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SOME MODERN TRENDS AND ANALYTICAL PROBLEMS IN ENVIRONMENTAL BIOCHEMICAL TOXICOLOGY RESEARCH

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Summary. – *The full assessment of the biochemical implications from environmental trace metal exposure requires analytical quality–assurance research for the reliable and accurate measurement of trace metal levels in biological samples such as tissues and biochemical components. Nuclear and radiochemical techniques such as neutron activation analysis (NAA) and radiotracers with very high specific radioactivity are very suitable methods for such a type of research. In particular they are very powerful techniques: a) for analytical control of contaminations and losses occurring during sampling, sample pretreatments and biochemical fractionations of cellular components for the identification of metallobiocomplexes; b) for developing routine methods for the microdetermination of trace metals such as atomic absorption spectroscopy (AAS). In this context NAA can be used as reference technique while the use of radiotracers improves our understanding of the atomization characteristics of the element being investigated and on the possible interferences from the matrix elements affecting the trace metal analysis.*

Riassunto (Prospettive e problemi analitici nella ricerca tossicologica, biochimica e ambientale). – *La valutazione delle possibili implicazioni biochimiche, derivanti da esposizioni a elementi in tracce, richiede ricerche di controlli analitici di qualità per rendere attendibili ed accurate le misure dei livelli attuali degli elementi in campioni biologici come tessuti e composti biochimici. Le tecniche nucleari e radiochimiche quali la radioattivazione neutronica (NAA) ed i radiotraccianti ad elevata radioattività specifica sono metodi di indagine molto efficaci per tale scopo. In particolare tali metodi sono specialmente adatti: a) per controlli analitici di qualità relativi a contaminazioni e perdite durante il campionamento, i trattamenti del campione nelle fasi della sua preparazione per l'analisi ed i processi biochimici di frazionamento cellulare per l'isolamento di metallobiocomplessi; b) per sviluppare metodi di routine per la microdeterminazione di elementi come la spettroscopia in assorbimento atomico (AAS). In tale contesto l'NAA può essere usata come tecnica di riferimento mentre l'uso dei radiotraccianti permette di aumentare le nostre conoscenze sulle caratteristiche di atomizzazione dell'elemento considerato e nello studio di possibili effetti interferenti di elementi costituenti la matrice inorganica dei campioni in esame.*

Introduction

Environmental trace metal pollution is an important contributory factor to some chronic diseases [1, 2]. It is hardly surprising, therefore, that there is a growing interest in the setting of health protection standards for trace metals which implies in turn a knowledge of the relations between the biochemical changes to long–term low–level exposure and the levels to which man is exposed from all pathways including air, food and water [3]. This requires the determination of the concentrations of trace elements in the various compartments of the body as well as a knowledge of their biotransformations taking place in the tissues [4]. Thus, the analytical aspect plays a fundamental role in the setting of protection standards.

Despite the great number of studies on trace elements in human tissues and body fluids, progress about the assessment of their impact on human health remains quite slow. A major factor responsible for this limited progress is almost certainly due to analytical difficulties involved in the accurate measurement of trace levels in the range of sub–$\mu g \cdot g^{-1}$ to sub–$\mu g \cdot g^{-1}$ as they often are in biological specimens. Although data on some trace elements in human tissues, particularly in blood and urine, are relatively abundant [5-7], they cannot generally be used in pratice for toxicological evaluations because of the absence of any quality assurance.

Many of the toxic trace metals of major concern are present in the tissues in concentrations lower than those in supra–pure chemical reagents and quartz or plastic ware. Thus, analytical data from samples collected in unpolluted areas often reflect the pollution

Step	Objective of the quality assurance study	Use of neutron activation analysis (NAA) and radiotracers
Sampling	Contamination and loss	NAA: determine the levels of trace metals in materials coming into contact with the sample
Sample pretreatments	Contamination and loss during freeze–drying, mineralization and preseparation steps	NAA: determine the levels of trace metals in acid solution for the mineralization and chemicals for the preparation
		Radiotracers: quantify losses during the pretreatment steps
Fractionation of cellular components	Contamination and loss during the biochemical procedures for the identification of metallobiocomplexes	NAA: determine levels of trace metals in biochemicals and different materials used for the cellular fractionation
		Radiotracers: study the behaviour of trace metals during the biochemical procedures for cellular fractionation
Development of routine techniques such as ET–AAS	Quantitation of the analyte and matrix behaviour at each step of the determination. Study of the the reaction mechanisms such as vaporization behaviour	NAA: references technique
		Radiotracers: label the analyte and the matrix elements

Fig. 1 – Analytical quality assurance research at the JRC–Ispra for trace metal microdeterminations in biological specimens such as tissues, body fluids and biochemical components

conditions of analytical laboratories, chemical reagents and glassware and not those of the original environment.

There is a great need for the quality assurance of the analytical data to be used for the evaluation of biochemical implications of trace metals on human health. The quality control must be applied not only to the determination of the *true* values of the total content of trace metals, but also, to sampling and sample pretreatment. The sources of potential contaminations during these operations are largely unknown and generate a considerable number of erroneous values, thus being "the Achilles' heel" [8] of environmental biochemical toxicology research carried out at ppb level. Thus, a major trend is to relate the routine techniques used in traditional laboratories to the use of analytical methods recognized as reference techniques such as neutron activation analysis (NAA) and isotope dilution mass spectrometry (IDMS).

The objective of this paper is to discuss some problems related to the combined use of nuclear and radioanalytical methods with analytical techniques, such as electrothermal atomic absorption spectrometry (ET–AAS) for analytical quality assurance studies of the microdetermination of trace metals in biological samples, such as tissues and biochemical components.

Experimental and results

Analytical quality assurance research

Fig. 1 outlines the quality assurance research planned and the techniques used in environmental toxicology studies, to study the parameters and factors affecting the analytical microdetermination of trace metals at various steps, such as:

a) sampling and sample pretreatment including the removal of the organic matrix and the development of preseparation procedures;

b) cellular fractionation for the isolation of metallobiocomplexes;

c) development of routine methods such as AAS by means of reference techniques such as NAA.

Sampling

Fig. 2 shows the approaches used in the identification and quantification of possible causes of contamination or loss during sampling of tissues and biochemical components for the microdetermination of trace elements. Three approaches are used [9]:

a) NAA of the materials such as scissors, needles, syringes which come into contact with the sample;

b) simulation of sampling using neutron activated materials and counting by high resolution gamma–ray spectrometry of the radioactivities released;

c) NAA of *uncontaminated* samples using the maximum precautions and special materials such as quartz knives and comparison of these with the same *heavily handled* sample.

Table 1 reports the analytical control data related to the determination of rare earths in human lungs and lymph nodes of a photoengraver professionally exposed to cored arc light carbon fumes [10]. Rat lung tissue was used to check possible contaminations arising during sampling and sample handling. The results show

Approach	Objective
NAA of the materials which come into contact with the sample (scissors, needles, syringes, containers)	Give information on the type of contaminant as well as on the potential level of contamination. Identify critical materials
Simulation of sampling using neutron activated materials which come into contact with the sample and counting of the radioactivities released	
NAA of aliquots of "uncontaminated" and "heavily handled" samples	Quantify the degree of contamination or loss under the sample conditions. Give the degree of uncertainty about the reliability of the results

Fig. 2 – Approaches used in the identification and quantification of possible causes of contamination or loss sampling

Table 1. – *Analytical quality control of rare earth determinations in human specimens as carried out by NAA*

	Approach used						
	NAA of materials which come into contact with sample (ppb)			Simulation of sampling by neutron activated surgical instruments (max. release,	NAA of "uncontaminated" and "heavily handled" rat lung (ppb)		Estimated risk of contamination in our determinations
Element	scalpel	forceps	scissors		uncontaminated	heavily handled	
La	–	–	–	< 10	< 20	< 50	none
Ce	< 250	< 231	< 20	< 100	< 70	< 100	none
Nd	20	31	< 50	< 50	100	120	none
Eu	< 10	< 70	50	< 3	0.8	2.1	none
Tb	< 200	20	50	< 2	< 2	4	1 (a)

(a) Impossible to estimate from present data

that the contribution of contamination is negligible with respect to the levels of rare earths found in the sample analysed.

