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

Part II. Measurement of Recoveries

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Abstract

Measurement of Na, K, Mg and Ca concentrations in natural fresh (non-mineralized) water samples can be performed in the same sample solution with little or no dilution, in acetylene-air flame with the addition of lanthanum chloride (La 15 g/L), caesium chloride (Cs 1.0 g/L) and hydrochloric acid (HCl 2.0% V/V) by flame atomic emission (Na, K) and absorption (Mg, Ca) spectrometry. Examined remaining influence of other major elements and main interfering components (i.e. sulphates(VI) and silicon) on measured elements was found to be minimal. The recoveries for various concentrations of individual elements in test solutions that had considerably different concentrations of Na, K, Mg and Ca and various participation of sulphates and silicon as well as different values of mineralization were found to be 98.9÷100.6 %, 99.2÷100.6 %, 99.1÷100.9 % and 99.1÷100.9 % for sodium, potassium, magnesium and calcium, respectively.

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

Introduction

In Part I of this work current Polish Standard methods for the determination of sodium, potassium, magnesium and calcium in natural fresh (non-mineralized) water were compared with other official standards, mostly from the U.S. (ASTM, USEPA, USGS) regarding recommended top level concentrations of these elements in measured solution and methods of regulating the sensitivity of measurements. Some of the disadvantageous limitations of conditions and ways of performing the spectrometric measurements that exist in Polish Standards were shown [1, 2, 3].

The aim of this research, results of which have been presented below, was to establish the extent of systematic errors that may occur in the process of measuring 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 specified conditions – F-AAS technique for measuring of calcium and magnesium and F-AES technique for measuring sodium and potassium.

Methods of Research

Measurement capabilities of F-AAS and F-AES techniques, as well as metrological parameters of measure-

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*Corresponding author; e-mail: jonca@ios.edu.pl ments, were established by the use of synthetic multicomponent test solutions representing selected chemical types of natural water.

It was assumed that test solutions corresponded with a specific method of preparing natural samples for the spectrometric measurements. This method is based on filtering and/or acidification with hydrochloric acid (1 mL of acid (1+1) to 100 mL of analyzed water) and, if need be, also mineralization by ultraviolet light exposure. That guarantees the clarity, acidification to pH of about 2 and absence of organic compounds of natural origin in measured solutions. This kind of preparation involves only insignificant dilution, e.g. proportion of 100+2, which comes from the addition of hydrochloric acid into the sample and the possible addition of hydrogen peroxide solution preceding the UV exposure of acidified samples [4, 5].

It was agreed that besides the influence of variable proportions of major cations, the research would have taken into consideration the participation of only two additional components in the test solutions: sulphates(VI) and silicon in the form of orthosilisic acid H_4SiO_4 and polysilisic acids. The aforementioned two components are the only significant sources of interference in unpolluted fresh water that, if there is no counteraction, can greatly disturb the analytical signals of major elements, mostly calcium and magnesium [1].

In prepared test solutions concentration values of sulphates resulted from their specific participation in cationic and anionic balance. Therefore, in the case of pure sulphate composition of dissolved salts, equalization of major cations, i.e. Na, K, Mg, Ca was present in the solution. The constant addition of silicon (Si about 25 mg/L) represents a relatively high concentration of this element that is sometimes present in natural ground water.

Disparity of test solutions according to mutual proportions of four major elements of cationic composition, i.e. sodium, potassium, magnesium and calcium, was selected first of all due to the need of even occupation of planned variability interval of cationic composition and, on the other hand, in order to emulate basic hydrochemical regularity existing in natural fresh water. Seven chemical test solutions (I÷VII) were planned (Table 1).

For two types of test solutions the proportion of calcium to magnesium amounted to 4:1, which was close to the average value of proportion of Ca/Mg in surface and ground fresh water used for living, agricultural and industrial purposes [6]. In the case of sodium and potassium, proportion 1:1 was chosen for two chemical types of test solutions with dominant calcium and magnesium participation. Increasing sodium participation in cationic composition from the values close to the potassium participation up to the dominant participation corresponds to those known in hydrogeochemistry direction of chemical changes of ground water with its increasing mineralization [7]. The addition of a constant quantity of silicon imitates hydrogeochemical regularity ascertained in cases of ground waters in which low mineralised waters have higher participation of silicon in total of substances dissolved, and this participation decreases rapidly with the rise of water mineralization [7].

Experimental Procedures

Laboratory Equipment

MILIPORE unit 185 Plus (Austria). RADWAG WPS 360 and WPS 2100 balances (Poland). Atomic absorption and emission spectrometer JENOPTIK AAS30 (GDR). Hollow cathode lamps: Mg NARVA (GDR) and Ca CPI (USA). Flame atomizer UNICAM SP9 (Great Britain) with a 100 x 0.50 mm single slot burner. GILSON peristaltic pump "Minipuls 3" (France). Acetylene purifier WSL "WANZA" A-55 (Poland). Compressed air. Technically pure acetylene. Glass volumetric flasks 250 and 500 mL, individually calibrated. Automatic measuring pipettes.

Reagents and Materials

Sodium carbonate *p.a.* (POCh). Hydrochloric acid 36% *p.a.* (POCh) and "Tracepur®" (MERCK). Silicon solution ca. 100 mg/kg prepared by means of fusing quartz glass pieces with sodium carbonate, dissolving the alloy in water, acidification with hydrochloric acid to pH 3.0, and then passing through strongly acidic cationic bed Wofatit KPS in the hydrogen form. Caesium chloride *puriss*. AR (KOCH-LIGHT LAB.). Lanthanum chloride (REACHIM) purified two or three times by hydroxide precipitation with ammonia and dissolution in hydrochloric acid. Titrisol® concentrates for sodium, potassium, magnesium and calcium (MERCK). Sulphuric acid concentrates of 0.05 mol (POCh). Water with conductivity below 0.2 μS/cm.

