

# Verification of Measurement Capabilities of Flame Atomic Spectrometry for the Determination of Sodium, Potassium, Magnesium, and Calcium in Natural Fresh Water

## Part I. Comparison of Recommended Methods

Z. Jońca<sup>1\*</sup>, W. Lewandowski<sup>2</sup>

<sup>1</sup>Environmental Monitoring Laboratory, Institute of Environmental Protection, Krucza 5/11d, 00-548 Warsaw, Poland

<sup>2</sup>Chair of Chemistry, Institute of Environmental Engineering and Protection, Białystok Technical University, Zamenhofa 29, 15-435 Białystok, Poland

*Received: 8 April 2003*

*Accepted: 20 May 2003*

### Abstract

Current Polish Standard methods for the determination of sodium, potassium, magnesium, and calcium in natural fresh water were compared with other official standards, mostly from the U.S. (ASTM, USEPA, USGS), regarding recommended top concentrations of measured elements in measured solutions and methods of regulating the sensitivity of measurements.

Some of the disadvantageous limitations of conditions and methods of performing the spectrometric measurements that exist in Polish Standards were shown.

**Keywords:** natural water analysis, flame atomic spectrometry, determination of sodium, potassium, magnesium, and calcium

### Introduction

The Flame Atomic Absorption Spectrometry (F-AAS) and Flame Atomic Emission Spectrometry (F-AES) are the most often used instrumental techniques for the determination of many elements in different types of natural waters, including rain waters, fresh waters, mineral waters, brines and wastewaters. According to the Institute of Water Supply and Environmental Protection of the Cracow University of Technology, there are at least 850 laboratories specializing in water analysis in Poland.

Besides easily measured major elements, i.e., sodium, potassium, magnesium, calcium and silicon, the flame technique usually also has a sufficient detectability in measurement of iron, manganese, zinc, copper, strontium,

lithium and aluminium. In the case of wastewater analysis, one can count on proper detectability of cadmium, nickel, cobalt, chromium, lead, barium, silver, and beryllium.

The flame atomic spectrometry technique is still being developed, with emerging new solutions that enhance the overall instrument performance, its quality of measurement, and ease of use. Meanwhile, there is lack of compatibility between the high measurement capabilities of modern F-AA/AE equipment and the Polish standardized analytical methods (PN-ISO & PN-EN-ISO), based on standard methods published by the European Committee for Standardization (EN) and the International Organization for Standardization (ISO) that are intended for direct flame measurement without preliminary separation of measured elements.

This is especially true regarding major elements, i.e. sodium, potassium, magnesium and calcium, commonly

---

\*Corresponding author; e-mail: jonca@ios.edu.pl

Table 1. Top values of the range of measured concentrations in chosen F-AAS methods recommending significant dilution of fresh water samples. Concentration values in parenthesis correspond with measurements performed using acetylene-nitrous oxide flame.

Methods	References	Na	K	Mg	Ca
		mg/L			
USEPA 1974/1983	[2]	1	2	0.5	7
ASTM D4191-82	[3]	3			
ASTM D4192-82 (87)	[4]		4		
ASTM D511-84	[5]			3.5	15
SEV 1983	[6]	1	2	0.5	7
ISO 7980-1986	[7]			0.5 (0.2)	5 (2)
FRESENIUS 1988	[8]	1	1	(2)	(2)
GREENBERG 1992	[9]	1	2	2	20
ISO 9964-1,2:1993	[10]	1	1		
PN-ISO 9964-1,2:1994	[11]	1	1		
EN-ISO 7980-2000	[12]			0.5 (0.2)	5 (2)
PN-EN-ISO 7980-2002	[13]			0.5 (0.2)	5 (2)

determined in living, agricultural and industrial water. The above-mentioned methods do not take full advantage of the flame spectrometers' measurement capabilities, even in older models.

Although Polish Standards are not mandatory, unless required by specific law, in fact, they remain the main source of detailed analytical information for most of the national laboratories and they are very often used by these laboratories [1]. Another reason that Polish Standards are so commonly used is because the requirement for detailed process documentation is less strict than in the case of non-standard methods.

