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Determination of Tetrafluoroborate and Chloride Anions by Capillary Isotachophoresis and Suppressed Ion Chromatography★

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This paper presents, discusses, and compares the results of determination of tetrafluoroborate and chloride anions by isotachophoresis (ITP) and ion chromatography (IC) with conductometric detection. Tetrafluoroborate and chloride anions are the ones of the most important (and most often used) anions in the molecules of ionic liquids. The achieved limit of detection (10 μg L^{-1}) was very satisfactory for the routine analysis. Thanks to the low cost and high throughput, the presented method can be used as an interesting alternatives for the current procedures. It was validated and basic validation parameters were estimated.

W pracy przedstawiono i porównano wyniki oznaczania anionów tetrafluoroboranowego i chlorkowego za pomocą izotachoforezy (ITP) oraz wysokosprawnej chromatografii jonowej (IC). W obu technikach wykorzystano detekcję konduktometryczną. Aniony tetrafluoroboranowy i chlorkowy są najpopularniejszymi anionowymi składnikami cieczy jonowych. Zaprezentowana metoda (granica wykrywalności 10 μg L^{-1}) może być wykorzystana w praktyce w rutynowych analizach próbek środowiskowych. Opracowaną metodę poddano walidacji i wyznaczono podstawowe parametry walidacyjne takie jak liniowość, precyzja, granica wykrywalności i granica oznaczalności.

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★ Dedicated to Professor Rajmund Dybczyński on the occasion of his 75th birthday.

Room-temperature ionic liquids (RTIL) – the salts that are liquid at ambient temperature – are normally composed of relatively large organic cations and inorganic or organic anions. Unlike molecular liquids, ionic liquids as polar solvents are environmentally benign, nonvolatile, and nonflammable. Typical ionic liquids consist of an organic cation with delocalized charges and a small anion – most often fluoroanion such as BF_4^-, PF_6^- or Cl^- of weak coordinating properties [1]. Most of them are well soluble in water and stable in air [2]. In addition, by varying the length and branching of alkyl chains of the anionic core and the cationic precursor, it is possible to design ionic liquid solvents for specific applications. Due to the above mentioned properties, ionic liquids are widely used as new solvent media in heterogeneous catalysis, organic synthesis, electrochemistry, sensors, battery applications, analysis and separation [2, 3].

Ionic liquids are toxic xenobiotics (at concentrations > 50 μmol L^{-1}) and can be rated as persistent organic pollutants (POPs) [4]. Thus, monitoring of concentration of ionic liquids in different parts of ecosystems (water, soils, or sediments) is necessary. Development of new analytical methods for rapid and reproducible separation and identification of ionic liquids is therefore prerequisite for future biological and environmental research on these substances.

Analysis of a cationic part of RTIL molecules is usually performed by chromatographic [3–5, 15–17] or electrophoretic techniques [1, 6].

Isotachophoresis (ITP) [18, 19] with direct conductivity detection is useful and powerful method for highly sensitive determination of both anionic and cationic components of RTIL [1]. Isotachophoresis has been successfully used for environmental analysis of water, wastewater, sewage sludge, and compost samples [7–11].

US, EPA, and EU directives, as well as Polish regulations, recommend ion chromatography with different types of detection (conductivity, UV, amperometric) as the method for routine analysis of anionic species in different matrices [12].

The main aim of this study was to demonstrate and compare the use of isotachophoresis and ion chromatography for determination of tetrafluoroborate and chloride anions. The quantitative analytical performance of the developed methods was satisfactory. Basic validation parameters were estimated.

EXPERIMENTAL

Instrumentation

An EA 102 (Villa Labeco, Spisska Nova Ves, Slovakia) isotachophoretic analyzer equipped with two FEP (fluoroethylenepropylene polymer) columns (pre-separation column: 0.8 mm × 90 mm; analytical column: 0.3 mm × 160 mm), two contact conductometric detectors, and a sample loop of 30 μL was used.

Driving current of 50 μA was set for the detection step. Isotachophoretic data were acquired and processed using ITPPro 32 software (KasComp, Bratislava, Slovakia) PC class.