Sample pretreatments

The preparation of biological samples for trace metal microdetermination can involve various steps such as: a) freeze–drying; b) destruction of the organic matrix; c) use of preseparation and preconcentration methods (Fig. 3). The number of pretreatment steps depends on the type of the sample as well as on the level and type of trace metal to be determined.

In the case of many soft tissues and of elements originating long lived radioisotopes by neutron activation, freeze–drying is a sufficient step for the analysis. On the other hand, the determination of elements such as vanadium present at the ppb level and originating ^{52}V (T 1/2 = 3.77 min) under neutron irradiation requires the destruction of the organic matrix and the preseparation of the element before irradiation.

Freeze–drying. – In addition to contaminations, losses due to sample–container interactions or volatilization during this process can occur. Regarding the recovery of the elements after lyophilization great advantage is taken by the use of radiotracers in *metabolized* form, because different behaviours have been observed in the freeze–drying of inorganic radiotracers added to the biological sample with respect to their *metabolized* forms. These latter compounds are prepared by administering low doses of radioactively labelled trace metal to laboratory animals and collecting the metal–labelled tissues and body fluids of interest.

Table 2 reports the losses during freeze–drying of inorganic trace metal solutions under standardized conditions [11]. Among 33 elements tested, As(III) and Hg(II) are the only elements showing significant losses, while the losses of other elements are judged to be negligible.

Destruction of the organic matrix. – This step is carried out using a teflon bomb apparatus. By this method fast digestion of the sample, small volumes and very low reagent blanks can be achieved. Losses of small amounts by volatilization are virtually eliminated during pressure decomposition (less than 1% for at least 41 elements). Ultrapure nitric acid is used for the dissolution of the

Table 2. – *Losses during freeze–drying of inorganic ions as determined by radiotracers. Operating time: 24-28 hs; operating pressure: 0.1 mbar; starting temperature: - 80 °C; final temperature: 25 °C*

Labelled element and oxidation state	Loss (%)
^{24}Na (I)	⩽ 1
^{42}K (I)	⩽ 1
^{45}Ca (II)	⩽ 1
^{46}Sc (III)	⩽ 1
^{48}V (IV or V)	⩽ 1
^{51}Cr (III)	⩽ 1
^{59}Fe (III)	⩽ 1
^{60}Co (II)	⩽ 1
^{63}Ni (II)	⩽ 1
^{65}Zn (II)	⩽ 1
^{72}Ga (III)	⩽ 1
^{74}As (III)	30
^{74}As (V)	⩽ 1
^{86}Rb (I)	⩽ 1
^{85}Sr (II)	⩽ 1
^{99}Mo (VI)	⩽ 1
^{103}Ru (IV)	⩽ 1
^{110}Ag (I)	⩽ 1
^{109}Cd (II)	⩽ 1
^{114}In (III)	⩽ 1
^{113}Sn (IV)	⩽ 7
^{125}Sb (V)	⩽ 1
^{134}Cs (I)	⩽ 1
^{131}Ba (II)	⩽ 1
^{181}Hf (IV)	⩽ 2
^{182}Ta (V)	⩽ 3
^{187}W (VI)	⩽ 1
^{198}Au (I)	⩽ 1
^{203}Hg (II)	10
^{201}Tl (I)	⩽ 1
^{203}Pb (II)	⩽ 1
^{140}La (III)	⩽ 1

sample and the organic matter destruction.

Table 3 shows typical trace metal contents in ultrapure HNO_3 (Merck, Darmstadt, FRG) used in the teflon bomb process as determined by NAA. Considering that the dissolution of the sample requires at least 2 ml of acid the purity of this reagent is satisfactory for many practical purposes. With the exception of blood, the estimated amounts of trace metal impurities introduced do not exceed the typical values in the tissues.

Preseparation and preconcentration procedures. – After mineralization of tissue samples the solutions to be analysed contain all elements in inorganic forms. Some of them, such as Na, P, Ca, K, Cl, are matrix elements and can interfere in the NAA determination of short–level induced radioisotopes. It is therefore necessary to remove the bulk of these elements using procedures which can also concentrate the element to be determined. Chelex–100 resin, which strongly absorbs many elements, is used for this purpose. In view of the extensive use of the resin for separation and concentration treatments before irradiation, different radiotracers were used for systematic study of the behaviour of trace metals on the resin (Table 4), and trace metal impurities determined in the resin by NAA. We can note that the matrix elements are removed by this treatment, while the resin retains most of the trace metals which can then be eluted and simultaneously measured by NAA.

Table 3. – *NAA of trace element impurities in ultrapure HNO_3 used for the mineralization of human tissues and body fluids during the wet digestion in teflon bomb*

Element	Concentration (ppb)	Estimated amount added in teflon bomb (ng)
As	0.3	0.6
Br	16	32
Cd	< 25	< 30
Co	0.06	0.12
Cr	2	4
Cs	0.01	0.02
Cu	2	4
Fe	32	64
Hg	< 10	< 20
Mn	6	12
Mo	0.4	0.8
Rb	0.5	1
Sb	0.05	0.1
Se	0.1	0.2
Sn	< 10	< 20
Sr	0.06	0.12
Th	< 0.02	< 0.04
U	0.008	0.016
Zn	3	6

Use of cellular fractionation methods

The cellular fractionation of the tissues for the isolation of metallobiocomplexes can involve the following steps (Fig. 3): homogenization in appropriate buffer, differential centrifugation for the preparation of the intracellular fractions, use of a biochemical technique of fractionation such as gel fractionation, electrophoresis, ion–exchange chromatography, isoelectrofocusing, high pressure liquid chromatography, dialysis, ultrafiltration and affinity chromatography [12]. The body fluids (blood and urine) can be directly fractionated by one of these latter methods.

When the cellular fractionation procedures must be applied for the identification of metallobiocomplexes of human origin it is absolutely necessary to know qualitatively and quantitatively the trace metals in materials and media to be used in the fractionation. These include buffers, resins and membranes for ultrafiltration. NAA with its multielement character is a very suitable technique for these determinations [13].

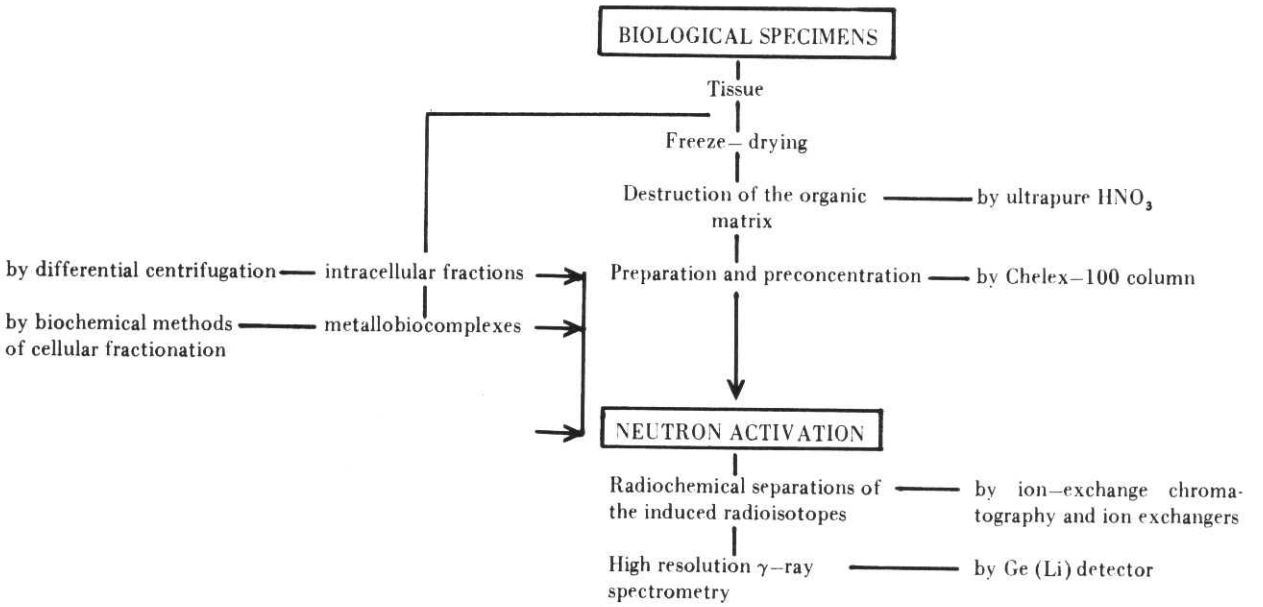

Fig. 3 – Outline of the steps for the preparation of biological samples for trace metal microdetermination

