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# Contactless conductivity detection in capillary zone electrophoresis<sup>☆</sup>

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## Abstract

Some basic performance parameters of a high-frequency contactless conductivity detection technique originally designed for capillary isotachopheresis (ITP) were evaluated from the point of view of its use in capillary zone electrophoresis (CZE). These parameters included the response characteristic (a response of the detector to changes of the specific conductivity in the on-column detection cell), short-term noise and the detection sensitivity. A series of seven detectors, provided with capillary tubes (300  $\mu\text{m}$  I.D.) that were made either of PTFE (six detectors) or fused-silica (one detector), was taken into the evaluation. A certain scatter of the noise/detection sensitivity ratios of the tested detectors (attributable to differences in the on-column detection cells of the same construction) was found. These differences were also associated with different limits of detection (LODs) attainable for the test analytes (inorganic anions) by the evaluated detectors. For the detector characterized by minimum values of noise/detection sensitivity ratios for the test anions, the LOD (a 200-nl sample injection volume) ranged from 0.3  $\mu\text{mol/l}$  (sulfate) to 0.7  $\mu\text{mol/l}$  (fluoride) in the carrier electrolyte solution, which had a pH value of 3.5. These LOD values were two–eight times higher in comparison to those attainable by an on-column contact conductivity detector under otherwise identical working conditions. A lower sensitivity of the contactless conductivity detector can be more than compensated for in practical situations by its operational robustness. These features were proved effective in the CZE analyses of aqueous extracts of soil samples of high humic acid content (these samples are known to contaminate surfaces of the detection electrodes of the contact conductivity detectors). Here, 1–3% RSD values in the determinations of chloride, nitrate and sulfate could be achieved in large series of CZE runs, with no disturbances linked with the performance of the contactless conductivity detector even in situations when the sample matrix precipitated in the capillary. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Detection, electrophoresis; Conductivity detection; Inorganic anions

## 1. Introduction

Conductivity detection techniques play a key role in the detection of zones in capillary isotachopheresis (ITP) separations [1–9]. In spite of the fact that conductivity detectors were used in some of the pioneering work on capillary zone electrophoresis

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(CZE) [10–12], at present, these detectors are used in CZE only rarely [13–31]. However, in this context, we should note that several recent reports (see e.g., Refs. [17,24–31]) demonstrate some analytical advantages of conductivity detection, especially, in the CZE analysis of inorganic ions.

Extensive research linked with the developments of on-column contact conductivity detectors for ITP revealed that undesired electrochemical reactions can occur when some electrochemically active analytes come into contact with the detection electrodes and/or when samples containing matrix constituents exhibiting a strong adherence to the surface are analyzed. These reactions or associated changes of the surfaces of the detection electrodes may impair the performance of the contact conductivity detectors [8,32]. Undoubtedly, these disturbing phenomena can also occur in CZE separations. Their impact on data of analytical relevance may be even more significant, as, in CZE, often very small conductance changes are to be measured on a high background conductance of the carrier electrolyte. The availability of contactless conductivity detection eliminated these problems in ITP [33–36]. For analogous reasons, the use of this detection technique is also of interest in CZE. So far, however, only very limited attention was paid to this subject [37–39].

This work was aimed at investigating some basic performance parameters [short-term noise, sensitivity (response to conductance changes), reproducibility of the response] of a high-frequency contactless conductivity detection system in CZE separations. A series of CE columns provided with on-column contactless conductivity detection devices originally designed for ITP and based on the detection principle proposed by Gaš et al. and Vacík et al. [33–36] was employed in this investigation. The columns were fitted with capillary tubes (300  $\mu\text{m}$  I.D.) made either of PTFE or fused-silica. CZE separations of inorganic anions present in water samples and in matrices known to disturb the contact conductivity detection (soil extracts containing humic acids at high concentrations) were used to assess some practical aspects of the use of contactless conductivity detection. A comparison of the detection possibilities of contactless conductivity detection with those provided under similar

working conditions by its contact counterpart was carried out.

