

SPECTRAL METHODS IN WATER ANALYSIS

Contents: 1. Introduction. 2. Absorption and atomic fluorescence spectrometry. 3. Atomic emission spectrometry. 4. X-ray fluorescence spectrometry. 5. Other methods. 6. Conclusions; Streszczenie; References.

1. INTRODUCTION

Natural waters include sea waters, surface waters (rivers, lakes, ponds), ground waters (saline waters, deep waters, spring and mineral waters) as well as industrial waters and sewage. A still wider term is the „aquatic environment” including suspended matter, organisms living in water and bottom sediments. Consequently, all chemical elements occurring in the Nature can be expected to be found in the aquatic environment. Already in the 19th century it was foreseen that all elements of the Periodic Table occur in sea water. Recent studies confirmed the presence of 73 elements in the seas and oceans. Most of these elements occur in trace amounts. Earlier studies on the composition of sea and deep waters were aimed either at identification of their mineral resources or the solving of hydrological and geological problems. Nowadays new problems have emerged, concerned with studies on the trophic chain of elements in the ecosystem and the protection of the environment [27]. Interest in the role of trace elements and their toxicity in Nature [25] including rare-earth elements and noble metals, has grown.

In most cases the determination of one or several elements is of no value. Analysts are frequently required to carry out simultaneous determinations of a dozen or even tens of elements in very small samples containing only their traces [37]. Further requirements claim differentiation of various organic and inorganic forms of metallic elements [20]. In Tables 1 and 2 an example has been given of the mean elemental composition of sea water and requirements as to the detection limits of some elements in deep and drinking waters.

Table 1. Mean elemental composition of sea water [30, 37]
 Tab. 1. Średni skład pierwiastków wód morskich [30, 37]

Content — Zawartość, $\mu\text{g/ml}$	Elements — Pierwiastki
Major components Składniki główne	
10^4 — 10^3	Cl, Na, Mg
10^2 — 10^1	S, Ca, K, Br, C
100	Sr, B, Si, F
Trace elements Pierwiastki śladowe	
10^{-1}	Li, N, Rb
10^{-2}	Al, Ba, Fe, I, Mo, P, Zn
10^{-3}	As, Cu, Mn, Ni, Ti, U, V
10^{-4}	Co, Se, Sn
10^{-5}	Ag, Bi, Cd, Cr, Hg, Pb
10^{-6}	Au, Be

Table 2. Minimum detectable limits required in the analysis of drinking water and some underground water [30, 34]

Tab. 2. Wykrywalności wymagane w analizie wód pitnych i niektórych wód podziemnych [30, 34]

Minimum detectable limit Wykrywalność $\mu\text{g/ml}$	Elements to be determined — Oznaczone pierwiastki	
	Underground water Wody podziemne	Drinking water Wody pitne
10^0		B, Ba, Cu, Sr, Zn
10^{-1}		Al, Fe, Mo
10^{-2}	Fe, Mg, P, Ti, Sr	Ag, As, Cr, Mn, Pb
10^{-3}	Ba, Br, Cr, Cu, Li, Ni, Rb Zn	Cd, Se
10^{-4}	Ag, As, B, Ce, Co, Cs, Ga Gd, Ge, I, La, Mo, Nb, Pb Pr, Sb, Sc, Sm, Sn, Th, U, V Y, Zr	Be
10^{-5}	Be, Cd, Dy, Er, Eu, Hf, Hg Ho, Se, Ta, Tb, Tl, W, Yt	
10^{-6}	Bi, In	
10^{-7}	Au, Pt, Pd, Te	
10^{-8}	Ir, Re	

