

SELECTED ANIONS AND CATIONS IN MINERAL WATERS

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WYBRANE ANIONY I KATIONY W WODACH MINERALNYCH

Zastosowano szybką, jednoczesną, izokratyczną technikę tłumieniowej dwukolumnowej chromatografii jonowej z detektorem konduktometrycznym do oznaczania głównych anionów (F^- , Cl^- , NO_3^- , SO_4^{2-}) i kationów (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) w wodach mineralnych. Optymalny rozdział anionów uzyskano stosując eluent $1,7 \text{ mmol/dm}^3 Na_2CO_3 + 1,5 \text{ mmol/dm}^3 NaHCO_3$ z przepływem $1,3 \text{ cm}^3/\text{min}$ i czasem analizy 20 min.

Do analizy kationów zastosowano eluent $1,0 \text{ mmol/dm}^3 HNO_3 + 1,0 \text{ mmol/dm}^3$ 1,4-dichlorofenyloaminę z przepływem $0,6 \text{ cm}^3/\text{min}$ i całkowitym czasem analizy 12 min. Przedstawiono wyniki analiz anionów i kationów w czternastu, dostępnych w handlu, polskich wodach mineralnych.

S u m m a r y

The rapid, simultaneous isocratic suppressed ion chromatographic determination of common anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) in mineral waters has been performed using the dual column ion chromatograph and conductivity detector.

Optimum separation of the anions was achieved using $1.7 \text{ mmol/dm}^3 Na_2CO_3 + 1.5 \text{ mmol/dm}^3 NaHCO_3$ eluent with flow rate $1.3 \text{ cm}^3/\text{min}$ and analytical run time 20 min. For cation analysis $0.1 \text{ mmol/dm}^3 HNO_3 + 1.0 \text{ mmol/dm}^3$ 1,4-dichlorophenylamine eluent with flow rate $0.6 \text{ cm}^3/\text{min}$ and total run time 12 min was used. The results of the analysis of anions and cations in fourteen commercially available Polish bottled waters are presented.

INTRODUCTION

The concentrations of cations and anions in different water samples are usually determined by classical methods or instrumental techniques (e.g. flame emission spectroscopy, atomic absorption spectroscopy, photometric methods). Recently ion chromatography has become a standard method for the determination of ions in water [6–9, 16].

Since its introduction in 1975 [15] ion chromatography has been the most popular instrumental technique applied to determine of inorganic and organic ions in environmental samples [1, 2, 12, 14, 18, 19]. This paper was an important milestone, in particular because for the first time it presents the possibility of rapid separation and measurement of common inorganic and organic anions.

This method is so-called „suppressed” or „dual-column” ion chromatography because of relatively high electrical conductivity of eluent necessary to be used in second suppressed column. These columns are packed with high capacity ion-exchange resin of opposite type to the separator columns.

The careful selection of separation column and eluent allows the application of only one analytical column. This „one-column” or „non-suppressed” ion chromatography was introduced by Gjerde *et al.* in 1979 [3]. Detectors used in ion chromatography are the same as those used in HPLC. These can be divided into two classes: optical and electrochemical. The electrical conductivity detector is most commonly used in ion chromatography. Because all of species separated by ion exchange are partially or completely dissociated ions during their separation, they share the capability of conductivity electric charge of solution. Because of this, the electrical conductivity detector is the most commonly useful detector following ion exchange separation.

The detector must be very stable and sensitive, for it must measure small conductivity changes against background perhaps a thousand times higher than the signals observed.

Originally the chromatography of anions was more important than the chromatography of simple inorganic cations. Most cations come from metals and metallic elements can be determined spectroscopically. The determination of inorganic anions on the other hand was very difficult until the development of ion chromatography.

If anion analysis by using ion chromatography is nowadays well known and relatively easy to carry out, the first cation exchange column for suppressed ion chromatographic determination of alkali and alkaline earth metals was introduced in 1979 [17].

