

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS IN ENVIRONMENTAL RESEARCH

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INTRODUCTION

The introduction of Ge-semiconductor detectors and laboratory computers has strongly stimulated the development of neutron activation analysis (NAA) over the past two decades. The high energy resolution of Ge(Li)-detectors and apparently unlimited computing facilities made chemical separations superfluous for many sample materials (1). The detection limits are not as low as obtained when applying chemical separation, but in many types of samples such as geological materials, soils, air particulates, refuses, industrial wastes and plant materials, tens of elements can be determined simultaneously by a purely instrumental technique. Instrumental neutron activation analysis (INAA) is very well suited for application in environmental research and monitoring. It has been discussed extensively in literature (2) and at meetings such as the IAEA symposium "Measurement, Detection and Control of Environmental Pollutants" held in 1975 (3) and the five consecutive conferences on "Nuclear Methods in Environmental and Energy Research", organized by the ANS. In his contribution at the most recent of these conferences (Mayaguez, Puerto Rico, 1984) Steinnes (4) stressed the pertaining importance of nuclear analytical techniques in environmental research along with other techniques such as atomic absorption spectrometry and emission spectroscopy. The advantages of neutron activation analysis in general have been discussed recently by Greenberg (5). The characteristics of instrumental NAA when applied to environmental samples can be summarized as

- high sensitivity for many relevant elements
- high accuracy for a variety of sample types
- insensitive for light elements
- information on many elements simultaneously
- economically attractive.

These characteristics are discussed in more detail in the next section.

At Delft, INAA is used in a variety of environmental research projects. A description of the IRI system for INAA will be given, with some recent results obtained in monitoring heavy metal air pollution using lichens. Finally, some ideas will be presented regarding the position of INAA in environmental research and monitoring in the near future.

CHARACTERISTICS OF INAA, RELEVANT FOR ENVIRONMENTAL APPLICATIONS

Sensitivity

Although lower than what is achievable by radiochemical NAA, the sensitivity of INAA is still such that many (potentially) toxic elements can be detected in the environment far below detrimental concentration levels. Therefore, the behaviour of such elements in the environment can be studied often at natural concentration levels. When using INAA in environmental monitoring, increases of heavy metal concentration levels can be observed - and the necessary measures are taken - long before they have developed into an acute environmental problem. This is illustrated by the detection limits of INAA for some elements in air filters, and the maximum permissible ion mission concentrations (MIC-value) for these elements, presented in Table I. The filters (cellulose, 5 cm², 10 m³ of air) were analysed with the IRI-system for INAA which will be discussed in the next section.

Be and Pb are the only elements of environmental concern to which INAA is not applicable: the determination of lead using ²⁰⁷Pb is regarded as inadequate when compared to the determination by AAS.

Accuracy

The low risks of contamination of element loss, typical for NAA, are particularly important in the analysis of environmental samples, where the concentrations of interest are mostly in the ppb- to ppm-range. Equally important is the lack of matrix effects for a large range of matrix compositions. This makes it possible to obtain absolute and directly comparable concentration values for strongly differing materials such as surface water, air particulate matter, human and animal tissues, plant materials and soils. In addition, when using INAA, no destruction or chemical separations are applied, so that post-irradiation losses are avoided.

These factors are the basis of the high accuracy obtainable with NAA, reflected in the dominating role of this analytical technique in establishing certified concentrations of trace elements in reference materials (6,7).

Insensitivity for light elements

Of most light elements the thermal neutron cross-sections are very low, or the reactions lead to nuclides with very short half lives. Even when present at high concentrations, elements such as H, C, N, O, (Al,)P, S, Si and Ca do not interfere in the INAA procedure, neither directly by the induced activity or indirectly through neutron flux depression or self-shielding. As these elements are the major constituents of water, tissues, soils and filter materials, they are apparently absent in the analysis and do not hamper the detection of the heavier elements present at trace level.