Table 4. – *Behaviour of various ions in aqueous solutions (pH = 4-7) on column of Chelex–100 (7x30mm)*

Elements absorbed	Elements not absorbed
Al (III)	Na (I)
Sc (III)	Mg (II)
V (IV)	Cl (-I)
Cr (III)	K (I)
Mn (II)	Ca (II)
Fe (III)	V (V)
Co (II)	Cr (VI)
Ni (II)	Ge (IV)
Cu (II)	As (III)
Zn (II)	As (V)
Ga (III)	Se (IV)
Zr (IV)	Se (VI)
Mo (VI)	Br (-I)
Pd (II)	Rb (I)
Ag (I)	Sr (II)
Cd (II)	Sb (III)
In (III)	Sb (V)
Sn (IV)	I (-I)
Hf (IV)	Cs (I)
W (VI)	Ta (V)
Hg (II)	Ir (VI)
Pb (II)	Pt (IV)
Bi (III)	Au (III)
Pa (V)	Tl (I)
La (III)	
Ce (III)	
Eu (III)	
Lu (III)	

In addition, in order to avoid artifacts which are very common in such a research is also necessary to understand the behaviour of the *free element* and its recovery during the fractionation procedure. The use of radiotracers is particularly important for a systematic study of the behaviour of trace elements in the various steps of the biochemical methods [12].

Table 5 summarizes the NAA of trace metals in two salts used to prepare buffers such as HEPES (hydroxy-

Table 5. – *Typical NAA of HEPES(a) and ammonium acetate(b) used in the application of biochemical methods for cellular fractionation*

Element	Metal concentration (ppm)	
	HEPES	NH_4COOCH_3
As	0.06	< 0.002
Au	0.0001	0.00006
Cd	10.6	0.12
Co	0.14	0.01
Cr	0.2	0.07
Fe	55	< 40
Hg	0.06	< 0.015
Mo	0.22	< 0.15
Sb	0.03	< 0.002
Se	0.06	< 0.04
Zn	< 0.5	< 0.2

(a) N–2 hydroxyethylpiperazine–N –2 ethanesulphonic acid
(b) from Merck

Table 6. – *Arsenic in biochemicals and materials used for biochemical fractionation of cellular components*

Biochemical	Company	Use	As concentration (ng/g)
TRIS (a)	Serva		6
TRIS (a)	Sigma		34
HEPES (b)	Serva		60
HEPES (b)	Good Serva	Buffers	3
TRIZMA(c)	Sigma		< 1
TES (d)	Serva		3
NH4COOCH3	Merck		< 2
Affigel	BioRad	Affinity chromatography	7
SDS (e)	BioRad	Membrane solubilization	< 30
Ficoll	Pharmacia	Density gradient	70
Metrizamide	Nyegard	Isopycnic centrifugation	6
Polyacrylamide	BioRad	Disc electrophoresis	250
Sephadex G–25	Pharmacia		
Sephadex G–75	Pharmacia		
Sephadex G–100	Pharmacia	Gel filtration	< 1
BioGel P–20	BioRad		

(a) see table

(b) section: use of cellular fractionation methods (see)

(c) pure TRIS

(d) N–tris (hydroxymethyl) methyl–2 aminoethane sulphonic acid

(e) sodium dodecylsulfate

ethylpiperazine–ethanesulphonic acid). The results show that the acetate buffer has a higher degree of purity than the HEPES. This conclusion is not surprising because it is known that buffers such as HEPES and TRIS (tris (hydroxymethyl)methylaminoethanesulphonic acid) have complexing properties for trace metals [14] which are probably enriched in the salt used in the preparation of the buffer solution.

Table 6 reports the results of NAA of arsenic in different biochemicals and materials used for biochemical fractionation of cellular components. The highest concentration of arsenic was found in polyacrylamide gel electrophoresis followed by affigel for affinity chromatography and ficoll for density gradient centrifugation. A good purity can be observed for materials used in gel chromatography. These results suggest that the use of gel electrophoresis for the isolation of native As–biocomplexes should be avoided while gel filtration can be conveniently applied.

Routine techniques developed by means of radiotracers and reference techniques

Radiotracers and NAA are also used in developing atomic absorption methods for the microdetermination of trace metals in biological specimens. The use of radiotracers constitutes a very powerful tool that improves our understanding of: a) the atomization characteristics of the elements being investigated; b) the interferring action of some common matrix elements (*e.g.* sodium and chlorides).

Fig. 4 illustrates the vaporization behaviour of vanadium at different atomization temperatures ranging from 1500 to 2750 °C. For each temperature a different furnace tube was used and the ^{48}V radioactivity, used to label ^{48}V–vanadate solutions, measured after one complete cycle. The absorbance value was also determined at each atomization cycle. From this curve two main conclusions can be drawn: 1) ^{48}V radioactivity starts decreasing and the absorbance starts increasing at approximately the same temperature (about 2000 °C). This observation tends to support the mechanisms of formation of VO in gaseous form which would dissociate to give free vanadium and oxygen [15]; and 2) at the temperature of the maximum absorbance the residual ^{48}V radioactivity is still large (about 40% of the initial one).

These findings suggest that vanadium is retained on the graphite in a very stable chemical form (possibly as carbide) which does not vaporize under the conditions used for the analysis.

Table 7 shows the behaviour of an inorganic matrix such as NaCl labelled with ^{22}Na radiotracer in the determination of aluminium and thallium. Two different behaviours can be observed. In the case of Al, at the temperature of charring, more than 95% of the Na is

Table 7. – *Behaviour of ^{22}Na–labelled Na^+ ions during the drying, ashing and atomization steps in the determination of thallium and aluminium*

THALLIUM *(a)*	Operating program			
	dry	ash	atomize	wash
Temperature (°C)	110	600	2350	2400
Time (s) –ramp	10	8	2	1
–hold	75	10	5	2
Residual ^{22}Na radioactivity (%)	100	96	0.05	–

ALUMINIUM *(b)*				
	dry	ash	atomize	wash
Temperature (°C)	250	1700	2400	2600
Time (s) –ramp	1	1	0	1
–hold	60	45	6	6
Residual ^{22}Na radioactivity (%)	100	4	0.7	–

(a) Final composition of sample solution: ^{22}NaCl saturated solution diluted 1:10; 0.1 M H_2SO_4; 0.01 M HNO_3. Volume of sample solution introduced into graphite tube: 50 µl

(b) Final composition of sample solution: ^{22}NaCl saturated solution diluted 1:10; 0.1 M HNO_3; 10.6 g/l of $Mg(NO_3)_2 \cdot 6H_2O$. Volume of sample: 20 µl introduced into L' VOV platform

vaporized. Thus, if Al would not be vaporized at this temperature no effect of Na on the determination of Al would occur. In the case of Tl at the charring temperature 96% of Na is still present in the sample. Thus, Na is vaporized together with Tl so that a matrix effect would be expected.

