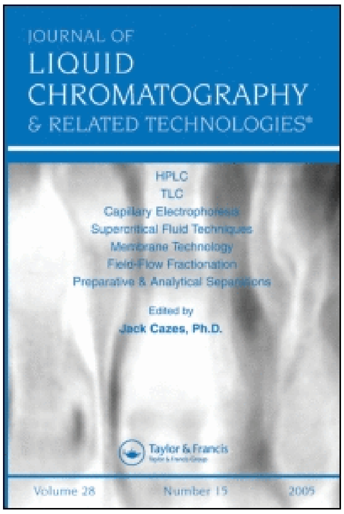

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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Przemyslaw Kosobucki[a]; Boguslaw Buszewski[a]
[a] Department of Environmental Chemistry and Ecoanalytics, Faculty of Chemistry, NCU, Toruñ, Poland

To cite this Article Kosobucki, Przemyslaw and Buszewski, Boguslaw(2006) 'Application of Isotachophoresis for Quality Control of Drinking and Mineral Waters', Journal of Liquid Chromatography & Related Technologies, 29: 13, 1951 — 1960

To link to this Article: DOI: 10.1080/10826070600758100

URL: http://dx.doi.org/10.1080/10826070600758100

Journal of Liquid Chromatography & Related Technologies®, 29: 1951–1960, 2006

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070600758100

Application of Isotachophoresis for Quality Control of Drinking and Mineral Waters

Przemyslaw Kosobucki and Boguslaw Buszewski
Department of Environmental Chemistry and Ecoanalytics,
Faculty of Chemistry, NCU, Toruñ, Poland

Abstract: Results of drinking and mineral waters quality control by isotachophoresis (ITP) are presented. This method was used to determine inorganic cations (potassium, sodium, calcium, and magnesium) and anions (nitrate, chloride, sulphate). Direct conductometric detection was applied in this investigation. As a result of the measurements, we have found a considerable difference between the value declared on the label and the examined one in many cases. Thanks to its low cost and high rate, the presented method can be used in routine analysis as an alternative technique to ion chromatography.

Keywords: Isotachophoresis, Water quality, Inorganic ions, Ecoanalytics

INTRODUCTION

Water, as one of the most important mediums present in the ecosystem, is necessary for life on the Earth. From this point of view, water analysis (qualitative and quantitative) is very significant. The typical analysis of surface, underground, mineral, and drinking (before and after conditioning) water using classical analytical methods is time and work consuming and an expensive task.[1] This is directly connected with numbers of examined parameters, 46 physicochemical and 6 biological parameters should be tested in the normal analysis for correctly estimated water quality.[2] A typical

Address correspondence to Boguslaw Buszewski, Department of Environmental Chemistry and Ecoanalytics, Faculty of Chemistry, NCU, 7 Gagarin Street, 87-100, Toruñ, Poland. E-mail: bbusz@chem.uni.torun.pl

control laboratory (eg., in a water conditioning factory) should be equipped with a wide range of instruments including expensive ones.

Electrochemical (ion selective electrodes–ISE), spectrophotometric (UV-VIS),[1] and chromatographic techniques (IC)[3] are very often used to analyse ionic compounds in water. In recent years, ion chromatography with and without suppression (suppressed and non-suppressed IC), mobile phase, and conductivity detection, and/or spectrophotometry are most popular in laboratories.[4] However, the high cost of a single analysis, as a consequence of the instruments' cost, is the significant disadvantage of the use of ion chromatography. Application of electromigration techniques in water analysis, especially isotachophoresis (ITP) or capillary zone electrophoresis (CZE), may be considered as an alternative. Isotachophoresis (ITP) with direct conductivity detection is a useful and powerful method for high sensitive determination of both anionic and cationic species.[5,6]

The aim of this contribution is to present results of the determination of some cations (sodium, potassium, calcium, magnesium) and anions (chloride, nitrate, sulphate) in drinking water, as well as in samples of eight selected mineral waters (accessible in Poland), by isotachophoresis with conductivity detection. Classical titration was used as a reference method.

EXPERIMENTAL

Instrumentation

An isotachophoretic analyzer EA 100 (VillaLabeco, Spisska Nova Ves, Slovakia) was used. This analyzer is provided with two PTFE columns (a pre-separation one: 0.8 mm × 90 mm, and an analytical one: 0.3 mm × 160 mm), one UV detector (254 nm), two conductometric detectors, and a sample loop 30 μL.