The major light element interference is due to ²⁴Na, the neutron activation product of sodium. The high concentrations of this element in most human and animal tissues or fluids and

sea materials severely limit the sensitivity for elements determined on basis of nuclides with intermediate half lives. For certain elements, the use of a nuclide with short or long half life as alternative for an otherwise more sensitive nuclide with intermediate half life, may lead to improved detectability. For example, the detection limit of Cu in toenails when measuring ^{64}Cu (12.7h) is approximately 10 ppm because of the high ^{24}Na -activity; when using ^{66}Cu (5.1h), the detection limit is lowered by a factor of 10 to less than 1 ppm. Self-evidently, high sodium contents such as present in whole blood, do not affect analyses using nuclides with long half lives (8). Limitations due to ^{24}Na can be avoided also by applying a hybrid of radiochemical and instrumental NAA, where the ^{24}Na is selectively separated using hydrated antimony pentoxide (9). But this approach is relatively laborious and the accuracy may be affected by losses in the chemical procedure.

Multi-element capability

The large number of elements determined simultaneously in an INAA-procedure is becoming increasingly important for many environmental applications. As it is often not known a priori which elements are matter of concern in a certain area, a "broad spectrum" analysis covering a large part of the Periodic Table, is of the first importance for environmental monitoring. In this respect, INAA is very suitable as it yields information on all (potentially) toxic elements except Be and Pb, when present at relevant levels.

Part of the information obtained refers to elements which are not of direct environmental concern. This additional information may play an essential role in the interpretation of the toxic element concentration data. As elements such as As and Sb are present in natural soils at ppm levels, it is important to distinguish between the "natural" amounts of these elements originating from that soil and the amounts from anthropogenic sources. Normalization of the observed concentrations on basis of the concentrations in the same sample of selected reference elements characteristic for soil (Al, Sc, Fe, R.E.) yields an Enrichment Factor (12) which allows to discriminate between these possible sources.

Possibly the most important application of the multi-element information obtained from INAA is the use of trace element patterns as fingerprints for identifying specific sources of inorganic pollutants. The basic idea is that the elements of primary interest are introduced into the environment in specific combinations with other elements, and that certain elements or element ratios are specific for different sources. Identifications of sources of pollutants on basis of element patterns of environmental samples mostly regard the elucidation of the origin of inorganic air pollution using the element concentration patterns observed in air filters. But applications have been reported also for other materials such as lichens used as biological indicator for pollution with heavy metals (13,14).

In the identification procedures reported, two basically different approaches can be distinguished. When the relevant sources and the compositions of the associated emissions are known, the "Chemical Element Balance" method can be used to estimate the relative contributions of each of these sources at a specific place or in a specific sample (15,16). When applying Factor Analyses procedures, a set of hypothetical components is calculated from the compositions of a large number of samples, without using a priori knowledge of actual sources or compositions. These hypothetical components can then be identified with realistic components or sources on basis of their calculated element concentration patterns. The Factor Analysis approach has been discussed thoroughly by Hopke (17); Chemical Element Balance and the Factor analyses methods were evaluated recently by Stevens (18).

Analysis costs

In environmental research and particularly in environmental monitoring, large numbers of samples and analyses are involved. Therefore, cost per analysis will be an important factor when judging the value of a specific analysis technique for such applications. INAA is often regarded as a complicated and expensive analysis technique, to be carried out by high level specialists. But since it is a purely instrumental technique, automation and computerization are possible to a high degree. At present, the capacity of laboratory computers is such that their use for automated measurement, spectrum analysis and interpretation, and administration may reduce considerably both amount and level of labor involved in INAA. Although the resulting savings in analysis costs will depend on local conditions such as the ratio between labor- and instrumentation/computer-costs, it will in general lead to appreciable cost reductions. For the system for routine INAA in use at IRI, the costs are DF1 125-200 (\$35-50) for a complete analysis involving two irradiations and three measurements (19). This is comparable to or even lower than the costs of the alternatives, which often include laborious and costly chemical manipulations.

THE IRI SYSTEM FOR ROUTINE INAA

Description of the system

The analysis system (20) is based on the use of the single comparator method of standardization (21) to take full advantage of the multi-element capabilities of INAA without the problems associated with the preparation and use of trace element standards covering two thirds of the periodic system. Zinc is used as mono-element standard; the element concentrations are calculated on basis of a weighed average of the ^{65}Zn - and ^{69m}Zn -activities, using experimentally determined conversion factors.