## 2. Experimental

### 2.1. Instrumentation

A CS isotachophoretic analyzer (Villa-Labeco, Spišská Nová Ves, Slovak Republic) was used in experiments performed in this work. It was assembled in a single-column configuration of the separation unit [40]. The separation unit consisted of a CZE injection valve with a 200-nl internal sample loop (Villa-Labeco), one of the columns described below (Villa-Labeco) and a counter-electrode compartment with a hydrodynamically (membrane) closed connecting channel to the separation compartment (Villa-Labeco).

The columns used in this work were provided with 300  $\mu\text{m}$  I.D. capillary tubes made either of PTFE (500  $\mu\text{m}$  O.D.) or fused-silica (430  $\mu\text{m}$  O.D.). The lengths of the capillary tubes to the detector ranged from 130 to 180 mm. Each of the columns was provided with a four-electrode on-column contactless conductivity detection cell (see Fig. 1) and an on-column part of the electronics (Villa-Labeco). A protective polyimide coating of the fused-silica capillary in the position of the detection cell was left intact.

The signal from the detector assembled in the separation unit was sent to a 486 DX computer via a Unilab data acquisition unit (Fitek, Šála, Slovak Republic). ITP Win software (version 2.31) obtained from Kascomp (Bratislava, Slovak Republic) was used for the acquisition and processing of the data.

A series of aqueous solutions of KCl (0.5–10 mmol/l) was used for the measurement of response characteristics (calibrations) of the detectors. The specific conductivities of these calibration solutions were determined using a previously described method [41] and an OK-102/1 conductimeter (Radelkis, Budapest, Hungary). In the measurement of the response characteristics, the capillary tube provided with the on-column conductivity detection cell was successively filled with the calibration solutions (without application of a driving current). A par-

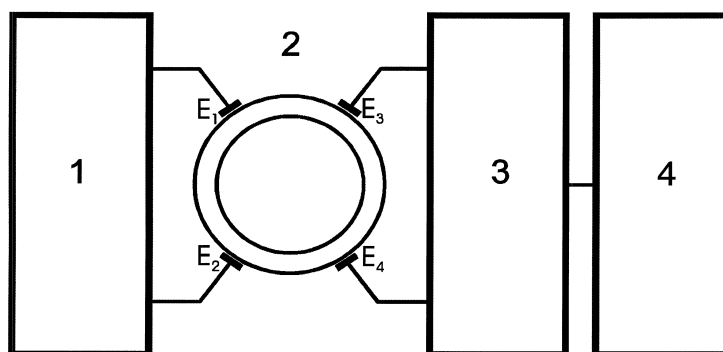


Fig. 1. Block scheme of a high-frequency contactless conductivity detector used in this work. 1, high-frequency generator (consisting of a 4-MHz oscillator, an amplifier and inverter, phasing elements and output voltage amplifiers); 2, four-electrode (capacitive) detection cell; 3, receiver (consisting of a pre-amplifier, a narrow-band amplifier, a selective filter, a high-frequency rectifier, a d.c. amplifier and a low band-pass filter); 4, a data acquisition unit;  $E_1$ – $E_4$ , detection electrodes. Generated from Refs. [34,35].

tical calibration solution was pumped through the capillary tube until a constant response of the detector was reached.

## 2.2. Chemicals

Chemicals used for the preparation of the carrier electrolyte solutions and model samples (potassium and sodium salts of inorganic acids) were obtained from Fluka (Buchs, Switzerland), Lachema (Brno, Czech Republic), Serva (Heidelberg, Germany), Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany). Methylhydroxyethylcellulose 30 000 (m-HEC), from Serva, served as a suppressor of the electroosmotic flow in the separation compartment [42]. The solutions of the carrier electrolytes were prepared in water that had been demineralized using a Pro-PS water purification system (Labconco, Kansas City, KS, USA) and, before use, they were filtered through disposable membrane filters (1.2  $\mu\text{m}$  pore size) obtained from Sigma.