Within the past few years numerous monographs dealing with water analysis [15, 26, 34, 39] have appeared. Every two years review papers devoted to methods of water analysis appear in „Analytical Chemistry”, similar reviews being made each year by the „Journal of the Water Pollution Control Federation”. A comprehensive discussion of various review papers and all monographic literature concerned with all, not only spectral, methods of water analysis can be found in the second chapter of the second volume of the book entitled „Applied Atomic Spectroscopy” [11]. This chapter also contains much valuable information about the basic principles and applications of all atomic spectroscopy methods. Even a superficial review of these monographs and papers shows that in the determination of metallic elements, and in particular their trace amounts, spectral methods predominate. Special monographs have been confined to these methods [12, 30]. A more detailed analysis of the data concerned with the application of different methods [19] confirms this statement. During 1975—1977 the contribution of particular analytical methods was as follows (per cent):

atomic absorption spectrometry	44
molecular spectrophotometry, colorimetry	15
electrochemical methods	12
atomic emission spectrometry	9
X-ray fluorescence	9
neutron activation analysis	8
mass spectrometry	2
others	1

Each year 200—300 articles on the determination of various elements in water appear all over the world, more than one-half of the number being concerned with atomic spectrometry and X-ray fluorescence spectrometry. In ARAAS [2], a publication providing information about all publications covering analytical atomic spectrometry only, 115 items concerning the application of these methods to analysis of waters and the aquatic environment were specified in 1976. In 1977 the number of publications increased to 150.

The main advantage of atomic spectrometry and X-ray fluorescence spectrometry is the very high specificity of these methods in respect of the elements analysed. The same specificity can be achieved only by mass spectrometry. Other important advantages of the spectral methods, in particular of mass spectrometry, are very low detection limits and the possibility of assaying all elements of the Periodic Table. Only the X-ray fluorescence techniques are limited to assays of only those elements whose atomic numbers are higher than 11.

2. ABSORPTION AND ATOMIC FLUORESCENCE SPECTROMETRY

In the history of analytical chemistry, the rapid development of atomic absorption spectrometry (AAS) is an exceptional phenomenon. The first communications about AAS appeared as late as in the mid-50-ties. Ten years later numerous firms were already manufacturing their own types of instruments and now almost all analytical laboratories the world over employ this technique. Hence, it is no wonder that AAS has become one of the most convenient and widespread methods employed to assay trace elements in waters and the aquatic environment.

In the western countries the AAS techniques are increasingly recommended by various official organisations and by standards as routine methods for the assaying, in water, of such elements as Cd, Cu, Hg, Mn, Pb and Zn. Other elements frequently assayed by this method are As, Cr, Fe, Ni and Se. Both Poland and the socialist countries are markedly behind in employing the AAS methods, although certain progress has been made during the past two years. The authors of the monograph [34] ascribe this delay to the lack of appropriate equipment. They emphasize the advantages of AAS, such as high precision, simplicity and speed of determinations, and postulate the necessity to make up for lost time.

Atomic absorption spectroscopy does not, principally, require isolation of the elements to be determined. The high specificity of atomic spectra enables one element to be assayed in the presence of others. This refers to all spectral methods utilizing characteristic features of either atomic structure (emission, absorption and atomic fluorescence spectroscopy, X-ray fluorescence spectroscopy) or whole ionized atoms (mass spectrometry). The presence of other elements, particularly in large quantities, frequently increases the detection limits of trace elements.

In regard to the mode of measurement, the AAS techniques are among the monoelement methods, which means that under particular conditions only one element can be determined. Despite many modifications, AAS will remain the method for assaying one or at best a few elements in one analytical cycle.

The description of the AAS techniques and their application for water analysis can be found in [2, 12, 30, 33]. The flame and flameless techniques are commonly used. They complement themselves and differ in the manner of atomization only. In the classical flame technique, the sample is converted into the state of atomic gas by means of the flame into which the sample is introduced in the form of an aerosol. The total concentration of a salt in the solution should not exceed 1 per cent. Flameless atomization is usually accomplished in an ohmically-heated graphite cuvette. For this reason the technique has recently been referred to as

electrothermal atomization [21]. This enables markedly better absolute detectability to be achieved (Table 3), but requires very small volumes of solution (5—100 μ l). The flameless technique can be employed for the analysis of various solutions, irrespective of the total salt concentration in them, and, in some cases, for the analysis of solids. However, the complexity of processes occurring in the cuvette and the necessity to handle microquantities of sample, decrease the accuracy and precision of the flameless methods.