The analyses are performed according to a standard protocol comprising a first irradiation of 15-30 s followed by a measurement after 0.5-20 m decay, and a second irradiation of 0.5-4 h followed by two measurements after 2-6 d and 3-5 w respectively. The irradiations are carried out in the Institute's 2Mw swimming pool reactor in a thermal neutron flux of $1 \times 10^{13} \text{ n/cm}^2 \cdot \text{s}$.

The irradiation facilities used are a fast rabbit system (transport time <15 s) for short irradiations and a slow rabbit system (transport time 8 s) for the long irradiations.

The spectrometers, equipped with coaxial and well-type Ge(Li)-detectors are integrated with a DEC PDP-11/44 computer through buffered input gates in a CAMAC interface system (Fig. 1). The well-type detectors are expensive but have the advantage of a high photopeak efficiency (5-50%, depending on γ -ray energy), so that good detection limits are obtained even after an irradiation of a few hours at a moderate neutron flux.

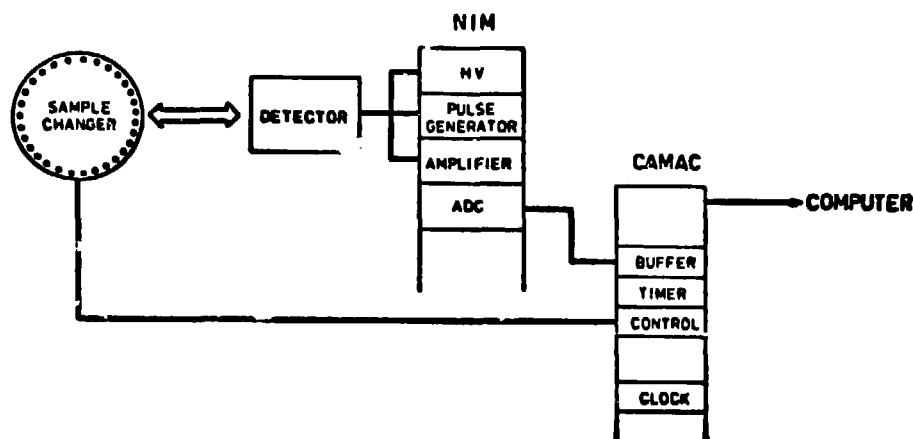


Fig. 1. γ -ray spectrometer used in INAA

The γ -ray spectra are converted into element concentrations using a set of dedicated computer programs (22,23). The INAA software package comprises the following main functions:

- spectrum analysis and interpretation, including conversion of the peak area data into element concentrations or estimated upper concentration limits. The isotope identification is based on a catalog of measured γ -ray energies and intensities (24);
- comparison and combination of the intermediate results obtained from measurements after different decay times, correction for blank and for contributions from interfering reactions;
- generation of the final analysis report in hard copy or on tape or disk;
- bookkeeping of the results obtained from reference materials for detection of systematic errors in the analytical procedure.

The results obtained in repeated analyses of reference materials indicate that the accuracy of the method is in general better than $\pm 5\%$, which is adequate for most environmental samples. Table I shows some detection limits obtained routinely in materials of environmental interest.

Table I. Routine INAA at IRI

Element	Detection limit				MIC-value in air (25) (ng/m ³)
	soil (ppm)	plants (ppm)	nails/hair (ppm)	air particulates (ng/m ³)	
V	3	1	1	1	250
Cr	1	1	0.3	1	100
Mn	1	1	1	1	25000
Fe	100	30	30	100	5000
Zn	10	1	1	10	10000
As	1	0.1	0.03	0.1	500
Se	3	1	0.3	1	-
Cd	1	1	0.3	1	500
Sb	0.3	0.1	0.01	1	2500
Hg	3	1	0.3	1	10

Environmental applications of the INAA system

Currently, more than half of the 4000 samples analyzed annually are related to studies of the transport of heavy metals in the environment. In these applications, the multi-element capabilities of INAA are essential, either to study a range of heavy elements simultaneously, or for source identification on basis of trace element patterns. Major projects are:

