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## DETERMINATION OF INORGANIC ANIONS IN RIVER WATER BY COLUMN-COUPLING CAPILLARY ISOTACHOPHORESIS

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### SUMMARY

Optimal operating conditions for the simultaneous determination of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{F}^-$  and  $\text{PO}_4^{3-}$  in river water by column-coupling capillary isotachophoresis were found. The time for the complete analysis was *ca.* 25 min and no sample pre-treatment was needed. Detection limits for constituents that are present in river water at lower concentrations ( $\text{NO}_2^-$ ,  $\text{F}^-$  and  $\text{PO}_4^{3-}$ ) were in the range 30–60 pmoles. Decomposition of  $\text{NO}_2^-$  during the separation was observed and a possible mechanism is proposed.

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### INTRODUCTION

Determinations of inorganic anions present in waters (river, drinking, rain and waste waters) are currently performed in laboratories involved in environmental control. Of these constituents, sulphate, chloride, nitrate, nitrite, fluoride and phosphate are routinely determined in river water. At present, mostly different titrimetric and spectrophotometric methods are used for this purpose<sup>1,2</sup>. In some instances better results can be achieved using ion-selective electrodes<sup>3</sup>. In general, these methods are instrumentally simple and the reactions used for the determinations are usually well understood<sup>1,2</sup>. On the other hand, sample pre-treatments are often necessary before the final analytical step and it may be necessary to determine each of the constituents in a separate aliquot of the sample, which makes the complete anionic analysis labour and time consuming and less reliable.

Recently, several papers dealing with the determination of the above anions in water by ion chromatography (IC) have appeared. Both suppressed<sup>4-7</sup> and non-suppressed<sup>8-12</sup> modes of this technique with conductivity and/or photometric detectors were found to be suitable for this purpose. Multiple ion analysis, little or no

sample pre-treatment, speed, sufficient sensitivity and automation of the analysis are the main advantages of IC in water analysis.

Very similar advantages are offered by capillary isotachopheresis (ITP)<sup>13,14</sup>. However, with the exception of the work by Boček *et al.*<sup>15</sup>, in which the determinations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in mineral water were demonstrated, little attention has been paid to this subject. The aim of this work was to show the analytical capabilities of ITP for the simultaneous determinations of six inorganic anions that are currently monitored in river water.

The concentrations of the constituents of interest in river water may differ substantially (three orders of magnitude is typical). Also, as their physico-chemical properties dictate the use of a universal detector (preferably with a high resolving power), both low detection limits of the detector and a high load capacity<sup>16</sup> of the separation unit are desirable. Whereas a low detection limit of a universal detector in ITP requires a small I.D. of the capillary tube<sup>17</sup> and a low concentration of the leading constituent, the load capacity is best maximized through an increase in the I.D. of the capillary tube and/or through an increase in the concentration of the leading constituent<sup>16</sup>.

A column-coupling technique introduced into ITP by Everaerts *et al.*<sup>18</sup> provides an optimal solution in this respect; by dividing the analysis into two stages it enables a high load capacity and a low detection limit to be achieved simultaneously without an appreciable increase in the analysis time. Therefore, the use of such a configuration of the separation unit was an obvious choice in this work.

## EXPERIMENTAL

The chemicals used for the preparation of the solutions of the leading and terminating electrolytes, obtained as analytical-reagent grade materials, when necessary were purified by conventional methods<sup>19</sup>. Triply distilled water was used for the preparation of the solutions throughout this work.

The separation unit of the home-made ITP instrument used is shown in Fig. 1. A 0.85 mm I.D. capillary tube made of fluorinated ethylene-propylene copolymer (FEP) was used in the pre-separation (first) stage and a capillary tube of 0.30 mm I.D. made of the same material served for the separation in the second stage. Both tubes were provided with conductivity detection cells<sup>20</sup> and an a.c. conductivity mode of detection<sup>13</sup> was used for making the separations visible. The driving current was supplied by a unit enabling independent currents to be pre-selected for the pre-separation and final analytical stages. The run of the analyser was controlled by a programmable timing and control unit. The zone lengths from the conductivity detector, evaluated electronically, were printed on a PT 1 line printer (Laboratorní přístroje, Prague, Czechoslovakia). A detailed description of the analyser will be given elsewhere.

