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Abstract

A review of the applications of Instrumental Neutron Activation Analysis (INAA) in the industrial and environmental fields is given. Detection limits for different applications are also given.

1. INTRODUCTION

In the last three decades, neutron activation analysis (NAA), namely its non-destructive mode (instrumental neutron activation analysis - INAA), has been found to be very useful for the determination of trace and minor elements in many industrial and especially environmental applications. This is due to advantageous features of the technique in both modes, i.e. INAA and radiochemical NAA - RNAA, which have recently been discussed in detail [1-3] and have also been mentioned in Ch. 4 of this document. Therefore, only two specific advantages are mentioned here which concern an inherent potential for accuracy and the completely independent principle compared to the other trace element analytical techniques. This makes NAA indispensable for quality control of chemical analysis, namely for the preparation of certified reference materials, i.e. for both homogeneity testing and certification analyses. Besides chemical metrology itself, these advantageous features are also very important in industrial and environmental applications, because use of inaccurate analysis results in any decision process would incur vast financial and other losses.

2. INDUSTRIAL APPLICATIONS

In industrial applications of NAA, the most appreciated advantages involve low up to extremely low detection limits of elements, and the nondestructive and multielemental character of analysis. The matrices analysed mostly include high purity and high-tech materials, plastics, often also geological materials, and in general, such materials that are difficult to convert quantitatively into a solution for subsequent analysis by other analytical techniques. Numerous NAA procedures have been developed for process research, testing, process control, and product-quality improvement since the sixties [4-7].

In the last ten years, most frequent industrial applications or most frequently analyzed industrial-related matrices in which predominantly trace and ultra-trace concentrations of elements were determined by various NAA procedures involve: alloys, catalysts, ceramics and refractory materials, coatings, electronic materials, detection of explosives, fissile and other safeguard materials, fertilizers, graphite, high purity and high-tech materials, integrated circuit packing materials, on-line, flow analysis, oil products and solvents, pharmaceutical products, plastics, process control applications, semiconductors, pure silicon and silicon processing, silicon dioxide and NAA irradiation vials, textile dyes, thin metal layers on various substrates, while in geology and geochemistry analysis of the following specimens was most frequently performed by NAA: asbestos, borehole samples, bulk coals and coal products, coal and oil

shale components, crude oils, kerosene, petroleum, cosmochemical samples, cosmic dust, coral, diamonds, exploration and biogeochemistry, meteorites, ocean nodules, rocks, sediments, soils, glacial till, ores and separated minerals [8-12]. However, it should be realized that in the competition with other trace element analytical techniques, namely ICP-MS, only those applications have remained viable until now which have also economic advantages of low cost and speed or where NAA has an indispensable position. Some examples are given in this report.

2.1. INAA FOR SILICON INTEGRATED CIRCUIT TECHNOLOGY

Very pure silicon wafers are needed for fabrication of integrated circuits, because concentrations of impurities in silicon are considered to be critical even at levels of 10^2 pg/g. However, during a large number of process steps, contamination may easily occur in the wafers and their top structure, often adversely affecting the properties of the product of a process step. A stringent control of contamination is therefore required throughout the entire manufacturing process as exemplified by various producers, for instance, in the Philips Research Laboratories, Eindhoven, The Netherlands. For this purpose, INAA proved to be extremely useful as demonstrated by contents of the impurities found and limits of detection of other elements in a very pure silicon wafer given in Table 1.

TABLE 1. Content of the impurities found (bold values) and detection limits of other elements in a Si wafer (for experimental details see [13])

Element, content, pg g ⁻¹	Element, content, pg g ⁻¹	Element, content, pg g ⁻¹	Element, content, pg g ⁻¹
Na < 500	Se < 2	Cs < 0.5	Hf < 0.3
K < 150	Br 2.4	Ba < 60	Ta < 0.5
Ca < 10000	Rb < 10	La < 0.15	W 25
Sc < 0.03	Sr < 250	Ce < 0.9	Re < 0.3
Ti < 3000	Zr < 150	Pr < 6	Os < 0.7
Cr < 2	Mo < 6	Nd < 10	Ir < 0.004
Mn < 15000	Ru < 1.5	Sm < 0.03	Pt < 4
Fe < 300	Pd < 60	Eu < 0.07	Au 1.6
Co < 0.5	Ag < 3	Gd < 6	Hg < 0.6
Ni < 150	Cd < 15	Tb < 0.1	Tl < 3000
Cu 560	In < 4	Ho < 3	Th < 0.2
Zn < 15	Sn < 200	Er < 40	U < 1
Ga < 1.5	Sb 180	Tm < 3	
Ge < 1000	Te < 4	Yb < 2	
As 33	I < 8000	Lu < 0.04	

In this case, the matrix is very favourable since the half life of the induced radioisotope (³¹Si) is only 2.6 hours, and induced radionuclides of the elements of interest (mostly transition metals and Au which are highly undesirable in semiconductor silicon) are much longer-lived and therefore extremely low detection limits can be obtained.

