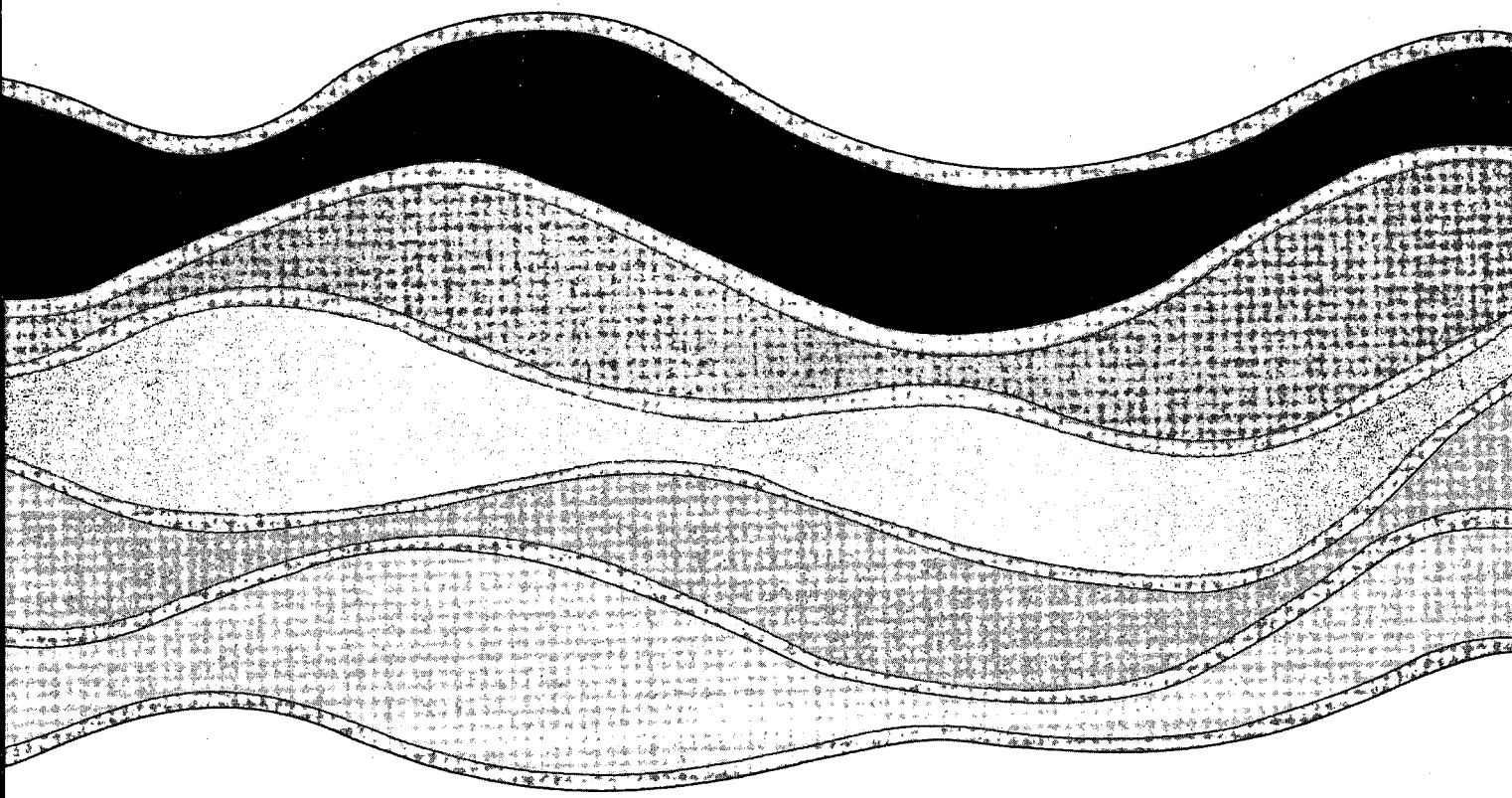


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DETERMINATION OF CHLORIDE, NITRATE,
SULPHATE, NITRITE, FLUORIDE AND
PHOSPHATE BY ON-LINE COUPLED
CAPILLARY ISOTACHOPHORESIS -
CAPILLARY ZONE ELECTROPHORESIS
WITH CONDUCTIVITY DETECTION

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DETERMINATION OF CHLORIDE, NITRATE, SULPHATE, NITRITE, FLUORIDE AND PHOSPHATE BY ON - LINE COUPLED CAPILLARY ISOTACHOPHORESIS - CAPILLARY ZONE ELECTROPHORESIS WITH CONDUCTIVITY DETECTION

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BRIEF

A capillary zone electrophoretic method with on-line isotachophoretic sample pretreatment accommodates the injection of μL sample volumes. Using this technique anions such as chloride, nitrate, sulphate, nitrite, fluoride and phosphate ions can be reliably quantified at sub-ppb levels in water without any pre-column sample preparation.

MANAGEMENT PERSPECTIVE

On-line isotachophoretic (ITP) sample pre-concentration with capillary zone electrophoresis (CZE) represents a novel analytical separation technique for environmental analysis of anionic species as an alternative to ion chromatography.

This report describes an evaluation of the ITP-CZE system for quantitation of anions such as chloride, nitrate, sulphate, nitrite, fluoride and phosphate ions.

A notable feature of this technique in comparison to currently-used ion chromatography is that ITP determination includes macro-constituent ions (chloride, nitrate and sulphate) simultaneously with microconstituents (nitrite, fluoride and phosphate) at ppt level. This work was performed at the Slovak University in Bratislava during Dr. Francis I. Onuska's two months development leave, September-October, 1993.

The outstanding performance of this method can be extended to the analysis of ionic analytes in various water matrices with minimal sample preparation.

