

Performance of ion chromatography in the determination of anions and cations in various natural waters with elevated mineralization

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Abstract

The performance of ion chromatography in the determination of anions and cations in natural mineral waters of different composition and different total mineralization was evaluated. Up to 12 ions of the 20 usually included in extended chemical analysis of natural waters were successfully determined by ion chromatography alone. At least 98.60% and up to 99.96% of total cation composition of mineral waters was determined by ion chromatography. Hydrogen carbonate predominated in anion composition of mineral waters and was determined titrimetrically. The percentage of anions determined by ion chromatography in the remaining anion composition of mineral waters was between 98.90% and 99.96%. The agreement between total concentrations of anions and cations in individual mineral waters determined predominantly by ion chromatography is very good and the performance of ion chromatography for the basic and for the extended chemical analysis of highly mineralized water samples is very high. Method development was assisted by previously developed algorithms and appropriate experimental conditions are also discussed.

Keywords: Water analysis; Inorganic anions; Inorganic cations

1. Introduction

Ion chromatography is already routinely used for the analysis of normal drinking water but it is also becoming more and more popular for the analysis of other ecological samples e.g. rainwater [1], acid rain, snow [2], ice core [3], organic-rich natural waters from peatlands [4,5] and so on. The samples within these groups are not so different as mineral waters are. Mineral waters significantly differ not only in total mineralization but also in chemical composition and proportion between individual constituents. In order to facilitate the analysis of such different water samples we have been previously working on the development of algorithms that facilitate the selection of appropriate experimental conditions for the

ion chromatographic determination of anions [6,7] and cations [8].

The aim of this work is the practical evaluation of the performance of ion chromatography in the analysis of mineral waters considering not only the number of parameters successfully determined but also the percentage, of total anion and total cation composition that were determined in different mineral waters by ion chromatography. The selection of appropriate experimental conditions using algorithms is also discussed.

2. Experimental

2.1. Apparatus and experimental conditions

For the determination of cations the Dionex

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(Sunnyvale, CA, USA) Model 4000i ion chromatographic apparatus was used, with an IonPac CS12 guard column and an IonPac CS12 separator column, a cation self-regenerating suppressor (4 mm) and a Dionex conductivity detector II (CMD). For the determination of anions an IonPac AG4A guard column, an IonPac AS4A separator column and an IonPac AS5 guard and IonPac AS5 separator columns, an anion micromembrane suppressor (4 mm) and, in addition to a conductivity detector, a spectrophotometric variable-wavelength detector was used. In the flow path the flow cells of the two detectors were positioned one after another and the conductivity cell was the last. Spectrophotometric detector was used for the determination of nitrite, nitrate, bromide and iodide. The injection volume and the eluent flow-rate were 25 μl and 1 ml min^{-1} for the determination of cations, and 50 μl and 2 ml min^{-1} for the determination of anions. A two-canal Chrom Jet integrator (Thermo Separation Products, CA, USA) was used.

2.2. Reagents and solutions

All stock standard solutions for determination of anions and cations were prepared at a concentration of 1 g l^{-1} from analytical reagent grade chemicals using deionised water obtained from a Milli-Q water-purification system (Millipore, Bedford, MA, USA). A stock standard solution of the cationic eluent with a concentration of 1 M was prepared from 98% methanesulphonic acid purchased from Merck-Schuchardt (Hohenbrunn bei München, Germany) and an eluent containing 20 mM methanesulphonic acid was prepared daily from it. Two different anionic eluents were used. The first one contained only sodium hydrogencarbonate at concentration 15 mM , the concentrations of sodium hydrogencarbonate and sodium carbonate in the second eluent were 1.7 and 1.8 mM . Both eluents were prepared daily from stock standard 100 mM solutions.

Hydrochloric acid (Titrisol) of concentration 100 mM was purchased from Merck (Darmstadt, Germany) and was used for the titrimetric determination of hydrogen carbonate in mineral waters.