Bulk analysis of the quartz used in the furnace for Si wafer processing is another example where INAA is highly suitable, and is routinely done either by the chip manufacturers or their quartz suppliers. Other materials that need bulk analysis in semiconductor industry include SiC (used in vertical furnaces), thin films of silicon dioxides,

Ti, TiN, W, etc., and also determination of U and Th as precursors of α -particle emitters in various plastic packaging materials is highly required [3]. Besides NAA, other techniques based on neutron interactions with matter, such as neutron depth profiling (NDP) and prompt gamma activation analysis (PGNAA), e.g. for depth profiling of boron in thin silicon oxide films prepared by chemical vapour deposition (CVD) and for measuring bulk hydrogen content of thin films produced in CVD process, respectively, play also an important role in the semiconductor industry [3].

2.2. APPLICATIONS OF INAA IN CHEMICAL INDUSTRY

Recently, numerous applications of INAA were reported from DSM Geleen, a Dutch company producing chemicals and materials [14]. Although INAA was introduced at DSM Research primarily for the determination of trace elements in high-purity silica, nowadays the use of this technique is much more diversified to meet special analytical requirements of the chemical plant.

One of many applications is panoramic analysis of liquid hydrocarbons (LHCs), the emphasis being placed on the determination of mercury and arsenic. LHCs, such as gas oil and naphtha, are used in very large amounts in huge chemical plants. Since oil and natural gas, from which LHCs are derived, contain significant amounts of Hg and As as contaminants, both elements are contained in LHCs. These elements can cause extensive damage to process equipment, affect adversely the performance of catalysts and pose a potential hazard to plant workers and to the public if released into the environment. INAA proved to be especially useful for this purpose for the following reasons:

- both elements and/or their compounds are volatile and can thus be lost during sample preparation for other analytical techniques, while no special sample preparation is needed in INAA
- possible matrix variations can cause problems to other analytical techniques, but not to NAA
- more other analytical techniques would be needed to deliver full panoramic quantitative information, resulting in much higher costs.

Another kind of samples for which INAA is especially suitable are Ziegler-Natta catalysts, based on the elements Ti, Cl, Mg, Al and V. Determination of these elements is quite difficult to carry out by other analytical techniques, because very often the catalysts are present in a slurry of organic materials which is difficult to handle with other analytical techniques, and because the catalysts readily decompose upon contact with ambient air and moisture, making sample preparation for other analytical techniques very difficult. A survey of typical samples at DSM Research analyzed at DSM Research by INAA and elements being determined is given in Table 2.

TABLE 2. Typical samples analyzed at DSM Research by INAA [14]

Sample type	Elements to be determined	Concentration
Liquid hydrocarbons	panoramic analysis	$\mu\text{g}/\text{kg}$ to mg/kg
Catalyst slurries	Ti, Cl, Mg, Al, V	mg/kg to %
Catalytic systems	Co, Pd, Mn, As, Rh, Fe, Ni	$\mu\text{g}/\text{kg}$ to %
Plastics	Cu, I, F	mg/kg to %
	heavy metals (Cr, Cd, Hg, Ni, Zn, Cu, As)	$\mu\text{g}/\text{kg}$
	Br, Sb	%

Determination of halogens and other impurities, such as Mn and Sb in polymers also appears to be a very important application of NAA in chemical industry [3,14]. On the other hand, fluorine compounds are added to some plastics to improve the behaviour of the polymer during processing and determination of this element by INAA is one of the best possibilities.

NAA is also in demand in photographic industry [3]. A very important process of the manufacturing of the photographic films is the precise doping of the silver halide crystals with ultra low level impurities, such as Ir, Rh and Au. Determination of these dopants was found to be best performed by NAA with a pre-irradiation separation. Most photographic films are chemically mixed halides, e.g. AgBrCl, AgBrI, etc. The mole ratio of the halides determines the sensitivity of colour films. The halide ratio in these mixed halides can be readily and reliably measured by INAA using a ^{252}Cf neutron source. Gelatine used as the emulsion in which Ag halides are dispersed is required to be of high purity. Presence of trace impurities such as Hg and Se is highly inhibitive to the photoactive process and latent image formation. A nuclear reactor based NAA (as in most of the above applications) of the gelatine was found to provide superior quality trace analytical data when compared with other techniques, such as hydride generation, and cold vapour atomic absorption spectrometry [3].

2.3. OTHER INDUSTRIAL APPLICATIONS

Determination of rare earth elements (REE), most of which can easily and reliably be performed by INAA, in geological materials is frequently required. Ratios of individual REE or the pattern of their contents normalized to those of C1 chondrites are extremely useful indicators in geochemistry of the origin and processes involved in the evolution of geological formations, structures, rocks, etc.