Conclusions

One of the main requirements of environmental biochemical toxicology research is the implementation of analytical quality assurance studies to assess the validity of the data being provided. This matter is of great practical interest to generate accurate and reliable data which can be used for toxicological assessment studies and the setting of protection standards.

The few examples reported here show the great advantage given by the use of nuclear and radiochemical techniques in the study of the parameters affecting

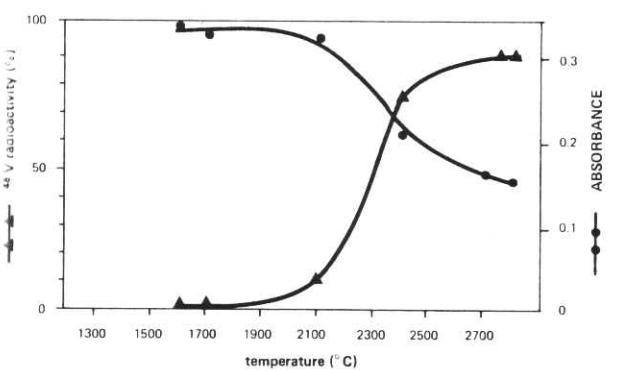

Fig. 4 – Vaporization behaviour of vanadium at different temperatures

Table 8. – *Aluminium content in NBS standard reference materials (not certified) bovine liver (SRM 1577)* [(a)]

Al content (ppm)	Reference
1.8	Good, 1977
2.0	Hislop, 1977
6.5	present lab., 1983
7.0	Brill, 1973
< 15	Capan, 1978
20.4	Nadkarni, 1977
20.4	Hofmann, 1974
20.8	Buono, 1977
23.4	Ward, 1979
37	Zitkowski, 1977
45.6	Nardkarni, 1977
50	Quater, 1979
51	Hoste, 1975
65	Capan, 1978

(a) Taken from reference [16]

trace metal determinations, such as contaminations or losses during the sequential analytical steps for the preparation of the sample for trace metal analysis, as well as in developing routine techniques, such as AAS.

We underline that the analytical quality controls must be applied not only to elements for which determinations at ppb levels are required, but even to the more common elements. The case of aluminium, generally present in biological specimens at ppm level, is an example of this. The great uncertainty related to its determination in biological materials is shown by the results on aluminium content reported by different authors in NBS reference material SRM 1577 such as bovine liver (Table 8).

Considering that these incredibly high differences are related to a standard material, one can easily imagine the tremendous problems involved in obtaining reliable analytical data on aluminium in biological specimens. If these differences are due to contamination or loss or to an erroneous use of the techniques or to other factors is difficult to say. Only analytical quality assurance research will be able to clarify their origin.

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ATOMIC EMISSION SPECTROSCOPY WITH A.C. INTERRUPTED ARC AND ATOMIC ABSORPTION SPECTROMETRY WITH GRAPHITE FURNACE AND COLD VAPOUR TECHNIQUE IN ENVIRONMENTAL PROTECTION STUDIES

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Summary. – *Use has been made of a.c. interrupted arc emission spectroscopy for survey analysis of trace metals in different soil and waste water samples. Trace metal content of the various water samples has been determined by atomic absorption spectrometry with graphite furnace atomizer. Elements such as Cd, Pb, Cr and Cu in soils and waste water is the concentration range of* 10^{-5} *- 1% have been studied and quantified. Trace elements are removed from the aqueous samples by means of an IDE–cellulose column. The ions of the metals under investigation are subsequently added at scaled concentrations. The method has been applied to the determination of trace metals in drinking and mineral waters. A method for the determination of mercury in water is also described.*

Riassunto (Spettroscopia di emissione atomica ad arco interrotto a c.a. e spettrofotometria di assorbimento atomico con fornetto di grafite e tecnica di vapori freddi in studi di protezione ambientale). – *E' stata utilizzata la spettroscopia di emissione ad arco interrotto a corrente alternata per un'indagine del contenuto di metalli in traccia in vari campioni di suoli e di acque di scarico. L'analisi dei campioni di acqua è stata effettuata per mezzo della spettrofotometria di assorbimento atomico, con fornetto di grafite. Sono stati studiati e quantizzati elementi come Cd, Pb, Cr e Cu nel suolo e nelle acque di scarico in concentrazioni da* 10^{-5} *a 1% . Gli elementi in esame sono stati separati dai campioni di acqua per mezzo di una colonna di IDE–cellulosa e quindi analizzati con il metodo delle aggiunte. Questo metodo è stato anche applicato per la determinazione di metalli in traccia in acque minerali e potabili. E' anche descritto un metodo per l'analisi del mercurio nell'acqua.*

Introduction

In analytical investigations for environmental protection, spectrochemical methods are very widely employed since they can be used for the determination of most of the metal and semi–metal components. Since the matrix of the samples may change over very wide limits, the measured emission or absorption depends to a great extent on the way of atomization and excitation. Therefore, a significant part of the spectrochemical investigations connected to environmental protection deals with atomization and excitation. The aim of these investigations is to accomplish conditions under which the excitation or atomization depends to the possible lowest extent on the composition of the sample, and thus the matrix effect is less significant. This work deals briefly with the results of our investigations on the a.c. interrupted arc generator with controlled arc circuit developed for semiquantitative analysis, with our special addition method developed for the determination of trace metal impurities in water by atomic absorption and with our method for the determination of organic mercury compounds in water.

Semiquantitative analysis with a.c. interrupted arc excitation

In environmental protection analysis it is often necessary and sufficient to carry out semiquantitative chemical emission analysis. This has the advantage that the full spectrum of the sample is taken, and thus the appearance of an eventual pollutant is observable even if we did not intend to determine it quantitatively.

For the analysis of samples of varying composition, containing volatile components and organic matter, a.c. interrupted arc excitation is widely applied. Its advantage is that due to the breaks between the burning periods, the heating of the sample is weaker than in the case of d.c. arc excitation. The application of a.c. interrupted arc was first suggested by Gerlach in the thirties. Critically investigating the method, Kaiser and Sohm have found that the use of interrupted arc improves the line intensity/background radiation ratio. The detection limits are thus lower and, owing to the better evaporation conditions, the reproducibility also improves.

Later, interrupted arc excitation has been more or less surpassed. For the investigation of metals mainly spark excitation was applied, whereas for the analysis

of powders – since they appear mostly in geological investigations and the task is then the determination of refractory materials – mostly d.c. arc excitation was used with total burning. One of the obstacles in the spread of a.c. interrupted arc excitation was the fact that the arc generators built in the fifties and sixties were controlled only in the ignition circuit, and when the current exceeds 8-10 A, particularly with the use of electrodes with poor thermal conductivity (like graphite), continuous arc develops. The application of lower currents, however, is unfavourable in the detection of refractory elements. To overcome these difficulties, we have developed a generator with controlled arc circuit. The first version was operated with thyratron tubes of xenon filling, the next was built with semiconductor components. In the latter, only the control unit was built in our laboratory, and this was connected to a DG–3 arc generator (USSR product). In principle, the control unit can be connected to any a.c. arc generator.

The scheme of the equipment can be seen in Fig. 1. The control unit built from thyristors and rectifiers

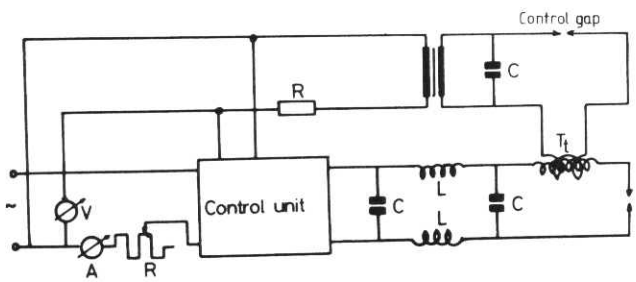

Fig. 1. – Circuit diagram of a.c. interrupted arc generator controlled in arc circuit

is inserted into the arc circuit of a Pfeilstricker–type generator. In the case of a.c. arc, according to Fig. 2a, only the thyristors are active, in antiparallel connection; d.c. arc can be produced according to Fig. 2b. In this case the system is operated as a bridged rectifier. In the case of a.c. arc position, a half–wave d.c. arc can be produced by the inhibition of one of the thyristors (polarized arc). The control unit can be applied up to 40 A, the DG–3 generator to 15 A.