## 2.3. Samples

Stock solutions containing the salts of inorganic acids at 10 mmol/l concentrations were used for the preparation of model samples. The model samples were prepared fresh before use, by appropriately diluting the stock solutions with water demineralized using a Pro-PS water purification system (Labconco).

Wet soil samples used in this work were kindly provided by Professor B. Juráni from the Department of Pedology of Comenius University (Bratislava, Slovak Republic). A 30-g amount of an actual soil sample was extracted for 15 min into 90-ml of demineralized water under sonication. The sample was then centrifuged for 10 min at 7000 rpm and the supernatant was diluted five-fold with demineralized water before analysis. Tap water samples were collected in the laboratory and placed in polyethylene sample containers. They were diluted appropriately with demineralized water or injected directly into the CZE equipment without any sample preparation.

## 3. Results and discussion

### 3.1. Some performance characteristics of the contactless conductivity detectors

Only very small changes in the specific conductivities can be associated with the CZE separands of analytical interest under current CZE separating conditions [11,43]. Therefore, any conductivity detector to be used in CZE has to provide the corresponding detection sensitivity. Response characteristics of the contactless conductivity detectors, as obtained in the context of ITP separations [33–36], showed that these detectors have their maximum

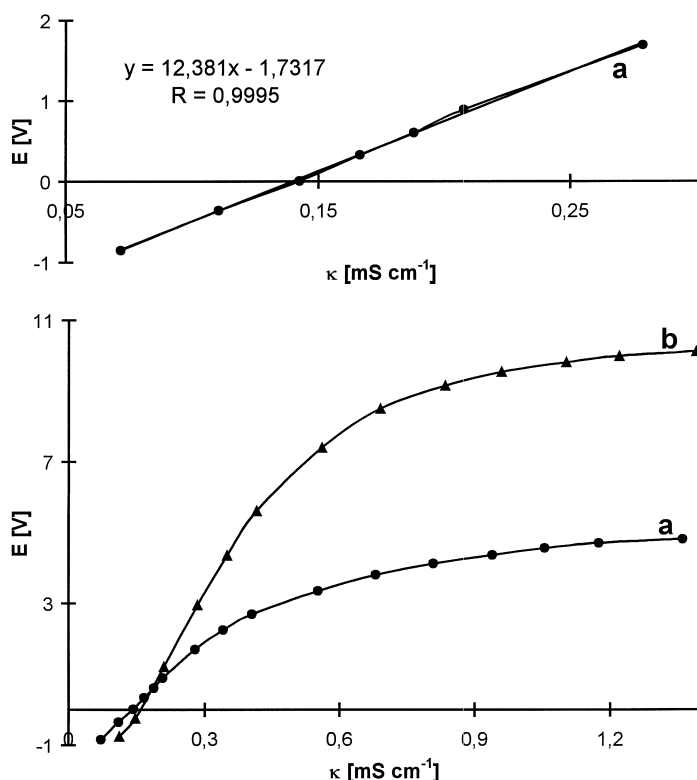


Fig. 2. Response characteristics of the on-column contactless conductivity detectors with the columns provided with PTFE (a) and fused-silica (b) capillary tubes. The characteristics were obtained for aqueous solutions of KCl with determined specific conductivities. A fragment of the response characteristic for the PTFE tube (PTFE “3” in Table 2) at the top corresponds to the specific conductivity interval linked with the CZE separations carried out in this work.

Table 1  
Electrolyte systems

Parameter	Electrolyte system number	
	1	2
Solvent	Water	Water
Anion	PEG-DC	Succinate
Concentration (mmol/l)	10	7
Counter ion	Bis-Tris propane	Bis-Tris propane
Concentration (mmol/l)	4.11	0.5
pH	3.5	3.55
Additive	— <sup>a</sup>	m-HEC
Concentration (% w/v)	—	0.2
Complexing additive	PVP 3600	PVP K90 (PVP 3600)
Concentration (% w/v)	7.5	5 (7.5)

<sup>a</sup> The capillary tube was coated with a 1% (w/v) aqueous solution of m-HEC before the CZE runs.