Preparation of Standard-Control Solutions and Test Solutions

Each of the chemical types of test solutions was prepared in three modifications (or subtypes) that differed in participation of sulphates in anionic composition (equivalent portions were 0%, 50%, 100%, respectively). Each of the 21 test solution subtypes (7 types with 3 modifications in each) occurred in a few concentrations of the total (except silicon) of dissolved components (i.e. concentration levels), increasing with geometrical progression (x2) up to the top concentrations that, depending on the subtype, were between 0.92÷2.44 g/L. Every combination of chemical cationic type and anionic modification and total concentration level of ionic constituents was performed in two variants – with no addition of silicon and with its constant addition (about 25 mg/L).

Numerical values, i.e. concentrations of respective mono-elemental solutions and solutions of sulphates and silicon, and concentrations of all measured elements contaminating all used solutions, were entered into the programmed spreadsheets of MS Excel. Masses of particular solutions were calculated due to the preparation of standard and test solutions with specified composition.

Table 1. Mutual proportions of Na, K, Mg and Ca concentrations in test solutions I-VII used for the measurement of recoveries.

Type No.	Chemical type of test solutions	Ca	Mg	Na	K
I	Ca>>Mg>>Na=K	16	4	1	1
II	Ca>>Na>>Mg=K	16	1	4	1
III	Na>>Ca>>Mg=K	4	1	16	1
IV	Na>>Mg>>Ca=K	1	4	16	1
V	Mg>>Na>>Ca=K	1	16	4	1
VI	Mg>>Ca>>Na=K	4	16	1	1
VII	Ca=Na>Mg>K	4	2	4	1

Mono-elemental standard-control solutions of chloride forms of measured elements dissolved in acidified water were prepared by putting the weighted amount of a given solution directly into the 500 ml measuring flasks. Test solutions were prepared by weighing portions of given four-elemental gravimetrically prepared solutions directly into the 250 mL measuring flasks with required additions of sulphates and/or silicon solutions. The temperature of solutions during filling-up and the verified individual capacities of volumetric flasks were taken into account in preparation of solutions and calculation of final concentration values. Solutions were kept in low-density polyethylene (LDPE) bottles.

All bottles containing standard-control solutions and test solutions were stored in hygrostats in 100% relative humidity to avoid an increase of concentration due to water vaporization from closed bottles. The above effect is essential in case of storing solutions for several months. For the 250 mL NALGENE LPDE 2003-0008 bottles, the mass loss was around 45 mg per month (year-long average in room temperature), which is close to 0.02% of total bottle content.

Spectrometric Measurements

During the measurement of recoveries 78 test solutions were ultimately used with the following respective concentrations (mg/L) of particular elements: sodium – 16, 64, 256; potassium – 16, 32, 64; magnesium – 16, 64, 128; calcium – 16, 64, 128, 256.

Na and K determination was performed by emission technique. Emission background corrections were negligibly low, and in case of the most disadvantageous proportion of dominant elements to the measured element achieved few μg/L for potassium and several μg/L for sodium.

Due to the lower cost, an acetylene-air flame was used instead of the more expensive acetylene-nitrous oxide flame. The economical aspect is nowadays one of the most important factors recognized by analytical laboratories when deciding on the choice of methods used. In addition, the technical and chemical methods were limited to those that can be implemented with the current F-AA/AE spectrometers.

Spectrometric measurements concerned exclusively solutions with added auxiliary substances, counteracting possible interference. The aim of these measurements was to find the remaining interference.

One set of auxiliary substances (at the same time releasing and deionising) known from literature as lanthanum-caesium-chloride "buffer," and often used in analytical practices, was exploited [5, 8, 9]. The buffer was used as a separate auxiliary solution containing respective concentrations of lanthanum chloride, caesium chloride and hydrochloric acid in slightly different proportions than the original formula. The original prescription gives the following proportions of La [g/L]: Cs [g/L]: HCl [% (V/V)] = 10: 0.79: 0.65, and the one used in this study was 15: 1: 2. Directly preceding its use, the auxiliary solution was degasified by simultaneously applied negative pressure and ultrasonic waves.

The traditional method of addition of auxiliary substances to the measured solutions, i.e. a beforehand addition of a known amount of concentrated auxiliary solution into each measured solution, was not considered. This was due to the possibility of changing the chemical conditions, i.e. the composition and concentration of solution introduced to the spectrometer by two aspirating tubes of a "DCS" system (*Double Capillary System*) [1, 5, 9].

The common DCS that is based on the negative pressure caused by the nebulizer itself (and is an excellent system in routine analyses) was not used at this time. In order to provide consistent values of solution flow rate in both capillary tubes, the DCS requires the use of tubes that are short and small in diameter. Additionally, it requires the distances between tubes' ends and the nebulizer's inlet, as well as the depth of immersion during each consecutive measurement, to be kept constant. An accuracy expressed in centimetres is satisfactory for routine measurements. The use of only one tube requires keeping similarly stable vertical distance between the end of the tube and the nebulizer's inlet.

Therefore, other reliable, convenient and practical methods were used during the spectrometric measurements. The measured and auxiliary solutions, in proper proportions, were aspirated by the peristaltic pump, then mixed together and passed into the nebulizer in two ways.

The initially used method relied on pumping the mixed solution directly to the nebulizer. However, due to the necessary use of pump tube compression higher than normal (because of significant negative pressure produced by the nebulizer) and high rotary speed of the pump head (to reduce pulsations) the used PVC tubes turned out to be not durable enough for steady input of solution during measuring sessions lasting several hours. Therefore, after completion of potassium measurements this method was discontinued. The second method, recommended in literature [10], depended on pumping of the mixed solution first to the overflow micro-cell and then aspirating it with a nebulizer. The nebulizer's aspirating tube had an inner diameter and length selected for a 4.2 mL/min flow rate. The dilution factor for measured solutions was between 3.7-3.8, for auxiliary solutions approximately 1.3, and was verified by flow

Table 2. Conditions and instrumental parameters for measurements of sodium, potassium, magnesium and calcium by flame atomic spectrometry.