Table 3. A comparison of the minimum detectable limits of the AAS method in the flame and in the HGA-2000 graphite cuvette

Tab. 3. Porównanie granic wykrywalności metody ASA w płomieniu i kuwecie grafitowej HGA-2000

Element Pierwiastek	Minimum detectable limit — Wykrywalność ng/ml	
	HGA — 2000 ^a	Flame — Płomień
Cd	0.001	0.6
Co	0.04	10
Cr	0.04	3
Cu	0.01	1
Fe	0.03	5
Mn	0.01	2
Ni	0.1	2
Pb	0.06	10
Zn	0.0006	1

^a Sample size: 100 μ l
Wielkość próbki: 100 μ l

The analysis of sea water is one of the more difficult problems, owing both to microtrace amounts of elements and the presence of relatively large quantities of mineral salts [4, 11, 12, 28]. In direct analysis by the flameless technique [14, 21, 28], additional difficulties are due to non-specific absorption. This requires the application of special background correctors.

During the analysis of trace metals in waters by the AAS methods, preliminary separation of the elements to be determined is frequently employed. This enables the detection limit to be markedly improved and eliminate interferences caused by main components. For the separation of the elements, extraction methods are usually employed with application of ammonium pyrrolidinedithiocarbamate [8, 29, 30, 33] or ion-exchange methods utilizing chelating ion exchangers such as Chelex 100

[24, 33, 42]. Of other methods of enrichment, those of coprecipitation [9] and electrodeposition directly on the wall of the graphite cuvette [4] should be mentioned.

The important advantage of most of the AAS methods is the possibility of their automation. Numerous methods of automatic assay of elements such as As [32], Fe [31] and Hg [1] have been developed so far utilizing mostly the commonly known Technicon equipment.

The methods of atomic fluorescence spectrometry utilize similar equipment as those of AAS. These methods, although characterized by markedly lower detection limits of Cd, Ag, Zn and Sb than AAS, have been infrequently employed for water analysis [35].

3. ATOMIC EMISSION SPECTROMETRY

Atomic emission spectrometry provides one of the oldest methods employed in water analysis (e.g. determination of sodium, potassium and rubidium by flame emission photometry).

In contrast to AAS, emission methods are mostly those of multielement analysis. They can be employed for simultaneous determination of many elements in a sample occupying a volume of several hundred microlitres. Those spectrographic methods in which the spectra are recorded on a polarographic plate have an additional advantage in that they provide an irreplaceable method for rapid quantitative analysis of a sample.

In quantitative analyses, spectrographic methods have recently been increasingly replaced by spectrometric analysis utilizing multichannel spectrometers with detection by means of photomultipliers [11, 23]. This technique has been used for water analysis, but it is particularly useful in multielement analysis of marine plankton or other living organisms or suspensions, i.e. in those cases when the size of the available sample is small (1—100 mg). The application of emission spectrometry utilizing multichannel instruments enabled and markedly facilitated the carrying out of studies on interrelationships in the occurrence of various elements in the whole marine environment. In this way, about 40 elements are now routinely determined in particular species of marine phytoplankton, fish, crustaceans, etc. [37]. This enables precise determination of the selectivity and concentration factors of various elements by various organisms living in this environment.

In atomic emission spectrometry, different methods of sample excitation have been used. The oldest one, still most frequently employed, is excitation in a d.c. arc [11, 23, 34, 37, 39] or in a spark. This technique requires adequate preliminary preparation of the sample. This usually consists in the evaporation of a definite volume of water, or solu-

tion, on graphite powder which is subsequently excited in the crater of auxiliary electrodes in the arc. The solution can also be evaporated directly on the electrode and the residue excited in the arc or in the spark. In the case of organic matter, this procedure has to be preceded by appropriate ashing (or wet combustion) of the sample.