- identification of sources of heavy metal air pollution using air filters or biological

indicators such as mosses and lichens. The air filter data are interpreted by correlation with meteorological data and by Factor analysis. The studies using lichens are discussed in some detail in the next paragraph;

- study of the uptake and translocation of heavy elements in plants. This study involves plants grown in actually polluted areas as well as plants grown under controlled conditions at the laboratory. In a complementary approach, trace element transport kinetics are studied in isolated plant parts with radionuclides of 15 elements simultaneously (26). A separate study is aimed at evaluating the use of selected plant species for "biological cleaning" of soils polluted with cadmium;
- evaluation of human toe-nails as an indicator of heavy metal uptake by populations in polluted areas. This study is combined with a survey using lichens in the same area;
- evaluation of bird feathers (27), mollusks and waterplants as possible indicators for heavy metal pollution in fresh water and estuarine areas.

Part of the studies are carried out in cooperation with chemists, physicists and biologists from Dutch universities.

USE OF LICHENS AS BIOLOGICAL MONITOR FOR HEAVY METAL AIR POLLUTION

Introduction

The major part of our effort in environmental research is focussed on the development, evaluation and application of epiphytic lichens as accumulating monitor for identifying sources of heavy metal air pollution. Various plant species have been used for such monitoring, especially in Scandinavia, Great-Brittain, Ireland and Canada (28,29,30,31), but the results have to be handled carefully to avoid misleading conclusions (32). Therefore, special attention is paid to mathematical techniques for a reliable interpretation of the element concentration patterns observed in sets of lichen samples.

In air pollution surveys, epiphytic lichens are collected at places regularly spread over an area under investigation. At the laboratory, the lichens are separated from the substrate bark, washed, dried and analyzed by routine INAA. In Table II, ranges and mean values are listed of element concentrations found in material collected in De Kempen, an industrialized area in the South of The Netherlands.

Besides mapping of the element concentrations, two additional procedures are applied to the concentration data, to obtain information on position and identity of any significant sources present in an area:

- mapping of the concentrations of individual elements after conversion to Enrichment Factors;
- application of Factor Analysis to the multi-element dataset and identification of sources of pollution and their contributions for each relevant element.

The relevance of careful data interpretation will be illustrated below with some of the results from two recent air pollution surveys in The Netherlands. The first survey covered the entire country, the second one was focussed on De Kempen, a small area along the Southern border (Fig. 2a), known to be polluted by heavy metals.

Table II. Trace elements in *Lecanora conizaeoides* from De Kempen

El.	av.conc.	range	el.	av.con.	range	el.	av.con.	range
	ppm	ppm		ppm	ppm		ppm	ppm
Na	680	200-1900	Fe	6100	1700-1700	Eu	0.15	0.052-0.40
Mg	1480	420-5100	Co	4.9	1.4-23	Dy	0.49	0.19 -1.1
Al	5200	1900-11000	Zn	590	120-7500	Yb	0.31	0.055-0.97
Cl	680	290-1200	As	11	2.4-41	Lu	0.057	0.011-0.20
K	4300	1400-11000	Se	2.5	0.80-8.1	Hf	1.0	0.25 -3.2
Sc	1.5	0.42-4.2	Br	50	7.5-140	W	1.3	0.25 -12
Ti	420	100-4300	Cd	5.0	1.0-33	Au	0.012	0.003-0.091
V	29	12-76	Sb	13	3.4-61	Hg	0.98	0.20 -13
Cr	30	9.7-88	La	4.4	1.3-12	Th	1.1	0.32 -2.6
Mn	97	43-175	Ce	8.3	2.8-22	U	0.56	0.13 -1.9

Application of Enrichment Factors

Our experiences so far indicate that straightforward geographical mapping of concentrations of individual elements and locating sources on basis of concentration gradients does not yield reliable results. Local differences in growing conditions of the lichens may lead to artifacts not related to the factors studied. Conversion of element concentrations into Enrichment Factors improves this situation as this conversion implies correction for differences in soil contribution or growth rate.