2.3. Analysis of mineral waters

Ten different mineral waters of Slovenia were

analysed. The samples A, C, G, H, K, P, were taken from Health resort Radenska, the samples 1, 2, 3, 6 were from the Prekmurje region. For the first six samples an extended chemical analyses was done. For the ion chromatographic analysis the samples of mineral waters that contained carbon dioxide were ultrasonically degassed (8 min). All the samples had to be diluted. If anions were determined and hydrogencarbonate eluent with concentration 15 mM was used, the hydrogencarbonate concentration in diluted samples was adjusted to that value. In all cases the method of calibration functions was used for quantitative analysis. For the determination of each ion, peak areas and peak heights of five calibration solutions with different concentrations were measured (Table 4). The first, the third and the last calibration solutions were injected twice. All the samples were injected at least twice. The concentrations of ions were calculated either from peak areas or from peak heights, depending on the value of correlation coefficients of the relating calibration functions. Peak heights generally gave better results. Peak areas were used only for the determination of chloride in samples 1, 2, 3, 6, C, H, P and also for the determination of sulphate in samples 1, 3, A, C, G, H, K and P.

3. Results and discussion

3.1. The performance of ion chromatography for the determination of ions in highly mineralized waters

For the periodical checking of quality of natural waters there are mostly two types of analysis: basic and extended (complete) chemical analysis.

In order to evaluate the performance of ion chromatography in the analysis of highly mineralized waters, extended chemical analysis that usually comprises 20 ions, was done and the results are summarized in Table 1. Six mineral waters analyzed were fairly different, the concentrations of total dissolved solids were between 788 mg l^{-1} and 6833 mg l^{-1} , but in all six samples 12 parameters of all 20 were successfully determined by ion chromatography alone. Even more important than the number of parameters was the percentage of total cation and the

Table 1
The results of extended chemical analysis of different mineral waters

	<i>c</i> (mg l ⁻¹)					
	Sample of mineral water					
	A	C	G	H	K	P
NH ₄ ⁺	1.5	0.3	0.2	0.8	1.0	0.3
Li ⁺	0.61	0.15	1.15	0.21	0.58	0.45
Na ⁺ (IC)	676	90.5	1334	100	653	680
K ⁺ (IC)	124	24.1	202	18.6	110	67.3
Ca ²⁺ (IC)	270	61.0	204	174	104	122
Sr ²⁺	1.46	0.25	2.1	0.62	1.47	1.09
Mg ²⁺ (IC)	85.3	19.6	89.8	60.0	41.8	38.7
Fe ²⁺	0.1	0.05	0.1	2.5	0.1	0.05
Mn ²⁺	0.06	0.2	0.03	0.20	0.2	0.4
Al ³⁺	<0.07	<0.07	0.07	0.07	<0.07	<0.1
F ⁻ (IC)	0.49	0.38	0.66	0.40	1.31	0.57
Cl ⁻ (IC)	66.1	8.95	157	9.52	54.5	175
Br ⁻ (IC)	0.37	0.040	0.85	0.045	0.30	0.77
I ⁻ (IC)	0.14	0.015	0.30	0.018	0.12	0.13
NO ₃ ⁻ (IC)	<0.012	<0.004	<0.020	<0.005	<0.010	<0.008
NO ₂ ⁻ (IC)	<0.012	<0.004	<0.020	<0.005	<0.010	<0.008
SO ₄ ²⁻ (IC)	131	8.05	337	18.6	119	92.3
HS ⁻	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
HPO ₄ ²⁻ (IC)	<0.08	<0.03	<0.14	<0.04	<0.07	<0.05
HCO ₃ ⁻	3050	539	4440	1170	2280	2135
TDS	4457	788	6833	1601	3410	3349

IC, determined by ion chromatography.

Ammonium, iron, aluminum and hydrogen sulphide were determined by spectrophotometry.