m-HEC, methylhydroxyethylcellulose; PVP, polyvinylpyrrolidone; PEG-DC, polyethyleneglycol dicarboxylic acid.

detection sensitivities in limited spans of the specific conductivities. The response characteristics of the detectors tested in this work were determined to find these maxima that would provide optimum detection conditions. A series of aqueous solutions of KCl with known specific conductivities was used for this purpose (for details, see Section 2.1). Typical characteristics obtained in this way for the columns provided with PTFE and fused-silica capillary tubes are plotted in Fig. 2. Their courses agree with those predicted for a capacitance type of contactless conductivity detection cell [33]. In addition, the plots in Fig. 2 show that there were significant differences between the characteristics obtained using the capillary tubes made of PTFE and those of fused-silica under otherwise identical experimental conditions. These differences could be expected [33] and they are probably linked with different capacitances of the walls of the capillary tubes (different materials and different thicknesses).

A non-linear course of the response characteristics of the contactless conductivity detector need to be taken into consideration when it is used in ITP separations in which the mobility data are calculated from its response (see e.g., Ref. [36]). Under our CZE separating conditions (see Table 1 for the compositions of the carrier electrolyte solutions), such a correction for the non-linearity of the response was not necessary. This was because the detectors were operated at the specific conductivities at which they gave linear responses (see Fig. 2). In this context, we should note that the ranges of the linear responses of the tested detectors covered intervals of the specific conductivities related to the changes of the concentrations of the CZE analytes by about three decadic orders of magnitude [38,39]. Such linear dynamic ranges can also be estimated by comparing the plots in Fig. 2 with the specific conductivity scales on the electropherograms (see Figs. 3, 5 and 6).

From the plots shown in Fig. 2, it is clear that an actual linear dynamic range of the detector depends on the specific conductivity of the carrier electrolyte solution. Therefore, the choice of carrier electrolyte solution to be used in the CZE separations monitored by the contactless conductivity detector has to reflect this fact. At first glance, this appears to be a serious practical disadvantage of the present contactless

detection technique. However, approximate estimations of the specific conductivities of carrier electrolyte solutions, as currently used in CZE separations employing contact conductivity detectors [10–31], show that these fit to the favourable linear parts of the response plots of the contactless conductivity detectors. Such a somewhat unexpected coincidence can be ascribed to the fact that the use of conductivity detection does not favour carrier electrolytes of high specific conductivity (problems associated with the measurements of small conductivity changes on high conductivity backgrounds). This, however, does not eliminate a need for a further extension of the range of specific conductivities within which the detector can operate with the highest attainable sensitivity.

In repeated measurements of the response characteristics of the detectors (recalibration of the detectors), performed with some time delays, we found that the characteristics changed only within random errors with which the specific conductivities of the calibration KCl solutions could be determined (1–2% RSD values). From these facts, we can conclude that very large series of CZE separations, performed between two successive calibrations (several hundred CZE runs), had no impact on these key performance characteristics of the detectors. Such robustness of the detector represents a significant improvement compared to contact conductivity detectors, which require regular cleaning of the surfaces of the detection electrodes [7,8].

Noise parameters of the detectors (peak-to-peak noise) were measured in the CZE runs without and with sample injections. The peak-to-peak noise of the detector signal at the baseline related to the amplitude of the signal corresponding to a unit concentration of the analyte (noise/sensitivity ratio) were obtained in these runs for a particular detector. Such a ratio effectively characterizes the performance of the detector in terms of the minimum detectability attainable for a given analyte [44]. Links of this ratio to the quality of the analytical data are illustrated in the electropherograms in Fig. 3.