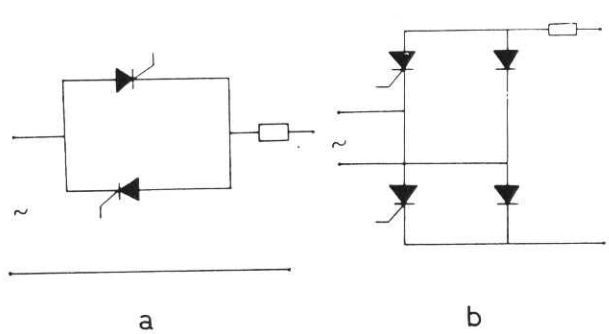

Fig. 2. – Circuit diagram of the control unit in the main (arc) circuit

Our experiments aimed at determining the conditions of application of the above equipment. Primarily, the effects of the phase position of arc ignition, of current and of the ratio of burning time to breaks were investigated. The investigations were carried out on sewage sludge and on soil samples. As model, garden soil was chosen. In this sample the concentration of elements studied was not too high, in fortunate cases below the detection limits. The elements to be studied were added to the appropriately pretreated (dried, pulverized) sample gradually, in the concentration range of $10^{-1} - 10^{-5}$ %.

The conditions of excitation were:
current: 4 - 16 A;
phase position of arc ignition: 70° and 90°;
burning times: 80, 120 and 200 ms;
break (cooling) times: 400, 600 and 700 ms.

Since the samples contained magnesium in sufficient concentration, on the basis of the Mg 279.8 nm and Mg 280.3 nm line pair the temperature of the plasma could be estimated. This line pair was applied for the determination of plasma temperature by Calker in 1956. According to our results, the plasma temperature is affected to a greater extent by the intensity of the arc current than the phase angle (position) of ignition. Higher currents involve higher plasma temperatures. The increase of plasma temperature favours the determination of those elements which, or the derivatives of which, are poorly volatile and the oxides of which have high dissociation energy (*e.g.* Ba). For volatile, easily dissociating compounds, the line–to–background intensity ratio is the most advantageous at medium (8-12 A) currents. Within one half period, the phase position of ignition has relatively little effect on line intensities. The intensity is the highest when ignition takes place before voltage maximum, but in this case deviations are also higher. Therefore, the arc is usually ignited at voltage maximum.

The determination of Cd is very important in environmental protection; this can be carried out easily with the above way of excitation. The line to background intensity ratio is much better with a.c. arc excitation than with d.c. arc. In the case of copper, cadmium and chromium the detection limit is ca. $10^{-4} - 10^{-5}$ %. The situation is less favourable for the detection of barium. If barium is present in the form of poorly dissociating compounds (phosphate, silicate or oxide), the detection limit becomes worse, and the line–to–background intensity ratio is better with d.c. arc.

The detection limits attainable with a.c. interrupted arc excitation are 1-3 orders higher than *e.g.* with atomic absorption analysis. However, in the investigation of solid samples the situation is not so unfavourable. By means of emission spectrography, solid samples can be investigated directly, whereas for atomic absorption the samples should be brought into solution. The concentration of the main constituent in the solution is at most 1-0.1 %, and thus the concentration of the trace elements to be determined is 2-3 orders lower in it. In the analysis of water samples or solutions, the analytes should be enriched by evaporation.

AAS investigations of trace metal pollutants of waters

The determination of trace metals in waters is an increasingly frequent task of environmental protection. The task is generally solved by atomic absorption methods, often by graphite furnace methods (GFA–AAS). This method meets the requirement generally well, with respect to sensitivity, detection limit and selectivity. However, the matrix effect is not negligible. Alkali metal and alkali earth metal elements are present in concentrations exceeding the concentrations of trace metals by several orders, and they strongly affect evaporation and atomization processes. Owing to this matrix effect, the atom concentration produced in the furnace on atomization may significantly differ from the concentration in the sample, and this may lead to serious errors.

In the atomic absorption analysis of the trace metal content of waters, for the compensation or suppression of interference effects a special addition method and a separation–enrichment method have been developed. In both methods, IDE–cellulose (imino–diacetic acid–ethylecellulose) prepared in our laboratory was applied (Fig. 3).

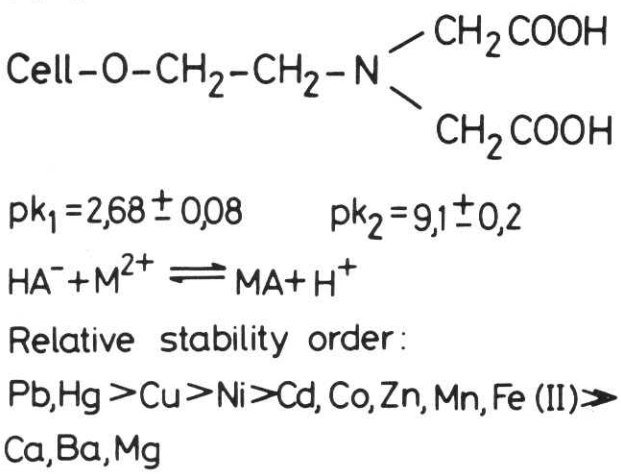

Fig. 3. –IDE–cellulose: iminodiacetic acid ethyl–cellulose

The complex formation ability of this dibasic acid, (iminodiacetic acid) is similar to that of EDTA, forming complexes mainly with the heavy metals. Complex formation ability is pH–dependent and it is generally preferable to work at pH = 5-6. The relative stability order of the complexes is as follows:

Pb, Hg >Cu >Ni >Cd, Co, Zn, Mn, Fe(II) >>Ca, Ba, Mg.

IDE–cellulose as ion exchanger has the following main advantages:

a) ion exchange is fast;

b) the bonded metal ions can be eluted easily and rapidly with relatively dilute acid;

c) it is well applicable in the separation of heavy metal ions from alkali and alkali earth metal ions;

d) IDE–cellulose itself is insoluble in water and dilute acids, and thus does not cause interference in the subsequent steps of analysis.

On the basis of these properties, IDE–cellulose is very advantageous in quantitatively binding the heavy metal content of various water samples without changing the concentration of main constituents. Our special addition and enrichment separation method is based on these properties.

The essence of our special addition method is that the standards necessary for water analysis are prepared from the water sample itself. In the first step, an appropriate fraction of the sample is passed through an IDE–cellulose column. The heavy metals are bonded on the column, their concentration in the filtrate is below the detection limit, but the macro–components (alkali metal and alkali earth metal ions) remain in practically unchanged concentration. If the metal ions to be analysed are added in appropriate concentrations to the resulting filtered water, standards are obtained in the matrix the same as in the unknown samples.

The advantage of this special addition method over other addition methods is that it starts with zero concentration, and thus the eventual curvature of the analytical line causes no problems. On the other hand, over the ion exchange method it has the advantage that if the concentration of main constituents does not change significantly, it is not necessary to carry out separation in each case. The standards can be stored for long periods, even for 1-2 years, in acidic medium in plastic containers. As a further advantage, it can be mentioned that this method can also be used for the more or less precise determination of metal ions, in colloidal form, whereas by ion exchange or other separation methods they are hard to determine, if possible at all. For acidification nitric acid is applied, in the presence of which the matrix effect is weaker than with hydrochloric acid.

The filtered water samples prepared in the described way can be used to study matrix effect. We have studied, *e.g.*, how in waters of different hardness the matrix effect reduces the signal obtained in the determination of lead with electrothermal atomization. The results are shown in Table 1. The concentrations of the matrices of the water samples investigated are given in Table 2. The reduction of absorbance was related to that of lead measured in high–purity water. The strongest reduction of absorbance was measured in the case of the hardest well–water. High–purity water was prepared from distilled water by filtration through a cation– and anion–exchange column filled with cotton–form cellulose. The concentration of the elements in this water is below or equal to the detection limit of atomic absorption with electrothermal atomization (Table 3).