The Enrichment Factor of an element x on basis of a reference element y is defined as:

$$EF_{x,y} = \frac{\left(\frac{C_x}{C_y}\right)_{\text{lichen}}}{\left(\frac{C_x}{C_y}\right)_{\text{soil}}}$$

In our studies, the Enrichment Factors are calculated with scandium as reference element, using the element-scandium ratios experimentally determined for "clean" Dutch soils. Fig. 2a and b show maps of the arsenic concentrations and arsenic Enrichment Factors of *Parmelia*

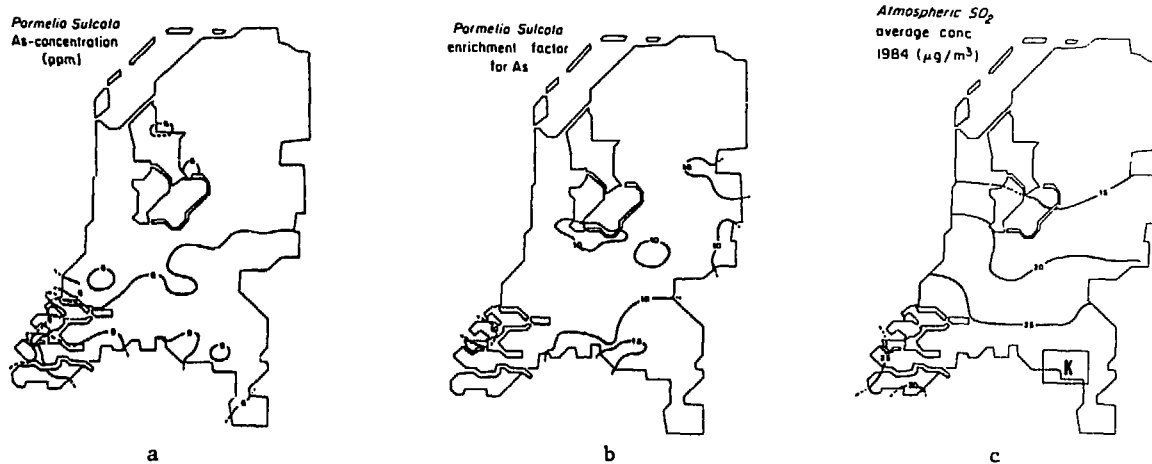


Fig. 2. Distribution over The Netherlands of arsenic in lichens and the average atmospheric SO_2 -concentration.
K = De Kempen

sulcata collected over the country. The first map shows a concentration gradient towards the South-Western border, suggesting a major source of arsenic in that direction. The arsenic Enrichment Factor however has a rather flat distribution. This suggests that the high As-content is due to locally high soil contributions, or that the arsenic is emitted together with soil elements in a natural ratio.

Fig. 2c represents the distribution of the atmospheric SO_2 -concentrations over the country. The similarity between the SO_2 - and the arsenic-distributions suggest either a common source of the two (e.g. coal burning), or a casual relationship between the two concentrations. Influence of the atmospheric SO_2 -concentrations on trace element concentrations in lichens is not unlikely since high SO_2 -concentrations are known to inhibit lichen growth (33).

It will be clear from this example that one has to be very careful with conclusions based only on concentrations of single elements.

Application of Factor Analysis

De Kempen is an area along the Dutch-Belgian border which has been for a long time, and still is, polluted by emissions from metallurgical industries. Several zinc smelters have been in operation for more than a century and the area also houses a branch of a large electronic industry. Part of the zinc smelters have changed their production process recently to reduce heavy metal emission. Contributions to the air pollution can also be expected from the center of industrial activities around Antwerp, appr. 50 km in Westerly direction (fig. 3).