SOMMAIRE À L'INTENTION DE LA DIRECTION

La préconcentration isotachophorétique en direct des échantillons (ITP) avec électrophorèse à zone capillaire (EZC) constitue une nouvelle technique de séparation analytique pour l'analyse environnementale d'espèces anioniques, qui peut servir à remplacer la chromatographie ionique.

Ce rapport décrit une évaluation du système ITP-EZC pour l'analyse quantitative d'anions tels que le chlorure, le nitrate, le sulfate, la nitrite, le fluorure et le phosphate.

Par rapport à la technique de la chromatographie ionique présentement utilisée, cette technique comporte une caractéristique remarquable : les dosages ITP donnent les valeurs des macroconstituants ioniques (chlorure, nitrate et sulfate) en même temps que celles des microconstituants ioniques (nitrite, fluorure et phosphate) à l'échelle des parties par billion. Ces travaux ont été effectués à l'Université slovaque de Bratislava au cours du congé du développement de deux mois de M. Francis I. Onuska, en septembre et octobre 1993.

Cette méthode très performante peut être appliquée à l'analyse de substances ioniques dans diverses matrices aqueuses, avec une préparation minimale de l'échantillon.

ABSTRACT

Capillary zone electrophoresis (CZE) coupled with capillary isotachopheresis (ITP) in the column-coupling configuration of the separation unit was studied for the determination of nitrite, fluoride and phosphate present in a large excess of chloride, nitrate and sulphate. Such distributions of these anions are typical for many environmental matrices and it was shown that the ITP-CZE tandem enables the ITP determination of the macroconstituents while ITP-preconcentrated microconstituents cleaned-up from the macroconstituents can be determined by CZE with a conductivity detector. This approach was effective when the concentration ratio macro-/microconstituents was less than $2\cdot 3\cdot 10^4$.

The limits of detection achieved for the microconstituents (200, 300 and 600 ppt for nitrite, fluoride and phosphate, respectively) also enabled their determinations at low ppb concentrations in instances when the concentrations of sulphate or chloride in the samples were higher than 1 g/l. Although in such situations the load capacity of the ITP column was not sufficient to provide the quantitation of the macroconstituents, the ITP sample clean-up enabled the CZE determinations of the microconstituents present in the samples at 10^5 - 10^6 fold lower concentrations. Experiments with samples of such extreme compositions showed that anionic impurities from the ITP electrolyte solutions transferred together with the analytes onto the CZE column are probably the main hindrances in extending this dynamic concentration range by decreasing the limits of the detection to a level associated with the noise characteristics of the conductivity detector.

RÉSUMÉ

On a étudié le couplage de l'électrophorèse à zone capillaire (EYC) et de l'isotachophorèse capillaire (ITP) (en une configuration à colonnes couplées dans l'unité de séparation) pour le dosage des ions nitrite, fluorure et phosphate présents dans un important excès de chlorure, de nitrate et de sulfate. De telles distributions de ces anions sont caractéristiques d'un grand nombre de matrices environnementales, et il a été démontré que le tandem ITP-EYC permet le dosage ITP des macroconstituants, tout en permettant le dosage par EYC, à l'aide d'un détecteur de conductivité, des microconstituants préconcentrés par ITP, extraits des macroconstituants. Cette approche était efficace à un rapport de concentration macroconstituants/microconstituants inférieur à $2-3 \times 10^4$.

Les limites de détection obtenues pour les microconstituants (200, 300 et 600 parties par billion pour le nitrite, le fluorure et le phosphate, respectivement) ont également permis leur dosage aux faibles concentrations (de l'ordre de quelques parties par milliard) dans des cas où les concentrations des ions sulfate ou chlorure des échantillons étaient supérieures à un 1 g/L. Bien que, dans ces cas, la capacité de charge d'une colonne ITP ne soit pas suffisante pour permettre le dosage des macroconstituants, l'extraction de l'échantillon ITP a permis des dosages EYC des microconstituants présents dans les échantillons à des concentrations 10^5 - 10^6 fois moindres. Des essais avec des échantillons caractérisés par de telles compositions extrêmes ont montré que les impuretés anioniques de solutions d'électrolytes ITP transférées en même temps que les substances à analyser sur une colonne EYC constituaient probablement les principaux obstacles à l'extension de la plage de concentration dynamique, car elles abaissent les limites de détection à une valeur associée aux caractéristiques de bruit de fond du détecteur de conductivité.

INTRODUCTION

At present, ion chromatography (IC) has a dominant position among the separation methods used for the analysis of inorganic anions (see, e.g., refs.1-4). However, when the separation efficiencies as typically achieved by IC are compared to those characterizing capillary zone electrophoresis (CZE) for the same group of analytes (ref. 5) it is apparent that the latter technique has advantages. In principle, the separation of analytes by isotachopheresis is determined by the effective mobilities of the sample components, which are closely related to their absolute mobilities, their pK_a values (refs.5,6) and to the pH of the leading electrolyte buffered by a suitable non-ionic additives (refs.7,8). Other selectivity factors (ref.9), are favourable for achieving rapid resolutions of the analytes by CZE.

Although in some instances it is possible to determine very low concentrations of inorganic anions by CZE (refs.10,11), problems occur when the concentrations of the sample constituents differ considerably. This is due to the fact that the determination of microconstituents may require the sample load to have a negative impact on both the migration velocities and the resolutions of the analytes (ref.12). The use of indirect detection, as preferred in CZE of inorganic anions (see, e.g., refs.5, 10, 11) is also less favourable in achieving adequate load capacities since low detection limits are met through a low concentration of the carrier constituent (ref.13). In this context it is to be noted that the load capacity limits may hinder the CZE determination of inorganic anions in instances when the analytes are determined by detection techniques having no prior restrictions with respect to the concentration of the carrier electrolyte (ref.14).