The data from the detectors were acquired and processed by an ITPWin ver. 2.31 software (KasComp, Bratislava, Slovakia) installed on a Pentium computer.

An EM-Bürette (Hirschmann Laborgeräte, Eberstadt, Germany) was used for chloride ions determination.

Sample sonification was performed in an ultrasonic bath UM-2 (Unitra Unima, Olsztyn, Poland).

Chemicals

Hydrochloric acid, ammonium acetate, zinc acetate and citric acid were obtained from P. O. Ch. (Gliwice, Poland). Hydroxyethylcellulose, polyethylene glycol 600, β-alanine and Bis-tris propane (BTP) were purchased from Sigma-Aldrich (Steinheim, Germany). All chemicals utilized for electrolytes, standard solutions, and sample preparation were pure per analysis (*p.p.a.*) class.

Deionised water was used from Milli–Q RG (Millipore, Molsheim, France).

Sample Preparation

Before isotachophoretic analysis samples (all from examined series) were sonicated in 10 minutes. It was necessary to remove dissolved gases (especially carbon dioxide) from the liquid sample. One sample (eg., mineral water-*Krystynka*) was diluted (100 × times) using distillated water, because the measured zone length of the undiluted sample was too long and did not fit in linear range of the calibration curve (Table 1).

Method Validation

The isotachophoretic method was validated.[7,8] Precision, recovery, linearity, and the limit of detection were determined. Table 1 shows the data obtained from the validation and characteristics of qualitative and quantitative analyses. Compared with titration, the presented method was characterized by a wider range of linearity as well as by a higher precision that did not exceed 5%. The calibration curve method was used. Standards of examined species were injected (in duplicate) from water stock solutions at five levels (Table 1) utilizing a sample valve with fixed volume (30 μL).

Our preview study on the determination of ionic constituents in the different environmental matrixes shows that data obtained from isotachophoresis are directly correlated ($R^2 > 0.9997$) with data from capillary zone electrophoresis.[5] Other researchers validated data from isotachophoresis with, eg., ion chromatography techniques.[10]

RESULTS AND DISCUSSION

Table 2 presents composition of leading (LE) and terminating (TE) electrolytes used to separate inorganic ions by isotachophoresis in water samples. The anion analysis system makes possible determination of other anions. Simultaneous analysis of ions such as Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, PO_4^{3-}, F^- is easy to perform; but we have examined only chloride and sulphate ions' concentrations in the samples because contents of only these two anions are declared on water labels.

Figure 1 shows typical isotachophoregrams obtained from analyses of the different water samples (distillated water, drinking water, and *Muszynianka* mineral water, for example).

Table 1. The characteristics of the method for the analysis of the studied species

		Analytes					
		Anions		Cations			
Characteristic	Value	Chlorides	Sulphates	Potassium	Sodium	Calcium	Magnesium
RSH		0.000	0.120	0.179	0.465	0.586	0.719
Intra-assay[a]	%	2.2	1.2	3.6	2.8	3.1	2.9
Accuracy[b]	%	87.2 ± 6	96.6 ± 1	84.6 ± 1	88.4 ± 8	81.1 ± 5	80.7 ± 7
Linearity[c]	mg/L	2–100	10–100	1–20	1–20	10–50	10–50
Detection limit[d]	mg/L	1	1	0.5	0.5	1	1

Where: RSH –relative step height, parameter to isotachophoretic qualitative analysis.

[a] Repeated injection of the same sample, RSD, n = 4.

[b] Sample spiked with 1 mg/L analyte solution, n = 3.

[c] Correlation coefficient (min. 0.99).

[d] Based on the signal-to-noise ratio n = 3.

Table 2. Operational systems for isotachophoretic separations ions in water samples

	Anions		Cations	
Parameter	LE	TE	LE	TE
Ion	Cl^-	CITR	NH_4^+	Zn^{2+}
Concentration (mM)	8	2	10	10
Counter ion	BALA	H^+	CH_3COO^-	CH_3COO^-
Co-counter ion	BTP	—	PEG	—
Concentrartion	3 mM	—	30 %	—
pH	3.55	—	5.40	—
Additive	0.1% HEC		0.1% HEC	

where: LE—leading electrolyte, TE—terminating electrolyte, BALA—β-alanine, CITR—citric acid, PEG—polyethylene glycol 600, BTP—1,3-bis[tris(hydroxymethyl)-methylamino]propane, HEC—hydroxyethylcellulose.