The determination of monovalent and divalent cations was possible but not within the same run. The newest column offers further advantages. It has a shorter run time, higher capacity, better sodium-ammonium-potassium selectivity. The sulphonic functionality characteristics for all previous columns were replaced by carboxylic functionality which enables the use of low strength eluents for the isocratic elution of I and II group ions [10].

In literature there have been several articles on application of ion chromatography to determine alkali and alkaline earth metals in mineral water. Gros and Gorenc [5] described rapid, simultaneous, isocratic ion chromatographic analyses of lithium, sodium, ammonium, potassium, magnesium and calcium in highly mineralized waters. These authors have worked out an expert system which permits planning of appropriate dilutions and the prediction of suitable detector output ranges for the successful quantitative analysis of individual ions in particular samples [4]. For simultaneous determination of six common cations in mineral water from South Korea, one-column ion chromatography was applied [11].

The aim of this work was to present suppressed ion chromatography for determination of some anions and cations in different mineral waters available on the Polish market.

EXPERIMENTAL

APPARATUS

The Biotronik ion chromatographic system model IC 5000 (Biotronik, Maintal, Germany) consisting of dual piston high pressure isocratic pump (BT 0512), conductivity detector (BT 0331) and a CR6A integrating system (Shimadzu, Japan). The analytical columns for separation of anions and cations (4.5 x 200 mm I.D.) contained suitable ion-exchange resins.

CHEMICALS AND SOLUTIONS

All chemicals (Na_2CO_3 , NaHCO_3 , 1,4-dichlorophenylamine and HNO_3) used for eluents preparation were purchased from Merck (Merck, Darmstadt, Germany).

Prior to the analysis the water samples were filtered through a $0.45\ \mu\text{m}$ Sartorius filter and degassed for about 30 min in ultrasonic bath. Deionized water with resistivity $< 0.05\ \mu\text{S}/\text{cm}$ purified by reverse-osmosis and filtrated through activated charcoal (Millipore, Milli-Q) was used for the preparation of standards and eluents and for sample dilutions when necessary.

Eluents were prepared daily with freshly deionised degassed water. As stock solution of anions and cations commercial solution in concentration of $1.000\ \text{mg}/\text{dm}^3$ each ions was used.

The concentrations of ions in calibration solutions were prepared taking into account their expected concentration in water samples. Fourteen commercially available mineral and table waters and one therapeutic water from different producers were purchased and common anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were analyzed.

RESULTS AND DISCUSSION

DETERMINATION OF FLUORIDE, CHLORIDE, NITRATE AND SULFATE ANIONS

The analysis of anions in calibration solutions and mineral water samples were carried out in the following analytical conditions:

Analytical column	–	BT I ANS,
Suppersor column	–	BT S AG,
Eluent	–	$1.7\ \text{mmol}/\text{dm}^3\ \text{Na}_2\text{CO}_3 + 1.5\ \text{mmol}/\text{dm}^3\ \text{NaHCO}_3$,
Flow rate	–	$1.3\ \text{cm}^3/\text{min}$,
Prenotessure	–	48 bar.

Calibration curve obtained using two point's calibration method. Results are given in Table 1.

Table 1. Calibration coefficients and anions concentrations in standard solutions

Anion	Retention time [min]	Calibration coefficient	Anion concentration [mg/dm^3]
F^-	3.03	$3.8572\ \text{E}-7$	1
		0.100824	10
Cl^-	4.37	$1.2522\ \text{E}-6$	1
		0.51694	100
NO_3^-	7.12	$2.1732\ \text{E}-6$	1
		0.20483	10
SO_4^{2-}	16.48	$3.9104\ \text{E}-6$	1
		0.64484	100

DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM CATIONS

The analysis of cations in calibration solutions and mineral water samples were carried out in the following analytical conditions:

Analytical column	–	BT IV KA,
Suppressor column	–	BT SKG,
Eluent	–	0.1 mmol/dm ³ HNO ₃ + 1.0 mmol/dm ³ 1,4-dichlorophenylamine,
Flow rate	–	0.6 cm ³ /min,
Pressure	–	57 bar.