Of the inorganic anions which are currently monitored in water, chloride, sulphate, and nitrate can be considered anionic macro-constituents. These are typically accompanied by nitrite, fluoride and phosphate present in water

samples at 10^2 - 10^5 - fold lower concentrations. Such a wide concentration span probably cannot be covered by CZE, especially, when restrictions of detection in the indirect mode are taken into account (ref.15). It appears that at present CZE offers only a modest improvement relative to the state in early days of this technique (ref.16).

Capillary isotachophoresis (ITP) in the column-coupling configuration of the separation unit provides a two-step procedure (integrated into one electrophoretic run) for the simultaneous determination of anionic macro- and microconstituents in water (ref.17). However, its use is limited when the concentrations of the macroconstituents are ca. 10^3 - fold higher than those of the microconstituents. Two independent ITP runs provide a way to perform these measurements when the concentration ratio macro- /microconstituents is in the range 10^3 - 10^4 (ref.18). For higher values of this ratio the determination of the microconstituents is possible only when a suitable sample preparation procedure is employed. For fluoride and phosphate such procedures which are compatible with the ITP determinations are described in the literature (refs. 19,20). However, their use are both time and labour intensive.

It was shown recently that an on-line combination of ITP with CZE in the column-coupling capillary electrophoresis instrument is a convenient capillary electrophoretic (CE) alternative to the analysis of trace ionogenic constituents present in a large excess of matrix ions (refs.21,29). The aim of this work was to study the analytical capability of such a CE approach to the determination of chloride, nitrate, sulphate, nitrite, fluoride and phosphate in the concentration range within which these anions are found in water samples. In previous work, the ITP stage in the ITP-CZE combination was used merely for the clean-up of samples and/or for the preconcentration of trace analytes. Here, we extend the use of this procedure to the determination of sample macroconstituents while maintaining the clean-up and preconcentration capabilities.

EXPERIMENTAL

Instrumentation

An Isotachophoretic Analyzer (Villa-Labeco, Spišská Nova Ves, Slovak Republic) that enables CE separations in the column-coupling mode was used. The separation unit of the analyzer was assembled from components provided by the manufacturer and also from those developed in this laboratory.

The ITP column was constructed from a 0.85 mm I.D. capillary tube (O.D. ~ 1.15 mm) made of fluorinated ethylene-propylene (FEP) copolymer. The distance from the inlet of the capillary tube to the conductivity cell was 150 mm. The CZE columns used a 0.30 mm I.D. (O.D. ~ 0.65 mm) capillary tube made of FEP (the distance from the inlet to the conductivity cell was 150 mm) and with a 0.35 mm I.D. (O.D. ~ 0.70 mm) capillary tube made from the same material (the distance from the inlet to the detection cell was 150 mm). The capillary tubes were placed in compartments made of plexiglass that allowed efficient dissipation of heat produced during the analysis.

The samples were injected with the aid of a sampling valve with a 30 μL internal sampling loop.

The data from the detectors were acquired and processed by an ITP.SOFT program (KasComp, Bratislava, Slovak Republic) which runs on a 386 PC computer.

Chemicals

Chemicals used for the preparation of the electrolyte solutions were obtained from Serva (Heidelberg, Germany), Sigma (St. Louis, MO, U.S.A.), Reanal (Budapest, Hungary) and Lachema (Brno, Czech Republic). Some of them were purified by conventional methods while analytical grade chemicals were

used as delivered. Methylhydroxyethyl cellulose 30,000 (m-HEC) served as an anticonvective additive in the electrolyte solutions. A stock aqueous solution containing 1% (w/v) of the chemical standard was purified on a mixed-bed ion exchanger (Amberlite MB-1; Serva).

Water from an Aqualabo two-stage demineralization unit (Aqualabo, Brno, Czech Republic) was further purified by circulation in a laboratory made demineralization system made of polytetrafluoroethylene which was packed with Amberlite MB-1 mixed-bed ion exchanger (Serva). At the outlet, water was filtered through a 0.45 μm filter (Gelman, Ann Arbor, MI, U.S.A.).

RESULTS AND DISCUSSION

Separation conditions

As mentioned above, in our approach the ITP determination of chloride, nitrate and sulphate was combined with the CZE determination of nitrite, fluoride and phosphate. In such a combination of electrophoretic techniques three basic configurations of the electrolyte system can be distinguished (ref.30). Of these, the one using identical terminating and carrier constituents was preferred in this work because it does not require replenishment of the electrolyte solution in the ITP column after the sample fraction of analytical interest is transferred onto the CZE column. Additionally, in the selection of the leading and terminating electrolytes the following facts were taken into the consideration:

- (1) The leading electrolyte has to provide the ITP separation of the macroconstituents and at the same time a group separation and concentration of the microconstituents into a narrow band. This enables the ITP quantitations of the former constituents and an ideal transfer of the latter into the CZE stage.
- (2) To achieve an efficient use of the ITP column, it is necessary that the microconstituents migrate with lower effective mobilities than the

macroconstituents (ref.31). Such a migration configuration is favourable also for a removal of the macroconstituents from the separation compartment after their detection in the ITP stage.

- (3) To reduce the number of anionic migrating constituents, i.e., to reduce the number of potential interfering anionic constituents a low pH of the leading electrolyte is mandatory.