### Recommended Analytical Methods

Until recently, Polish Standards recommended for determining major elements in fresh water (drinking and industrial water) by flame atomic absorption spectrometry included only standards for Na and K (PN-ISO 9964-1,2,3:1994 – translation of ISO standard, 1993). In March 2002, the PN-EN ISO 7980:2002 standard for determination of Ca and Mg in raw and drinking water by F-AAS was introduced. This standard has been in existence without any changes as an international standard since 1986 and in the European Union since 2000.

In our opinion, these standards (PN-EN ISO 7980-2002 and absorption versions: PN-ISO 9964:1994) disadvantageously assign (as the top level of the range of measured concentrations of determined elements) values that are very small compared with those usually occurring in water samples. Concentrations accepted in these standards are as follows: 1.0 mg/L for sodium and potassium, 0.5 mg/L for magnesium, and 5.0 mg/L for calcium. This requires a multiple increase of the dilution factor, often

several or even tens of times, e.g. when higher concentrations of sodium or magnesium are present. In general, this requires preparation of solutions using different dilution factors for each of the four elements, i.e. four separate solutions from the same laboratory sample.

Since the analyst usually does not know the element concentrations in analyzed samples, preliminary measurements have to be performed in order to establish approximate element concentrations and to calculate the proper dilution factors. Unfortunately, these standards do not provide straightforward directions for performing preliminary measurements.

Because the aforementioned standards do not allow for exceeding the top value of the range of measured concentrations, the preliminary measurements need to be carefully performed in order to obtain a correct dilution factor. The use of a much higher dilution factor than the one based on preliminary measurements may result in preparation of a solution in which the measured element concentration is too small. Consequently, this may also negatively affect the accuracy of measurements due to possible effects by contamination.

In that respect, it is much easier to determine sodium and potassium following PN-ISO 9964-3:1994 (FAES), where for both elements the top value of the range of measured concentrations is accepted at 10 mg/L.

Similarly disadvantageous is the requirement (unequivocally defined in the standard for magnesium and calcium and not so clearly described in parts 1 and 2 of the standard for sodium and potassium) of limiting the range of measured concentrations to the linear region of calibration dependency without giving the linear criterion and ways to confirm its value. Meanwhile, the spectrometers manufactured even in the 1960's were equipped with attachments allowing for a

Table 2. Top values of the range of measured concentrations in chosen F-AAS/AES methods recommending instrumental ways of lowering the measurement sensitivity and small sample dilutions. Concentration values w/o parentheses correspond to the parallel position of the slot burner. Sign „ $\lambda$ ” means the use of low-sensitivity analytical line and sign „ $\neq$ ” – perpendicular or oblique position of the slot burner.

Methods	References	Measuring technique	Na	K	Mg	Ca
			mg/L			
FISHMAN, DOWNS 1966	[14]	F-AAS ( $\lambda$ )	10 (60)	10	2 (50)	20
BROWN <i>et al.</i> 1970	[15]	F-AAS ( $\neq$ )	6 (60)	10	2 (50)	?
SKOUGSTAD <i>et al.</i> 1979	[16]	F-AAS ( $\neq$ )	(80)	10 (100)	10 (50)	60
JOŃCA <i>et al.</i> 1986	[17]	F-AAS ( $\neq$ )	(100)	(20)	(50)	(100)
FISHMAN <i>et al.</i> 1989	[18]	F-AAS ( $\neq$ )	1,0 (80)	1,0 (10)	5 (50)	5 (60)
JOŃCA <i>et al.</i> 1997	[19]	F-AES ( $\neq$ )	(60)	(40)		(160)
		F-AAS ( $\neq$ )			(30)	

conversion of the value of measured analytical signal into a corresponding value of concentration preceded by linearization of the calibration curve. They have been constantly improved, finally becoming today's modern, high-performance, computerized versions. There is no reason for continuation of recommendations that exclude the possibility of significantly increasing the range of measured photometric values. Therefore, one may conclude, there is a need to establish one standard for determining all major elements, including silicon, by flame atomic absorption spectrometry.