Similar to the AAS methods, the detection limits of many elements directly in water, particularly in sea water, are unsatisfactory in atomic emission spectrometry. For this reason, preliminary separation techniques (mostly extraction or coprecipitation) are also used in this method.

Classical methods of arc and spark excitation, still widely used in emission analysis, are charged with large errors [5, 23], being therefore less precise than the AAS techniques. For this reason, high-frequency excitation sources utilizing plasma have proved a revelation during the past few years. The most commonly known and widely used in routine analyses is inductively coupled argon plasma, commonly known as ICP (Inductively Coupled Plasma) or ICAP (Inductively Coupled Argon Plasma). So far the number of publications covering the application of this method to water analysis is small [2, 11, 12, 40]. This source, however, has excellent stability, comparable with that of the flame in AAS and improved detectability as compared with that in arc or spark, frequently higher than in AAS. The shortcoming of the ICP sources, similar to that of the flame techniques of AAS, is the necessity to use relatively dilute solutions. Hence, they cannot be applied directly to the analysis of sea water.

Another excitation source worth mentioning, utilizing plasma, is MIP (Microwave-Induced Plasma). This source has increasingly been used in gas chromatography [2, 6, 36] as a detector and also for direct excitation of very small samples of solutions (several hundred microlitres). The excitation in MIP sources enables the obtaining of atomic spectra of both metals and nonmetals (F, Cl, Br, I, N, S, P, C) [2]. Coupled with the chromatographic technique, spectrometric MIP detectors enable the assaying of individual organometallic compounds and other compounds containing halogens, sulphur or phosphorus (e.g. pesticides, surfactants etc.).

4. X-RAY FLUORESCENCE SPECTROMETRY

Two atomic fluorescence techniques have been employed in analysis of the aquatic environment [13, 16, 19]: a conventional technique with wavelength dispersion and a modern energy-dispersive technique. In systems with energy dispersion [7, 13, 16], X-ray lamps have mostly been

used as the sources of exciting radiation. Radioisotopic sources have, however, also been employed occasionally for that purpose.

As in atomic emission spectrometry, X-ray fluorescence is a multielement method of analysis. As mentioned, its sole limitation is that it cannot be employed to assay elements of small atomic numbers. In practice, it is usually used to assay elements heavier than magnesium. This method does not ensure as high a detectability of the elements as AAS or atomic emission spectrometry. Its main areas of application involve the determination of major components or impurities at levels exceeding 10^{-3} per cent. Accordingly, the determination of trace amounts requires preconcentration.

In the analysis of the aquatic environment, X-ray fluorescence has been applied mostly to particulate matter, plankton and bottom sediments [37]. Attempts have also been made to use this technique, in conjunction with appropriate separation on filters, for direct assay of trace amounts of elements [38].

5. OTHER METHODS

The methods considered in the preceding sections have long been routine ones in the analysis of water and the aquatic environment. In analyses, where low detection limits of all elements are essential, the spark source mass spectrometry is of value [17]. For this purpose, high-resolution double-focusing spectrographs are employed. Thus, the instrumentation differs slightly from that used in the organic analysis and gas analysis. Spectra recorded on photographic plates also enable complete qualitative analysis to be carried out relatively easily. By the mass spectrometric method all elements of the Periodic Table can be determined, including the isotopic composition of the samples. The detection limits of the majority of elements are of the order of ppb [5, 16]. Mass spectrometry, however, requires special preparation of the samples. Neither solutions (the vacuum in the spectrometer is of the order of 10^{-8} Tr) nor large samples can be analysed directly by mass spectrometry.

Recently, a new technique appeared in the trace analysis, referred to as PIXE (Proton Induced X-ray Excitation) [41]. In conventional X-ray spectrometry, a beam of electrons or the γ -radiation (X-rays) are used for sample excitation. In both cases, strong background of bremsstrahlung or the Compton background appears in the spectra. Replacement of electrons by markedly heavier protons enables the background to be reduced by a factor of 10^6 . The use of 2.5-MeV proton beams for the bombardment of the sample lowers the detection limit of the ele-

ments considerably, enabling quantities of the elements of the order of 10^{-12} g (10^{-1} — 10^{-2} ppm) to be determined. Taking into account the range of the proton beam, however, this type of analysis can be considered rather as a microanalysis affording information on the composition of a very small area only. Despite this shortcoming the technique has frequently been applied to investigations of water and the aquatic environment [13, 41].