The leading electrolyte solution fulfilling requirements stated above for our type of samples is described in Table I under column ITP-1 (refs. 17,32-35). Further the microconstituents, and a small part of the macroconstituents are transferred onto the CZE column. This is due to diffusion of the leading electrolyte constituents onto the CZE column during the ITP separation (the solutions in the columns are in direct contact in the bifurcation block) and a small part is transferred with the microconstituents to achieve their high recoveries during the transfer. Therefore, the separating conditions in the CZE stage were chosen not only to provide the resolutions of nitrite, fluoride and phosphate but also to speed up their defocusing from the macroconstituents (ref.36). From the ionic mobilities of the anions involved and from pKa values of the corresponding acids (ref.6) it is clear that a low pH of the carrier electrolyte is an optimum. Further, in the choice of the carrier constituent (serving also as a terminating anion in the ITP stage) it was also necessary to take into consideration requirements related to the use of the conductivity detector in the CZE stage to get favourable molar responses of the detector to the analytes (ref.37), while the electromigration dispersion (ref.37) is kept to a minimum. The composition of the carrier electrolyte as used in this work (System CZE in Table I) was a reasonable compromise considering all the above requirements.

ITP determination of chloride, nitrate and sulphate

Working conditions (leading electrolyte, sample injection volume, I.D. of the capillary tube, driving current) employed in the ITP determination of chloride,

nitrate and sulphate were identical to those used for the same purpose in the ITP-ITP tandem (refs.17, 18). Therefore, analytical performance data describing the ITP determination in this work (Table II) were close to those reported in the quoted references.

A series of model mixtures containing chloride, nitrate and sulphate at varying concentrations were analyzed to find maximum concentrations of these anions that can be determined simultaneously with the microconstituents in one run. It is apparent (Table III) that the concentration of nitrate in the sample (having the intermediate effective mobility between that of chloride and sulphate) limited an overall sample load. This is what was expected from a theoretical treatment of the ITP separation process (refs.31, 38). From a practical point of view, it means that such a load capacity of the ITP stage enables the determination of the anions in a wide variety of water samples.

CZE determination of nitrite, fluoride and phosphate

As is clear from electropherograms in Fig.1 that nitrite, fluoride and phosphate were baseline-resolved under the separation conditions employed in the CZE step. It is also apparent that the transferred macroconstituents (a large peak migrating in front of nitrite in Figs.1a and 1b) did not interfere with their determination. The reproducibility of the migration times of the CZE analytes was 1% or less when the concentrations in the sample were below 40 - 50 ppb. At higher concentrations, migration times were systematically biased by electromigration dispersion (ref.37). This dispersive phenomenon had a negative effect on the separation efficiencies of the analytes, as is clear from the data in Table IV (see also ref.40). Nevertheless, parameters of the regression equations describing the calibration lines show that reliable quantitation of the microconstituents was possible under such conditions (Table V).

Besides separation, ITP also concentrated the ionic impurities present in the

leading and terminating electrolyte (originating from the components from which the solutions of the electrolytes were prepared). For example, in the CZE separations shown in Fig.1, peak areas of the impurities in the migration position of the analytes corresponded to ca. 2 ppb of nitrite and 1 ppb of fluoride.

An impurity peak migrating in the neighbourhood of phosphate (see the blank run in Fig.1b) was equivalent to ca. 3 ppb of this analyte. Fluctuations in the peak areas of these impurities (background noise) determined the limits of detection (LOD) for our analytes. Estimates of the relative standard deviations of the peak areas of the impurities as obtained in repeated blank runs (6 runs related to the experiments in Fig.1) served as a measure of these fluctuations. From the signal-to-noise ratio of three of these experiments LOD values of 200, 300 and 600 ppt for nitrite, fluoride and phosphate, respectively were obtained. These values are ca. 5-10 greater than those which were expected from the noise characteristics of the conductivity detector. As no special attention was paid to the purities of the chemicals used in the preparation of the leading and terminating electrolytes solutions, it is reasonable to expect that appropriate measures taken in this respect could reduce the LOD values, making them comparable to those of the conductivity detector.

Analytical potentialities of the ITP-CZE tandem

Electropherograms given in Fig.2 illustrate the use of tandem ITP-CZE with conductivity detectors for the analysis of a practical sample. In this instance a CZE column of larger I.D.(0.35 mm) was employed to test a column of a higher load capacity. Relevant data (see figure legend) show that under such conditions very reproducible CZE determinations were possible.

In some instances (see, e.g., refs.18-20, 39) it is necessary to analyze samples containing chloride, sulphate and nitrate in a very large excess relative to nitrite, fluoride and phosphate. The potential for using tandem ITP-CZE for the analysis of such sample types was evaluated with a series of model mixtures containing

constant concentrations of the microconstituents while the concentrations of chloride and sulphate varied (see Table VI). As is apparent from the data in Table III the concentrations of chloride and sulphate were in some of the model samples several times above the load capacity of the ITP column for these anions. The data in Table VI show that microconstituents were fully recovered by the ITP pretreatment when the concentration of chloride was 2 g/l or less, or the concentration of sulphate 1.25 g/l or less. As low ppb concentrations of the microconstituents could also be determined at such concentrations of sulphate and/or chloride, we can state that tandem ITP-CZE enables the CZE determination of nitrite, fluoride and phosphate in a 10^5 - 10^6 -fold excess of the macroconstituents. The main problems in these experiments were associated with the purities of the chemicals from which the model mixtures were prepared. For example, from the electropherograms in Fig.3 we can see that the injection of sulphate at a 1.25 g/l concentration was responsible for an increase in the peak area of phosphate equivalent to ca.10 ppb concentration of this anion in the sample (see the electropherograms in Figs.3a and 3c). The origin of this peak was confirmed in a run with a chloride sample (containing chloride at a concentration leading to the same prolongation of the ITP separation while the background signal in the migration position of phosphate was identical to that in the blank run (Fig.3a)). Therefore on spiking the sample with a 10 ppb concentration of phosphate it was necessary to make a correction for a significantly higher blank value and thus introduce a higher random error into the determination. Similarly, for nitrate spikes, even considerably higher nitrite concentrations were detected. A prolongation of the ITP pretreatment by injecting the samples containing 1.25 g/l of sulphate (12 minutes longer ITP separation in comparison to the blank run in Fig.3a) led to an increase of the peak areas of some of the unidentified constituents (see, e.g., a peak migrating immediately behind phosphate in Fig.3). In this instance the origin of these peaks was associated with impurities in the ITP electrolyte solution.