In many analytical methods recommended by official institutions the top values of the range of measured concentrations are set at the level of single mg/L and lower (Table 1).

Dilution of more concentrated samples in order to lower the element's concentration to the value listed in Table 1, besides the time and effort spent, exposes the samples (and the calibration solutions) to contamination at every stage of the analytical procedure. It is easy for such a contamination to take place in a laboratory that is not sufficiently prepared for performing trace analysis; one that does not have filtered air blowers, equipment made of adequate materials, high purity reagents and, most of all, an analyst who is experienced enough to perform this kind of analysis.

In professional literature there are known methods that in order to avoid significant sample dilutions decrease the measurement sensitivity of flame AA spectrometers by using various technical measures. Beginning with the use of low-sensitivity analytical lines, e.g. in the case of sodium and magnesium [14], to the easiest method of reducing the path length by burner rotation [15-19]. Standards used by the U.S. Geological Survey (USGS), that utilize these methods, are especially well known [14-16, 18] (Table 2).

Despite that, these simplest methods recommended in atomic spectrometry monographs as well as by the manufacturers of AA/AE spectrometers had not been included in ISO and EN standards.

Based on the author's experience it has been concluded that there is a technically simple and fairly accurate way of measuring Ca, Mg, Na, and K in the same

solution where the measured element concentrations are much higher than those recommended by current Polish Standards [17,19]. This means measuring these elements in a solution that is diluted only a little compared with the original natural (non-mineralized) water sample using Double Capillary System (DCS) as well as slot burner rotation, and possibly less sensitive analytical lines. DCS is used to dilute the measured solution with an auxiliary substance solution while both solutions are being aspirated into the same nebulizer [20-23].

It was not clear, however, if the results of the conducted measurements, despite their precision, were free of systematic errors, big enough to eliminate the advantage of shorter measurement preparation time and the facilitation of measurement procedures.

### Influence of Fundamental and Secondary Components on Accuracy of Measurement of Major Elements

The negative influence of some natural components present in analyzed water on the accuracy of measurements of major elements by F-AAS and F-AES techniques, especially calcium and magnesium, but also sodium and potassium, has been known for a long time. Also since then, during the spectrometric measurements of these kinds of samples, preventive measures were used, including the addition of various auxiliary substances whose purpose was to avert the interference on the determined element.

Calcium and magnesium, as the most susceptible to interference, were carefully investigated in the past. It was concluded that in acetylene-air flame the possible interaction caused by even high concentrations of iron, aluminium, phosphates, and nitrates could be easily eliminated by the addition of appropriate auxiliary substance to the measured solution. The most commonly used are lanthanum salts, mostly in the form of chloride and in hydrochloric acid solution [24, 25].

The common factor in the basic research on these interferences – directed toward analytical practice – was

the assessment of influence of the usually high concentrations of interfering constituents (mostly aluminium, silicon, iron, phosphates(V), sulphates(VI), perchlorates, fluorides and nitrates(V) among others) on low concentrations of measured elements (calcium, magnesium, sodium, and potassium). The reason for conducting research on these systems was the need to analyze materials that consisted mainly of silicon, aluminium and iron, where calcium and magnesium, as well as sodium and potassium, were among the minor elements. Those systems were different rocks, mineral materials, soils, semi-manufactured metallurgic, ceramic, and glass materials, as well as glass and other industrial materials (in analyzing which flame the AA/AE spectrometry has been particularly useful) converted into a solution using acids or melted with fluxes.

Although the natural trace constituents found in fresh water, such as iron, aluminium, phosphates, fluorides, ammonia ion, and nitrates, exist sometimes as minor (or sporadically even as major components), they actually never achieve concentration levels that are high enough to prevent the measurements of sodium, potassium, magnesium, and calcium to be accurate [24]. Concentrations of these constituents in natural, clean waters usually do not exceed, accordingly, few mg/L (aluminium, phosphates, nitrates, fluorides), a dozen or so mg/L (ammonia ion) or tens of mg/L (iron) [26-29].