An ICS–1000 (Dionex, Sunnyvale, USA) ion chromatograph with an IonPacAG22 guard column and an IonPac AS22 analytical column was used in chromatographic experiments. The system was equipped with a sample loop of 25 μL, an ASRS-Ultra II suppressor system, and a conductometric detector. The chromatographic data were acquired and processed using Chromeleon software (Dionex, Sunnyvale, USA).

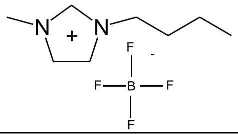
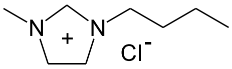
Chemicals

All chemicals used as electrolytes were of ppa (pure per analysis) grade and were purchased from Sigma–Aldrich (Steinheim, Germany).

1-butyl-3-methyl-imidazolium tetrafluoroborate [BMIM][BF_4] and 1-butyl-3-methyl-imidazolium chloride [BMIM][Cl] salts were purchased from Sigma–Aldrich (Steinheim, Germany). Basic physicochemical properties of these compounds are given in Table 1.

Deionized water (18 MΩ cm) was obtained using a Milli–Q RG filtering system (Millipore, Molsheim, France).

Table 1. Physicochemical properties of the examined compounds [3]

Chemical name	Chemical formula	Abbreviation	Structure	Molecular mass, g mol^{-1}	λ_{max}, nm
1-butyl-3-methyl-imidazolium tetrafluoroborate	$C_8H_{15}N_2BF_4$	[BMIM][BF4]		226	210
1-butyl-3-methyl-imidazolium chloride	$C_8H_{15}N_2Cl$	[BMIM][Cl]		174	212

Operational systems

Table 2 presents compositions of the leading (LE) and terminating (TE) electrolytes used to separate anions by isotachophoresis. Composition of these electrolytes was established in our previous study [1] and was occasionally applied in the ITP analysis of anions.

Table 2. Operating conditions for isotachophoretic separation of tetrafluoroborate anion; LE – leading electrolyte, TE – terminating electrolyte, BALA – b-alanine, CITR – citric acid, BTP – 1,3-bis[tris(hydroxymethyl)-methylamino]propane, HEC – hydroxyethylcellulose

Parameter	LE	TE
Ion	Cl^-	CITR
Concentration [mmol L^{-1}]	8	2
Counter ion	BALA	H^+
Co-counter ion	BTP	–
Concentration [mmol L^{-1}]	3	–
pH	3.55	–
Additive	0.1% HEC	–

RESULTS AND DISCUSSION

Isotachophoresis in the anionic mode enabled identification of anionic components of RTILs. Figure 1 shows the results of identification of the components of the model mixture of RTILs using conductivity detection. In isotachophoregram sharp and clear step corresponding to $[BF_4^-]$ can be observed. Relative step height (RSH) of this step is 0.346 ± 0.018 ($n = 5$). Chloride anion can be identified from the extension of the leading electrolyte signal. LE for the anionic analysis contained Cl^- (Tab. 2); Cl^- from LE and RTIL summed and produced finally the extended LE signal (this effect can be used in quantitative analysis as an internal standard method). Total analysis time in the anionic mode was about 20 min for the examined species (tetrafluoroborate and chloride anions).