Results of calibration are shown in Table 2.

Table 2. Calibration coefficients and cations concentrations in standard solutions

Cation	Retention time [min]	Calibration coefficient	Cation concentration [mg/dm ³]
Na ⁺	2.65	9.68655 E-7	1
		0.21566	100
K ⁺	4.31	5.4027 E-7	1
		0.97325	10
Mg ²⁺	6.37	2.2606 E-7	1
		0.28797	100
Ca ²⁺	10.09	7.85784 E-6	1
		0.64271	100

Samples were analyzed three times and the average results as well as producer's data, pH value before degassing and some statistical data are given in Tables 3 and 4. Examples of chromatograms are shown in figure 1 (anions) and 2 (cations). Owing to ion-exchange capacity of separator columns samples no. 13 and no. 5 (in the case of cation analysis) were diluted with deionized water prior to the analysis in the ratio of 1: 25.

The human body consists of 65–70% of water. One of sources of water can be mineral waters consumed in recent years in large amounts. According to Polish regulation [13] so-called „mineral water” can be divided into several groups:

- „Mineral water” is defined as „ground water obtained from subterranean water-bearing strata that in its natural state contains soluble matter”;
- „Carbonated water” as water that has been saturated with carbon dioxide under pressure;
- „Mineralized water” as water, saturated or not with carbon dioxide under pressure, to which mineral salts have been added;
- „Soda water” as carbonated water or carbonated water to which carbonate or bicarbonate salts of sodium or potassium have been added.

Moreover, these can be distinguished soft drink as a product prepared from water,

mineral water or mineralized water and flavorings and „packaged water” as water for human consumption other than mineral water. Mineral water is required to be labeled with a typical analysis of mineral constituents.

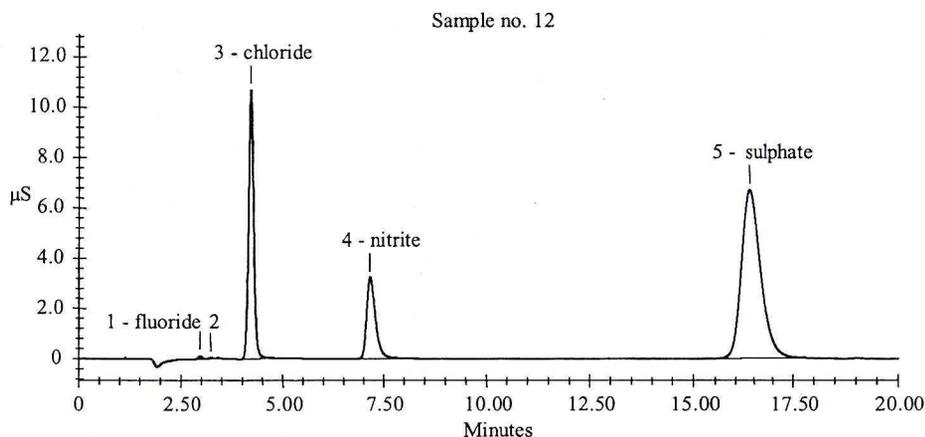


Fig. 1. Chromatogram of anion analysis (sample 12, measurement no. 1)
 Analytical conditions for the determination of fluoride, chloride, nitrate and sulphate ions:
 Analytical column – BT I ANS,
 Suppressor column – BT S AG,
 Eluent – $1.7 \text{ mmol/dm}^3 \text{ Na}_2\text{CO}_3 + 1.5 \text{ mmol/dm}^3 \text{ NaHCO}_3$,
 Eluent flow rate – $1.3 \text{ cm}^3/\text{min}$,
 Back pressure – 52 bar.