Conditions and instrumental parameters	K			Na			Mg			Ca			
Element concentrations in measured solutions	16 mg/L	32 mg/L	64 mg/L	16 mg/L	64 mg/L	128 mg/L	16 mg/L	64 mg/L	128 mg/L	16 mg/L	64 mg/L	128 mg/L	256 mg/L
Spectrometric technique	F-AES						F-AAS						
Analytical line	766.5 nm			589.6 nm			285.2 nm			422.7 nm			
Monochromator slits spectral width	0.20 nm									0.60 nm			
Source of analitycal radiation	flame						HCL NARVA Mg(Ar)			HCL CPI Ca(Ne)			
Lamp current using							2.5 mA	2 mA		6 mA			
Burner type	single slot 100 mm x 0.50 mm												
Flame kind	acetylene-air												
Air pressure on nebulizer inlet	135 kPa												
Air underpressure on nebulizer outlet	- 56 kPa												
Air flow rate	6.7 L/min												
Acetylene cylider pressure	0.5 - 0.8 MPa												
Flame stochiometry	slightly lean, i.e. with primary combustion zone of 4-6 mm												
Burner position angle in view of measuring beam	oblique			perpendicular			oblique		perpendicular	parallel		oblique	
Measuring zone location above the burner	13 mm						8 mm						
Nebulized solution flow rate	4.2 mL/min												
Measured solution dilution factor	3.68			3.83									
Kind of auxilary substances adding to measured solutions	$LaCl_3$, CsCl , HCl												
Concentrations od auxiliary substances in nebulized solution	La 15.0 g/L, Cs 1.0 g/L, HCl ca. 2% (V/V)												

rate measurements. Accordingly, the auxiliary solution contained such concentrations of lanthanum, chloride and hydrochloric acid that after mixing it with measured solution, the nebulized solution contained 15.0 g/L of La, 1.00 g/L of Cs and 2.0 % (V/V) HCl. Both methods produced equivalent results regarding the composition and concentration of nebulized solution when compared with a traditional method of aspirating the previously prepared solution, including auxiliary substances by means of one tube.

A 100mm x 0.5mm single-slot burner was used. After polishing the internal surface of a slot, the burner does not clog up even after a few hours lasting nebulization of measured solutions containing the abovementioned concentrations of lanthanum chloride and other salts, except the coating close to the edges. A 50 x 0.40 mm burner clogs up at a fast rate and is not suitable for solutions having this kind of chemical composition.

Most of the measurements were performed in very low sensitivity conditions. Lower sensitivity line of 589.6 nm was selected for sodium. In case of all four elements, an oblique to perpendicular position of the burner relative to the measuring beam was used. The impact bead was not used, i.e. the impact bead was in the furthest position from the nebulizer's outlet. In order to intensify the mixing of gases with the nebulized solution and to lower the sensitivity of measurement (by decreasing the amount of aerosol reaching the flame), an extra flow spoiler was inserted in the mixing chamber. Removal of large droplets from the aerosol was particularly beneficial in this case.

An acetylene-air lean flame, i.e. with a decreased amount of acetylene (primary combustion zone height of 4÷6 mm) was used. Measuring zone location above the burner that is the burner height (from the burner edge to the beam axis) was adjusted for sodium and potassium as 13 mm and for magnesium and calcium as 8 mm. The burner height was selected in order to obtain minimum noise and lower sensitivity variation in comparison with lower or higher locations.

Participation of acetone vapour in acetylene (thereby the flame temperature) was standardized by keeping an acetylene cylinder pressure in the range of 0.5÷0.8 MPa. The flame was supplied from five combined cylinders refilled from a full one.

All spectrometric measurements were accomplished in similar conditions: nearly the same dilution factor of measured solution, the same type and concentration of auxiliary solution, the same type of burner, the same type and stoichiometry of flame, one burner height for sodium and potassium and the other one (somewhat lower) for magnesium and calcium. The same nebulizer was used for all the performed tests. The burner head was arranged differently in order to decrease the signal in case of high concentrations of highly sensitive elements (sodium, potassium, magnesium) or to increase the signal in case of low concentrations of calcium that has a much lower sensitivity than magnesium in an acetylene-air flame. Conditions and detailed instrumental parameters are presented in Table 2.

Concentrations of measured solutions (standard-control and test) were converted from the mg/L to conventional units. This was done so the concentrations of a standard solution used for direct comparison with a given group of test solutions was equal to 10,000, high enough to disregard a possible resolution error. Concentrations of test solutions were also converted in the same manner.

After standardization of instrument readings, analytical signals of a given test solution were 6-9 times and alternately compared with the respective signals of a control solution containing almost the same concentration of the measured element.

The following spectrometer readings were registered:

- Absorbance values for calibration dependence.
- Analytical signals values for specified pair of control and test solution (with 25 sec integration time of signal measurement).
- Noise of analytical signal (RSD in % for 10 repetitions with 2.5 sec signal integration time).

During measurement sessions, around 4000 of numerical values for measuring signals (except the noise signal values) were collected. These data were corrected for drift influence and used for calculating statistical parameters.

Corrections and Calculations of Statistical Parameters

Collected data for individual element concentrations in respective test solutions were inserted into the programmed MS Excel spreadsheets for the following purpose:

- Correction decreasing an influence of sensitivity change, especially sensitivity drift and zero level drift.
- Verification of outliers with Dixon Q test (at 80% confidence level).
- Individual results standard deviation, arithmetic mean, median, mean standard deviation and percentage recovery calculations.
- Student's t-test (at 95% of confidence level) of significance for differences between mean and true values.

Calculated numerical values are saved in Tables 3, 4, 5, and 6, which contain the following data:

- "Min", mineralization value; i.e. total of nominal sodium, potassium, magnesium and calcium concentrations and respective concentrations of chlorides and sulphates in given test solutions.
- "n", i.e. number of individual results for recovery measurement of a specified element, which were held in a given measuring cycle.
- "Q", i.e. number of individual results as above rejected by Dixon Q-test.
- "RSD", i.e. relative standard deviations of results accepted by test, as above.
- Recovery.
- "HW", i.e. half value width of recovery confidence interval at the confidence level of 95%.
- "R", i.e. value of R index.