Related to NAA are analytical techniques used in the geochemistry and geophysics for well logging, i.e. to measure properties of reservoirs of gas and oil from inside the well casing. In this type of well logging, a probe consisting of a pulsed source of fast neutrons and γ -ray detectors, is pulled through the formations traversed by the borehole. As the logging probe is pulled slowly (e.g. at 2 m/s) along the borewell, the formations are irradiated and measured at the interface. Spectra are collected during the source pulse (mixed energy neutron field) and after the pulse (thermal neutron field). The data from the mixed energy neutron field is separated into capture and inelastic scattering events. These resolved spectra are mapped to elemental constituents; of particular interest are inelastic scattering by carbon and oxygen (oil and water). More information about this technique and other applications of nuclear techniques in the exploitation of mineral resources can be found in proceedings of an IAEA specialized symposium on these topics [15] and in proceedings of a topical meeting on Industrial Radiation and Radioisotope Measurements and Applications [16].

Of the emerging techniques, analysis of large samples (kg-size) by NAA should be mentioned. Most analytical techniques deal with portions in the order of μL to mL, and of mg to grams, whereas the amount of sampled material may easily be in the order of litres to kilograms, due to aspects of representativity and ease of operation. Thus it is usually necessary to reduce the particle size and to homogenize the sample before the subsampling takes place; sometimes the material characteristics are such that homogenization to a representative sample of a few mg is almost impossible. Further, in all these sample preparation processes, contamination and/or element loss may occur, while care is needed to avoid segregation. Therefore, a facility has been developed at the Interfaculty Reactor Institute, Delft, The Netherlands for INAA of kg-size samples. The maximum dimensions of the samples that can be handled in the facilities for irradiation and counting are 1 m in length, 15 cm in diameter, and about 50 kg in mass [17]. Applications of large sample INAA should be sought for in the

first place with materials difficult to dissolve, which may be considered macroscopically homogeneous but which are grossly too inhomogeneous for direct subsampling without extensive homogenization. Examples are materials from the waste recycling industries, e.g. plastics, shredded materials from electronic devices, domestic waste, waste from construction sites, etc. Also, the geological market segment might be interested in large sample INAA, particularly for analysis of samples (rocks, drill-cores, as well as sediments) with inhomogeneously distributed depositions [17].

3. ENVIRONMENTAL APPLICATIONS

Applications of reactor-based NAA in environmental studies are by far more extensive compared to industrial applications. It is therefore hardly possible to provide a comprehensive and exhaustive review of such applications in this type of report. Therefore, the importance of employing NAA in environmental applications will be demonstrated mostly using examples of air pollution monitoring and biological monitoring of environmental pollution.

3.1. AIR POLLUTION STUDIES

Large amounts of pollutants are yearly discharged into various compartments of the environment world-wide, although many countries have already establishing measures towards decreasing pollution of the environment. Many pollutants enter primarily the atmosphere in the form of inorganic or organic gases and inorganic or organic particulates. The major sources of atmospheric pollution are generally recognized to be industry, power generation and home-heating, transport, and waste incineration. The material discharged into the atmosphere is dispersed in aerosols, tiny liquid or solid particles. The processes involved in the formation of the atmospheric aerosol are schematically depicted in Fig. 1 [18]. The solid component of this aerosol, which has diameters in the range from about 1 nm to „giant“ particles of several hundred μm , is frequently referred to as airborne particles or air particulate matter (APM). However, most of their mass is in the size range from about 0.1 μm to 10 μm . Depending on the particle size and the atmospheric conditions, APM resides in the air for various periods of time, typically from a few days to a few weeks, and can be transported by the winds over distances of thousands of kilometres. Eventually, APM is removed by precipitation in rainfall or by gravitational fallout. Therefore, there is a continual transfer of contaminants from the atmosphere into the hydrosphere or into the soil, so that the air provides a route for the contamination of the rest of the biosphere.

Because of the variability in production and the relatively short lifetime, the concentrations, size distributions and chemical composition of APM vary widely in time and space. Although aerosols form only a small part of the total mass of the atmosphere (about 1 part in 10^9), they play an important role in atmospheric chemistry, have effects on human and animal health and welfare, and they influence climate [19]. The climatic effect of aerosols is in the direction of cooling (under most circumstances) and is of a magnitude comparable to that of the greenhouse gas warming [20,21]. However, there is still a large uncertainty associated with the estimate of climate forcing which reflects the unsatisfactory knowledge regarding the sources, distributions, and properties of atmospheric aerosols.

