metals. In other environmental materials these concentrations are orders of magnitude lower. However it was shown that for the three environmentally important elements Cd, Pb and Tl, a radiochemical procedure yields detection limits of 6, 25 and 44 ng g<sup>-1</sup> (ref. 134); <sup>111</sup>In, <sup>206</sup>Bi and <sup>203</sup>Pb were separated by an ion exchange procedure.

In earlier work (ref. 135) the promptly emitted  $\alpha$ -particles were counted during irradiation with 1.4 to 2 MeV protons for the determination of the light elements Li, B and F in particulates collected in a marine atmosphere (ref. 121).

**Table 6:** Nuclear reactions used in CPAA with 12 MeV protons (ref. 125)

Element	Nuclear Reaction	Threshold Value (MeV)	t <sub>1/2</sub>	$\gamma$ -energy used (MeV)	Detection limit ( $\mu\text{g g}^{-1}$ )*
Ca	<sup>44</sup> Ca(p,n) <sup>44</sup> Sc	4.5	3.93 h	1157.0	660
	<sup>44</sup> Ca(p,n) <sup>44m</sup> Sc	4.5	2.44 d	271.4	2500
Ti	<sup>48</sup> Ti(p,n) <sup>48</sup> V	4.9	16.1 d	983.5	10
Cr	<sup>52</sup> Cr(p,n) <sup>52m</sup> Mn	5.6	21.3 min	1434.3	35
	<sup>52</sup> Cr(p,n) <sup>52</sup> Mn	5.6	5.7 d	744.3	43
Fe	<sup>56</sup> Fe(p,n) <sup>56</sup> Co	5.5	77.3 d	1283.3	120
Cu	<sup>63</sup> Cu(p,n) <sup>63</sup> Zn	4.2	38.1 min	962.1	470
	<sup>65</sup> Cu(p,n) <sup>65</sup> Zn	2.1	243.8 d	1115.5	
Zn	<sup>64</sup> Zn(p, $\alpha$ ) <sup>61</sup> Cu	0.8	3.41 h	283.0	3400
	<sup>68</sup> Zn(p,n) <sup>68</sup> Ga	3.8	67.8 min	1077.4	1300
	<sup>67</sup> Zn(p,n) <sup>67</sup> Ga	1.8	78.2 h	300.2	320
Sr	<sup>87</sup> Sr(p,n) <sup>87</sup> Y	2.7	80.3 h	388	51
Y	<sup>89</sup> Y(p,n) <sup>89</sup> Zr	3.6	78.4 h	909.1	5
Zr	<sup>90</sup> Zr(p,n) <sup>90</sup> Nb	7.0	14.6 h	1129.1	7
Cd	<sup>111</sup> Cd(p,n) <sup>111</sup> In	1.6	2.83 d	245.4	47
Sn	<sup>118</sup> Sn(p,n) <sup>118m</sup> Sb	4.5	5.0 h	1229.6	3000
	<sup>122</sup> Sn(p,n) <sup>122</sup> Sb	2.4	2.70 d	564.1	270
Pb	<sup>206</sup> Pb(p,n) <sup>206</sup> Bi	4.4	6.24 d	881.0	250

\* obtained by ICPAA for incineration ash (BCR-CRM 176)

It should be realized that while INAA is certainly the most appropriate technique for multielement analyses of many solid environmental samples, IPAA can often be complementary for the elements not detected after neutron irradiation. CPAA can hardly be considered as a routine technique for environmental investigations but should be applied in special cases such as where the highest accuracy is required i.e., mostly with radiochemical separations, or when the highest accuracy is needed as for certification purposes. Only the determination of Pb in dust collected on a filter can be performed routinely by CPAA.

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