R index was calculated as a quotient of absolute value of difference between mean and true value and a product of standard deviation of mean and two-sided, t-Student test critical value with the confidence level of 95%. R index shows the probable cause of difference between the mean and true value. Values greater than one indicate high probability that the mean, besides random error, is loaded with systematic error.

Discussion

Relative standard uncertainties of the values of recoveries having their source in uncertainties of concentration values for particular comparable pairs of measuring solutions, i.e. standard-control and test solution, were between 0.03% and 0.05%, if calculated according to [12].

Sodium

Recovery values for all concentrations are placed in the 98.9-100.6% range. Median values of recoveries for all three measured concentration levels (16 mg/L, 64 mg/L, 256 mg/L) are 99.5%, 99.9%, and 100.0%. Just seven recoveries among 42 were indicated as loaded with systematic error by R index.

Within specified chemical types there are no statistically significant differences in recoveries depending on sulphate participation or silicon presence because the confidence intervals of recoveries belonging to the one chemical type overlap each other.

The tendency in slightly smaller recovery of silicon variant for one pair of recoveries belonging to the one modification is noticeable. It is especially clear in the case of type IV Na>>Mg>>Ca=K. For 21 pairs in total, 16 recovery pairs belonging to the same modification silicon variant, indicates slightly lower recovery than the non-silicon.

Table 3. Recoveries and statistical parameters for sodium. See the explanation of abbreviations in text.

Chemical types, modifications and variants of test solutions			Min	n	Q	RSD	Recovery	HW	R
Type. Concentration of measured element	Modification	Variant	mg/L			%			
Type I Ca>>Mg>>Na=K (16 : 4 : 1 : 1) Na 16 mg/L	Cl 100%		1031	7	0	0.8	100.3	0.8	0.4
		Si		7	0	0.6	99.4	0.5	1.0
	Cl 50% SO_4 50%		1151	7	0	0.8	99.7	0.7	0.5
		Si		7	0	0.5	99.6	0.5	0.7
	SO_4 100%		1272	7	0	0.7	99.4	0.6	0.9
		Si		7	0	0.5	99.3	0.5	1.5
Type II Ca>>Na>>Mg=K (16 : 4 : 1 : 1) Na 64 mg/L	Cl 100%		965	8	0	0.8	100.2	0.7	0.2
		Si		7	0	0.5	100.1	0.5	0.1
	Cl 50% SO_4 50%		1073	7	0	0.3	99.8	0.3	0.6
		Si		7	0	1.0	100.0	0.9	0.0
	SO_4 100%		1182	8	0	0.4	100.0	0.4	0.1
		Si		7	0	0.6	100.0	0.5	0.0
Type III Na>>Ca>>Mg=K (16 : 4 : 1 : 1) Na 256 mg/L	Cl 100%		921	7	0	0.3	100.0	0.3	0.1
		Si		7	0	0.4	99.7	0.4	0.7
	Cl 50% SO_4 50%		1022	8	0	0.4	100.0	0.4	0.0
		Si		7	0	0.8	99.9	0.8	0.1
	SO_4 100%		1123	7	0	0.5	100.1	0.5	0.3
		Si		7	0	0.5	100.0	0.5	0.0
Type IV Na>>Mg>>Ca=K (16 : 4 : 1 : 1) Na 256 mg/L	Cl 100%		976	7	0	0.4	100.1	0.4	0.2
		Si		7	0	0.7	99.7	0.6	0.5
	Cl 50% SO_4 50%		1087	7	0	0.4	100.0	0.4	0.1
		Si		8	0	0.4	99.7	0.4	0.7
	SO_4 100%		1198	7	1	0.4	100.5	0.5	1.0
		Si		8	0	0.7	99.6	0.6	0.7
Type V Mg>>Na>>Ca=K (16 : 4 : 1 : 1) Na 64 mg/L	Cl 100%		1240	7	0	0.6	100.2	0.5	0.3
		Si		7	0	0.6	99.9	0.5	0.2
	Cl 50% SO_4 50%		1398	7	0	0.5	99.4	0.5	1.2
		Si		8	0	0.5	99.8	0.4	0.5
	SO_4 100%		1555	7	0	0.5	99.7	0.4	0.8
		Si		8	0	0.6	99.1	0.5	1.9
Type VI Mg>>Ca>>Na=K (16 : 4 : 1 : 1) Na 16 mg/L	Cl 100%		1251	7	0	1.1	100.1	1.0	0.1
		Si		8	0	0.8	99.9	0.6	0.2
	Cl 50% SO_4 50%		1411	8	0	0.9	99.3	0.8	0.9
		Si		8	0	1.0	99.0	0.9	1.1
	SO_4 100%		1570	8	0	0.7	98.9	0.6	1.9
		Si		8	0	0.7	99.8	0.6	0.3
Type VII Na=Ca>Mg>K (4 : 4 : 2 : 1) Na 256 mg/L	Cl 100%		1983	8	1	0.4	100.2	0.4	0.5
		Si		7	0	0.7	100.6	0.7	0.9
	Cl 50% SO_4 50%		2210	7	0	0.8	100.4	0.8	0.6
		Si		8	0	0.6	100.2	0.5	0.3
	SO_4 100%		2437	7	0	0.5	100.3	0.5	0.6
		Si		7	1	0.5	100.1	0.5	0.2

Table 4. Recoveries and statistical parameters for potassium. See the explanation of abbreviations in text.