The values of the noise/sensitivity ratios as obtained for the tested detectors are summarized in Table 2. Significant differences between some of the detectors as far as this performance parameter is concerned are apparent from these data in spite of

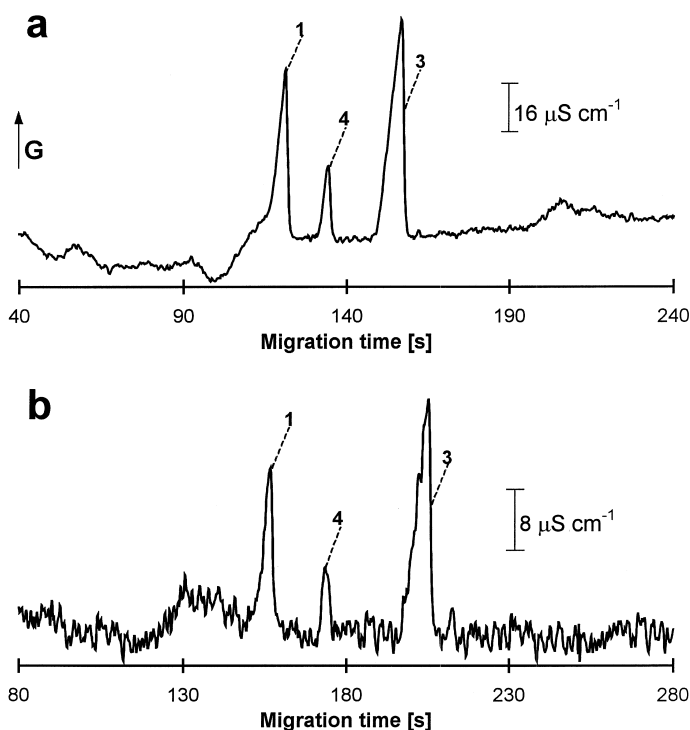


Fig. 3. Electropherograms from the CZE separations of chloride (1), nitrate (4) and sulfate (3) in the PTFE capillary tubes using contactless conductivity detection cells with different detection performances. The anions were present in the injected samples at  $10 \mu\text{mol/l}$  concentrations. (a) The electropherogram obtained using the detector with the lowest peak-to-peak noise/sensitivity ratio (see Table 2); (b) the electropherogram obtained using the detector with the highest peak-to-peak noise/sensitivity ratio (see Table 2). [A group of six columns with contactless conductivity detectors was used for these tests; the columns were provided with PTFE capillary tubes of  $300 \mu\text{m}$  I.D. and  $500 \mu\text{m}$  O.D., from an identical production lot, and the detection cells were of the same construction (see Fig. 1)]. The CZE separations were carried out in electrolyte system No. 1 (Table 1) with the driving current stabilized at  $50 \mu\text{A}$ .

Table 2  
Noise performance characteristics of the tested contactless conductivity detectors

Column	Noise/sensitivity ratio ( $\mu\text{mol/l}$ ) <sup>a</sup>		
	Chloride	Nitrate	Sulfate
PTFE "1"	0.94	1.04	0.73
PTFE "2"	1.01	0.99	0.65
PTFE "3"	0.25	0.20	0.19
PTFE "4"	0.49	0.34	0.32
PTFE "5"	1.68	1.69	1.15
PTFE "6"	0.46	0.35	0.31
FS	0.22	0.14	0.14

<sup>a</sup> Noise/sensitivity ratio is a ratio of the peak-to-peak noise of the detector to its response to the peak corresponding to a unit concentration of the analyte.

PTFE, polytetrafluorethylene capillary; FS, fused-silica capillary.

the fact that the detectors were provided with the electronics of very close performance parameters. It is logical to ascribe these differences to different performances of the detection cells. Their origins may be in different asymmetries of the detection electrodes ( $E_1$ – $E_4$  in Fig. 1) [33–36]. Whether the limits of the present method of contactless detection are set by this parameter of the detection cell is not yet clear.