CONCLUSIONS

From the results presented in this work it appears that the on-line coupling of ITP with CZE in the column-coupling configuration of the separation unit offers a very promising alternative to the determination of the studied anions in situations where their concentrations differ considerably. It is also apparent that the load capacity of the ITP column sets a limit for the simultaneous determination of both macro- (sulphate, nitrate and chloride) and microconstituents (nitrite, fluoride and phosphate). Thus when the concentration ratio macro-/microconstituents was higher than $2\cdot 3\cdot 10^4$ the analysis had to be divided into two runs (separate determinations of both groups of anions). In this way, the ITP clean-up provided a way to determine the microconstituents present in samples with a 10^5 - 10^6 - fold excess of macroconstituents.

The anionic impurities from the electrolyte solutions accumulated in the ITP stage between the leading and terminating zones and were the main interferences in the CZE analysis of microconstituents. The use of high purity chemicals in the preparation of the electrolyte solutions for the ITP stage should be used to determine detection limits of the ITP-CZE tandem in this respect. The use of conductivity detector in CZE has some inherent limitations (ref.37). Nevertheless, this work showed that its performance was not limiting in achieving sub-ppb detection limits for the studied analytes. In this context it can also be concluded that advances related to the purities of the electrolyte solutions in the ITP stage will define its limitations and, eventually, initiate further research related to the technique.

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TABLE I

ELECTROLYTE SYSTEMS

Parameter	Electrolyte				
	ITP - 1		ITP - 2		CZE
	L	T	L	T	C
Solvent	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O
Anion	Cl ⁻	Asp	Cl ⁻	Asp	Asp
Concentration (mM)	8	4	8	4	10
Counter ion	BALA	BALA	BALA	BALA	BALA
Co-counter ion	BTP	-	-	-	-
Concentration (mM)	3	-	-	-	-
pH	3.4	4	3.4	4	3.4
Additive	MHEC	-	MHEC	-	MHEC
Concentration (% w/v)	0.2	-	0.2	-	0.2

MHEC = methylhydroxyethylcellulose; BALA = β -alanine; Asp = Aspartic acid;

BTP (bis-tris propane) = 1,3 - bis(tris(hydroxymethyl)methylamino)propane;

L = leading; T = terminating; C = carrier.

TABLE II

PARAMETERS OF THE REGRESSION EQUATIONS FOR THE CALIBRATION LINES, LIMITS OF DETECTION AND REPRODUCIBILITIES OF THE ITP DETERMINATIONS OF CHLORIDE, NITRATE AND SULPHATE

Anion	Regression equation*			LOD	RSD
	a(s)	b(s.l/mg)	CC	mg/l	(%)
Chloride	0.56	0.4279	0.9984	5	4.2
Nitrate	-0.11	0.2635	0.9998	2	1
Sulphate	0.49	0.319	0.9999	1	0.5

a = intercept; b = slope; CC = correlation coefficient; LOD = limit of detection; RSD = median of the relative standard deviations for 5 samples (each sample analyzed 5 times).

*the calibration data were obtained from 60 runs for calibration mixtures containing chloride in the range 20-90 mg/L; nitrate in the range 5-40 mg/L and sulphate in the range 25-125 mg/L.

TABLE III

MAXIMUM TOLERABLE CONCENTRATIONS OF CHLORIDE AND SULPHATE FOR VARYING CONCENTRATION OF NITRATE IN THE ITP DETERMINATION

Concentration of Nitrate (mg/l)	Maximum concentration	
	Chloride (mg/l)	Sulphate (mg/l)
5	100	125
10	75	125
20	75	125
30	75	100
40	50	125

*when both anions are present in the sample.

TABLE IV

SEPARATION EFFICIENCIES FOR NITRITE, FLUORIDE AND PHOSPHATE FOR VARIOUS CONCENTRATIONS*

Concent. ($\mu\text{g/L}$)	Separation efficiency (N/m)		
	Nitrite	Fluoride	Phosphate
5	224,000	84,000	-
10	150,000	56,000	174,000
15	120,000	58,000	-
20	88,000	55,000	160,000
30	-	-	121,000
40	-	-	84,000
50	68,000	27,000	-
100	68,000	15,000	79,000

*sample volumes were 30 μL ;

N/m = number of theoretical plates per metre.

TABLE V

REGRESSION EQUATIONS OF CALIBRATION LINES AND REPRODUCIBILITIES OF CZE DETERMINATIONS OF NITRITE, FLUORIDE AND PHOSPHATE

Anion	Regression Equation			RSD (%)	
	a (mV.s)	b, mV.s/ppb	CC	A	B
Nitrite	1.38	0.153	0.9994	0.87	0.95
Fluoride	2.71	0.597	0.9999	0.7	1.11
Phosphate	0.86	0.0987	0.9999	2.21	2.36

a = intercept; b = slope; CC = correlation coefficient; RSD = relative standard deviation; A = model sample contained: 15 ppb of nitrite, 15 ppb of fluoride and 30 ppb of phosphate; B = model sample contained 20 ppb of nitrite, 20 ppb of fluoride and 40 ppb of phosphate. The calibration solutions contained 5 - 375 ppb of nitrite; 5 - 375 ppb of fluoride and 10 - 750 ppb of phosphate and the regression equations were calculated from 14 data points.