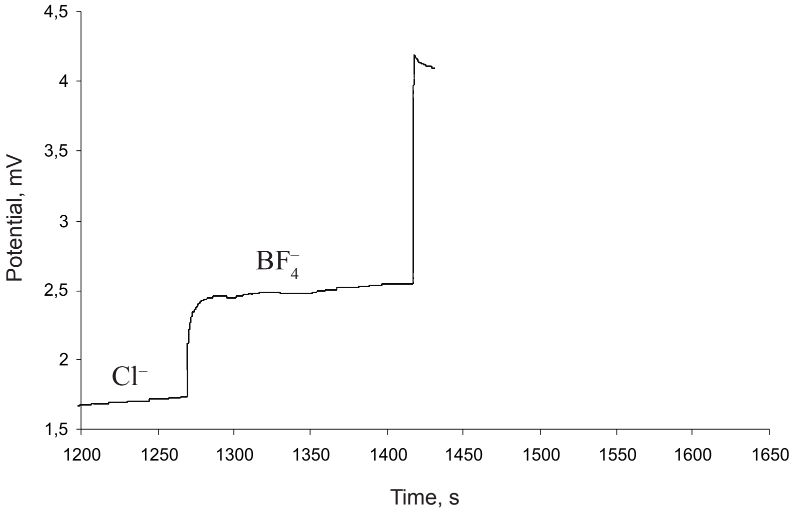


Figure 1. Isotachophoregram of the standard mixture containing tetrafluoroborate and chloride anions obtained under optimum conditions. Buffers – (Tab. 2), I_2 = 50 μA. Concentrations of BF_4^- and Cl^- are 0.369 mmol L^{-1} and 0.1066 mmol L^{-1}, respectively

The chromatographic method used was adapted from the procedure proposed by Dionex for determination of inorganic anions [13] and was preformed without addition of any organic modifiers to the mobile phase. The aim of our research was to apply this method using strongly polar column bed (AS22) to the analysis of tetrafluoroborate and chloride anions at the concentration level 0.1–12.0 mg L^{-1}. The applied column bed contained supermacroporous polyvinylbenzyl ammonium polymer cross-linked with divinylbenzene and bonded alkyl/alkanol quaternary ammonium functional groups. The results of the experiments performed under optimum conditions (flow rate, mobile phase composition) are shown in Table 3.

Exemplary chromatogram of the standard sample containing 0.369 mmol L^{-1} BF_4^- and 0.1066 mmol L^{-1} Cl^- in deionized water is shown in Figure 2. In the chromatogram three peaks can be distinguished. The first peak was attributed to the free fluoride (t_R = 3.43 min) and probably originated from the sample impurities. The second peak was assigned to chloride t_R = 4.47 min; this peak was characterized by high asymmetry coefficient (f_{AS}= 1.57). AS22 column efficiency on 5800 theoretical plates was calculated. The third peak at t_R = 10.29 min was the signal from tetrafluoroborate anion, the main component of the model mixture. This peak was characterized by high asymmetry coefficient (f_{AS}= 1.46), too. In this case column efficiency (AS22 column) on 4500 theoretical plates was calculated.

Table 3. Optimal conditions for chromatographic separation of tetrafluoroborate and chloride anions

Analytical column	IonPac AS22
Guard column	IonPac AG22
Supressor	ASRS-Ultra II
Supressor current	31 mA
Eluent	4.5 mmol L^{-1} Na_2CO_3 + 1.4 mmol L^{-1} $NaHCO_3$
Flow rate	1.2 mL min^{-1}
Injection volume	25 μL
Detection	Conductivity

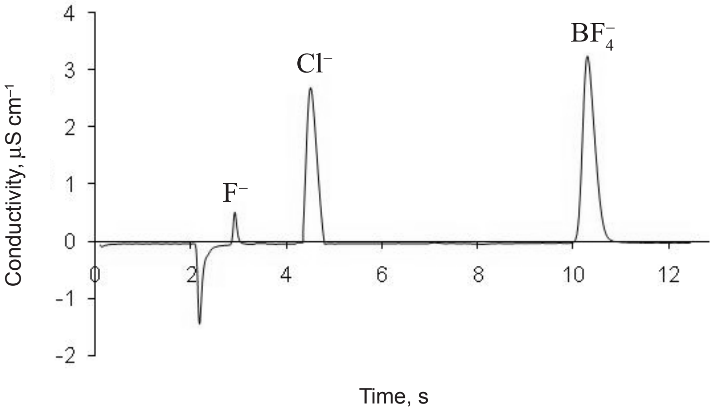


Figure 2. Chromatogram of the sample containing 0.1066 mmol L^{-1} Cl^- (t_R = 4.47 min) and 0.369 mmol L^{-1} tetrafluoroborate anion (t_R = 10.29 min). For chromatographic conditions see Table 3

Method validation

Both methods were validated. Precision, recovery, and linearity of the isotachophoretic method were determined. Validation data as well as method's characteristics obtained from qualitative and quantitative analyses are given in Table 4. The presented method is characterized by wide linearity range and high precision (RSD not exceeding 3%).