APM larger than 1 μm show a high sedimentation velocity and can move independently of the wind, while APM smaller than 1 μm show a low sedimentation velocity and move with the wind. It is probable, therefore, that APM smaller than 1 μm exert a strong influence on human health and the environment [22]. The potential negative effects of aerosols on human health have been recognized many years ago. Recently, renewed interest in the health risks of aerosols has been generated by the finding of a correlation between the

increased mortality and the concentration of airborne particles in metropolitan areas in the United States [23]. The US studies, together with similar research in the European Union, Brazil and elsewhere, consistently link higher levels of APM to increased risks of respiratory-, cardiovascular-, and cancer-related mortality, as well as pneumonia, lung functions loss, hospital admissions, asthma, and other respiratory problems. In most studies, the correlations examined were those between mortality and PM 10 particles (smaller than 10 μm equivalent aerodynamic diameter - EAD), but other studies indicated that the association with increased mortality was even higher when PM 2.5 particles were examined instead of those with PM 10. This is probably due to the relationship between the diameter of the APM and its precipitation in the human lungs. The respiratory air passages begin at the nasal cavity, pass through the trachea, bronchi and bronchioles, and end at the alveoli. The diameter of these passages and the velocity of air flow through them also decrease in this order. Larger APM are therefore unable to penetrate into the narrow branches of passages, but smaller particulates can easily reach the alveoli (Cf. Fig. 2). Clearly, therefore, it is important to investigate the size distribution of APM in addition to simple quantitative observations on their total mass. For these purposes, various sampling techniques of APM exist which has already been reviewed [23,24]. Details of INAA methodology and a survey of reference materials available for quality assurance of air pollution studies have also been described [24].

3.1.1. Data reporting and treatment

Results for the element concentrations in APM are usually expressed in a mass of an element per cubic meter of air, i.e. in ng m^{-3} , $\mu\text{g m}^{-3}$, etc. Therefore, it should be emphasised that at least the same attention should be given to the appropriateness and quality assurance of sampling of APM, i.e. calibration and control of the air flow through a collection device, checking of tightness of the device to avoid possible leakages, etc., as to its analysis, because otherwise larger uncertainties of results may be expected due to the sampling process than those of analysis. In addition, the concentration of an element in APM can be calculated as a mass fraction. However, in this case the exact mass of the material collected must be known. This means that proper weighing procedures must be followed [24].

A first exploratory step in the interpretation of the element concentrations determined is to compare the level of pollution in the impact (polluted) and clean (background) regions, and to evaluate time trends, especially if sampling was performed in regular intervals for a sufficient period of time. More broadly, this type of the data treatment concerns evaluation of spatial and seasonal variability of elemental composition of APM.

A useful way of the data evaluation is the use of enrichment factor (EF) calculations. An EF is defined as the double ratio of the concentration of the element of interest, c_x , in APM to that of a reference element, c_r , in APM divided by the ratio of the same elements in a reference material (e.g. the earth crust, soil, seawater, etc.) according to the relation

$$EF = \frac{\left(\frac{c_x}{c_r} \right)_{APM}}{\left(\frac{c_x}{c_r} \right)_{ref}} \quad (1)$$

In general, for EF calculations in APM, aluminium or scandium is taken as the reference element both in APM and the reference material for which the earth crust is most frequently employed. Evaluating of EF presumes that the atmosphere is always loaded with

APM originating both from the natural (soil erosion, sea aerosol) and anthropogenic (man-made) sources. An EF value close to one is indicative that the main source is of the crustal and/or marine origin, while values of EF exceeding ten (sometimes these values can reach several thousands) are indicative of significant anthropogenic contribution.

In order to develop rational and effective strategies for improving air quality, it is necessary to have an understanding of the relationship between the pollutant sources and their impact at receptor sites. Qualitative information of this kind can be inferred from the increased occurrence of specific elements which serve as markers for particular source emissions. Examples of marker elements are given in Table 3 [24]. More sophisticated approaches involve source or dispersion models which predict the concentration of pollutants at a receptor site using diffusion models with emission inventories and meteorological data. The predicted element concentrations can then be compared with the measured ones.

TABLE 3. Characterization of emission sources according to marker elements [24]

Source	Elements
Coal-fired plants	As, Se, S
Oil-fired plants	V, Ni, rare earths
Motor vehicles	Br, Pb
Refuse incineration	Ag, Zn, Sb, Cd, Sn, Pb
Limestone/concrete	Ca, Mg
Soil	Al, Fe, Mn, Sc, Si, Ti
Wood burning	C (elemental and volatile), K
Refineries	Rare earths
Sulphide smelters	In, Cd, As, Se, S

There is a number of multivariate statistical techniques which can be used for these purposes. *Receptor modelling* infer source contributions at receptor sites using statistical models with the data measured at the receptor site. *Principal component analysis* (PCA) is frequently employed for identifying pollutant sources. PCA attempts to explain the variance of a large set of intercorrelated variables (measured element concentrations in APM) with a smaller set of independent variables (the principal components). PCA is one of method of qualitative and quantitative techniques for data analysis which are collectively termed *factor analysis*. An introduction to data analysis of airborne particle composition has recently been published within the framework of one the IAEA Research Co-ordinated Programmes in this field [25] and there are numerous literature sources on this topic, as well, for instance [26,27]. Moreover new techniques are being developed, such as APCA, "Source profiles by unique ratios technique" (SPUR), "Positive matrix factorization" (PFA) [28,29]. *Chemical mass balance* (CMB) methods are designed to apportion the APM mass of each sample quantitatively amongst a number of contributing sources. This is possible if each source is characterized by a specific chemical pattern (source profile) and as many variables are available as sources.