TABLE VI

INFLUENCE OF A VARYING EXCESS OF MACROCONSTITUENTS ON CZE DETERMINATIONS
OF TRACE CONCENTRATIONS OF NITRITE, FLUORIDE AND PHOSPHATE

Sample	Microconstituents						Macroconstituents	
	Nitrate (ppb)		Fluoride (ppb)		Phosphate (ppb)		Sulphate (ppm)	Chloride (ppm)
	No.	Taken	CZE	Taken	CZE	Taken	CZE*	
1	5	5.6	5	4.8	10	11.3	250	-
2	5	4.7	5	5.3	10	11.3	500	-
3	5	5.1	5	6.1	10	12.3	750	-
4	5	5.4	5	4.6	10	10	1,250	-
5	5	4.5	5	4.7	10	10	-	1,000
6	5	4.9	5	5.1	10	10	-	2,000
7	5	0	5	2.8	10	12.2	-	2,500

*Mean values from two parallel runs.

LEGENDS TO THE FIGURES

Fig.1. Electropherograms from the separation of a model mixture of inorganic anions.

(nitrate = 6 mg/l; sulphate = 2.5 mg/l; nitrite = 5 ppb; fluoride = 5 ppb; phosphate = 10 ppb; chloride present in the sample coincided with the leading electrolyte zone (L)). The ITP separation (lasting 8 minutes) was carried out in the electrolyte system ITP-1 (Table I) and the carrier electrolyte CZE (Table I) was used in the separation of microconstituents. The migration positions of the microconstituents as obtained in a blank run (b) are marked with asterisks (compare the run the sample (a)). The driving currents were 250 and 75 mA in the ITP and CZE stages, respectively. R, G, t = increasing resistance, conductance and time, respectively. L, T = leading and terminating zones, respectively.

Fig.2. ITP and CZE determinations of macro- and microconstituents in a river water sample (Yamaska River, PQ, Canada). The sample directly injected into the analyzer was found to contain 15.0 mg/l (RSD = 2.6%) of chloride, 7.3 mg/l (RSD = 0.5%) of nitrate, 5.9 mg/l (RSD = 0.9%) of sulphate, 13.1 ppb (RSD = 0.9%) of fluoride and 60.9 ppb (RSD = 3.4%) of phosphate. Nitrite was below the limit of detection (200 ppt). The quantitations were based on 5 parallel runs. The separation conditions, driving currents and the meaning of the symbols is the same as in Fig.1.

Fig.3. Electropherograms from the CZE determination of ppb concentrations of microconstituents present in a model mixture containing 1.25 g/l of sulphate.

a = blank run (the terminating electrolyte was injected); b = sample containing microconstituents and sulphate at a 10 mg/l concentration; c = sample containing 1.25 g/l of sulphate; d = the same as (c) only the sample contained also 5 ppb of each nitrite and fluoride and 10 ppb of phosphate. Asterisks in the runs (a) and (c) mark the migration positions of the microconstituents. The ITP separation was carried out in the system No.ITP-2 (Table I) and the carrier electrolyte CZE (Table I) was used in the CZE column. The driving currents were 250 and 75 mA in the ITP and CZE stages, respectively. G = increasing conductance.