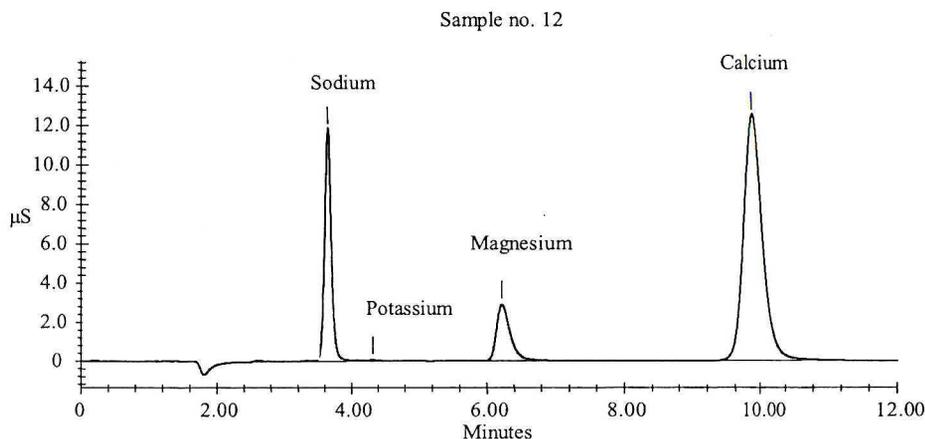


Fig. 2. Chromatogram of cation analysis (sample 12, measurement no. 1)
 Analytical conditions for the determination of sodium, potassium, magnesium and calcium ions:
 Analytical column – BT IV KA,
 Suppressor column – BT S KG,
 Eluent – $0.1 \text{ mmol/dm}^3 \text{ HNO}_3 + 1.0 \text{ mmol/dm}^3 \text{ 1,4-dichlorophenylamine}$,
 Eluent flow rate – $0.6 \text{ cm}^3/\text{min}$,
 Back pressure – 57 bar.