The special addition method was used for the determination of the heavy metal trace impurities of the water of lake Balaton. The samples were taken, in collaboration with the Biological Research Institute of the Hungarian Academy of Sciences, at places shown in Fig. 4 on the same day. The standard solutions were prepared from purified samples (filtration on

Table 1. – *The change of absorbance by the GFA–AAS determination of lead in different waters*

Waters	High purity water	Tap water		Well water		Balaton water	
ng Pb / 20 µl	A	A	%	A	%	A	%
1.0	0.1337	0.0894	–33	0.0580	–57	0.0706	–47
2.0	0.2326	0.1518	–35	0.1013	–56	0.1203	–48

Table 2. – *The cation and anion content of some waters purified on cellulose column*

Cations	Tap water	Well water	Balaton water
Na^+	9.03	54.9	22
K^+	2.50	100.0	5.9
Ca^{2+}	44.2	130.0	36
Mg^{2+}	21.1	56.3	43
Anions			
HCO_3^-	280	339	220
CO_3^{2-}	20	31.5	17
Cl^-	24	102	20
SO_4^{2-}	16	245	89

membrane filter of 0.45 µm pore size and then on IDE–cellulose). The samples were acidified with bidistilled nitric acid (0.3 ml / 100 ml sample). The results are given in Table 4.

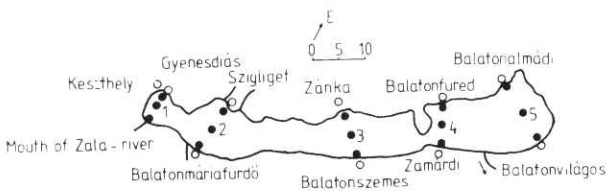

Fig. 4. – Sampling stations in lake Balaton

Table 3. – *Metal content of high purity water determined GFA–AAS*

Metal	µg/dm³
Cd	< 0.005
Cu	< 0.02
Pb	< 0.02
Mn	< 0.02
Zn	< 0.01
Fe	< 0.3
Ca	< 1.0
Hg	< 0.06
As	< 0.02

With the filtered and unfiltered samples, there is a quite great difference in the iron and manganese concentrations. This indicates that the amount of suspended matter cannot be neglected in lake Balaton, and this contains iron and manganese. The concentrations of Cu, Cr and Pb are below the detection limit in the lake. Table 5 shows the cadmium content of the lake (the measurements were carried out in three seasons: spring, summer and autumn). Cadmium can be detected in the autumn sample, but its concentration does not even reach the limit permissible in drinking water.

Table 4. – *Metal concentrations in Lake Balaton water samples GFA–AAS (1981)*

Station	Fe		Mn	
	µg/dm³			
	Labile unfiltr.	Dissolved filtrated	Labile unfiltr.	Dissolved filtrated
Keszthely	70	3.9	13	< 0.5
Mouth of	80	2.2	17	< 0.5
Zala–River	30	3.0	14	< 0.5
Szigliget–	230	3.4	17	< 0.5
Balatonmária–	110	3.6	15	< 0.5
fürdő	125	3.0	13	< 0.5
Zánka–	70	5.4	7.2	< 0.5
Balatonszemes	30	11.0	7.8	< 0.5
	70	1.8	7.8	< 0.5
Balatonfüred–	70	9.0	6.8	< 0.5
Zamárdi	70	7.5	6.8	< 0.5
	80	6.8	5.6	< 0.5
Balatonalmádi	80	3.4	4.0	< 0.5
Balatonvilágos	70	3.0	6.3	< 0.5
	90	3.4	4.4	< 0.5

Cu–content in filtrated and unfiltrated water samples < 3 µg/dm
Pb–content in filtrated and unfiltrated water samples < 5 µg/dm
Cr–content in filtrated and unfiltrated water samples < 2 µg/dm

Table 5. – *Cadmium content of Balaton water samples (1981)*

	Cd content µg/dm³		
	April	June	October
Keszthely	< 0.05		0.26
Mouth of	< 0.05	< 0.05	0.14
Zala–river	0.50		0.10
Szigliget–	< 0.05		0.05
Balatonmária–	0.50	< 0.05	0.18
fürdő	< 0.05		0.12
Zánka–			0.10
Balatonszemes	< 0.05	< 0.05	0.28
			0.48
Balatonfüred–		0.10	0.12
Zamárdi	< 0.05	< 0.05	0.05
		< 0.05	0.05
Balatonalmádi–	< 0.05		0.05
Balatonvilágos	< 0.05	< 0.05	0.05
	0.4		0.05

Our results indicate that the special addition method is well applicable for the determination of the heavy metal content of surface waters.

In very hard waters or in the case of extremely large salt content, even the special addition method fails to give reliable results. Owing to the high salt content, the blank value and the noise level increase, and even with the application of background correction the reliability of the results is poor. In such cases the detection limit and the precision (reproducibility) can be improved by means of IDE–cellulose ion exchange enrichment separation. This method was first elaborated in connection with the flame atomization technique. The procedure, *mutatis mutandis*, can also be combined with GFA–AAS measurements. In this technique, the ions to be analysed are measured in the eluate. For the elution 1 N HNO_3 is used. In this case, however, the amount of alkali earth metals bound to the column cannot be neglected; before determination they should be selectively eluted. According to this procedure, heavy metals can be measured in the ppb range.

Determination of organic mercury compounds in waters

Cold vapour atomic absorption techniques are increasingly widespread for the determination of the mercury content of water samples. Accordingly, mercury content is reduced with $SnCl_2$ or $NaBH_4$ into elementary (free metal) mercury, the latter is expelled from the solution with neutral gas stream, and conducted into a cell with quartz windows. Then, the measurement runs according to the usual principles of atomic absorption. The technique is at a first glance free of matrix effect. It is, in fact, not so, if it is taken into account that the reduction strongly depends on the bonding type of mercury in the actual derivative. In the solution of stable organic mercury compounds only a small fraction of the metal is in dissociated state, and thus reduction is imperfect. In environmental protection analysis mercury pollution in organic compounds may be frequently encountered (seed–dressings of mercury content, formation of organic mercury derivatives from inorganic derivatives in sludges via putrescence, etc.).

For the determination of the organic mercury compounds in water, $KMnO_4$ + HCl or BrCl breakdown is suggested. From these compounds chlorine or bromine, respectively, are formed which decomposes the organic mercury derivatives according to the following reactions:

$$HgR_2 + Cl_2 \rightleftharpoons RHgCl + RCl$$
$$RHgCl + Cl_2 \rightleftharpoons HgCl_2 + RCl$$
$$BrO_3^- + 2Br^- + 3Cl^- + 6H^+ \rightleftharpoons 3BrCl + 3H_2O.$$

Of the two reagents, BrCl has the faster decomposition effect. If the concentration of BrCl exceeds 0.005M the decomposition of even the most stable mercury derivatives requires no more than 30 min. For the decomposition of organic mercury derivatives, recent zonic irradiation is also recommended. It is claimed as advantage that no reagents are required, and thus the risk of contamination is lower. It should be noted, however, that a conserving agent is required here as well. In the BrCl or MnO_4^- + HCl decomposition, the reagent itself is the conserving agent. If the water sample is taken directly in the measuring flask and the reagent is added to it, the time elapsed during the transport of the sample into the laboratory is certainly enough for the decomposition.

In the determination of mercury after the decomposition of organic mercury derivatives, the sensitivity and detection limit were the same as with the determination of inorganic mercury compounds.