In distillated water prepared by the Millipore Milli-Q RG system, the examined ionic species were not found. The high quality of the deionised water was confirmed and, thus, we used it as a reference or blank water in qualitative and quantitative investigations.

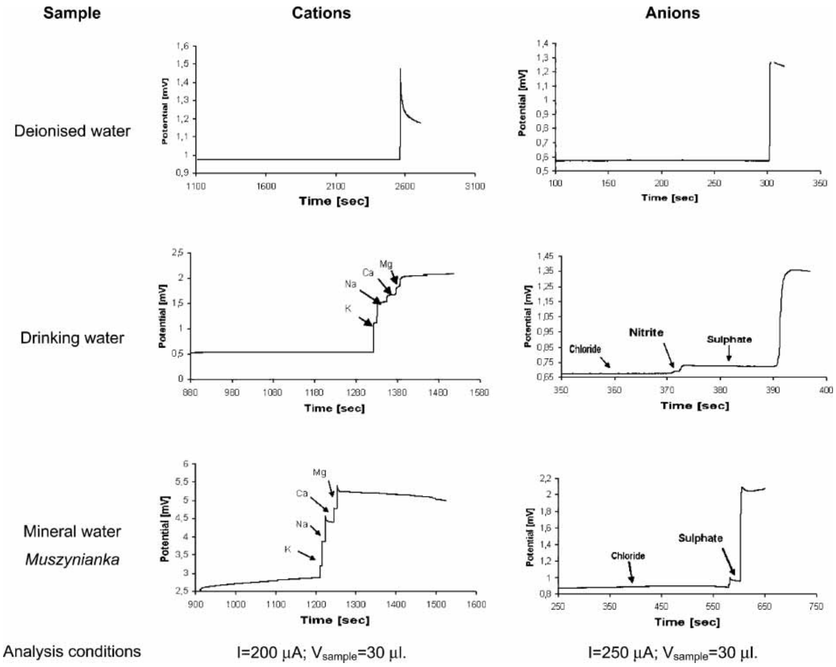

Figure 1. Determination of ions in various water samples by isatochophoresis.

Potassium, sodium, calcium, and magnesium ions were detected in drinking water in the amounts 2.32 ± 0.47 mg/L, 9.60 ± 0.98 mg/L, 24.15 ± 1.23 mg/L, and 7.83 ± 0.75 mg/L, respectively. Chloride and sulphate contents were determined as 124.69 ± 5.07 mg/L and 48.26 ± 2.39 mg/L. Extra nitrate was observed in 4.21 ± 0.61 mg/L amount. The established amounts of both cations and anions did not exceed the limited values for drinking water and for water of household/economic destination.[2]

In *Muszynianka* mineral water the contents of anions, chlorides, and sulphates are 18.82 ± 2.02 mg/L and 15.45 ± 3.43 mg/L, respectively. Concentrations of potassium, sodium, calcium, and magnesium cations are 10.67 ± 0.45 mg/L, 135.65 ± 6.78 mg/L, 185.34 ± 9.83 mg/L, and 134.31 ± 7.45 mg/L, respectively. Data on *Muszynianka* labels and the rest of the mineral water produced are presented in Table 3.

The results of the experiments demonstrated differences between values on the labels and the corresponding values measured by isotachophoresis in many cases. The observed differences' in quantities are from a few percent (potassium in *Muszynianka)* to dozens of percent (sulphates in *Naleczowianka)*, that is probably correlated with the time period of the mineral water analysis. Bottled water was analyzed a few times during the exploration period of the aquifer; however, ionic composition of the water could change during exploration. From this point of view, monitoring of the quality of mineral waters is necessary. Physicochemical control of drinking water is usually performed because water is conditioned with different elementary processes (coagulation, chlorination, ozonation) and physicochemical data are necessary to correct the process.[9]

We applied titration for chloride ion analysis to certify the data of isotachophoresis. Polish regulations recommend the classical Mohr's method to determine chloride in water samples.[2] Figure 2 shows results of chloride determination in *Muszyna Minerale* mineral water by isotachophoresis and titration.