Chemical types, modifications and variants of test solutions			Min	n	Q	RSD	Recovery	HW	R
Type. Concentration of measured element	Modification	Variant	mg/L			%			
Type I Ca>>Mg>>Na=K (16 : 4 : 1 : 1) K 16 mg/L	Cl 100%		1031	7	0	0.6	99.9	0.6	0.1
		Si		8	0	0.7	99.3	0.6	1.2
	Cl 50% SO_4 50%		1151	7	1	0.5	99.7	0.5	0.7
		Si		7	0	0.8	99.7	0.7	0.5
	SO_4 100%		1272	7	0	0.8	99.6	0.7	0.6
		Si		7	0	0.7	99.6	0.6	0.6
Type II Ca>>Na>>Mg=K (16 : 4 : 1 : 1) K 16 mg/L	Cl 100%		965	7	0	1.0	100.0	0.9	0.0
		Si		8	0	0.7	100.1	0.6	0.2
	Cl 50% SO_4 50%		1073	7	0	0.8	99.4	0.7	0.9
		Si		7	0	0.4	99.9	0.4	0.3
	SO_4 100%		1182	8	0	0.6	99.7	0.5	0.5
		Si		7	0	0.6	99.4	0.6	1.0
Type III Na>>Ca>>Mg=K (16 : 4 : 1 : 1) K 16 mg/L	Cl 100%		921	8	0	1.0	99.5	0.8	0.6
		Si		7	1	0.3	99.9	0.3	0.3
	Cl 50% SO_4 50%		1022	7	0	0.7	99.5	0.6	0.7
		Si		7	0	1.0	99.7	0.9	0.3
	SO_4 100%		1123	8	1	0.6	99.7	0.6	0.6
		Si		7	0	0.6	99.6	0.5	0.7
Type IV Na>>Mg>>Ca=K (16 : 4 : 1 : 1) K 16 mg/L	Cl 100%		976	7	0	0.4	100.0	0.4	0.1
		Si		7	0	0.5	99.6	0.5	1.0
	Cl 50% SO_4 50%		1087	7	0	0.4	99.4	0.4	1.5
		Si		7	0	0.8	99.7	0.7	0.5
	SO_4 100%		1198	7	1	0.4	99.5	0.4	1.4
		Si		9	0	0.7	99.3	0.6	1.2
Type V Mg>>Na>>Ca=K (16 : 4 : 1 : 1) K 16 mg/L	Cl 100%		1240	7	0	1.0	99.8	0.9	0.2
		Si		7	0	0.4	99.6	0.4	1.1
	Cl 50% SO_4 50%		1398	7	1	0.4	99.5	0.4	1.2
		Si		7	0	0.5	99.2	0.4	1.7
	SO_4 100%		1555	7	0	0.6	99.9	0.5	0.2
		Si		7	0	0.7	99.6	0.7	0.7
Type VI Mg>>Ca>>Na=K (16 : 4 : 1 : 1) K 16 mg/L	Cl 100%		1251	8	0	0.8	99.9	0.7	0.1
		Si		7	0	0.9	99.8	0.8	0.2
	Cl 50% SO_4 50%		1411	7	0	1.1	100.0	1.0	0.0
		Si		8	0	1.0	99.8	0.8	0.2
	SO_4 100%		1570	7	1	0.2	99.4	0.2	2.8
		Si		8	0	1.0	99.3	0.8	0.9
Type VII Na=Ca>Mg>K (4 : 4 : 2 : 1) K 16 mg/L	Cl 100%		496	7	0	1.0	100.1	0.9	0.1
		Si		7	1	0.1	99.6	0.1	2.9
	Cl 50% SO_4 50%		553	7	0	0.6	99.3	0.6	1.1
		Si		8	2	0.4	99.9	0.4	0.2
	SO_4 100%		609	7	0	1.0	99.9	0.9	0.1
		Si		8	0	0.5	99.7	0.4	0.8

Table 4 continues on next page...

Type VII Na=Ca>Mg>K (4 : 4 : 2 : 1) K 32 mg/L	Cl 100%		992	9	0	0.5	100.1	0.4	0.3
		Si		7	0	0.9	100.3	0.9	0.3
	Cl 50% SO_4 50%		1105	7	0	0.8	100.6	0.8	0.7
		Si		7	0	0.4	99.2	0.4	1.9
	SO_4 100%		1218	7	0	0.9	100.1	0.8	0.2
		Si		8	0	0.6	100.0	0.5	0.0
Type VII Na=Ca>Mg>K (4 : 4 : 2 : 1) K 64 mg/L	Cl 100%		1983	7	0	0.4	99.6	0.4	1.2
		Si		7	0	0.7	99.9	0.6	0.2
	Cl 50% SO_4 50%		2210	6	0	0.3	100.2	0.3	0.6
		Si		6	0	0.4	99.5	0.5	1.0
	SO_4 100%		2437	8	0	0.3	99.9	0.2	0.5
		Si		9	0	0.3	99.7	0.2	1.3

Table 5. Recoveries and statistical parameters for magnesium. See the explanation of abbreviations in text.

Chemical types, modifications and variants of test solutions Type. Concentration of measured element	Modification	Variant	Min mg/L	n	Q	RSD %	Recovery %	HW %	R
Type I Ca>>Mg>>Na=K (16 : 4 : 1 : 1) Mg 64 mg/L	Cl 100%		1031	7	0	0.7	99.8	0.6	0.2
		Si		8	0	0.6	100.5	0.5	0.9
	Cl 50% SO_4 50%		1151	8	0	0.6	100.4	0.5	0.9
		Si		8	0	1.0	99.7	0.8	0.4
	SO_4 100%		1272	7	0	0.4	99.4	0.4	1.6
		Si		8	1	0.6	99.7	0.6	0.5
Type II Ca>>Na>>Mg=K (16 : 4 : 1 : 1) Mg 16 mg/L	Cl 100%		965	8	0	0.8	99.3	0.6	1.1
		Si		7	1	0.3	99.3	0.3	2.0
	Cl 50% SO_4 50%		1073	8	0	0.9	99.4	0.8	0.7
		Si		8	0	0.5	99.5	0.5	1.0
	SO_4 100%		1182	7	0	1.0	99.5	1.0	0.5
		Si		8	2	0.3	99.1	0.3	2.8
Type III Na>>Ca>>Mg=K (16 : 4 : 1 : 1) Mg 16 mg/L	Cl 100%		921	8	0	0.7	99.2	0.6	1.4
		Si		7	0	0.7	99.5	0.7	0.7
	Cl 50% SO_4 50%		1022	7	0	0.5	99.9	0.5	0.2
		Si		7	0	0.5	99.6	0.4	1.0
	SO_4 100%		1123	8	0	0.8	99.5	0.6	0.8
		Si		7	0	1.1	99.7	1.0	0.3
Type IV Na>>Mg>>Ca=K (16 : 4 : 1 : 1) Mg 64 mg/L	Cl 100%		976	7	1	0.3	99.7	0.3	0.8
		Si		8	0	0.7	100.4	0.6	0.7
	Cl 50% SO_4 50%		1087	8	1	0.8	99.4	0.7	0.8
		Si		8	0	1.5	99.9	1.3	0.1
	SO_4 100%		1198	8	0	0.9	100.9	0.7	1.3
		Si		8	0	0.8	100.1	0.7	0.1
Type V Mg>>Na>>Ca=K (16 : 4 : 1 : 1) Mg 128 mg/L	Cl 100%		620	7	0	0.5	100.0	0.5	0.1
		Si		7	0	0.5	100.3	0.5	0.6
	Cl 50%		699	7	0	0.8	99.8	0.8	0.3
	SO_4 50%	Si		7	1	0.3	100.4	0.4	1.2
	SO_4 100%		778	7	0	0.6	99.9	0.5	0.2
		Si		7	1	0.6	99.7	0.6	0.5