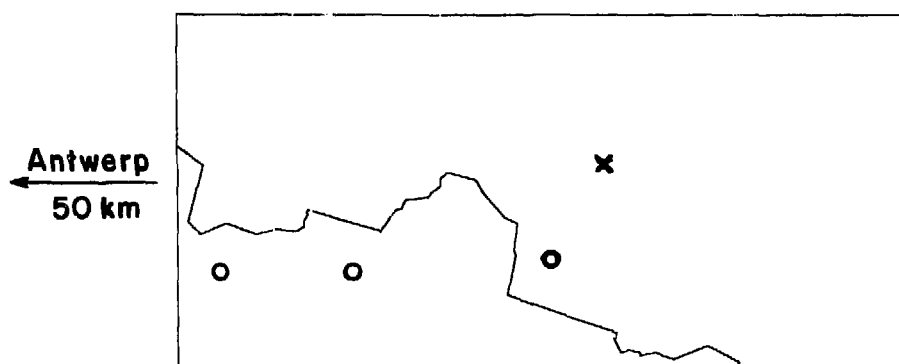


Fig. 3. The 20 x 50 km area surveyed in De Kempen.
o = zinc smelter; x = electronic industry

The lichen *Lecanora conizaeoides* was collected in an area of 20 x 50 km at in total 140 sampling points positioned on a lath of 3 x 3 km. Factor Analysis was applied to the element concentration dataset, using the information on 17 elements: Al, K, Sc, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Cd, Sb, Eu, W and Th. The Factor Analysis procedure yielded 5 factors or hypothetical components, accounting in total for more than 85% of the variance present in the dataset. The normalized

elemental compositions of these components are listed in Table III.

Table III. Results of Factor Analysis

Element	Factor composition				
	factor 1	factor 2	factor 3	factor 4	factor 5
Cd				4.7	<u>1000</u>
As	1.5		210	3.6	
Sb	2.9		310	4.2	
Zn				<u>1000</u>	
Al	940	320			
K		540			
Se	0.25	0.24			
V	6.6				
Cr	2.9	5.7			
Mn	17	6.1			
Fe	<u>1000</u>	<u>1000</u>			
Co	1.5	0.67	71		
Se	0.37		30	0.68	
Br			<u>1000</u>		
Eu	0.01	0.02			
W					800
Th	0.15	0.17			

Factors 1 and 2 can be identified with contributions from the soil, either separated artificially into two components, or representing two real soil components.

Factor 3 consists of a group of volatile elements, originating from high temperature industrial processes, including coal burning and refuse incineration, and from automobile exhaust (Br).

Factor 4, with a characteristic Zn/Cd-ratio of appr. 200, is associated with zinc ore processing.

Factor 5 does not reflect a typical emission pattern, but the cadmium and tungsten may originate from independent processes at the same location.

A next step in the source identification procedure was the calculation of an estimate of the contributions of the individual factors or aerosol components to the element concentrations in each of the lichen samples. Geographical maps of these individual contributions to the concentrations of a certain element give direct insight into the position of the associated sources and into the contributions of each of the sources to the total concentration of an element at a specific place.

Fig. 4 shows a map of the unprocessed cadmium concentrations and maps of the separate parts of the cadmium concentrations originating from the cadmium-containing factors 4 and 5.

Part of the sources of factor 4, and the source of factor 5 can be identified with industrial activities indicated in fig. 3. The largest source of cadmium in factor 4 can not be correlated directly with an industrial process actually going on, but it may originate from secondary emissions from dumps of zinc ashes.

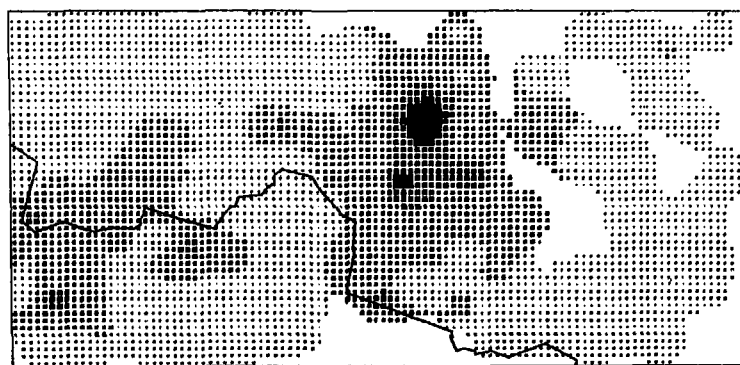
Fig. 5 shows a similar series of maps for antimony. An appreciable part of the antimony originates from soil contribution. The major source of antimony is associated with factor 3, comprising the volatile elements. The source of the corresponding component is possibly positioned just at the border of the area studied, but may be as well at greater distance in westerly direction. In the map of antimony from component 4 appears the same, yet not well identified, source as found for cadmium.