Studies of elemental composition of APM in remote (background) and impact regions reveal the extent of environmental pollution due to various anthropogenic activities, time trends, geographical variations of pollution, and how various pollution sources, e.g. combustion processes, industrial activities, transport, etc. contribute to the overall level of pollution. However, in order to be able to control the level of pollutants and/or their abatement, it is very important to study the elemental composition of APM in the place of its origin.

Since the combustion processes are the main sources of anthropogenic APM in many countries, a study has recently been started in the author's laboratory on elemental composition of APM originating from the combustion of lignite using an experimental fluidized bed combustor with the thermal output of 100 kW. The samples analyzed included bottom ash, coarse fly ash collected by a hot cyclone (five fractions were obtained with the particle size range of < 40 up to > 200 μm) and fine fly ash separated by a cascade impactor into eleven fractions with the aerodynamic cut-off diameters from 0.016 to 14.3 μm . Using INAA (and PIXE for some elements), significant enrichment was found for many trace elements, including toxic ones, such as As, Cd, Ni and Pb, in the finest particles compared to bottom ash [30]. In the presence of additives, such as limestone and lime hydrate, the volume concentrations of most of these and also matrix elements in combustion aerosols decreased [31]. This is especially important for the abatement of the toxic elements in power plants, because namely the ultrafine particles easily penetrate through the common separation devices. Thus, use of the INAA (and PIXE) data on elemental composition of combustion aerosols helped in explaining of the mechanism of the abatement of both trace and matrix elements on lignite combustion with the additives. It has been shown that both a reduction of the total mass of emitted particles and specific absorption of some elements, namely As, in the additives employed were responsible for the abatement of the pollutants, and consequently for a reduction of the environmental pollution due to combustion of lignite [32].

3.2. BIOLOGICAL MONITORING OF ENVIRONMENTAL POLLUTION

Biomonitoring, i.e. the use of biological indicators to detect changes in the physical and chemical properties of the abiotic environment, represents an interesting alternative to direct measurements of the physical and chemical properties of the environment. Biological indicators are those tissues, organisms or populations of which their occurrence, vitality and responses change under the impact of environmental conditions [33]. Biomonitoring takes one of two approaches: i) direct monitoring which is based on measuring the quantity of pollutants in suitable organisms rather than in samples from the environment; ii) indirect monitoring which is based on interpreting of biological signals due to changes of the environment such as the study of morphological, physiological and cytological responses of organisms, changes of abundances of certain species, etc. Only the former approach is discussed in the present report.

Although data provided by physical and chemical monitoring are indispensable for evaluating the changes of the environment, application of an (ideal) biomonitor can show several advantages compared to the use of direct monitoring techniques:

- the concentration of pollutants in the monitor tissue or organism are often higher than in the system to be monitored. This may facilitate accurate sampling and analysis, which are very difficult at the low levels occurring in many compartments of the environment;
- sampling of the tissue or organism used as a biological monitor is in general easier than most direct sampling procedures and no long term use of expensive sampling equipment is required;
- the intricate equilibria existing in many parts of the environment can easily be distorted by sampling itself, which may lead to erroneous results. When using biological monitors, this distortion is minimized;
- most tissues and organisms reflect external conditions averaged over a certain time, depending on e.g. the biological half-life of a specific substance in that organism. This is important when monitoring levels may change rapidly in time;

- concentrations of pollutants in organisms may give insight into the bio-availability of that pollutant. This information may be as relevant as the absolute concentration in a certain part of the environment;
- biological monitors are already present in the environment and monitoring continuously.

In direct biomonitoring of atmospheric element pollution, the relevant information is deduced from concentrations of elements in the monitor tissues. They have to meet specific requirements which have been described elsewhere [34].

Many human, animal and plant species can be used for air pollution monitoring, because they can meet most of the requirements. Human and animal species and/or tissues usually reflect complex changes of the environment, i.e. air, water, soil pollution, and element intake from their diet, so that their use for studying only air pollution may be rather difficult to interpret. Nevertheless, some of them proved to be very useful, such as analysis of human and/or animal hair and other ectoderm derivatives, for instance nails. Certain plant species appear to be especially suitable to indicate elemental air pollution and therefore their use as biomonitors of air pollution is also briefly discussed.