Table 5 continues on next page...

Type VI Mg>>Ca>>Na=K (16 : 4 : 1 : 1) Mg 128 mg/L	Cl 100%		626	8	0	0.6	100.1	0.5	0.3
		Si		8	0	0.4	100.5	0.4	1.3
	Cl 50% SO$_4$ 50%		705	7	0	0.6	100.4	0.5	0.8
		Si		8	2	0.2	100.4	0.2	1.9
	SO$_4$ 100%		785	7	0	0.6	100.1	0.6	0.2
		Si		7	0	0.5	99.8	0.5	0.4
Type VII Na=Ca>Mg>K (4 : 4 : 2 : 1) Mg 128 mg/L	Cl 100%		1983	7	0	0.4	100.0	0.4	0.0
		Si		7	1	0.2	99.6	0.2	2.3
	Cl 50% SO$_4$ 50%		2210	7	0	0.4	99.7	0.4	0.7
		Si		7	0	0.2	99.8	0.2	0.9
	SO$_4$ 100%		2437	7	0	0.4	99.9	0.4	0.2
		Si		7	0	0.4	99.8	0.3	0.7

Potassium

Recovery values for all concentrations are situated in the 99.2-100.6% range. Median values of recoveries of specified concentrations (16 mg/L, 32 mg/L, 64 mg/L) are 99.7%, 100.1%, 99.8%, respectively. The two last concentration levels of potassium are represented by merely six solutions each. Concentration of 16 mg/L was examined in 42 solutions and recoveries in 11 of them were explicitly (as demonstrated by R index) loaded with negative systematic error (recoveries in 99.2%-99.6% range). The rest of 16 mg/L concentration recoveries are placed between 99.3% and 100.1% and most of them are lower than 100%.

Just as in the case of sodium the confidence intervals of recoveries within the same chemical type overlap.

Among 27 pairs in total in 17 pairs of recoveries within the same modification the silicon variant showed slightly lower recovery than the non-silicon one.

Magnesium

Recovery values for all concentrations are placed in the range of 99.1-100.9%. Median values for specified concentration recoveries (16 mg/L, 64 mg/L, 128 mg/L) amounted to – 99.5%, 99.9%, 100.0%, respectively. Only 12 out of 42 recoveries were demonstrated by R index as loaded with systematic error, among them only 4 from 18 in case of the most concentrated solution 128 mg/L and 2 from 12 in case of 64 mg/L concentration.

Just like in the case of sodium and potassium, the confidence intervals for recoveries within the same chemical type overlap each other.

For 21 pairs of the same modification in 9 pairs silicon variant shows slightly lower recovery than the non-silicon variant.

Calcium

Recovery values for all concentrations are placed in the 99.1-100.9% range. Median values for specified concentration recoveries (16 mg/L, 64 mg/L, 128 mg/L, 256 mg/L) achieved 99.7%, 100.0%, 100.1%, and 100.0%, respectively.

Only 10 recoveries out of 60 are indicated by the R index as loaded with systematic error, among them only two from 18 in the case of the higher concentration 256 mg/L; just two from 18 in case of 128 mg/L; three from 12 in case of 64 mg/L and three from 12 in case of 16 mg/L.

As in the case of previous elements, the confidence intervals of recoveries within the same chemical type overlap each other with just a few exceptions.

In the case of 19 pairs of recoveries for 30 pairs in total within the same modification the silicon variant shows slightly lower recovery than the non-silicon.

Summary

Average repeatability obtained for all spectrometric measurements (median interval of RSD for individual results of recoveries for respective concentrations achieved 0.5-0.8% for Na, 0.4-0.7% for K, 0.5-0.7% for Mg, 0.4-0.8% for Ca) enables finding the systematic error in given mean recovery, i.e. the presence of matrix impact on measuring element, not smaller than several tenths of a percentage point.

Calculated confidential intervals overlap each other in the case of almost all recoveries of specified elements within one chemical type as well as most recoveries for all types together. Therefore, a statistically proven conclusion regarding the influence of the kind of chemical composition in specified test solutions on the obtained recovery result different than 100% cannot be drawn. This is true even if the presence of systematic error was confirmed by statistical test, which happened in 43 cases out of 198 examined recoveries.

Therefore, these impacts are too small to be annotated to the sulphates and/or silicon influence. Only the tendency in slight difference of recovery in case of silicon presence is noticeable when compared to the recoveries within modifications.

Table 6. Recoveries and statistical parameters for calcium. See the explanation of abbreviations in text.