Table 3. Concentration [mg/dm³] of anions and cations in tested water – part I

Water number	MN	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	pH	
1	1	0.05	5.73	12.23	22.09	35.27	1.2	18.67	49.23	6.82	
	2	0.05	5.58	12.40	22.04	35.09	1.3	18.89	49.12		
	3	0.07	5.51	12.49	22.17	35.14	1.3	19.02	49.91		
	Mean	0.05	5.61	12.37	22.10	35.17	1.27	18.86	49.42		
	PD	ND	7.96	ND	12	38.5	2	17.69	51.94		ND
	S _x	0.01	0.07	0.13	0.07	0.09	0.02	0.13	0.43		-
	V _x	20.38	1.17	1.07	0.30	0.26	1.21	0.70	0.87	-	
2	1	0.03	212.59	0.04	200.7	212.78	0.1	39.45	126.34	7.6	
	2	0.03	215.52	0.03	203.8	215.45	0.1	40.15	122.6		
	3	0.04	216.17	0.03	204.8	214.82	0.1	40.33	125.8		
	Mean	0.03	214.7	0.03	203.1	214.3	0.10	39.98	124.9		
	PD	ND	<270	ND	<190	ND	ND	>40	>85		ND
	S _x	0.01	2.14	0.01	2.14	1.40	0.01	0.01	2.02		-
	V _x	17.32	1.00	17.32	1.05	0.65	5.77	0.01	1.62	-	
3	1	0.28	16.74	0.05	57.86	23.13	1.8	19.45	117.45	5.83	
	2	0.29	16.71	0.05	57.82	22.78	1.8	19.07	118.31		
	3	0.27	16.34	0.05	58.26	22.82	1.8	19.44	117.77		
	Mean	0.28	16.60	0.05	57.98	22.91	1.80	19.32	117.8		
	PD	ND	21.3	ND	50.7	13.3	1.9	19.5	115.8		ND
	S _x	0.01	0.24	0.00	0.24	0.19	0.01	0.00	0.43		-
	V _x	3.57	1.47	0.00	0.42	0.84	0.56	0.00	0.37	-	
4	1	0.66	11.9	1.63	80.17	4.98	0.1	28.96	39.41	7.15	
	2	0.63	11.78	1.65	79.35	4.87	0.1	29.56	39.89		
	3	0.67	11.89	1.62	79.5	4.89	0.1	28.71	39.56		
	Mean	0.65	11.86	1.63	79.67	4.91	0.10	29.08	39.62		
	PD	ND	8.0	ND	29.0	5.0	ND	29.0	39.0		ND
	S _x	0.02	0.44	0.02	0.44	0.06	0.00	0.02	0.25		-
	V _x	3.19	3.68	0.94	0.55	1.19	0.00	0.05	0.62	-	
5	1	0.23	6.74	0.35	8.01	68.45	4.1	74.6	568.1	5.64	
	2	0.27	5.77	0.32	7.89	68.34	4.1	75.12	572.1		
	3	0.22	7.15	0.36	8.56	67.98	4.2	75.32	560.3		
	Mean	0.24	6.55	0.34	8.15	68.26	4.13	75.01	566.8		
	PD	0.1	10.3	ND	6.2	59.5	6.5	73.2	550.1		ND
	S _x	0.03	0.36	0.02	0.36	0.25	0.03	0.02	6.00		-
	V _x	11.02	5.45	6.06	4.38	0.36	0.64	0.03	1.06	-	
6	1	0.4	7.22	0.15	1.15	80.28	8.3	11.67	38.47	5.84	
	2	0.39	7.89	0.17	0.91	80.34	8.3	11.72	38.25		
	3	0.41	7.43	0.15	1.04	81.03	8.2	11.98	39.06		
	Mean	0.40	7.51	0.16	1.03	80.55	8.27	11.79	38.59		
	PD	0.38	53.5	ND	ND	81.1	9.3	11.6	38.8		ND
	S _x	0.01	0.12	0.01	0.12	0.42	0.01	0.01	0.42		-
	V _x	2.50	1.60	7.37	11.63	0.52	0.12	0.10	1.09	-	
7	1	0.07	1.74	0.81	35.4	36.21	1.2	12.62	38.71	6.71	
	2	0.07	1.72	0.79	35.06	36.78	1.2	12.93	38.33		
	3	0.05	1.76	0.84	35.4	36.29	1.1	12.71	39.11		
	Mean	0.06	1.74	0.81	35.29	36.43	1.17	12.75	38.72		
	PD	0.1	7.09	ND	41.2	28.2	1.34	17.8	40.6		ND
	S _x	0.01	0.20	0.03	0.20	0.31	0.01	0.03	0.39		-
	V _x	18.23	11.28	3.09	0.56	0.85	0.99	0.20	1.01	-	

Notes: PD – Producer Data;

S_x – standard deviation [mg/dm³]V_x – relative standard deviation [%]