3.2.1. Hair

The feasibility of human hair as a material easily accessible for non-invasive sampling in individuals or population groups, to demonstrate criminal, occupational or environmental exposure to toxic elements has received a great deal of attention in the literature. Besides many papers scattered in various journals, two monographs, one chapter in another monograph, and two review articles have been published [35-39]. Hair analysis is also facilitated by the availability of the generally recognized washing procedure which has been suggested in one of the IAEA Research Co-ordinated Programmes in the mid- seventies [40]. It is very important to use a standardized hair cleaning, because there is no single washing procedure which would completely remove the external contamination without influencing the endogenous element contents. While a generally accepted washing procedure exists for hair (for monitoring of environmental pollution) and thus comparable data on elemental hair composition are available from many countries, no such standardized washing is widely used for nail cleaning which can also be used for biological monitoring as another ectoderm derivative.

Numerous examples of application of hair analysis for studying environmental pollution can be found in the above (and other) literature sources. Therefore, the usefulness of hair analysis for these purposes will only be shown in one example which demonstrates a correlation between arsenic content in hair of children living in various distances from a pollution source and the expected degree of arsenic contamination of the air (Cf. Fig. 3 [41]). Noteworthy, a similar correlation was obtained when urinary arsenic levels of children were determined (Cf. Fig. 4 [41]). This demonstrates that urine is also a very suitable indicator to assess environmental exposure, however, the arsenic (and many other elements) determination in urine is much more difficult compared to hair, because RNAA is required for this purpose to eliminate high matrix activity.

Similarly to human hair, the hair of some rodents, such as the Common Hare (*Lepus europaeus*) and the Common Vole (*Microtus arvalis*) proved to be a very useful indicator of environmental pollution. This can be supported by the finding that similar haematological changes were found in hares as in children living in regions burdened with industrial emissions [42].

TABLE 4. Detection limits of 45 elements in selected environmental matrices by INAA*

Element	Coal mg/kg	Coal fly ash mg/kg	Atmospheric particulate matter, ng m ⁻³	Soil, sediment mg/kg	Spruce needles mg/kg
Ag	0.5	1.5	0.04	0.7	0.05
Al	20	35	5	30	15
As	0.05	0.25	0.015	0.45	0.05
Au	0.001	0.01	0.005	0.01	0.001
Ba	20	100	3	50	3
Br	0.05	0.3	0.1	0.4	0.04
Ca	100	500	30	500	300
Cd	0.5	4	0.1	5	0.3
Ce	0.15	1.5	0.15	1	0.2
Cl	50	300	15	400	50
Co	0.015	0.1	0.03	0.05	0.01
Cr	0.5	3.5	1	1.5	0.2
Cs	0.05	0.1	0.03	0.1	0.015
Cu	1	5	1	15	0.4
Dy	0.05	0.05	0.01	0.05	0.03
Eu	0.015	0.04	0.005	0.03	0.005
Fe	30	150	10	75	10
Ga	0.5	3	0.2	10	0.08
Hf	0.05	0.15	0.01	0.1	0.015
Hg	0.05	1	0.02	1	0.05
I	2	15	0.4	20	1
In	0.02	0.05	0.03	0.05	0.02
K	20	100	10	300	20
La	0.03	0.07	0.05	0.15	0.01
Lu	1	2.5	0.25	1	0.05
Mn	2	5	0.5	8	1
Mo	0.1	2.5	0.35	2.5	0.3
Na	2	4	10	10	0.3
Ni	10	40	2.5	60	10
Nd	2	4	0.2	5	1
Rb	5	10	0.5	7.5	0.5
Sb	0.03	0.1	0.015	0.075	0.01
Sc	0.005	0.010	0.003	0.005	0.001
Se	1	4	0.1	3	0.15
Sm	0.01	0.02	0.005	0.03	0.005
Sr	30	100	2	50	5
Ta	0.05	0.2	0.01	0.07	0.01
Tb	0.05	0.3	0.02	0.1	0.05
Ti	300	500	6	400	150
Th	0.03	0.1	0.015	0.05	0.015
U	0.1	0.5	0.03	0.5	0.01
Yb	0.1	0.3	0.05	0.3	0.03
	0.3	1	0.05	1.5	0.05
W	0.2	0.5	0.03	1	0.05
Zn	2	10	1	5	0.5

*Experimental conditions: Short- and long-time irradiation of 100-200 mg samples (except for APM which mass amounts to 0.5- 1 mg) in a neutron fluence rate of $5.10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ for 1 min. and 10 h, respectively, followed by gamma-ray spectrometric measurements using a HPGe detector (rel. efficiency. 21%). For other details see Ref. [50].

3.2.2. Other biomonitors

Recently, a review has been published on using herbaceous plants, trees, bryophytes, and lichens for biomonitoring of air pollution [34]. Of these recognized biomonitors, bryophytes, especially some moss species, lichens, needles of coniferous trees, and tree bark showed many advantages which are important for their application in this field as can be inferred from frequency of their use in various national and international programmes.