## RESULTS AND DISCUSSION

### *Choice of the operational systems*

The ionic mobilities of the constituents of interest decrease in the order  $\text{Cl}^- \geq \text{NO}_2^- \geq \text{NO}_3^- \geq \text{SO}_4^{2-} > \text{F}^- > \text{H}_2\text{PO}_4^-$  (at concentrations typical of the steady

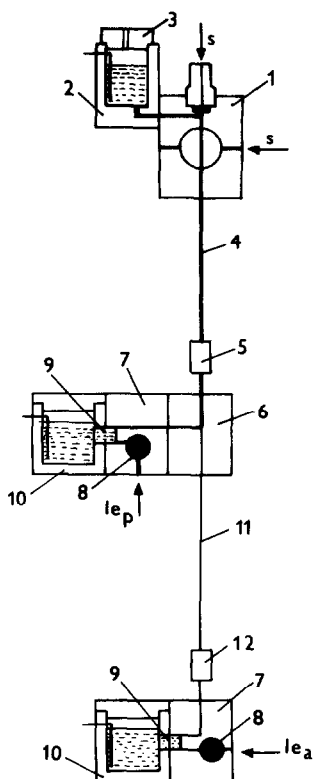


Fig. 1. Separation unit in a column-coupling configuration as used for the analysis of anions in river water. 1 = Sampling block with a 30  $\mu$ l sampling valve; 2 = terminating electrolyte compartment with a cap (3); 4 = 0.85 mm I.D. capillary tube (pre-separation column); 5, 12 = conductivity detectors; 6 = bifurcation block; 7 = refilling block with needle valve (8); 9 = mechanically supported membranes; 10 = leading electrolyte compartments; 11 = 0.30 mm I.D. capillary tube; s = positions for the sample introduction (valve or microsyringe);  $I_{e_p}$ ,  $I_{e_a}$  = positions for refilling of the columns used for the first and second stages, respectively.

state in ITP when water is used as the solvent). From the point of view of their abundance in river water we can divide them into two groups, viz., macro-constituents ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and micro-constituents ( $\text{NO}_2^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ).

There are several possibilities for optimizing the effective mobilities of these constituents through an appropriate composition of the operational system<sup>13,14</sup>. However, owing to their very different concentrations in river water, not all of the possible alternatives giving full separations fit equally well with the other requirements (e.g., the time needed for the separation or the load capacity required<sup>16</sup>, or interferences due to other constituents present in the sample or due to impurities present in the leading and terminating electrolyte solutions).

The use of a column-coupling configuration of the separation unit provided the possibility of applying a sequence of two leading electrolytes in one analytical run<sup>18</sup>. Therefore, the choice of optimal separation conditions could be advantageously divided into two steps: (1) the choice of a leading electrolyte suitable for the separation and quantitation of the macro-constituents in the first stage (pre-separation

column), simultaneously having a retarding effect on the effective mobilities of micro-constituents; and (2) the choice of the leading electrolyte for the second stage in which only micro-constituents are separated and quantified (macro-constituents were removed from the analytical system after their evaluation in the first stage).

To satisfy the requirements for the properties of the leading electrolyte applied in the first stage and, consequently, to decide its composition, two facts had to be taken into account, *i.e.*, the pH value of the leading electrolyte needs to be *ca.* 4 or less (retardation of nitrite relative to the macro-constituents in this stage) and at the same time the separations of the macro-constituents need to be optimized by other means than adjusting the pH of the leading electrolyte (anions of strong acids). For the latter reason, complex equilibria and differentiation of anions through the charge number of the counter ions<sup>21</sup> were tested at a low pH as a means of optimizing the separation conditions for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in the presence of  $\text{NO}_2^-$ ,  $\text{F}^-$  and  $\text{PO}_4^{3-}$ .

The retardation of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  through complex formation with  $\text{Cd}^{2+}$ , enabling the separation of anions of interest<sup>15</sup> to be carried out, was found to be unsuitable for our purposes as the high concentration of  $\text{Cd}^{2+}$  necessary to achieve the desired effect led to the loss of  $\text{F}^-$  and  $\text{PO}_4^{3-}$  (probably owing to precipitation).

Similarly, the use of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as complexing co-counter ions<sup>22</sup> to decrease the effective mobility of  $\text{SO}_4^{2-}$  was found to be ineffective as a very strong retardation of  $\text{F}^-$  occurred.

Better results were achieved when a divalent organic cation was used as a co-counter ion in the leading electrolyte<sup>21</sup> employed in the first separation stage.