ND – No Data

Table 4. Concentration [mg/dm³] of anions and cations in tested water – part II

Water number	MN	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	pH
8	1	0.29	6.13	1.92	2.71	35.61	1.1	9.92	98.13	6.95
	2	0.30	6.10	1.99	2.65	36.18	1.2	9.54	98.52	
	3	0.29	6.07	1.93	2.69	36.72	1.1	9.73	97.94	
	Mean	0.29	6.10	1.95	2.68	36.17	1.13	9.73	98.20	
	PD	ND	8.8	ND	ND	12.0	4.8	22.8	117.3	7.0
	S _x	0.01	0.03	0.04	0.03	0.56	0.01	0.44	0.30	-
	V _x	1.97	0.50	1.94	1.14	1.53	0.51	4.52	0.30	-
9	1	0.44	18.45	1.67	25.9	7.44	1.1	7.34	56.81	6.25
	2	0.40	18.35	1.43	24.41	7.42	1.1	7.27	56.75	
	3	0.41	17.41	1.62	25.82	7.38	1.1	7.28	56.88	
	Mean	0.42	18.07	1.57	25.38	7.41	1.10	7.30	56.81	
	PD	ND	15.2	ND	35	6.5	1.4	9.5	64.5	ND
	S _x	0.02	0.84	0.13	0.84	0.03	0.02	0.13	0.07	-
	V _x	5.00	4.64	8.05	3.30	0.41	1.89	1.74	0.11	-
10	1	0.37	6.41	0.24	22.27	5.78	0.3	5.61	81.56	5.38
	2	0.36	6.37	0.26	22.9	5.81	0.3	5.49	82.04	
	3	0.32	6.34	0.28	23.23	5.77	0.3	5.69	82.18	
	Mean	0.35	6.37	0.26	22.80	5.79	0.30	5.60	81.93	
	PD	0.14	7.09	ND	95.0	3.1	0.9	8.75	90.1	ND
	S _x	0.03	0.49	0.02	0.49	0.02	0.03	0.02	0.33	-
	V _x	7.56	7.65	7.69	2.14	0.36	8.82	0.36	0.40	-
11	1	0.49	6.21	0.43	25.77	12.56	1.1	8.59	42.19	6.8
	2	0.45	6.7	0.45	25.61	12.74	1.1	8.83	42.79	
	3	0.46	6.55	0.42	25.42	12.49	1.1	8.74	43.15	
	Mean	0.47	6.49	0.43	25.60	12.60	1.10	8.72	42.71	
	PD	ND	12.4	ND	35.6	3.2	1.6	13.3	70.9	ND
	S _x	0.02	0.18	0.02	0.18	0.13	0.02	0.02	0.48	-
	V _x	4.46	2.70	3.53	0.68	1.02	1.89	0.18	1.14	-
12	1	0.137	3.94	4.51	16.46	13.71	1.5	27.04	48.27	4.28
	2	0.142	3.57	4.41	16.43	13.67	1.5	26.99	47.32	
	3	0.144	3.59	4.7	16.5	13.49	1.55	26.85	47.48	
	Mean	0.14	3.70	4.54	16.46	13.62	1.52	26.96	47.69	
	PD	ND	16.25	ND	42.28	10.17	2.54	35.59	51.7	ND
	S _x	0.00	0.04	0.15	0.04	0.12	0.00	0.15	0.51	-
	V _x	2.56	0.95	3.24	0.21	0.86	0.24	0.55	1.07	-
13	1	1.13	1133	4.49	60.47	5480	158	428	168	7.15
	2	1.16	1098	4.72	59.75	5420	160	458	164	
	3	1.17	1099	4.76	59.98	5470	155	452	168	
	Mean	1.15	1110	4.66	60.07	5456	157.6	446.0	166.6	
	PD	ND	616.5	ND	54.7	5600	200.3	464.2	184.7	ND
	S _x	0.02	0.37	0.15	0.37	32.15	0.02	0.15	2.31	-
	V _x	1.80	0.03	3.13	0.61	0.59	0.01	0.03	1.39	-
14	1	0.04	2.92	3.19	22.90	8.29	1.2	15.05	8.25	7.35
	2	0.04	2.90	3.18	22.94	8.56	1.2	15.18	8.18	
	3	0.04	2.86	3.16	22.97	8.47	1.2	15.21	8.22	
	Mean	0.04	2.89	3.18	22.94	8.44	1.20	15.15	8.22	
	PD	ND	11.8	ND	ND	5.1	ND	28.06	7.3	8.0
	S _x	0.00	0.04	0.02	0.04	0.14	0.00	0.02	0.04	-
	V _x	0.00	1.21	0.48	0.15	1.63	0.00	0.10	0.43	-

Notes: PD – Producer Data;

S_x – standard deviation [mg/dm³]V_x – relative standard deviation [%]

ND – No Data

EVALUATION OF CONCENTRATION OF ANALYZED IONS IN TESTED WATER

FLUORIDE

At concentration greater than 1.0 mg/dm^3 fluoride reduces the incidence of dental cavities, but in concentrations over 1.5 mg/dm^3 fluorosis may occur. In Poland, maximum acceptable concentration of fluoride in drinking water is 1.5 mg/dm^3 and in mineral water up to 2.5 mg/dm^3 . Concentration of fluoride anion in analyzed water was from limit of detection to 1.17 mg/dm^3 (in highly mineralized therapeutic water no. 13).