Both mass spectrometry and PIXE require sophisticated equipment and specialized laboratories, hence they cannot be employed for routine analyses. However, low detection limits of the techniques make them irreplaceable in certain instances.

6. CONCLUSIONS

Even the most accurate analytical methods fail to give adequate results when the sampling procedure, storage of sample and its pretreatment is wrong. This is particularly important in trace analysis, but frequently underestimated even by qualified analysts. It is only in recent years that due attention has been paid to these problems. It was found, for instance, that many results of analyses of aquatic environments reported many years ago aroused doubts after having been verified [10]. A classical illustration of these problems can be provided by adsorption of individual elements on the walls of vessels or diffusion of some components of plastics from which the vessels are made, to the sample [3, 43]. Another problem is provided by the preparation of samples for analyses (wet combustion, freeze-drying, evaporation, enrichment etc.) [3, 18].

The comparison of analytical methods [5, 16] is very difficult. In trace analyses, one of the basic criteria would be the minimum detectable limit of elements. Such a comparison of the atomic emission and absorption spectrometry has been shown in Fig. 1, in which the heights of the bars illustrate the relative number of elements characterized by given detection limits. The data refer to directly excited or atomized water in which matrix effects can be ignored. Consequently, the data do not account for the enrichment processes. The confrontation with data for the X-ray fluorescence and mass spectrometry is virtually impossible as the methods require preconcentration or separation of the elements in the case of water analysis.

The usefulness of the methods also depends on such factors as the possibility of carrying out qualitative analyses, number of elements determined, multielementability, mutual effects of elements, cost of equipment and single determination, and many others (Table 4). What is

also important is the size and number of samples and the aim of analysis (routine or comparative analyses, research work).