The LOD values provided by the contactless conductivity detectors for common inorganic anions ( $C_{A,LOD}$ ) were estimated using the following equation:

$$C_{A,LOD} = 3N_{p-p}/5S_A$$

where  $N_{p-p}$  is the peak-to-peak noise of the detector and  $S_A$  is the slope of the dependence of the peak

Table 3  
Comparison of the limits of detection for the inorganic anions using contact and contactless conductivity detectors

Anion	Limits of detection (nmol/l)	
	Contact conductivity detection	Contactless conductivity detection
Chloride	85	650
Bromide	75	480
Sulfate	42	270
Nitrate	48	330
Iodide	71	560
Nitrite	110	420
Fluoride	420	720
Phosphate	110	320

height on the concentration of analyte (for a 200-nl sample injection volume).

The LOD data obtained for the contactless detector with the best noise performance (PTFE “3” in Table 2) are summarized in Table 3. Complementary data obtained for a contact conductivity detector under identical CZE working conditions (system No. 2 in Table 1) serve as references. The electropherograms shown in Fig. 4 illustrate detection possibilities of both techniques in the CZE analysis of common inorganic anions. The electropherogram in Fig. 4b was obtained using the contactless conductivity detector that exhibited the lowest noise/sensitivity ratio (PTFE “3” in Table 2), while the one in Fig.

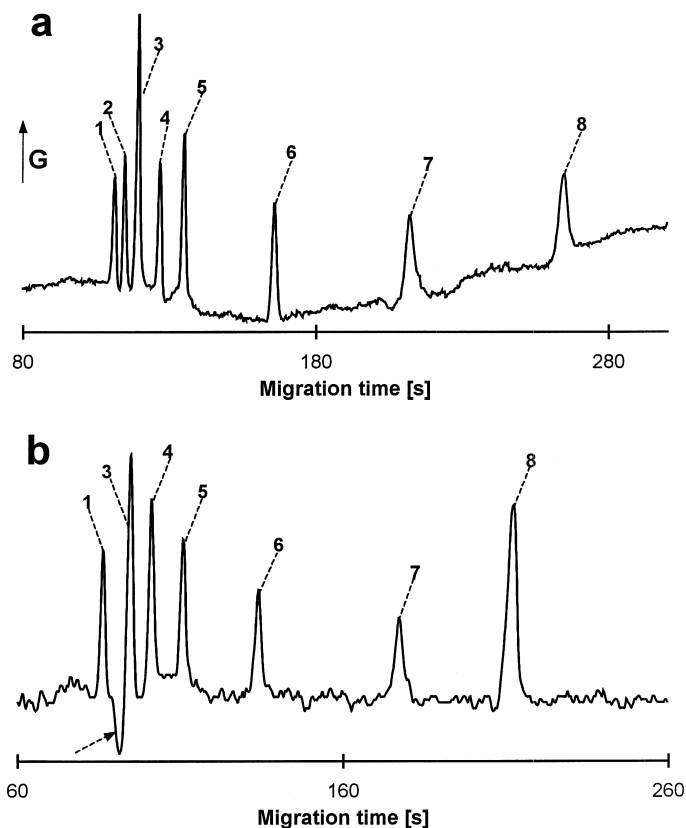


Fig. 4. Comparison of contact (a) and contactless (b) conductivity detectors in the CZE separation of common inorganic anions under similar working conditions. Peaks and the concentrations of the anions: 1=chloride at 2 (a) and 10 (b)  $\mu\text{mol/l}$ ; 2=bromide at 2 (a)  $\mu\text{mol/l}$ ; 3=sulfate at 2 (a) and 10 (b)  $\mu\text{mol/l}$ ; 4=nitrate at 2 (a) and 10 (b)  $\mu\text{mol/l}$ ; 5=iodide at 3 (a) and 10 (b)  $\mu\text{mol/l}$ ; 6=nitrite at 3 (a) and 10 (b)  $\mu\text{mol/l}$ ; 7=fluoride, 10 (a) and 10 (b)  $\mu\text{mol/l}$ ; 8=phosphate at 3 (a) and 10 (b)  $\mu\text{mol/l}$ . An arrow indicates the migration position of bromide. In both instances, the separations were carried out in electrolyte system No. 2 (Table 1) with the driving current stabilized at 30  $\mu\text{A}$ .