CHLORIDE

High concentration of chloride anions may result in an objectionable salty taste and sporadically laxative effect. Even maximum acceptable concentration (300 mg/dm^3) is not dangerous for human health. Concentration of chloride in analyzed water was from 1.72 mg/dm^3 (sample no. 7) up to 216.17 mg/dm^3 (sample no. 2) excepted sample no. 13.

NITRATE

Nitrate can be dangerous for health. Level higher than 45 mg/dm^3 may cause methemoglobinemia. The concentration of nitrate in analyzed water was definitely lower than 20 mg/dm^3 (maximum acceptable concentration) even in strong ionized waters.

SULPHATES

Water containing high levels of sulphates, particularly magnesium and sodium sulfate may have a laxative effect and have characteristic taste. For these reasons the upper recommended limit for sulphates in drinking water is 250 mg/dm^3 . The concentration of sulfate ions in analyzed water was from very low level (0.91 mg/dm^3 , sample no. 6) up to 204.84 mg/dm^3 (sample no. 2).

CALCIUM AND MAGNESIUM

Magnesium concentrations greater than 125 mg/dm^3 may have laxative effect on some people. Calcium and magnesium are important elements for human health. There is no maximum acceptable concentration of magnesium and calcium in mineral water. Water containing more than $50 \text{ mg/dm}^3 \text{ Mg}$ and $150 \text{ mg/dm}^3 \text{ Ca}$ is classified as „natural mineral water contains magnesium and calcium”. Relatively high concentration of calcium and magnesium was in the range of $8.18 \text{ mg/dm}^3 \text{ Ca}$ (sample no. 14) up to $572.18 \text{ mg/dm}^3 \text{ Ca}$ (sample no. 5) and from $5.49 \text{ mg/dm}^3 \text{ Mg}$ (sample no. 10) up to $458 \text{ mg/dm}^3 \text{ Mg}$ (sample no. 13).

POTASSIUM AND SODIUM

Potassium concentration in water was generally small – from $0.1 \text{ mg/dm}^3 \text{ K}$ (sample no. 2) up to $8.3 \text{ mg/dm}^3 \text{ K}$ (sample no. 6), except highly mineralized therapeutic water no. 13 (158 mg/dm^3). Human intake of sodium is mainly influenced by the consumption of sodium

chloride. In analyzed water the lowest concentration was at level from several to a few dozens mg/dm³, except very high concentration in water no. 13.

CONCLUSION

No mineral water producer provides information on the concentration of nitrate. Limit of detection of the analyzed ions in described conditions is 0.01 mg/dm³, except potassium (0.1 mg/dm³).

According to statistical data in table 3 and 4, standard deviation as well as relative standard deviation is on good acceptable level. Unfortunately, in several cases the obtained data are not compatible with producer's data. It concerns especially water no. 8, 10, 11, 12 13 and 14. Water no. 13 was highly mineralized therapeutic water.

Because ion chromatography is an accuracy and repeatable method (Table 3 and 4) these disagreements can be explicable in this way, that concentration of organic and inorganic compounds in water can be changeable in time and producers are obliged to do these analyses only once a year.

Ion chromatography is a useful technique for the analysis of inorganic compounds in various environmental samples including mineral water. In comparison to classical methods that are time and chemical-consuming ion chromatography has many advantages such as:

- possibility of simultaneous determination of several ions in a short time (5–20 min);
- limit of detection at mg/dm³ level or lower;
- small volume of samples necessary for analysis;
- high selectivity in complex matrix;
- easy sample preparation.

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