Chemical types, modifications and variants of test solutions			Min	n	Q	RSD	Recovery	HW	R
Type. Concentration of measured element	Modification	Variant	mg/L			%			
Type I Ca>>Mg>>Na=K (16 : 4 : 1 : 1) Ca 128 mg/L	Cl 100%		515	9	0	0.6	99.8	0.5	0.4
		Si		7	0	0.8	99.8	0.8	0.3
	Cl 50% SO_4 50%		576	7	0	0.6	100.1	0.6	0.2
		Si		7	0	0.6	100.2	0.6	0.3
	SO_4 100%		636	7	0	0.6	100.3	0.6	0.5
		Si		7	0	0.7	99.8	0.6	0.3
Type I Ca>>Mg>>Na=K (16 : 4 : 1 : 1) Ca 256 mg/L	Cl 100%		1031	7	0	0.3	99.9	0.3	0.4
		Si		7	2	0.1	100.1	0.1	1.8
	Cl 50% SO_4 50%		1151	7	1	0.1	100.3	0.1	2.9
		Si		8	0	0.2	99.9	0.2	0.3
	SO_4		1272	7	0	0.4	100.4	0.4	0.9
		Si		7	1	0.3	99.7	0.3	0.8
Type II Ca>>Na>>Mg=K (16 : 4 : 1 : 1) Ca 128 mg/L	Cl 100%		482	7	0	0.6	99.8	0.5	0.3
		Si		7	0	0.7	100.2	0.7	0.3
	Cl 50% SO_4 50%		537	7	1	0.3	100.3	0.4	0.9
		Si		7	0	0.6	99.5	0.5	0.9
	SO_4 100%		591	7	1	0.3	100.9	0.4	2.4
		Si		7	1	0.3	99.8	0.3	0.8
Type II Ca>>Na>>Mg=K (16 : 4 : 1 : 1) Ca 256 mg/L	Cl 100%		965	7	0	0.4	99.8	0.3	0.5
		Si		7	0	0.3	100.1	0.3	0.4
	Cl 50% SO_4 50%		1073	7	0	0.6	100.2	0.5	0.3
		Si		7	0	0.5	100.3	0.5	0.7
	SO_4 100%		1182	7	0	0.7	100.0	0.6	0.0
		Si		7	0	0.6	99.7	0.6	0.4
Type III Na>>Ca>>Mg=K (16 : 4 : 1 : 1) Ca 64 mg/L	Cl 100%		921	7	0	0.4	100.0	0.4	0.1
		Si		7	0	0.7	99.9	0.7	0.1
	Cl 50% SO_4 50%		1022	7	0	0.6	100.1	0.6	0.2
		Si		7	1	0.2	99.5	0.2	2.2
	SO_4 100%		1123	7	0	1.0	100.1	0.9	0.1
		Si		7	1	0.2	100.4	0.2	1.6
Type IV Na>>Mg>>Ca=K (16 : 4 : 1 : 1) Ca 16 mg/L	Cl 100%		976	7	0	1.1	99.8	1.0	0.2
		Si		8	0	1.1	99.5	0.9	0.5
	Cl 50% SO_4 50%		1087	7	0	0.4	99.4	0.4	1.4
		Si		7	0	0.6	100.2	0.5	0.4
	SO_4 100%		1198	7	0	1.1	100.0	1.0	0.0
		Si		8	0	0.9	99.5	0.8	0.6
Type V Mg>>Na>>Ca=K (16 : 4 : 1 : 1) Ca 16 mg/L	Cl 100%		1240	7	0	0.4	99.5	0.4	1.2
		Si		7	0	0.6	99.1	0.5	1.7
	Cl 50% SO_4 50%		1398	7	0	1.0	100.0	0.9	0.0
		Si		7	0	0.9	99.6	0.8	0.6
	SO_4 100%		1555	7	0	0.8	99.9	0.7	0.1
		Si		7	1	0.5	99.8	0.5	0.3

Table 6 continues on next page...

Type VI Mg>>Ca>>Na=K (16 : 4 : 1 : 1) Ca 64 mg/L	Cl 100%		1251	8	0	0.6	99.4	0.5	1.1
		Si		7	0	1.1	99.3	1.0	0.7
	Cl 50% SO_4 50%		1411	7	0	1.0	99.5	0.9	0.6
		Si		7	0	0.9	99.2	0.8	0.9
	SO_4 100%		1570	7	0	0.7	100.6	0.7	0.9
		Si		7	0	0.8	100.0	0.8	0.0
Type VII Na=Ca>Mg>K (4 : 4 : 2 : 1) Ca 128 mg/L	Cl 100%		992	8	0	0.1	100.1	0.1	1.0
		Si		7	0	0.5	99.5	0.4	1.2
	Cl 50% SO_4 50%		1105	8	0	0.6	100.1	0.5	0.1
		Si		7	0	0.8	99.7	0.7	0.4
	SO_4 100%		1218	7	0	0.4	100.1	0.4	0.1
		Si		7	0	0.8	100.1	0.8	0.1
Type VII Na=Ca>Mg>K (4 : 4 : 2 : 1) Ca 256 mg/L	Cl 100%		1983	7	0	0.5	99.6	0.5	0.7
		Si		7	0	0.8	99.7	0.8	0.4
	Cl 50% SO_4 50%		2210	7	0	0.7	99.9	0.6	0.1
		Si		7	0	0.8	100.1	0.7	0.2
	SO_4 100%		2437	8	0	0.4	100.0	0.3	0.0
		Si		8	0	0.4	99.8	0.4	0.6

On the contrary, it could be generally concluded that possible impacts would not exceed 1% and in most cases would achieve negative values. In more than a half (163 per 198 cases) the examined cases, impacts have not exceeded 0.5%. This happened in 33 out of 42 cases for sodium, in 43 out of 54 for potassium, 33 out of 42 for magnesium and 54 out of 60 for calcium.

Recoveries of the highest concentrations of all four elements are characterized with the smallest range and/or median values closer to 100% than the lowest element concentrations, i.e. 16 mg/L (Table 7).