A few conclusions may be arrived from these data. Isotachophoresis and titration methods provide the approached results with the measure error lower than 4%. But these data differ totally from the same on *Muszyna Minerale* mineral water label (5.3 mg Cl^-/L). ITP is a more precise analytical method in comparison with titration (8.98 ± 0.73 mg Cl^-/L and 8.86 ± 1.78 mg Cl^-/L, respectively).

Results of chemometric analysis (PCA) are presented in Figure 3. Data obtained from this analysis show that isotachophoretic investigations confirmed chemical compositions (similar underground water sources) of mineral water and the difference between measurement and label value can be ignored (no statistical significance). PC 1 is directly connected with excess of chloride in water (macrocomponet), the rest of the examined ions (microcomponents) have no significance in the total value of PC 1.

Table 3. Results of the determination of ions in various mineral water samples (n = 3, $\alpha = 0.95$)

	Chloride [mg/L]		Sulphate [mg/L]		Potassium [mg/L]	
Sample	Measured	Producer	Measured	Producer	Measured	Producer
1	nd	8.9	22.46 ± 1.12	45.52	8.4 ± 1.09	5.5
2	7.51 ± 1.24	8.9	22.06 ± 1.08	45.52	9.31 ± 0.98	5.5
3	11.23 ± 1.56	8.9	26.45 ± 0.76	45.52	8.67 ± 1.32	5.5
4	8.98 ± 0.87	8.9	25.65 ± 1.06	45.52	8.85 ± 1.23	5.5
5	18.82 ± 2.02	12.91	15.45 ± 3.43	19.8	10.67 ± 0.45	10.75
6	15.29 ± 3.11	12.91	23.87 ± 2.21	19.8	8.35 ± 2.04	10.75
7	n.d.	5.3	50.67 ± 4.08	47.5	11.52 ± 1.65	10.9
8	8.98 ± 2.13	5.3	37.56 ± 2.1	47.5	7.62 ± 2.87	10.9
9	4.56 ± 1.11	7.09	55.93 ± 4.65	32.5	1.31 ± 0.05	1.56
10	7.9 ± 0.67	7.09	18.02 ± 1.44	10.05	10.58 ± 2.7	7.84
11	9.03 ± 1.76	7.09	16.45 ± 1.98	10.05	5.35 ± 1.33	7.84
12	18.69 ± 2.08	10.6	34.67 ± 2.38	27.2	39.98 ± 4.65	46
13	26.66 ± 2.43	19.14	19.3 ± 2.87	20	4.6 ± 0.94	1.1
14	1122.98 ± 23.46	1659.2	45.93 ± 3.03	55	17.4 ± 2.87	18.8

(*Continued*)

Table 3. Continued

	Sodium [mg/L]		Calcium [mg/L]		Magnesium [mg/L]	
Sample	measured	producer	measured	producer	measured	producer
1	25.71 ± 4.54	13.3	63.53 ± 7.21	115.1	25.17 ± 4.54	23.3
2	14.19 ± 2.43	13.3	177.33 ± 9.67	115.1	29.99 ± 5.65	23.3
3	18.8 ± 2.29	13.3	124.24 ± 6.64	115.1	12.54 ± 2.31	23.3
4	18.76 ± 3.01	13.3	96.83 ± 8.34	115.1	17.45 ± 1.96	23.3
5	135 ± 65 ± 6.78	127.31	185.34 ± 9.83	206.21	134.31 ± 7.45	148.2
6	80.86 ± 4.41	127.31	169.86 ± 7.45	206.21	151.14 ± 8.08	148.2
7	67.12 ± 6.09	42.1	376.8 ± 11.34	485	56.29 ± 6.54	42.7
8	41.35 ± 5.58	42.1	365.91 ± 12.54	485	48.27 ± 4.23	42.7
9	4.86 ± 1.67	2.78	118.49 ± 7.54	88.18	10.52 ± 1.43	15.81
10	81.67 ± 7.73	66.2	487.49 ± 15.87	530.66	51.63 ± 3.45	73.02
11	89.45 ± 8.21	66.2	456.26 ± 16.65	530.66	111.28 ± 7.97	73.02
12	106.9 ± 9.32	132	280.16 ± 9.65	360.5	77.56 ± 3.92	65.9
13	4.29 ± 0.76	5.65	126.24 ± 8.82	86.57	22.5 ± 2.11	15.65
14	451.54 ± 10.23	950	121.31 ± 9.33	174.11	48.53 ± 3.5	62.61

Where: nd not detected.