Lithium, strontium and manganese were determined by atomic absorption spectrometry.

percentage of total anion composition covered by one single analytical technique. The results in Table 1 showed that 99.59% of total cation composition (TCC) of sample A was determined by ion chromatography, 98.60% of TCC of sample C, 99.71% of TCC of sample G, 99.96% of TCC of sample H, 99.52% of TCC of sample K and 99.67% of TCC of sample P. In anion composition of mineral waters hydrogencarbonate highly predominates, but it is very simply determinable titrimetrically and the percentage of anions determined by ion chromatography in the remaining anion composition of mineral waters are as follows: 99.90% (sample A), 98.90% (sample C), 99.96% (sample G), 99.30% (sample H), 99.88% (sample K), 99.93% (sample P). Ion chromatography together with acidimetric titration of hydrogencarbonate enables the determination of the vast majority of total composition of mineral waters.

Contrary to extended chemical analysis, basic chemical analysis which is practically more important and more widely spread, includes only the main

ions. For another four mineral waters basic chemical analysis was done. The results are summarized in Table 2. All parameters with the exception of hydrogencarbonate were determined by ion chromatography. In order to evaluate the reliability of the analysis as a whole, concentrations in mequiv.l⁻¹ are given in Table 2 in addition to concentrations in mg l⁻¹. The results in mequiv.l⁻¹ are a sort of controlling parameter enabling the evaluation of the agreement between total anion and total cation composition of mineral waters. The difference between total cation composition and total anion composition compared to total anion composition was -4.3% for sample 1, 0.0% for sample 2, +1.5% for sample 3 and -1.7% for sample 6. The agreement between concentrations of anions and cations determined predominantly by ion chromatography is very good and the performance of ion chromatography for the basic and for the extended chemical analysis of highly mineralized water samples is very high.

Table 2
The results of basic chemical analysis of different natural mineral waters

	Sample 1		Sample 2		Sample 3		Sample 6	
	mg l ⁻¹	mequiv. l ⁻¹	mg l ⁻¹	mequiv. l ⁻¹	mg l ⁻¹	mequiv. l ⁻¹	mg l ⁻¹	mequiv. l ⁻¹
Na ⁺	738	32.10	754	32.82	373	16.23	322	14.00
K ⁺	68.1	1.74	44.2	1.13	9.86	0.25	7.78	0.20
Mg ²⁺	8.69	0.72	4.00	0.33	1.25	0.10	0.97	0.08
Ca ²⁺	22.9	1.14	15.4	0.77	5.74	0.29	6.39	0.32
Total		35.70		35.05		16.87		14.60
Cl ⁻	150	4.22	120	3.38	11.1	0.31	122	3.45
SO ₄ ²⁻	30	0.64	1.90	0.04	1.88	0.04	0.99	0.02
HCO ₃ ⁻	1938	31.76	1927	31.58	993	16.27	695	11.39
Total		37.32		35.05		16.62		14.86

All ions except HCO₃⁻ were determined by ion chromatography.

Mequiv. l⁻¹ is not an SI unit, but it is unavoidable for the representation of the agreement between total anion and total cation composition.

3.2. The diversity of samples of mineral waters and selection of appropriate experimental conditions

Diversity in composition of all ten mineral waters analyzed by ion chromatography is more realistically represented by triangular diagrams in Figs. 1 and 2, than by figures. For the highest possible simultaneity and practical effectiveness of ion chromatographic analysis of such different water samples more planning of appropriate experimental conditions including dilutions, sequences of detector output ranges and most effective combinations of calibration solu-

tions were needed. The predictions were based on and facilitated by the previously developed algorithms [6–8].

In order to achieve the highest possible simultaneity the flow cell of the spectrophotometric detector was inserted between the suppressor and the flow cell of the conductometric detector. Thereby seven anions—fluoride, chloride, bromide, nitrite, nitrate, hydrogenphosphate and sulphate—all previously separated on the IonPac AS4A column, were determined within the same run. The concentrations of inorganic contaminants such as nitrite, nitrate and hydrogenphosphate were undetectably low in all