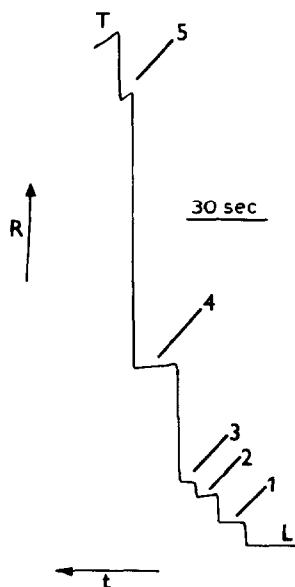


Fig. 2. Isotachopherogram from the separation of anions in the first stage using operational system No. 1. 1 = Nitrate (40 mg/l); 2 = sulphate (20 mg/l); 3 = nitrite (20 mg/l); 4 = fluoride (20 mg/l); 5 = phosphate (20 mg/l). Driving current, 250  $\mu\text{A}$ . L, T = leading and terminating anions, respectively; R = increasing resistance; t = increasing time. The sample was introduced with the aid of a 30- $\mu\text{l}$  valve.

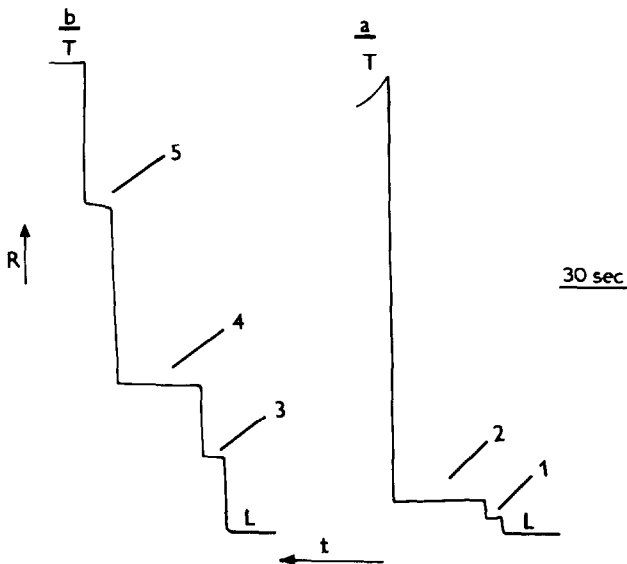


Fig. 3. Isotachopherograms from the analysis of a model mixture of anions present in the sample at concentrations approaching those in river water. 1 = Nitrate (30 mg/l); 2 = sulphate (100 mg/l); 3 = nitrite (0.5 mg/l); 4 = fluoride (0.5 mg/l); 5 = phosphate (0.5 mg/l). Operational system No. 1. Driving currents, 250 and 7.5  $\mu\text{A}$  for the first (a) and second (b) stages, respectively. Other symbols as in Fig. 2.

When, simultaneously, the pH of the leading electrolyte was 4 or less, the steady-state configuration of the constituents to be separated was  $\text{Cl}^- - \text{NO}_3^- - \text{SO}_4^{2-} - \text{NO}_2^- - \text{F}^- - \text{H}_2\text{PO}_4^-$ . The detailed composition of the operational system of this type used for quantitative analysis is given in Table I (system No. 1).

The choice of the leading electrolyte for the second stage, in which the micro-constituents were finally separated and quantitatively evaluated, was straightforward: a low concentration of the leading constituent (low detection limit) and a low pH of the leading electrolyte (separation according to pK values). The operational system used throughout this work in the second stage is given in Table I.

An isotachopherogram from the analysis of a model mixture of anions obtained in the first separation stage is shown in Fig. 2. This isotachopherogram merely indicates the differences in the effective mobilities of the anions of interest, as the concentrations of  $\text{NO}_2^-$ ,  $\text{F}^-$  and  $\text{PO}_4^{3-}$  in river water are usually too low to be detected in the first stage (see Fig. 3a).

As mentioned above, both the cross-sectional area of the capillary tube and the concentration of the leading constituent used in the second stage were optimized with respect to the determinations of micro-constituents. The isotachopherogram in Fig. 3b illustrates the response of the conductivity detector to the micro-constituents present in a model mixture approaching the composition of river water.

The isotachopherograms shown in Fig. 4 are taken from the analysis of a river water sample (Danube, near Bratislava). These isotachopherograms are typical of river water having concentrations of inorganic anions slightly lower than the average concentrations found in this study.