Sample no: 1 is Nałęczowianka (batch no. 1); 2 is Nałęczowianka (batch no. 2); 3 is Nałęczowianka (batch no. 3); 4 is Nałęczowianka (batch no. 4); 5 is Musynianka (batch no. 1); 6 is Musynianka (batch no. 2); 7 is Musyna Minerale (batch no. 1); 8 is Musyna Minerale (batch no. 2); 9 is Kinga Pienińska; 10 is Kryniczanka; 11 is Kryniczanka; 12 is Staropolanka 2000; 13 is Ustronianka; 14 is Krystynka.

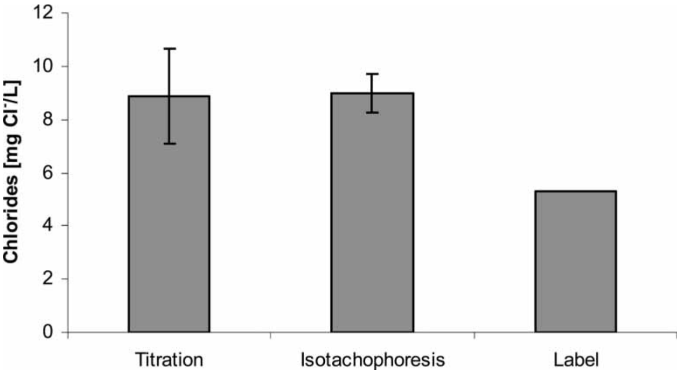

Figure 2. Comparison of the determination methods of chlorides Muszyna minerale (n = 3).

CONCLUSIONS

Results obtained in the measurements do not correspond to data declared by the producers. The differences between concentrations determined in our laboratory and those declared on labels of mineral waters reach even a dozen percent in some cases.

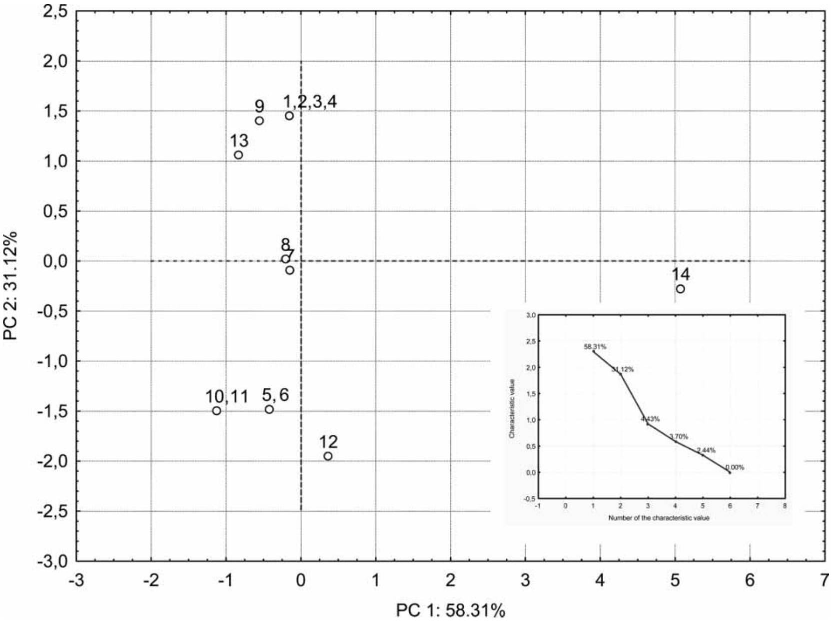

Figure 3. Principal Component analysis (PCA) of the examined mineral waters (abbreviations see Table 3).

The presented results state that the isotachophoresis offers a very promising alternative to the classic methods for analysis of the studied ions in water. The possibility of simultaneous determination of both macro- and micro consistuents in a reasonable time (up to 25 minutes) is the main advantage of ITP in this type of analysis. There is no sample pretreatment other than filtration required before analysis.

Thanks to its low cost and high rate, isotachophoresis could be useful in routine analysis. Additionally, isotachophoresis is a "*green chemistry technique*" because no toxic reagents and only small amounts of samples are utilized.

ACKNOWLEDGMENT

This work was supported by a grant (3 T09D 035 29) from the Ministry of Education and Science (Warsaw, Poland).

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Received January 8, 2006
Accepted February 10, 2006
Manuscript 6813