Table 4. Characteristics of isotachophoretic method for the analysis of the examined anions; RSH – relative step height, parameter to isotachophoretic qualitative analysis

Characteristic	Units	Cl^-	BF_4^-
RSH		0.000 ± 0.000	0.346 ± 0.018
Intra-assay[a]	%	1.9	2.8
Accuracy[b]	%	80.7 ± 8	91.4 ± 4
Linearity[c]	mg L^{-1}	0.1–20.0	0.1–12.0
LOD[d]	μg L^{-1}	15	10
LOQ[e]	μg L^{-1}	45	30

[a] Repeated injection of the same sample, RSD, n = 5.
[b] Sample spiked with 2.5 mg L^{-1} analyte solution, n = 3.
[c] Correlation coefficient (min. 0.999).
[d] Based on the signal-to-noise ratio n = 3 (zones shorter than 0.1 s were treated as a noise).
[e] LOQ = 3 · LOD.

Under the proposed isotachophoretic conditions (composition of LE and TE solutions, the magnitude of the applied current), tetrafluoroborate anion was determined in the range 0.1–12.0 mg L^{-1}. The applied analytical conditions seem to be well adjusted to provide good performance of the method – repeatability of RSH is often a weak point in ITP analysis. Relative standard deviations (RSDs) of the zone length were also reasonable and equalled to 2.8%. LOD (limit of detection) was calculated as 10 μg L^{-1} for the studied anion. This value is more than satisfactory and lower by few orders of magnitude than in the CZE method [6] for a comparable time. LOQ (limit of quantification) for tetrafluoroborate was 30 mg L^{-1}. This value fully suffices for the application of ITP in routine analysis.

Similar data were obtained for determination of chloride. Chloride was analysed in the wide concentration range 0.1–20.0 mg L^{-1}. The estimated accuracy was worse than for tetrafluoroborate. This can be explained by the lack of an additional step for chloride anion in isotachophoregram. In this case quality of LE is very important.

LOQ and LOD were estimated using a conventional chromatographic method and appropriate regression equation assuming that LOQ = 2.7 × LOD (in final calculations it was assumed that LOQ = 3 × LOD) [14].

The areas of the measured peaks were evaluated in order to validate the applied IC method. In order to verify precision, accuracy, linearity, detection limits, and quantification limits, 5 calibration solutions of tetrafluoroborate of the concentrations from the range 0.1–12.0 mg L^{-1} were prepared in deionized water and injected to the eluent stream. All calibration solutions were analysed in triplicate under optimal chromatographic conditions. The results of the calibration studies are summarized in Table 5.

Table 5. Chromatographic method validation parameters

Parameter	Units	Cl^-	BF_4^-
Retention time	min	4.47 ± 0.12	10.29 ± 0.26
Concentration range	μg L^{-1}	0.1–20	0.1–12
Standard deviation	μg L^{-1}	0.65	0.85
Accuracy	%	95 ± 0.96	96.75 ± 1.26
LOD	ng L^{-1}	1	2
LOQ	ng L^{-1}	3	6

The method was applied to the determination of the examined species in model mixtures. The investigated compound has not been detected in water or wastewater samples. However, its occurrence might become a problem in the near future.

Final remarks

New methods of identification of ionic liquids are required in ecological studies. The use of ion chromatography and isotachophoresis offers an interesting opportunity in this field. Ion chromatography with strongly polar column bed allows for analysis of inorganic anions *e.g.* tetrafluoroborate or chloride, which are the constituents of the room temperature ionic liquids.

The proposed method does not require any pretreatment (apart from filtration) of water and wastewater samples before the analysis. However, extraction of the analysed compounds from the solid matrix (soil or sediment samples) before the analysis is necessary.

The obtained results clearly show that the proposed methods are suitable for the analysis of ionic liquids in standard solutions and probably in environmental samples with high precision.

Acknowledgements

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