Mosses have been very popular in both local and long-term, large-scale studies in Nordic countries since seventies and use of these bioindicators have also been included in the Convention on Long-Range Transboundary Air Pollution [43,44]. In the Netherlands, national trace-element air pollution monitoring survey using epiphytic lichens has been started in 1982 and continues on international scale until now. These studies followed by a specific multivariate statistical procedure known as "Target Transformation Factor Analysis" have successfully been employed for apportionment of emission sources within and outside the country [45-47]. To obtain the relevant information of this kind, multielement analysis is required and INAA proved to be very effective tool for this purpose. Currently, the International Atomic Energy Agency is also conducting Co-ordinated Research Programme on "Applied Research on Plants as Biomonitors of Trace Atmospheric Pollution" using nuclear and related analytical techniques in which more than 10 countries participate.

On the other hand, it should be realized that without extensive calibration under all relevant conditions, the use of even the most suitable biomonitors frequently yields only qualitative information on the atmospheric level of pollutants as a function of time or place [48].

There are many more biomonitors and other matrices suitable for the assessment of the environmental pollution. For instance, from nation-wide surveys of natural surface soils in Norway it has become evident that the long-range atmospheric transport of heavy metals apparent in the moss survey is also reflected in the chemical composition of surface soil [43]. A similar relationship as for the level of pollution of the atmosphere and that of surface soil is usually found between surface waters and sediments and/or water suspended matter. Stratigraphic distribution of elements and other biomarkers in undisturbed lake sediments may even be used to trace the history of atmospheric and water pollution several hundred years back [49]. While for water analysis other analytical techniques are predominantly used, such as AAS, electrochemical methods, ICP-MS (because water is almost an ideal matrix for these techniques), for soil and sediment analysis INAA offers many advantages as it follows from detection limits for 45 elements in selected environmental matrices shown in Table 4.

REFERENCES

- [1] A.R. BYRNE, FRESINIUS J. *Anal. Chem.*, 345 (1993) 144-151.
- [2] A.R. BYRNE, J.KUCERA, *Proc. Int. Symp. Harmonization of Health Related Environmental Measurements Using Nuclear and Isotopic Techniques*, Hyderabad, India, 4-7 November 1966, IAEA Vienna 1997, pp. 223-238.
- [3] IAEA TECDOC on Enhancement of Research Reactor Utilization for Neutron Activation Analysis, IAEA Vienna, to be published
- [4] W.W. MEINKE, B.F. SCRIBNER (Eds.), *Trace Characterization; Chemical and Physical*, NBS Monograph 100, U.S. Department of Commerce, U.S. Government Printing Office, Washington DC, 1966.
- [5] R.F. BUNSAH (Ed.), *Modern Analytical Techniques for Metals and Alloys, Part 2.*, Interscience, New York 1970.