The results presented illustrate how multi-element information and use of appropriate data interpretation techniques can play an essential role in identifying sources of atmospheric pollutants. They underline the importance of multi trace-element analysis techniques such as INAA for environmental research and control.

Future position of INAA in environmental science.

It is always difficult to predict future developments in science and technology and one has to be very reserved when discussing the prospects of a specific technique. But there are no signs of developments in physics or chemistry, leading within the next decade to new routinely applied analytical technique for trace elements. Therefore, it may be worthwhile to discuss the future prospects of INAA, starting from the presently available alternative analytical techniques.

When regarding INAA as a routine method for the simultaneous determination of many trace elements present at often low concentration levels, the only realistic alternatives are inductively coupled plasma emission spectroscopy (ICPES), X-ray fluorescence analysis (XRF) and charged particle induced X-ray emission spectroscopy (PIXE). Atomic absorption spectroscopy can not be regarded as a multi-element analysis method, whereas analytical techniques based on inorganic mass spectroscopy are not suitable for application on a routine scale.



CD - CADMIUM

MIN: 1.00

• < 5.00

• ≥ 5.00

• ≥ 10.00

• ≥ 15.00

• ≥ 20.00

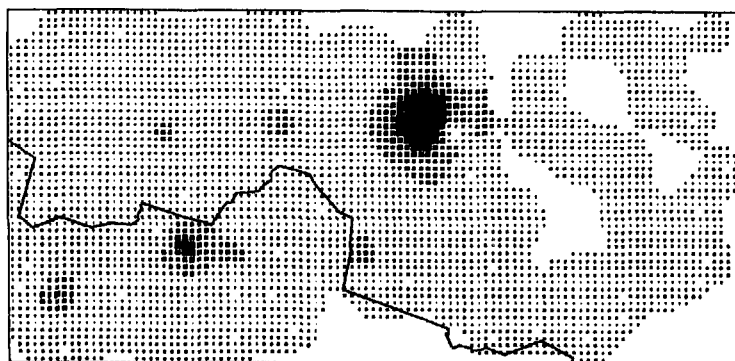
UNKNOWN CONC.

MAX: 32.72

PPM

CD-CONCENTR. IN
LECANORA CONIZ.
IN "DE KEMPEN"IRI
RESEARCH IS
SERVED DELFT

a



CD IN FACTOR 4

MIN: 0.00

• < 2.50

• ≥ 2.50

• ≥ 5.00

• ≥ 7.50

• ≥ 10.00

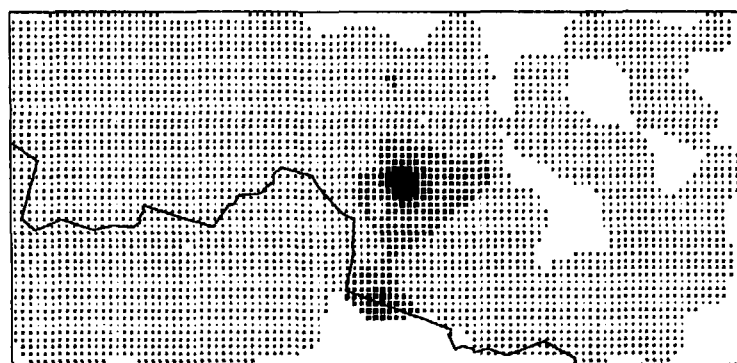
UNKNOWN CONC.

MAX: 31.01

PPM

CONCENTR. IN
LECANORA CONIZ.
IN "DE KEMPEN"IRI
RESEARCH IS
SERVED DELFT

b



CD IN FACTOR 5

MIN: 0.00

• < 2.50

• ≥ 2.50

• ≥ 5.00

• ≥ 7.50

• ≥ 10.00

UNKNOWN CONC.