Obtained results could be used more widely, i.e. equally good recoveries can be expected during measurements made with other F-AE/AA spectrometers and in other laboratories. Should the impact be found too high, the operator could easily change some of the parameters and measurement conditions used in this study. These parameters and conditions include the following:

- Significantly decreasing the flow rate of nebulized solution, e.g. from 4 ml/min to 2 mL/min.
- Increasing the dilution of measured solution.
- Use of a nebulizer with better sensitivity.

Conclusions

Determination of sodium, potassium, magnesium and calcium in fresh water samples with mineralization up to 1g/L as well as in water with higher mineralization, e.g. in the type VII up to 2.4 g/L, can be performed successfully by flame atomic spectrometry with an acetylene-air flame as described above, which means:

- Sodium and potassium by emission technique, magnesium and calcium by absorption technique.

Table 7. Comparison of recoveries and their range for highest and lowest concentrations of measured elements.

Elements	Concentration in measured solution	Dilution factor of measured solution	Percentage recoveries		
			n	Median	Range
Sodium	16 mg/L	3.8	12	99.5	98.9 ÷ 100.3
	256 mg/L		18	100.0	99.6 ÷ 100.6
Potassium	16 mg/L	3.7	42	99,7	99.2 ÷ 100.1
	64 mg/L		6	99.8	99.5 ÷ 100.2
Magnesium	16 mg/L	3.8	12	99.5	99.1 ÷ 100.9
	128 mg/L		12	100.0	99.6 ÷ 100.5
Calcium	16 mg/L	3.8	12	99.7	99.1 ÷ 100.2
	256 mg/L		18	100.0	99.6 ÷ 100.4

- Concentrations of all four elements can be measured in the same solution containing lanthanum chloride, caesium chloride and hydrochloric acid in respective concentrations of: 15.0 g/L, 1.00 g/L, 2.0% (V/V).
- If an operator does not use a diluting device for measured solution during the aspiration process, maximum concentrations of particular elements in measured solutions can reach – in the conditions described in this study – about 70 mg/L for sodium, about 17 mg/L for potassium, about 33 mg/L for magnesium, about 70 mg/L for calcium and for silicon about 6 mg/L.
- If an operator uses the DCS system or one with similar function, maximum concentrations of particular elements in measured solutions will depend on the applied dilution factor and for dilution factor e.g. equal to 4 can achieve about 270 mg/L for sodium, about 70 mg/L for potassium, about 130 mg/L for magnesium, about 270 mg/L for calcium, and about 25 mg/L for silicon in case of the same conditions as described above.
- In order to adapt sensitivity of spectrometric measurement to the needed value of absorbance or emission intensity (and curvature of calibration dependence) an operator can change independently the slot burner position angle in view of measuring beam from parallel to perpendicular position without significantly worsening the precision and accuracy of measurements.

Possible systematic error does not exceed about 1%, which is sufficient for most recipients of analytical information. Due to the common practice of preparation of multielemental standards with similar proportions of measuring elements to the one present in samples, possible systematic errors could be even smaller.

It is especially not necessary to worry about committing even so small a systematic error in case of surface water analyses (i.e. river and lake water samples) with bicarbonate composition (i.e. with secondary participation of sulphates) apart from the main cation, so in predominant part of water analyses destined for maintenance and economical purposes. Moreover, these water samples, in general, contain smaller silicon concentrations than applied in this work test solution concentration of 25 mg/L and possible minimal influence of silicon in these samples will be even smaller if the operator uses the DCS or similar system.

If, however, possible systematic error up to the 1% value cannot be accepted, some earlier mentioned methods could be performed. Lastly, standard solutions containing sulphates and silicon concentrations similar to the one in samples can be applied.

In any case, the dilution of laboratory samples to the so small and strictly specified concentration of an element required by current official methods – PN-ISO and PN-EN-ISO [2, 3] is not essential.

Radical decrease of laborious preparation of samples for spectrometric measurements as well as measurements itself in case of lack of knowledge about sample compositions is a big advantage of described method of fresh water analyses. Using higher measuring element concentrations also simplifies the preparation of standard solutions and facilitates the technical side of spectrometric F-AA/AE measurements.

Especially convenient for an operator is the DCS system or any other similar one. It allows for preparation of just one solution for all four elements and the same solution can be also used for measuring many other elements, e.g. Si, Fe, Mn, Zn, Al, Sr, Li, Cu, Ag etc., by flame technique or other atomic spectrometry techniques. Consequently, this system facilitates multi-elemental analyses and quality control of analytical results obtained at a given laboratory.

The other advantage is the low cost of used materials during analyses. Not only reagents and water, which do not have to be high purity, are cheaper but also gases, due to the use of an acetylene-air flame, are less expensive.

In this respect USGS standard methods were always more feasible and easier to use [11, 13-15]. However, the instrumental method recommended by USGS of decreasing measuring sensitivity by changing the slot burner arrangement from parallel through oblique to perpendicular was not accepted in the old and the current methods USEPA, ASTM, SEV, ISO, EN. This method was not accepted**,** even though it does not cause significant deterioration in repeatability and accuracy of measurement and is an easy and quick method of regulating sensitivity in the absorption as well as emission measurements.

Rejection of this method as well as the computational method of correcting the calibration dependence and other possible technical adaptations to particular measuring conditions unnecessarily increases the operator's workload and the laboratory's expenses, and exposes the measured solutions to contamination and mistakes during their preparation and measurement.

In the authors' opinion, major changes of PN-EN-ISO standards are required. It would be best to prepare a completely new single standard method for determining all four elements (possibly including silicon) that would consider measurement capabilities of modern flame spectrometers, as well as USGS recommendations and conclusions of this work.

Most laboratories performing natural water analyses will be using flame spectrometry as a main technique for sodium, potassium, magnesium and calcium determination in the near future. This statement is supported by:

- The current use of flame spectrometers at these laboratories;
- Ongoing improvement in the construction, performance and auxiliary equipment of new spectrometer models offered by the leading manufacturers;
- Significant and sustained price difference between the FAA/FAE and e.g. the ICP-AES spectrometers.

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