This is different in cases of higher concentrations of sulphates and/or silicon. Sulphates, which show in an acetylene-air flame a weaker suppression effect toward calcium than phosphates, may be the main anion component of some water types. On the other hand, silicon (as orthosilicic acid and colloidal dispersed polymeric forms of silicic acids) is known for its very strong interfering properties towards calcium and magnesium. Its influence can already be detected at a level of few mg/L and it is significant at higher concentrations.

Lanthanum chloride was recommended to remove the interference toward calcium and magnesium caused by sulphates [24]. The same monograph offers different opinions regarding the effectiveness of using lanthanum to remove the silicon suppression effect on calcium and strontium, as well as sodium and potassium signals. The comment on page 211 states that lanthanum only partially corrects these interferences. In other chapters of the same monograph (pp. 188, 190, 341-345) there are no statements regarding its supposed inefficiency. Significantly, in this monograph [24, p. 180] the complete lack of interference is grouped together with the negligible interference and given the value of permissible error equal to  $\pm 5\%$ . At that time, this corresponded with the average measurement accuracy requirements for F-AA measurements. This tolerance is definitely too high considering the needs of current environmental research and the capabilities of modern F-AA/AE spectrometers.

There is no current literature dedicated to the inadequate flame measurements that may occur despite technical (instrumental) and chemical preventive mea-

asures being used for determination of higher amounts of calcium, magnesium, sodium, and potassium in natural fresh waters.

One of the older references [30] describes the influence of sulphates (in equal molar concentrations) on magnesium, measured in acetylene-air flame. Although, at Mg concentrations of up to 2 mg/L, the difference between the sensitivity of measurement of magnesium sulphate solution and magnesium chloride solution was negligible, in higher concentrations (up to 15 mg/L) a decrease in measurement sensitivity caused by sulphates (measured with the burner in perpendicular position) was reaching tens of percent. In this research the use of two different types of F-AA spectrometers, different types of burners and different positions of impact bead, produced significant differences in intensity of the suppression effect. However, generally the suppression effect was increasing fast when accompanied by a decrease of the observation zone and an increase of the amount of acetylene in flame. Similar differences in measurement sensitivity were observed during measurements with low sensitivity Mg 202.5 nm line with the burner positioned in parallel. Therefore, the authors recommend either a dilution of the measured solutions or an increase of the observation zone with the use of flame with reduced amount of acetylene, possibly using an especially designed burner (triangle head section is the best) or a suitable "buffer".

As is well known, matrix interference in the nebulized solution caused by the presence of components that create thermo-resistant compounds with the measured element can be minimized or even completely eliminated by removing the biggest droplets from the aerosol before it reaches the flame.

In 1979, a simple device called *impact cup* was introduced. It was used either instead of or together with the impact bead, mostly in order for the analyst to be able to move the impact cup in front of the nebulizer or out of the way as needed, without having to shut the flame off. This device was not only lowering the sensitivity of measurement a dozen or so times, but was also catching the biggest droplets, decreasing the matrix effect [22, 31].

Unfortunately, an attempt by the author's of this research to use such an impact cup in a mixing chamber of SP9 atomizer (UNICAM) failed. Despite adding an extra flow spoiler to the mixing chamber, the impact cup was disturbing the flow of the carrying gas to such a degree that the process of mixing both the carrying gas and the combustible gas was incomplete, thus causing flame instability.

Several years' later, special inserts were introduced (positioned in an additional segment between the front cap and the mixing chamber), which were designed to stop the biggest droplets due to the collision effect [32]. Although the use of these inserts significantly lowered the sensitivity of measurements, the somewhat cumbersome manipulation required for going back to normal measurement conditions (shutting off the flame, disconnecting

atomizer parts to remove the additional segment, and connecting all parts again) caused the described invention to not be accepted as a mainstream measurement procedure.