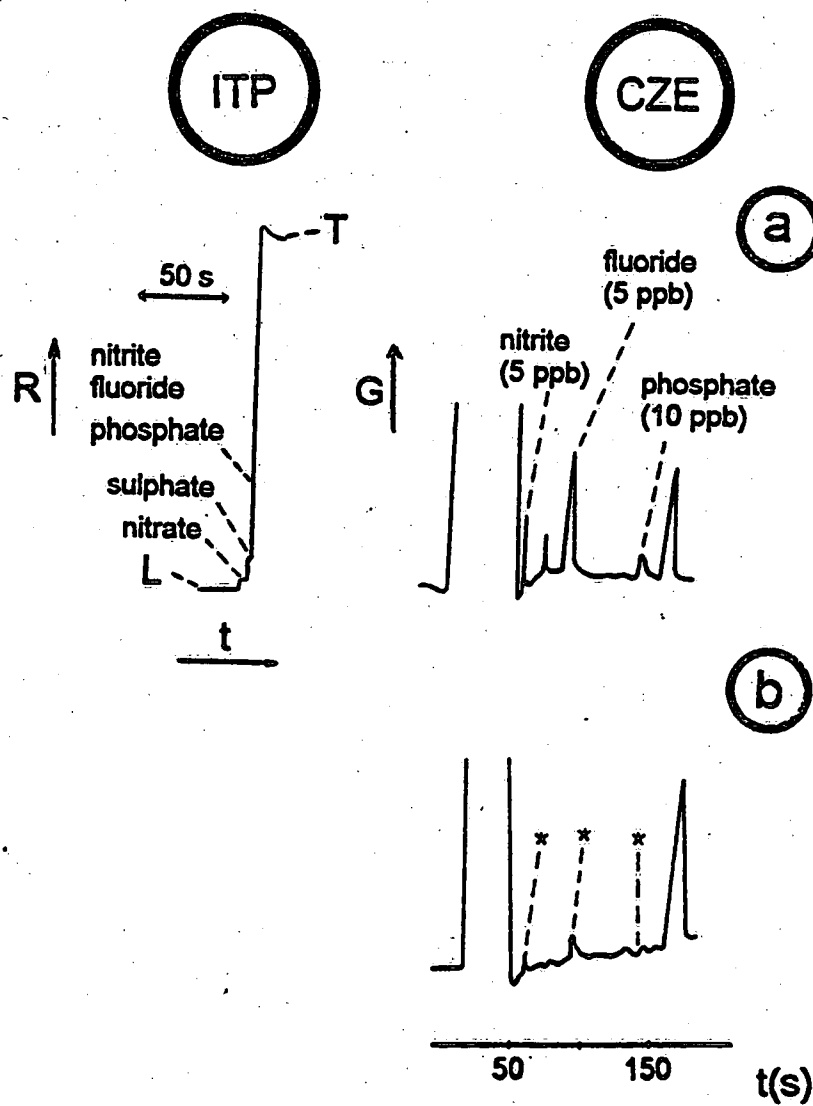


Fig. 1

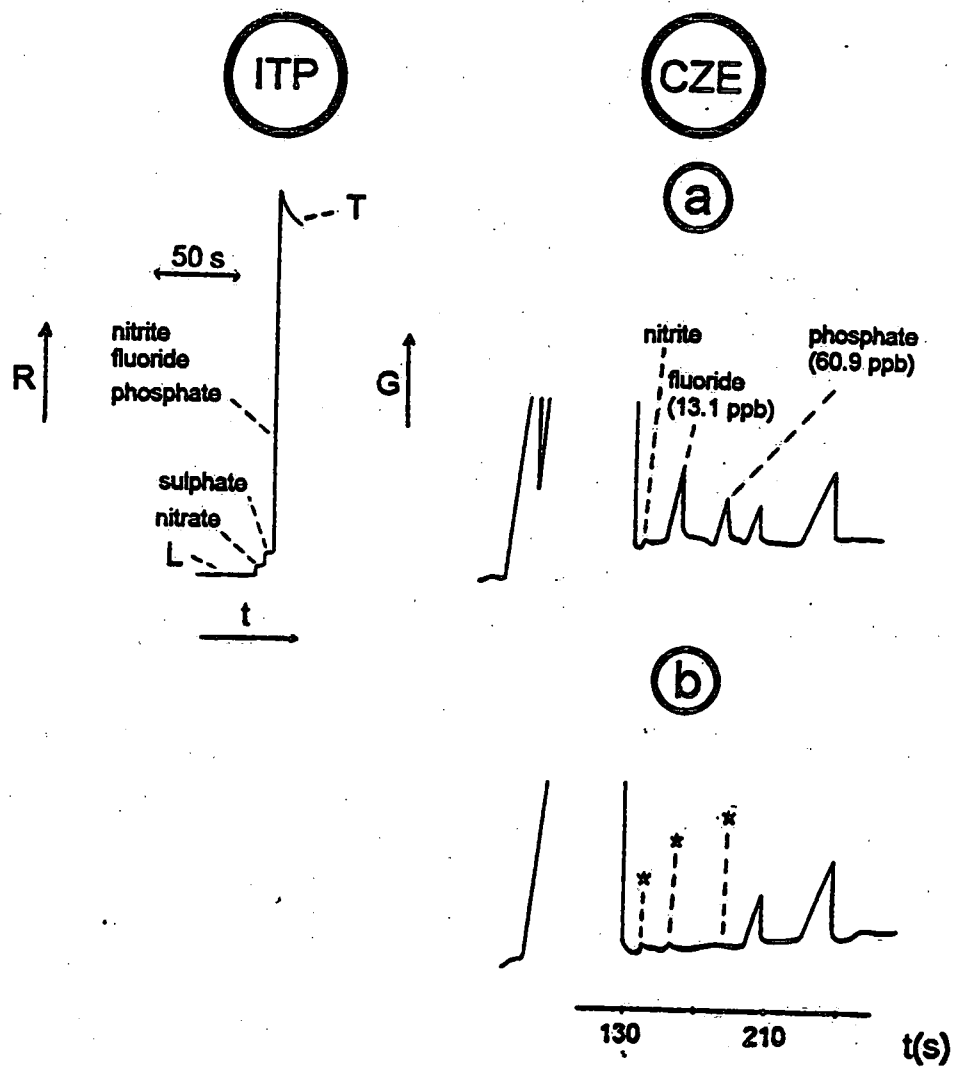


Fig. 2

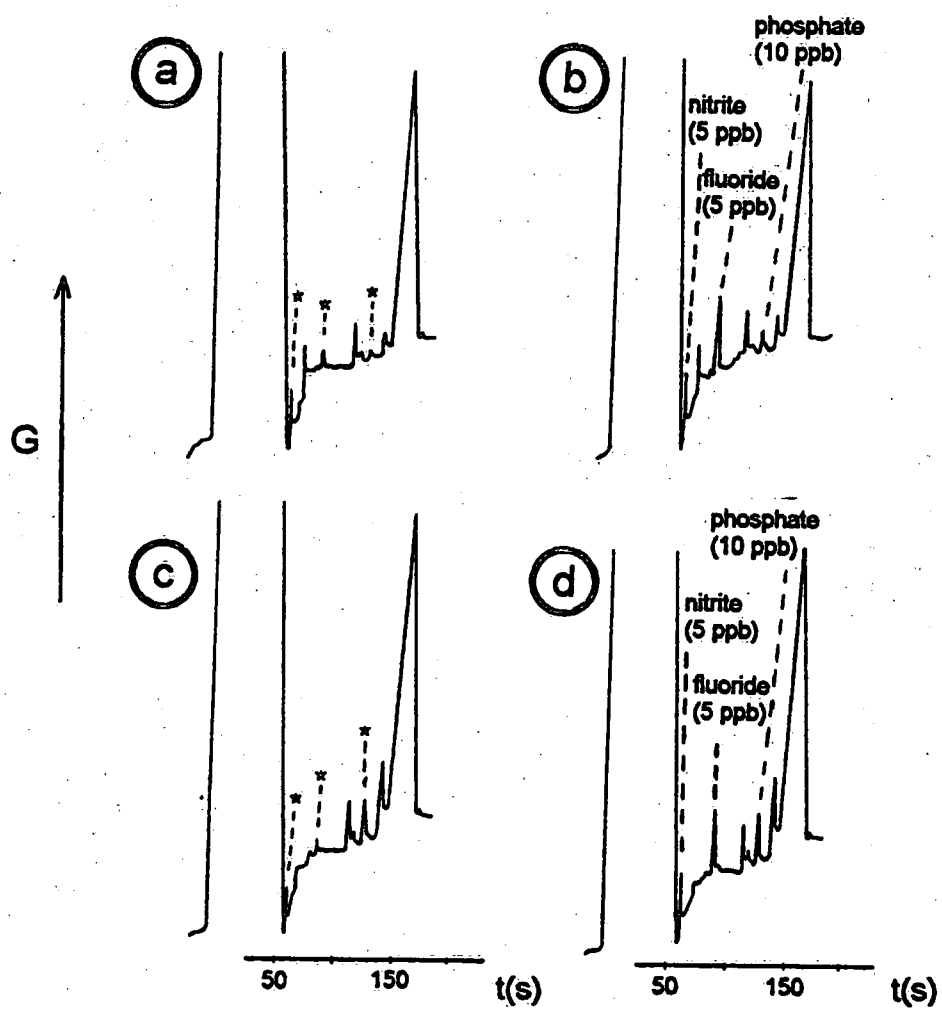
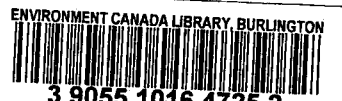