In a search for optimal separating conditions, operational system No. 2 (Table

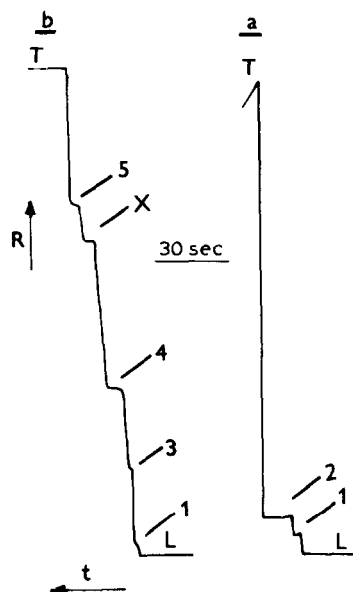


Fig. 4. Analysis of anions present in a water sample taken from the River Danube near Bratislava. 1 = Nitrate (13.0 mg/l); 2 = sulphate (31.8 mg/l); 3 = nitrite (0.16 mg/l); 4 = fluoride (0.16 mg/l); 5 = phosphate (0.36 mg/l). Chloride (16.6 mg/l) was determined as described in the text. Operational systems and other experimental conditions as in Fig. 3. Symbols as in Fig. 2.

TABLE I

## OPERATIONAL SYSTEMS

Abbreviations: BALA =  $\beta$ -Alanine; CITR = citric acid; BTP = 1,3-bis[tris(hydroxymethyl)methyl-amino]propane; HEC = hydroxyethylcellulose.

System No.	Parameter	Leading electrolytes		Terminating electrolyte
		1st stage	2nd stage	
1	Anion	Cl <sup>-</sup>	Cl <sup>-</sup>	CITR
	Concentration (mM)	8	1	2
	Counter ion	BALA	BALA	H <sup>+</sup>
	Co-counter ion	BTP	—	—
	Concentration (mM)	3	—	—
	Additive to the leading electrolyte	0.1% HEC	0.1% HEC	—
pH	3.55	3.55	ca. 3	
2	Anion	Cl <sup>-</sup>	Cl <sup>-</sup>	CITR
	Concentration (mM)	1	1	1
	Counter ion	H <sup>+</sup>	H <sup>+</sup>	H <sup>+</sup>
	Additive to the leading electrolyte	0.1% HEC	0.1% HEC	—
	pH	3.0	3.0	ca. 3

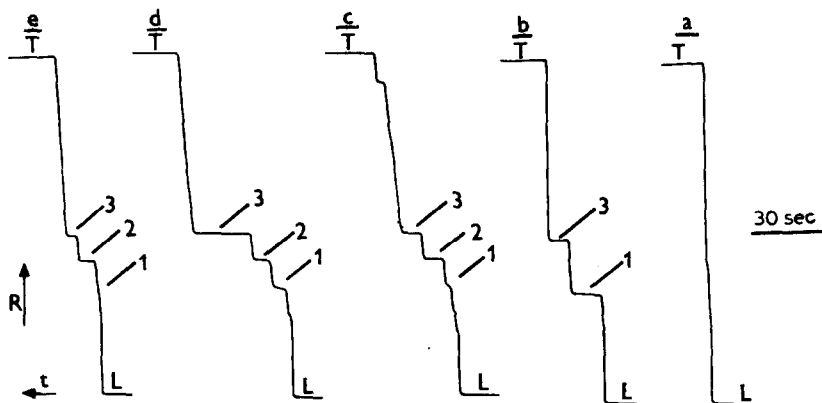


Fig. 5. Isotachopherograms from the detector used in the second stage registered from the analyses of anionic micro-constituents present in water samples. (a) Blank run (terminating electrolyte introduced into the sampling valve); (b) analyses of nitrite (1 mg/l) and phosphate (0.5 mg/l); (c), (d) river water samples; (e) drinking water. 1 = Nitrite; 2 = fluoride; 3 = phosphate. Operational system No. 2. Driving currents, 100 and 15  $\mu$ A for the first and second stages, respectively. Symbols as in Fig. 2.

I) was used for the determinations of micro-constituents. The isotachopherograms in Fig. 5, taken from the second separation stage (analytical column), illustrate the analyses of some water samples using this system. In spite of the good differentiation of the micro-constituents its use, *e.g.*, for separation in the second stage, is less favourable for the reasons given below.

As only anionic constituents of relatively strong acids can achieve the effective mobilities within the chloride-phosphate mobility interval at low pH, the number of possible interfering constituents (*e.g.*, organic anions associated with biological processes in water) is also reduced using the proposed operational systems.