An operator who has no such additional equipment can still control the size of droplets reaching the flame by choosing the right nebulizer that allows obtaining the highest sensitivity and, if technically possible, by adding an extra flow spoiler to the mixing chamber as well as by lowering the flow rate of the nebulized solution. In practice, the technical variations of a *nebulizer-mixing chamber-burner* system are combined with the addition of auxiliary substances to properly diluted measured solutions.

Many of the analysts utilizing the flame atomic spectrometry in water analyses use these methods on a daily basis. However, these methods are not accepted by the EN and ISO, nor by some of the U.S. (ASTM, USEPA) standards.

The purpose of this research, results of which are presented in Part 2, is to establish the extent of systematic errors that may occur in the process of measuring concentrations of calcium, magnesium, sodium, and potassium in undiluted samples of fresh water characterized by significant differences in the amount of dissolved constituents while using, in strictly controlled conditions, the F-AAS technique for measuring calcium and magnesium and F-AES technique for measuring sodium and potassium.

### Acknowledgements

The authors are grateful to Professor Barbara Gworek (Institute of Environmental Protection, Warsaw, PL) for helpful discussion.

### References

- BATEROWICZ A., WÓJTOWICZ A. Report on the inter-comparison of heavy metal determination in water. The Cracow University of Technology. Institute of Chemistry and Inorganic Technology. Analytical Chemistry Department. Kraków 2001 (in Polish).
- US EPA. Methods for Chemical Analysis of Water and Wastes. EPA/600/4-79/020. March 1983.
- ASTM D4191-82. Standard Test Method for Sodium in Water by Atomic Absorption Spectrophotometry.
- ASTM D4192-82(87). Standard Test Method for Potassium in Water by Atomic Absorption Spectrophotometry.
- ASTM D511-84. Standard Test Method for Calcium and Magnesium in Water. Method B – Atomic Absorption Spectrophotometric.
- SEV. Soveshhanie rukovoditelej vodokhozajjstvennykh organov stran-chlenov SEV. Unificirovannye metody issledovaniya kachestva vod. Chast' I. Metody khimicheskogo analiza vod. Tom 1. Osnovnye metody. Izdanie 4-oe. Moskva 1987. Tom 2. Metody atomno-absorpcionnoj spektrofotometrii. Izdanie 4-oe. Moskva 1983 (in Russian).
- ISO 7980-1986 (E) Water quality. Determination of calcium and magnesium. Atomic absorption spectrometric method.
- FRESENIUS W., QUENTIN K.E., SCHNEIDER W. (Eds.). Water Analysis. A Practical Guide to Physico-Chemical, Chemical and Microbiological Water Examination and Quality Assurance. Published by: Deutsche Gesellschaft für Technische Zusammenarbeit (GZT) GmbH. Springer Verlag. Berlin+Tokyo 1988.
- GREENBERG A.E. (red.). Standard Methods for the Examination of Water and Wastewater. Prepared and published jointly by: American Public Health Association, American Water Works Association, Water Environment Federation. 18-th Edition. Washington 1992.
- ISO 9964-1,2,3:1993 (E) Water quality. Determination of sodium and potassium. Part 1. Determination of sodium by atomic absorption spectrometry. Part 2. Determination of potassium by atomic absorption spectrometry. Determination of sodium and potassium by flame emission spectrometry.
- PN-ISO 9964-1,2,3:1994 Water quality. Determination of sodium and potassium (in Polish).
- EN-ISO 7980-2000 (E) Water quality. Determination of calcium and magnesium. Atomic absorption spectrometric method.
- PN-EN-ISO 7980:2002 Water quality. Determination of calcium and magnesium. Atomic absorption spectrometric method (in Polish).
- FISHMAN M.J., DOWNS S.C. Methods for Analysis of Selected Metals in Water by Atomic Absorption. A manual of procedures for determining Ca, Cu, Li, Mg, Mn, K, Na, Sr, and Zn in atmospheric precipitation, fresh waters, and brines by atomic absorption spectroscopy. U.S. Geological Survey. Water-Supply Paper 1540-C. 1966.
- BROWN E., SKOUGSTAD M.W., FISHMAN M.J. Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases. Techniques of Water-Resources Investigations of the United States Geological Survey. Book 5. Chapter A1. 1970.
- SKOUGSTAD M.W., FISHMAN M.J., FRIEDMAN L.C., ERDMANN D.E., DUNCAN S.S. Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Techniques of Water-Resources Investigation of the US Geological Survey. Chapter A1. Book 5. Laboratory Analysis. US Gov. Printing Office. Washington 1979.
- JOŃCA Z., MAJZNER E. Determination of sodium, potassium, magnesium, calcium and total iron in natural waters by flame atomic absorption spectrometry. In : Chemical Analysis of Natural Waters. Determination of Principal Components. Instytut Geologiczny. Instrukcje i metody badań geologicznych. Zeszyt 46. Wydawnictwa Geologiczne. Warszawa 1986 (in Polish).
- FISHMAN M.J., FRIEDMAN L.C. Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Techniques of Water-Resources Investigation of the US Geological Survey. Chapter A1. Book 5. Laboratory Analysis. Third Edition 1989.
- JOŃCA Z. The method for elemental analysis of environmental water samples with atomic spectrometry F-AAS, F-AES, PN-ICP-AES, USN-ICP-AES in use at "IOŚ Environmental Monitoring Laboratory-Warsaw". In : Śnieżek T. (Ed.) Integrated Monitoring of the Natural Environment. Base Station "Puszcza Borecka". PIOŚ. Biblioteka Monitoringu Środowiska. Warszawa 1997 (in Polish).
- JOŃCA Z. Some practical aspects of use flame atomic spectrometry. In : Bulska E., Pyrzyńska K. (Eds.) Applications of Analytical Atomic Spectrometry in Industry and Environmental Protection. Komisja Analitycznej Spektrometrii Atomowej Komitetu Chemii Analitycznej PAN. Warszawa 1999 (in Polish).
- SINGHAL K.C., SINHA R.C.P., BANERJEE B.K. Applications of double capillary in atomic absorption spectrophotometric analysis. Technology. 7, 271, 1970.