- [6] M. ZIEF AND R. SPEIGHTS (Eds.), *Ultrapurity: Methods and Techniques*, Marcel Dekker, New York, 1972.
- [7] T. BRAUN AND E. BUJDOSO (Eds.), *Proceedings, Int. Conf. on Modern Trends in Activation Analysis*, Paris, 1972, Elsevier, Amsterdam, 1972.
- [8] W.D. EHMAN, S.W. YATES, *Anal. Chem.*, 58 (1986) 49R-65R.
- [9] W.D. EHMAN, S.W. YATES, *Anal. Chem.*, 60 (1988) 42R-62R.
- [10] W.D. EHMAN, J.D. ROBERTSON, S.W. YATES, *Anal. Chem.*, 62 (1990) 50R-70R.
- [11] W.D. EHMAN, J.D. ROBERTSON, S.W. YATES, *Anal. Chem.*, 64 (1992) 1R-22R.
- [12] W.D. EHMAN, J.D. ROBERTSON, S.W. YATES, *Anal. Chem.*, 66 (1994) 229R-251R.
- [13] M.L. VERHEIJKE, H.J.J. JASPERS, J.M.G. HANSEN, M.J.J. THEUNISSEN, *J. Radioanal. Nucl. Chem., Articles*, 113 (1987) 397-404.
- [14] D.A.W. BOSSUS, R. VAN SLUIJS, *Proc. 13th Radiochemical Conference, Mariánské Lázně, Czech Republic, 19-24 April 1998*, in press in *Czech. J. Physics*.
- [15] *Nuclear Techniques in the Exploration and Exploitation of Energy and Mineral Resources*, Proc. IAEA Symp., Vienna, 5-8 June 1990, IAEA, Vienna, 1991.
- [16] *Industrial Radiation and Radioisotope Measurements and Applications (IRRMA)*, 1996, Proc. IRRMA Meeting, *Appl. Rad. Isotopes*, 48 (1997) 1273-1708.
- [17] R.M.W. OWERWATER, P. BODE, J.J.M. DE GOEIJ, *ANAL. Chem.*, 68 (1996) 341-348.
- [18] J. O. BUFFLE, H. P. VAN LEEUWEN (Eds.), *Environmental Particles*, Vol. 1., Lewis Publishers Inc., Boca Raton, Chelsea, Michigan, USA.
- [19] R. J. CHARLSON, J. HEINTZENBERG (Eds.), *Aerosol Forcing of Climate*, John Wiley & Sons, Chichester, 1994.
- [20] J. T. HOUGHTON et al. (Eds.), *Climate Change 1994: Radiative Forcing of Climate and an Evaluation of the 1992 Emission Scenario*, Intergovernmental Panel on Climate Changes (IPCC), Cambridge University Press, Cambridge, UK.
- [21] S.E. SCHWARTZ, *J. Aerosol Sci.* 27 (1996) 359-382.
- [22] K. OIKAWA, *Trace Analysis of Atmospheric Samples*, A Halsted Press Book, Kodansha Ltd., Tokyo, John Wiley & Sons, New York, London, Sydney, Toronto, 1977.
- [23] T. REICHHARDT, *Environ. Sci. Technol.*, 29 (1995) 360A.
- [24] *Sampling and Analytical Methodologies for Instrumental Neutron Activation Analysis of Airborne Particulate Matter*, Training Course Series No.4, IAEA, Vienna, 1992.
- [25] P. K. HOPKE, *Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques*, NAHRES-19, IAEA, Vienna, 1994, p. 215.
- [26] P. K. HOPKE, *Receptor Modelling in Environmental Chemistry*, J. Wiley & Sons Inc., New York, 1985.
- [27] H. MARTENS AND T. NAES, *Multivariate Calibration*, John Wiley & Sons, Chichester, UK, 1989.
- [28] P. PAATERO, AND U. TAPPER, *Chemom. Intell. Lab. Syst.*, 18 (1993) 183.
- [29] P. PAATERO, AND U. TAPPER, *Environmetrics* 5 (1994) 111.
- [30] J. SMOLÍK et al., *Environ. Sci. Technol.*, submitted (1998)
- [31] J. SMOLÍK et al., *J. Aerosol. Sci.* 29, Suppl. 1, S451-S452 (1998).
- [32] J. KUCERA et al., *Proc. Int. Conf. Nucl. Anal. Methods in the Life Sciences (NAMLS)*, October 26-30, 1998, Beijing, China, p. 71, *Biol. Trace El. Res.*, submitted (1998)
- [33] M. KOVACS, (Ed.), *Biological Indicators in Environmental Protection*, Akadémiai Kiadó, Budapest 1992.
- [34] J. KUCERA, *Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques*, NAHRES-19, IAEA, Vienna, 1994, p. 265.
- [35] V. VALKOVIC, *Trace Elements in Human Hair*, Garland Publ. Inc., New York, 1977.

- [36] S. A. KATZ, A. CHATT, Hair Analysis, Application in the Biomedical and Environmental Sciences, VCH Publishers, Inc., New York, Weinheim, 1988.
- [37] T. SUZUKI, Hair and Nails: Advantages and pitfalls when used in biological monitoring, In: T. W. Clarkson, L. Friberg, G. F. Nordberg, P. R. Sater (Eds.), Biological Monitoring of Toxic Metals, Plenum Press, New York and London, 1988, pp. 623-640.
- [38] K. BENCZE, FRESENIUS J. Anal. Chem., 337 (1990) 867.
- [39] K. BENCZE, FRESENIUS J. Anal. Chem., 338 (1990) 58.
- [40] YU. S. RJABUCHIN, Report IAEA/RL/50, IAEA, Vienna, 1978.
- [41] V. BENCKO, Toxicology, 101 (1995) 29.
- [42] J. KUCERA, Chemosphere, 34 (1997) 1975.
- [43] E. STEINNES, Proc. Int. Symp. Appl. of Isotopes and Radiation in Conservation of the Environment, Karlsruhe, 9-13 March 1992, IAEA Vienna, 1992, IAEA-SM-325/174, p.387.
- [44] Convention on Longe-Range Transboundary Air Pollution (LRTAP), Field and LRTAP laboratory manual, National Board of Water and Environment, Environmental Data Centre, Helsinki, 1989.
- [45] M.DE BRUIN, P. M. VAN WIJK, J. Radioanal. Nucl. Chem., 123 (1988) 227.
- [46] J. E. SLOOF, H. TH. WOLTERBEECK, Water, Air, and Soil Pollution 57-58 (1991) 785.
- [47] J. E. SLOOF, H. TH. WOLTERBEECK, Lichenologist 23 (1991) 139.
- [48] M. DE BRUIN, Applying biological monitors and neutron activation analysis in studies of heavy-metal pollution, IAEA Bulletin 4/1990, 22.
- [49] J. VESELÝ et al., J. Paleolimnol., 8 (1993) 211.
- [50] J. KUCERA, L. SOUKAL, J. Radioanal. Nucl. Chem., Articles, 121 (1988) 245.