#### Quantitative analysis

Data important for quantitative analyses of the macro-constituents were derived from the residence times of their zones in the conductivity cell of the pre-separation column. The residence times for the zones of nitrate and sulphate were measured in the usual manner<sup>13</sup> (time separations between the peaks of the differential conductivity signal were evaluated electronically).

The zone length of chloride, causing a prolongation of the leading zone, was evaluated from the difference between the time of entrance of the first zone into the detector when the sample was injected and that when a blank run was carried out. In the latter instance the sampling channel (13, Fig. 1) was filled with the solution of the terminating electrolyte before the run. A high reproducibility of the time of entry of the first zone into the detection cell in a series of identical experiments is essential in order to achieve reliable results for the quantitative analysis of chloride performed in this way.

There are two possible sources of errors that can be responsible for deviations in the time of appearance of the first zone in the detection cell in identical runs (excellent performances of both power supply and detection electronics are assumed): (1) delivery of different amounts of the leading electrolyte into the separation com-

partment on refilling of the capillary tube(s); (2) undesired hydrodynamic flows of the solutions in the capillary tubes during the analysis.

A need to fill the separation compartment with the same amount of the leading constituent to achieve a very reproducible time of appearance of the first zone in the detector in a series of identical experiments is clear from the dynamics of ITP separations<sup>16</sup>.

The use of tight valves (8, Fig. 1), non-leaking membranes (9, Fig. 1) and leak-proof connections between different parts of the separation unit are obvious requirements for eliminating uncontrolled flows of the solutions in the separation compartment(s). Moreover, in an effort to reduce the deviations of the time of appearance of the first zone in the detector to values representing *ca.* 0.05% of the total analysis time in the first stage (*ca.* 650 sec), we found that mechanical support of the membranes (9, Fig. 1) from the side of the leading electrolyte compartments (10, Fig. 1) is necessary. Foils 1 mm thick made of a less flexible plastic material having a series of 0.5 mm I.D. holes at the positions of the connecting holes of the leading electrolyte compartments (electrically conductive connections) gave satisfactory results in this respect. In experiments with unsupported membranes made of different materials and of different thicknesses the deviations of the time of appearance of the first zone in the detector were up to ten times higher and, consequently, the determination of  $\text{Cl}^-$  was less reproducible than those of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

Approximately 50 samples of river water taken at different sampling profiles of rivers in West Slovakia were analysed by ITP and by classical methods<sup>1,2</sup>. Some typical results, summarized in Tables II and III, serve as an illustration of the degree of agreement of the quantitative analyses obtained by the two methods. In several instances the agreement of the results is good. However, large differences found for some sample constituents (especially macro-constituents) must be ascribed to a lower accuracy of the classical methods, as is clear from the analyses of model mixtures summarized in Table IV.

Detection limits for the micro-constituents obtained under our experimental

TABLE II

DETERMINATIONS OF INORGANIC ANIONIC MACRO-CONSTITUENTS PRESENT IN RIVER WATER

The relative standard deviations for ITP determinations were better than 2% whereas for the classical methods they varied within the range 2–15%.

Sample No.	Sulphate (mg/l)		Nitrate (mg/l)		Chloride (mg/l)	
	ITP	Titrimetry*	ITP	Spectrophotometry**	ITP	Titrimetry***
1	36.6	41.6	13.2	11.7	18.9	31.2
2	40.8	34.4	13.6	12.3	23.0	33.2
3	38.9	42.5	13.3	11.3	20.6	33.2
4	57.6	56.9	13.3	9.0	26.3	39.2
5	50.9	54.4	12.4	10.3	22.2	35.5
6	43.7	55.2	13.3	9.4	22.8	34.6

\* The procedure described in ref. 2 (p. 186) was used.

\*\* For details, see ref. 2 (p. 128) or ref. 1 (p. 127).

\*\*\* Mercurimetric determination (ref. 1, p. 302).



TABLE III

## DETERMINATIONS OF INORGANIC ANIONIC MICRO-CONSTITUENTS PRESENT IN RIVER WATER

The relative standard deviations for both ITP and classical methods were typically 5% or less.

Sample No.*	Nitrite (mg/l)		Fluoride by ITP (mg/l)***	Phosphate (mg/l)	
	ITP	Spectrophotometry**		ITP	Spectrophotometry <sup>§</sup>
1	0.25	0.13	0.17	0.61	0.55
2	0.29	0.13	0.18	0.56	0.51
3	0.33	0.11	0.18	0.49	0.44
4	0.33	0.16	0.14	0.23	0.16
5	0.33	0.16	0.13	0.27	0.22
6	0.22	0.13	0.10	0.34	0.27

\* Samples as in Table II.