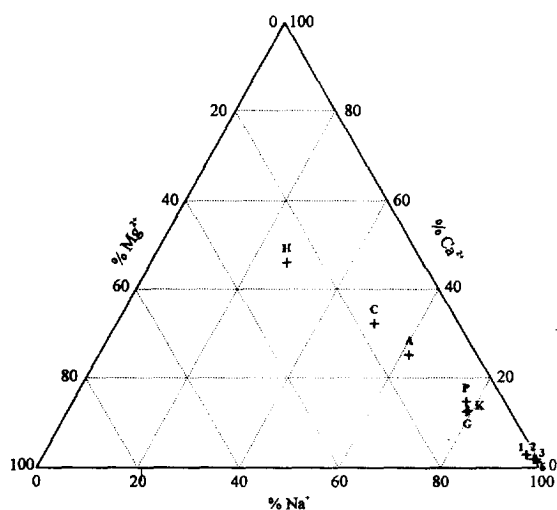


Fig. 1. Triangular diagram representing the proportions of the main three cations in different mineral water samples.

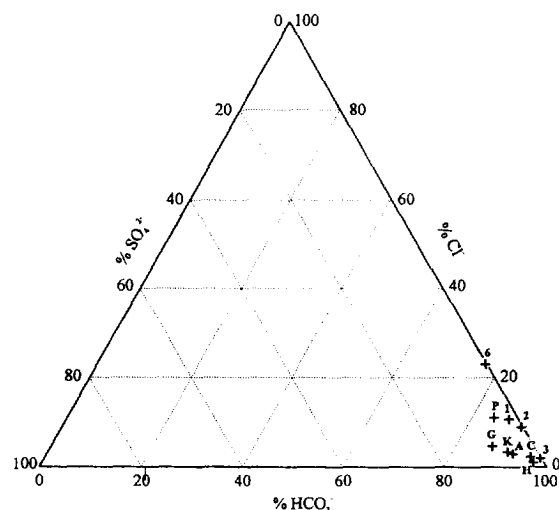


Fig. 2. Triangular diagram representing, the proportions of the main three anions in different mineral water samples.

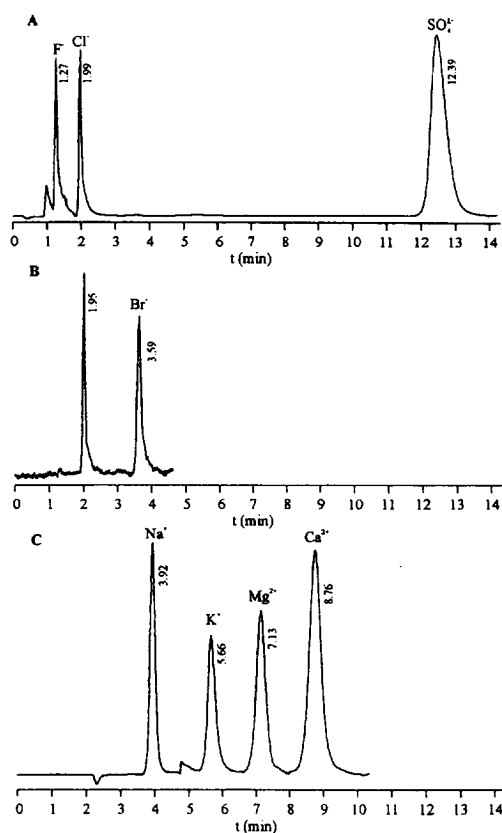


Fig. 3. Chromatograms for the determination of cations and anions in sample H.

mineral waters. Ion chromatographic analysis in connection with a previously developed computer program [7] enabled the estimation of the concentration limits that are certainly not exceeded in

individual mineral waters. The estimations showed lower concentrations than are maximally allowed by international authorities [9]. Unfortunately iodide cannot be separated on the IonPac AS4A column simultaneously with the other seven anions, therefore the IonPac AS5 column had to be used for the determination of this constituent. Fig. 3 shows three representative chromatograms for the ion chromatographic determination of anions and cations in mineral waters.

In order to improve the performance of the ion chromatographic analysis we have already proposed changing of detector output ranges during elution [10]. Appropriate combinations of detector output ranges are summarized in Table 3. In the comparison with anions the analysis of cations was much simpler. Only two sets of calibration solutions were needed: one for samples A, C, G, H, K, P and one for samples 1, 2, 3 and 6. On the other three sets of calibration solutions were needed for the successful determination of anions in first six samples (Table 4). The concentration differences between anions that were determined by ion chromatography in a particular water sample were up to four orders of magnitude. On the other hand differences between cations were only exceptionally more than two orders of magnitude.