22. CRESSER M.S., EDWARDS A.C. A critical appraisal of the use of branched capillaries in analytical spectroscopy. *Spectrochim. Acta.* **39B**, 609, **1984**.
23. CRESSER M.S. *Flame Spectrometry in Environmental Chemical Analysis. A Practical Guide.* RSC Analytical Spectroscopy Monographs. Cambridge **1994**.
24. PINTA M. (Ed.) *Atomic Absorption Spectrometry. Applications in Chemical Analysis.* PWN. Warszawa **1977** (in Polish).
25. WELZ B., SPERLING M. *Atomic Absorption Spectrometry.* Third ed.. Wiley-VCh. Weinheim **1999**.
26. MACIOSZCZYK A., DOBRZYŃSKI D. *Hydrogeochemistry.* Wydawnictwo Naukowe PWN. Warszawa **2002** (in Polish).
27. POLAŃSKI A. *The Basics of Geochemistry.* Wydawnictwa Geologiczne. Warszawa **1988** (in Polish).
28. DOJLIDO J.R. *Chemistry of Surface Waters.* Wydawnictwo Ekonomia i Środowisko. Białystok **1995** (in Polish).
29. KABATA-PENDIAS A., PENDIAS H. *Biogeochemistry of Trace Elements.* 2-nd ed. Wydawnictwo Naukowe PWN. Warszawa **1999** (in Polish).
30. CRESSER M.S., MACLEOD D.A. Observations on the limitation imposed by interferences in flame atomic-absorption spectrometry at high analyte concentrations. *Analyst.* **101**, 86, **1976**.
31. CRESSER M.S. The impact cup. A simple aid in flame spectrometric analysis at high analyte concentrations. *Analyst.* **104**, 792, **1979**.
32. SMITH D.D., BROWNER R.F. Influence of aerosol drop size on signals in flame atomic absorption spectrometry. *Anal. Chem.* **56** (14), 2703, **1984**.