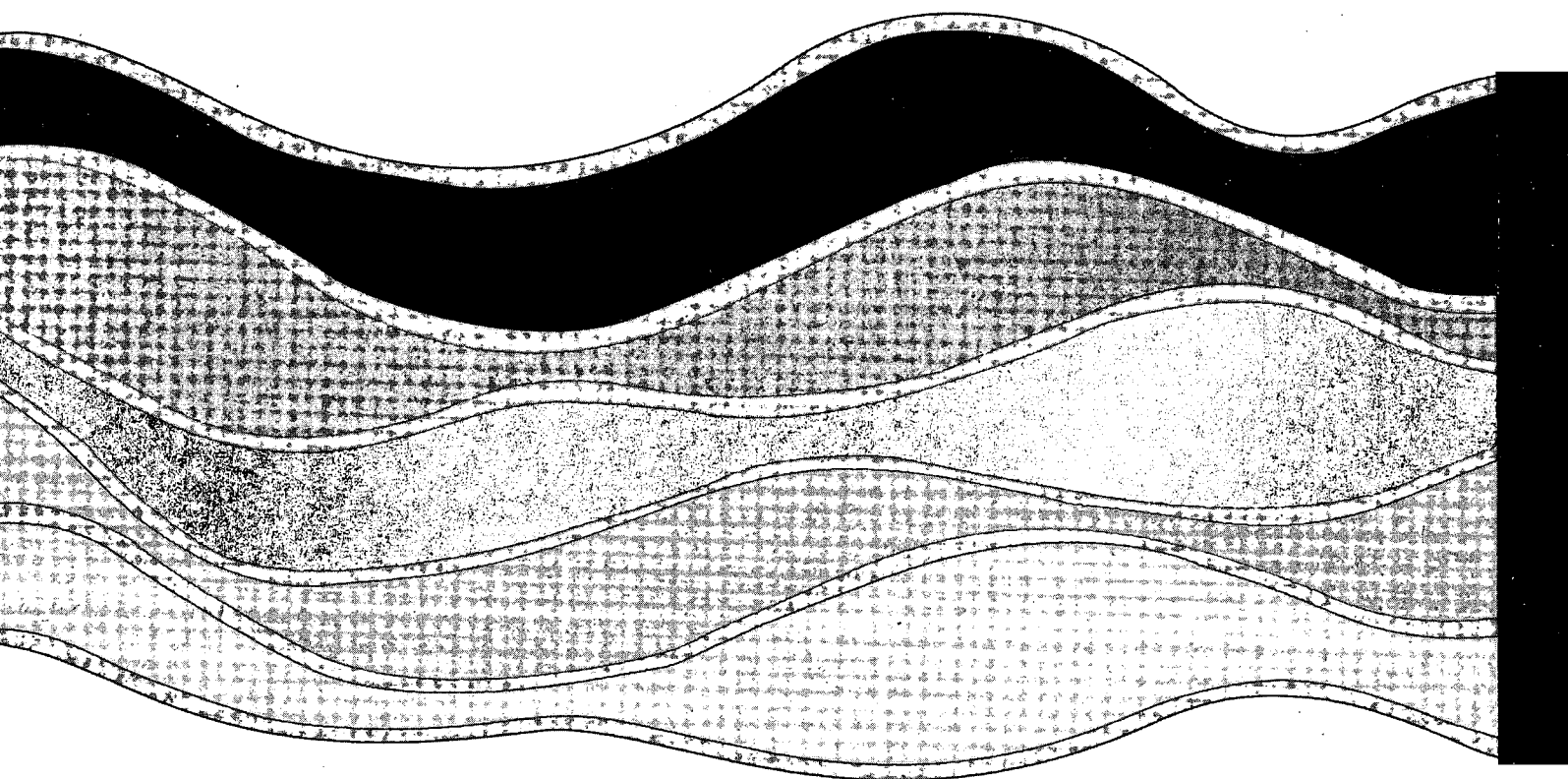


Fig. 3

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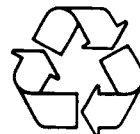


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