The matrix effect was also investigated. The analysis can be carried out in the presence of high amounts (3%) of NaCl. Of the solvents, the effects of methanol, ethanol and iso–propanol were studied in the concentration range of 10-100 µl/dm³. No interference was found. However, interference is caused by benzene, since it is not decomposed by BrCl or the $KMnO_4$ – HCl system, and it has a continuous absorption in the range 253.7 nm. Up to a concentration of 40 mg/dm³, this interference can be compensated by deuterium corrector.

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SOLUTION EMISSION SPECTROGRAPHIC AND SPECTROMETRIC ANALYSIS OF POWDERS FOR ENVIRONMENTAL PROTECTION

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Summary. – *The determination of components CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2 and MnO in aerial– transported powders has been carried out after precipitation with Na_2O_2 in aqueous HCl by spectrographic method. Trace elements such as As, B, Co, Cu, Mn, Mo and Zn in soils have been quantified in the µg/ml range. Excitation sources such as aerosol–fed high–tension spark with drilled electrodes, gas–stabilized arc according to Marinković and the Rotrode technique with axial argon–flux are compared. Powder samples of different origin have been analyzed for their content in V, Ti and Cr. Single components of the solution samples have been determined spectrometrically in a gas–stabilized d.c. arc by means of photoelectric detector system–double-beam detector for lines and background. The sequential direct analytical method and the simultaneous spectrographic tecnique are finally compared.*

Riassunto (Analisi spettrometrica e spettrografica in emissione di soluzioni di polveri in ricerche di protezione ambientale). – *La determinazione di CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2 e MnO nel particolato atmosferico è stata effettuata spettrograficamente dopo precipitazione con Na_2O_2 in una soluzione acquosa di HCl. In campioni di suolo elementi come As, B, Co, Cu, Mn, Mo e Zn sono stati ritrovati in concentrazioni dell'ordine del µg/ml. Sono state confrontate sorgenti di eccitazione come la scintilla ad alta tensione con elettrodi perforati per l'immissione dell'aerosol, l'arco a gas stabilizzato secondo Marinković e la tecnica Rotrode con flusso assiale dell'argon. Campioni di polveri di varia origine sono stati analizzati per il contenuto in V, Ti e Cr. I singoli componenti dei campioni in soluzione sono determinati con arco a c.c. a gas stabilizzato con rivelatore fotoelettrico a doppio raggio per la riga dell'elemento e per il fondo. Si confrontano infine i metodi diretti di analisi sequenziale con quelli spettrografici simultanei.*

Introduction

The chemical composition of airborne particulate samples can characterize their origin. The determination of both major components and trace (minor) elements is important in this aspect, and a number of suitable methods of emission spectral analysis have been elaborated. As the requirements of major and trace element determinations are quite different, the methods below are dealt with separately for these. Determination of toxic trace elements is even more important in matters of biosphere, such as soils, wastes, etc. This paper gives methods used today in our spectrochemical laboratory but based on earlier investigations which are also presented here.

Samples of unknown chemical composition are investigated preliminarly in *solid form* using total evaporation of 15-20 mg sample mixed with graphite powder (1+1) in a 8A d.c. arc source continuously in 180 s but recording 3 spectra: the first 30 s for the volatile parts, followed by a 60 s period, and 90 s at the end for the non volatile part (carbide–forming elements, etc.).

Determination of major components of airborne particulate samples [1]

Preparation of solutions: 50 mg powder sample, weighed in a silver cuyp onto 1 g previously given NaOH and partly (about 50 mg) Na_2O_2, is melted at about 600 °C. After 4-5 min fusion, the melt is dissoluted in HCl (1+1) and 50 ml solution (HCl 1+4) prepared, containing 4 mg/ml Cu as a reference element (or Co if also Cu is to be determined). Smaller samples (3 mg as a minimum) can be prepared in a similar way but with a proportionally smaller end volume. Samples hardly destroyed can be dissolved after treating in a sodium peroxide Parr bomb (8 ml) under pressure. Standard samples for the calibration of the method can be easily achieved synthetically, and control samples of SRMs are also available.

Spectrochemical analysis method: with the tube electrode spray method [2] 3-5 ml sample solution is put into a pneumatic nebulizer (Fig. 1), and the fine aerosol introduced with N_2 into a spark discharge ($U = 12\ kV_{eff}$, C= 12nF, L=1.5 mH).

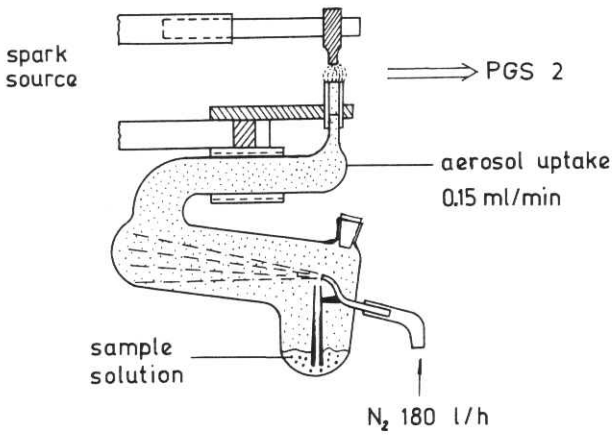

Fig. 1. – Pneumatic nebulizer and excitation source of the tube electrode spray method

Spectra are produced with a plane grating spectrograph (PGS 2, C. Zeiss, Jena), grating blazed at 280 nm, rec. lin. disp. 0.76 nm/mm, photographed on a fine graining emulsion (Agfa–Gevaert Scientia 23 D 50), and light power enhanced with a quartz cylindrical lens. Pre–sparking time 30 s, followed by double exposition of 15 s each.

Evaluation of the spectra performed on analysis line pairs:

Fe	275.5 nm	Cu 282.4 nm
Mg	277.9 nm	
Si	288.1 nm	
Mn	294.9 nm	Cu 296.1 nm
Al	308.2 nm	
Ca	315.8 nm	

Line blackenings(S)measured with a microdensitometer (G II, C. Zeiss, Jena) are transformed into I–values [3] and background corrected with a computer program to ΔY_{corr} values. An example of calibration graphs is shown on Fig. 2.

Analysis results of Austrian airborne dust samples [4]: samples collected in Vienna (W 1/1) and Graz (G 1/1) were analyzed applying various methods in seven analytical laboratories. Table 1 shows the results achieved with this spectrochemical method, and the averages from overall laboratories, with the calculated values of

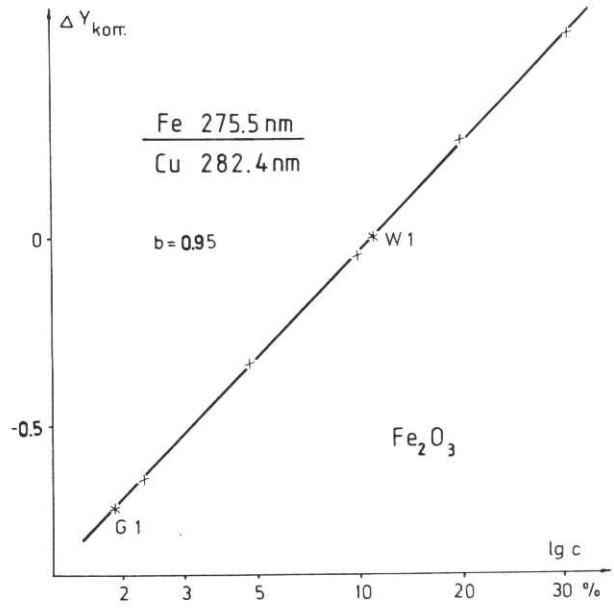

Fig. 2. – Calibration graph of the line pair Fe 275.5 – Cu 282.4 with the tube electrode spray method on the base of 9 parallel spectra. G1 and W1: results of SRMs of NBS–US Geological Survey

Table 1. – *Analysis results of Austrian airborne dust samples, in TU Veszprém, overall averages ($\bar{\bar{c}}$) and standard deviations (s)*

W 1/1 – Vienna	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	MgO (%)	CaO (%)
TU Veszprém	3.1	5.5	31.0	5.2	18.6
	3.2	5.8	32.0	5.5	20.5
	3.6	5.95	32.4	5.7	23.6
$\bar{c}$	3.3	5.75	31.8	5.5	20.9
overall $\bar{\bar{c}}$	3.23	5.50	37.35	5.42	21.45
overall s	0.09	0.32	6.81	0.39	1.87

G 1/1 – Graz	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	MgO (%)	CaO (%)
TU Veszprém	5.3	8.2	31.7	5.6	16.0
	5.6	8.3	36.5	5.7	19.0
$\bar{c}$	5.45	8.25	34.1	5.65	17.5
overall $\bar{\bar{c}}$	5.49	7.48	42.66	5.99	16.38
overall s	0.17	1.44	10.21	0.38	1.55

standard deviation. Report [4] accepted the results of Si determination only as orientative being extremely subject to the individual operating conditions. The results obtained show that the method used was suitable for determination of major components of dust samples, and can be easily applied in similar analyses.