Appropriate dilutions of mineral waters were very different and extended from 1:1.25 to 1:20 for determination of anions and from 1:12.2 to 1:183.5 for determination of cations. The dilution 1:20 was the only one suitable for the determination of anions in more than one mineral water (samples 1, 2 and 6). The recognition of the cation that determines the

Table 3

The diversity of experimental conditions necessary for the successful ion chromatographic determination of ions in mineral waters

Detector output range				Mineral water
F^- (μS)	Cl^- (μS)	SO_4^{2-} (μS)	Br^- (AU)	
3	100	30	0.005	A, G, K
3	30	10	0.002	C, H
3	300	30	0.01	P
—	30	0.1	—	1, 2, 6
—	30	1	—	3
Na^+ (μS)	K^+ (μS)	Mg^{2+} (μS)	Ca^{2+} (μS)	
10	1	1	1	A, C, G, H, K, P
10	0.3	0.3	0.3	1, 2, 3, 6

Table 4

The composition of three series or combined standard solutions (mg l^{-1}) for the quantitative determination of anions in mineral waters A, C, G, H, K and P

Solutions A				Solutions B		Solutions C			
F^-	Cl^-	Br^-	SO_4^{2-}	Cl^-	Br^-	F^-	Cl^-	Br^-	SO_4^{2-}
0.08	9	0.05	18	30	0.12	0.08	2	0.02	6
0.16	18	0.10	36	60	0.24	0.16	4	0.04	12
0.24	27	0.15	54	90	0.36	0.24	6	0.06	15
0.32	36	0.20	72	120	0.48	0.32	8	0.08	18
0.40	45	0.25	90	150	0.60	0.40	10	0.10	24

minimal necessary dilution [8] was necessary for the optimization of the dilution for the ion chromatographic determination of cations in mineral waters. Concentration level of sodium mostly determined dilution, but minimal necessary dilution of sample H was determined by calcium.

4. Conclusions

Although the mineral water samples were fairly different in total mineralization and chemical composition, up to 12 ions of the 20 usually included in extended chemical analysis of natural waters were successfully determined by ion chromatography alone. At least 98.60% and up to 99.96% of total cation composition of mineral waters was determined by ion chromatography. Hydrogencarbonate which predominated in the anion composition of mineral waters was determined titrimetrically. The percentage of anions determined by ion chromatography in the remaining anion composition of mineral waters was between 98.90% and 99.96%. The agreement between total concentrations of anions and cations in individual mineral waters determined predominantly by ion chromatography is very good and the per-

formance of ion chromatography for the basic and for the extended chemical analysis of highly mineralized water samples is very high. The optimization of experimental conditions is significantly facilitated by previously developed algorithms [6–8]. All this proves that ion chromatography is the method of choice not only for the analysis of normal drinking water but also for the analysis of different natural waters with higher mineralization.

References

- [1] P.A. Tanner and S.M. Chan, *J. Chromatogr. A*, 739 (1996) 249.
- [2] K. Oikawa, K. Murano, Y. Enomoto, K. Wada and T. Inomata, *J. Chromatogr. A*, 671 (1994) 211.
- [3] M. Legrand, M. De Angelis and F. Maupetit, *J. Chromatogr.*, 640 (1993) 251.
- [4] W. Shotyk, *J. Chromatogr.*, 640 (1993) 309.
- [5] W. Shotyk, *J. Chromatogr.*, 640 (1993) 317.
- [6] N. Gros and B. Gorenc, *Chromatographia*, 36 (1993) 251.
- [7] N. Gros and B. Gorenc, *J. Chromatogr. A*, 668 (1994) 385.
- [8] N. Gros and B. Gorenc, *J. Chromatogr. A*, 697 (1995) 31–43.
- [9] N.F. Gray, *Drinking Water Quality*, Wiley, New York, 1994, p. 20.
- [10] N. Gros and B. Gorenc, *Wat. Res.*, 29 (1995) 1591.