Nowadays the atomic absorption spectrometric methods are most

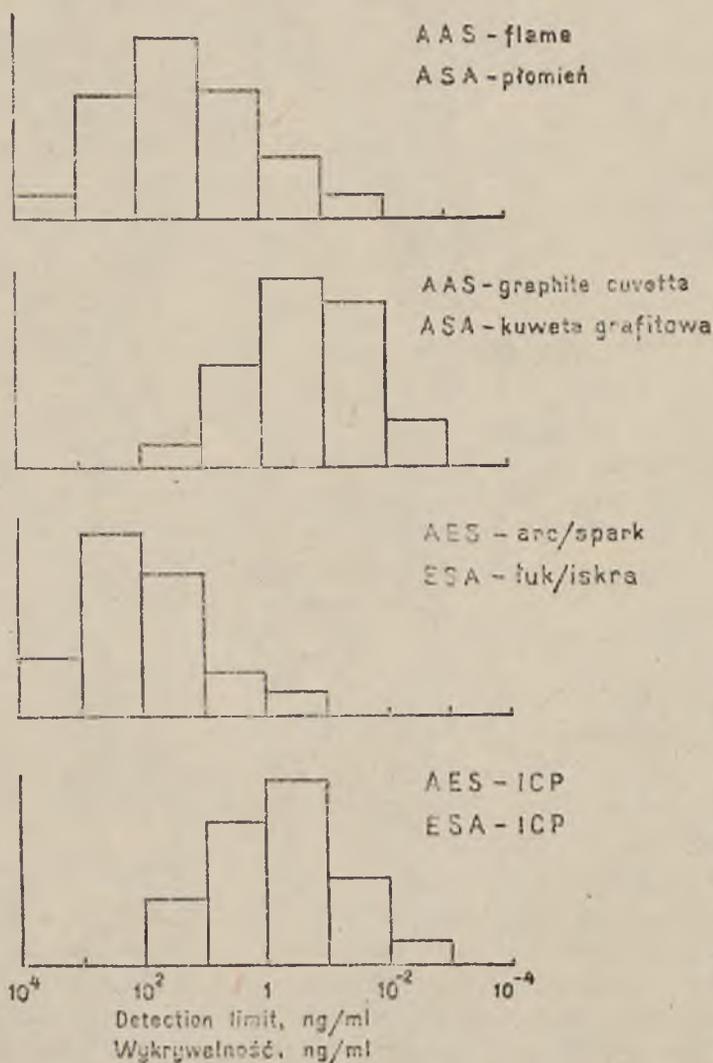


Fig. 1. Comparison of minimum detectable limits in the atomic absorption spectrometric (AAS) and atomic emission spectrometric (AES) methods

Rys. 1. Porównanie granic wykrywalności w metodach absorpcyjnej spektrometrii atomowej (AAS) i emisyjnej spektrometrii atomowej (AES)

- AAS — flame
płomień
- AAS — graphite cuvette
kuweta grafitowa
- AES — arc/spark
łuk/iskra
- AES — ICP

widely used. The appearance of plasma-induced sources of excitation (of the ICP type) may, however, effectively compete with the dominating AAS methods in the near future. It is worth noting that the most renowned firms producing equipment for AAS make efforts to introduce inductively coupled plasma sources (ICP) with emission techniques of measurements.

Table 4. A comparison of spectral methods. AAS — atomic absorption spectrometry; AES — atomic emission spectrometry; XRF — X-ray fluorescence; MS — mass spectrometry.

Tab. 4. Porównanie metod spektralnych. AAS — absorpcyjna spektrometria atomowa, AES — emisyjna spektrometria atomowa, XRF — fluorescencja rentgenowska, MS — spektrometria mas

Characteristic features Cechy	AAS	AES		XRF	MS
		Arc Łuk	ICP		
Qualitative analysis Analiza jakościowa	no nie	yes tak	yes tak	yes tak	yes tak
No. of elements determined Liczba oznaczanych pierw.	++	++	+++	++	+++
Multielement analysis Analiza wielopierwiastkowa	no nie	yes tak	yes tak	yes tak	yes tak
Sample preparation ^a Przygotowanie próbek ^a	+++	++	+++	++	+
Speed — Szybkość	+++	++	+++	+++	+
Mutual effect of elements Wzajemny wpływ pierwiastków	—	---	---	---	---
Cost of equipment Koszt aparatury	—	---	---	---	---
Cost of analysis — Koszt analizy	—	---	---	---	---
Qualifications of the analyst Kwalifikacje analityka	—	---	---	---	---

^a For measurements only, without accounting for wet combustion, enrichment, etc. — Tylko w celu dokonania pomiaru, bez uwzględnienia mineralizacji, wzbogacania itp.

+++ very many (very simple) — bardzo dużo (bardzo łatwo)

++ limited number (limited facility) — ograniczona liczba (ograniczona łatwość)

+ small (difficult) — mała (trudne)

--- large — duży; -- medium — średni; - small -- mały

METODY SPEKTRALNE W ANALIZIE WÓD

Streszczenie

Dokonano analizy piśmiennictwa światowego w latach 1975—1977 w zakresie częstości stosowanych metod analitycznych do wykrywania śladów metali w wodach. Omówiono zalety i wady, granice wykrywalności różnych organicznych i nieorganicznych form występowania śladów metali następujących metod: absorbcyjnej i fluorescencyjnej spektrometrii atomowej, emisyjnej spektrometrii atomowej, fluorescencyjnej spektrometrii rentgenowskiej i szeregu nowych technik, np. PIXE (Proton Induced X-ray Excitation). W ukazujących się co roku 200—300 pracach naukowych na temat oznaczania pierwiastków w wodach z wymienionych technik analitycznych ponad połowa opiera się na metodach spektrometrii atomowej i fluorescencyjnej spektrometrii rentgenowskiej.

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