\*\* The procedure described in ref. 2 (p. 136) was used.

\*\*\* Not determined by a classical method as only a very labour-consuming distillation method (ref. 2, p. 90) was available.

<sup>§</sup> For details, see ref. 1 (p. 471).

conditions are given in Table V. When the determined values of the detection limits are compared, the value obtained for nitrite is slightly higher. To explain this fact attention was paid to the behaviour of nitrite during the separation.

In inorganic chemistry it is known that nitrous acid takes a part in a reversible disproportionation reaction<sup>2,3</sup>:



Therefore, during ITP separation at low pH, part of the nitrite present in the form of the free acid must also participate in this disproportionation reaction. As a result, the zone of nitrite will always contain a certain amount of nitrate. The separation process will force more mobile nitrate out of the nitrite zone, thus shifting the course of the disproportionation reaction to the right. Consequently, continuous decomposition of nitrite will occur during the separation and a shorter zone of this constituent will be registered by the detector.

TABLE IV

## DETERMINATIONS OF ANIONIC MACRO-CONSTITUENTS PRESENT IN MODEL MIXTURES

For further details see the notes in Table II and the text.

Sample	Sulphate (mg/l)			Nitrate (mg/l)			Chloride (mg/l)		
	Taken	ITP	Titrimetry	Taken	ITP	Spectrophotometry	Taken	ITP	Titrimetry
A	50.0	49.7	32.7	15.0	14.4	14.3	25.0	25.4	29.9
B	100.0	100.5	103.7	30.0	30.2	34.2	50.0	49.8	57.5
C	150.0	149.6	—	45.0	*	44.0	75.0	*	83.7

\* Mixed zone of nitrate and chloride for the column used.

TABLE V  
DETECTION LIMITS FOR THE MICRO-CONSTITUENTS BY ISOTACHOPHORESIS

Constituent	Detection limit	
	<i>pmoles</i>	<i>ppm</i> *
Nitrite	60	0.1
Fluoride	30	0.02
Phosphate	30	0.1

\* For 30- $\mu$ l sampling volumes.

To confirm the suggested behaviour of nitrite during the separation, a series of experiments was carried out. Both columns were filled with the same leading electrolyte (No. 1 used for the first stage in water analyses). The experimental conditions were arranged in such a way that nitrate that could be present in the sample was removed from the separation system after the detection in the first stage. To increase the reliability of the removal of nitrate, sulphate was used for spacing of the zones of nitrate and nitrite. Thus the zone of nitrate detected in the second stage demonstrated the partial decomposition of nitrite.

In experiments with model mixtures a linear calibration graph was obtained for 0.1–2.0 ppm concentrations of  $\text{NO}_2^-$  using operational system No. 1 (Table I). Also, the reproducibilities of the zone lengths of this constituent, as measured by the conductivity detector in the second stage, were acceptable. In these experiments, however, the time for which the sample constituents migrated in the electric field was approximately constant and no further study aimed to evaluate, *e.g.*, the influence of the time of migration on the length of the nitrite zone was performed.

In spite of the partial decomposition the determinations of nitrite at concentrations down to 0.1 ppm are possible using the proposed operating conditions. Obviously, small deviations from the correct values must be tolerated when the same calibration line is used for the evaluation of nitrite contents in samples that differ substantially in composition.

## CONCLUSIONS

The results undoubtedly show the very promising potential of ITP in the analysis of inorganic anions that need to be monitored in river water. The main advantages of ITP in this application lie in the possibility of determining simultaneously both macro- and micro-constituents in a reasonable time (25 min under our experimental conditions) with detection limits of 30–60 pmoles for the micro-constituents. No sample pre-treatment or only filtration of particles is required before the analysis.

To introduce ITP into routine use in the river water monitoring, further work needs to be performed, as follows: (i) a detailed quantitative evaluation of the decomposition of nitrite in terms of possible systematic errors and the elimination of this undesirable phenomenon through a pre-column derivatization; (ii) a sufficiently wide series of comparative analyses for both model mixtures and river water samples of different compositions by different analytical methods in order to determine exactly

and to compare the analytical performance characteristics of ITP such as accuracy, day-to-day reproducibility and inter-laboratory coincidence of results<sup>24</sup>.

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