MAX: 14.47

PPM

CONCENTR. IN
LECANORA CONIZ.
IN "DE KEMPEN"IRI
RESEARCH IS
SERVED DELFT

c

Fig. 4. Geographical distributions of total cadmium (a), and cadmium from factor 4 (b) and factor 5 (c).

SB - ANTIMON - ANTIMONY



MIN: 3.37
 • < 10.00
 • ≥ 10.00
 • ≥ 20.00
 • ≥ 30.00
 ■ ≥ 40.00

UNKNOWN CONC.

MAX: 61.28
 PPM

SB-CONCENTR. IN
 LECANORA CONIZ.
 IN "DE KEMPEN"

IRI
 REKELMEC 18
 2079J0 DELFT

a

SB IN FACTOR 1



MIN: 0.00
 • < 5.00
 • ≥ 5.00
 • ≥ 10.00
 • ≥ 15.00
 ■ ≥ 20.00

UNKNOWN CONC.

MAX: 24.46
 PPM

CONCENTR. IN
 LECANORA CONIZ.
 IN "DE KEMPEN"

IRI
 REKELMEC 18
 2079J0 DELFT

b

SB IN FACTOR 3



MIN: 0.00
 • < 5.00
 • ≥ 5.00
 • ≥ 10.00
 • ≥ 15.00
 ■ ≥ 20.00

UNKNOWN CONC.

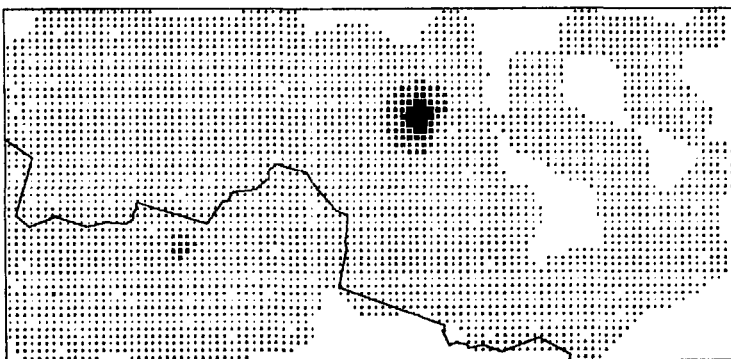
MAX: 27.88
 PPM

CONCENTR. IN
 LECANORA CONIZ.
 IN "DE KEMPEN"

IRI
 REKELMEC 18
 2079J0 DELFT

c

SB IN FACTOR 4



MIN: 0.00
 • < 5.00
 • ≥ 5.00
 • ≥ 10.00
 • ≥ 15.00
 ■ ≥ 20.00

UNKNOWN CONC.

MAX: 28.12
 PPM

CONCENTR. IN
 LECANORA CONIZ.
 IN "DE KEMPEN"

IRI
 REKELMEC 18
 2079J0 DELFT

d

Fig. 5. Geographical distributions of total antimony (a) and antimony from factor 1 (b), factor 3 (c) and factor 4 (d)

Of ICPEs the sensitivity seems on the average comparable to what can be obtained by INAA; for water, ICPEs seem even superior when no preconcentration is applied (35). For solid samples, the accuracy of ICPEs may be affected by contamination or losses in the dissolution step. For most elements, the detection limits obtainable by energy dispersive as well as wavelength dispersive XRF are higher than those for INAA or ICPEs (36). For PIXE, the minimum detectable masses are comparable to, and for some elements even lower than those for INAA (37). But since PIXE can only be applied to very thin specimens, it provides an alternative to INAA only for a limited number of sample types, such as air filters, thin slices of biological materials or trace elements in water after preconcentration. Moreover, application of PIXE is expensive because of the extensive use of a particle accelerator.

In the author's opinion three fields of application can be indicated where INAA is at present, and will be in the foreseeable future, the method of choice for multi-element trace analysis

- for routine analysis of materials which are difficult to convert into a solution suitable for ICPEs;
 - in cases where only milligram quantities of sample material are available;
 - as reference method for certifying standard materials or for testing other analytical techniques.
- A further increase of the supply of environmental samples for INAA can be expected as a result of increasing use of trace element pattern interpretation procedures in environmental research and monitoring.

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