Determination of trace elements in soils

After an alkaline fusion the sample components become as minor elements in an alkali chloride solution. The elements being originally traces cannot be determined with sufficient detectability. An acidic destruction of the sample, on the contrary, adds no matrix element to the solution, and especially using H_2F_2 a matrix reduction (SiO_2), *i.e.* some preconcentration of the other elements occurs.

Silicate based matters: first of all soils of different types were investigated, using a hydrogen fluoride destruction and three different spectrochemical solution analysis methods [5]. The tube electrode spray method with high voltage spark excitation and argon or nitrogen spraying gas was compared with the rotating disk spark technique using an axial argon blow in, and with the low current (6A) argon stabilized d.c. arc source according to Marinković. The trace elements determined in the soil solutions, the analysis lines and the estimated detection limits are listed in the Table 2.

It has been stated that the reproducibility of the Marinković arc is superior but matrix effects of different soil types are more depressed in spark excitation techniques, and detection limits show minimum values at the tube electrode argon spray method, as well as at the rotating disk argon blow in technique. Nitrogen gas excitation atmosphere is superior only in the presence of easily ionizable (alkaline) elements but in absence of the latter, argon plasma enhances the trace element intensities and reduces the standard deviation.

Trace element analysis of various environmental samples

The trace element analysis with the tube electrode spray method was further developed for various sample types of industrial wastes, dusts, ashes, etc. It was found that the destruction of samples can be performed easier and gives more reliable results in a teflon bomb under pressure, heated 1 h at a temperature of 130-140 °C. Traces of V, Cr, Ti, Mn, etc. were determined in HNO_3 containing solutions, with relative standard deviations between 5-10% . and detection limits of 0.01-0.1 μg/ml. Spectrographic analysis conditions were similar to those of major component determinations but in this case Pd was used as a reliable reference element, and argon as spraying gas.

Spectrometric (direct reading) trace analysis

Spectrographic analysis methods are advantageous if multielement determination are requested, and especially if any other element can be present in the samples which is not involved in the analysis (for this a given multielement spectrometric system is "blind"). On the other hand, also a single element spectrometric system can work "economically" if a series of results of one (or two) element in many samples in less time with better reproducibility are requested. For similar tasks [6], a photoelectric detector system was built and adapted for the plane grating spectrograph.

The detection system consists of a photomultiplier (EMI low noise end–on tube) working by time–sharing

Table 2. – *Detection limits (c) of trace element determinations in soil samples after a H_2F_2 destruction using various radiation sources* [5]

Analysis lines (nm)	Tube electrode spray–m. (Ar)	Tube electrode spray–m. (N_2)	Rot. disk m. (Ar)	Marink. arc m. (Ar)
As 234.9	2	2	2	2
B 249.7	0.5	1	0.5	5
Co 345.4	0.1	0.7	0.1	0.7
Cu 327.4	0.05	0.05	0.05	0.1
Mn 257.6 (or 293.3)	0.2	0.2	0.2	0.5
Mo 317.0 (or 379.8)	0.1	0.7	0.3	0.1
Zn 334.5	0.5	2	0.2	2

Reference lines: Bi 240.1; Bi 298.9; Bi 299.3; Bi 302.5

(c in μg/ml; 1 μg/ml corresponds to 0.005% in the sample)

(Fig. 3); adjusting a spectral line onto the entrance slit of the spectrograph, the movable part of the exit slit can be adjusted on a nearby situated spectral line, or as a rule, adjacent to the analysis line background. Applying a LED controlled chopper disk, background corrected spectral line intensity can be directly measured or recorded. By calibrating with synthetic standard solutions the intensity–concentration function of an element, rapid concentration determination with a relative standard deviation of 3-6% can be achieved.

A suitable radiation source for this detector system is the stabilized Marinković arc (Fig. 4) (a high voltage

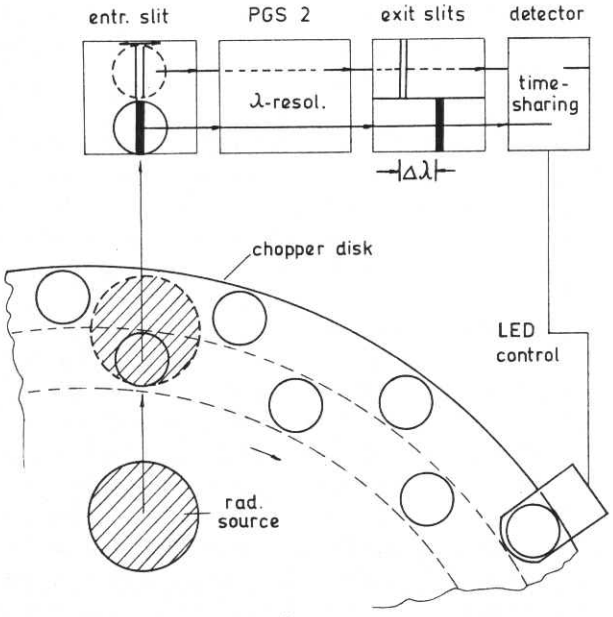

Fig. 3. – Direct reading detection system operating in time sharing mode

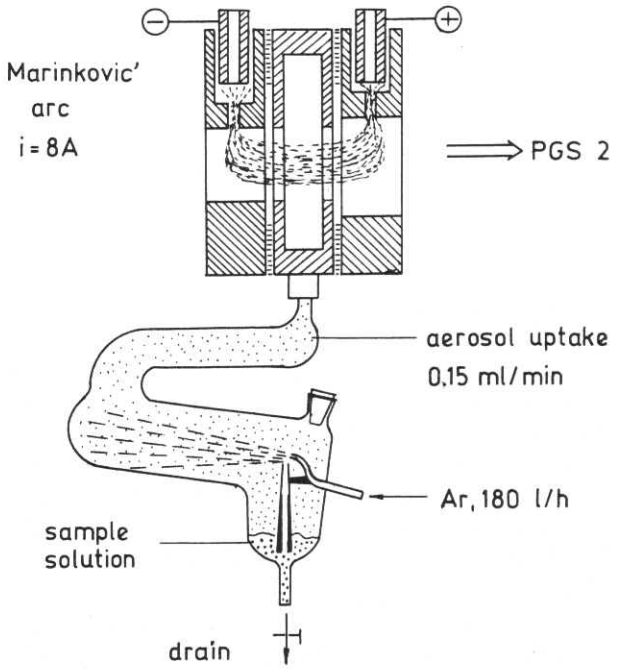

Fig. 4. – Stabilized d.c. plasma source according to Marinković with aerosol introduction using a modified pneumatic nebulizer

spark source causes hard shielding problems due to high frequency interference of the signals). The correctly adjusted long pathway of the plasma ensures stable radiation of enhanced intensity. To avoid memory–effects, care must be taken to accurately rinse and clean the nebulizer–source system. For measuring a second element, wavelength adjusting and concentration calibration have to be performed anew.

The choice of the suitable analysis method and detection system depends always on the task and analysis requirements.

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