4a was obtained using a contact conductivity detector under identical working conditions [25]. As could be expected (see the LOD data in Table 3), a better performance of the contact detector is demonstrated by these electropherograms.

The electropherograms in Fig. 4 indicate that the contactless conductivity detectors influenced the separation efficiency of the analytes more than the contact detector. This indication is in agreement with our recent results obtained with the contactless conductivity detector in a study aimed at the use of host–guest equilibria in the CZE separation of inorganic anions [38]. CZE experiments and computer simulations performed in that work showed that this detector influences the separation efficiency

data, especially for the most mobile analytes, with the time constant of the detector (0.5–0.7 s) being a main instrumental contributor to the plate height values.

### 3.2. Application potentialities

Our experiments, aimed at a practical use of the present contactless conductivity detector in the CZE of inorganic anions, were focused on water and soil samples. In our previous work dealing with the CZE analysis of inorganic anions [25], electrolyte system No. 2 (Table 1) was used. Water samples analyzed in this carrier electrolyte had to be diluted in the determination of macroconstituents (chloride, sulfate

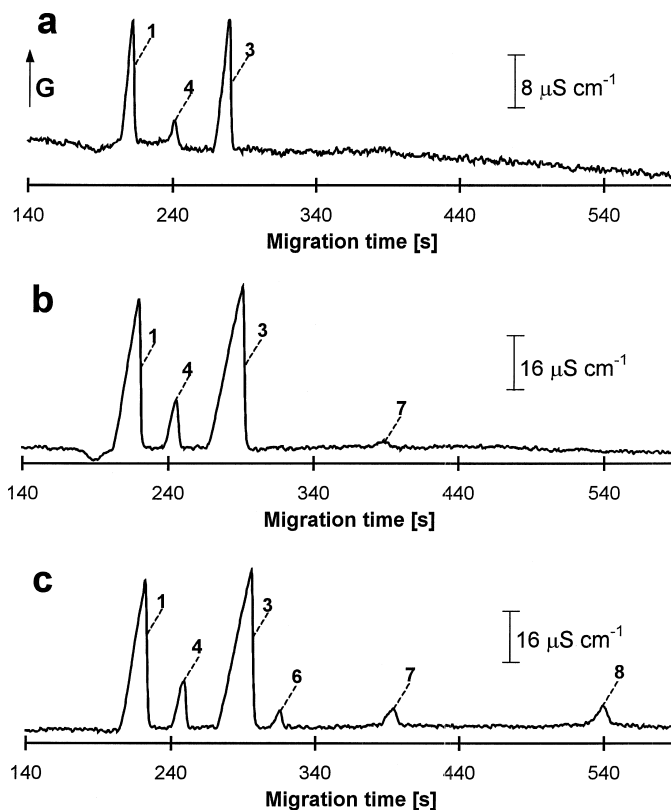


Fig. 5. Electropherograms from the CZE separation of inorganic anions present in drinking water. Peaks: chloride (1), sulfate (3), nitrate (4), nitrite (6), fluoride (7) and phosphate (8). (a) Drinking water diluted five-fold with demineralized water; (b) undiluted drinking water; (c) the same sample as in (b) only spiked with nitrite, fluoride and phosphate at 30  $\mu\text{mol/l}$  each. The separations were carried out in electrolyte system No. 1 (Table 1) using the PTFE column with the detection cell exhibiting the best detection performance among the tested cells (see Fig. 2a). The driving current was stabilized at 30  $\mu\text{A}$ . The inner wall of the capillary tube was coated with methylhydroxyethylcellulose to suppress the electroosmotic flow.



and nitrate), while the microconstituents (nitrite, fluoride and phosphate) had to be determined in separate CZE runs with undiluted samples. To solve these practical disadvantages, a new carrier electrolyte was developed in this work (System No. 1, Table 1). Enhancing both differences in the effective mobilities of the anionic macroconstituents and the sample load capacity of the separation system, this carrier electrolyte solution made it possible to obtain baseline resolution of the macroconstituents present in undiluted tap water samples (see Fig. 5). However, in contrast to the use of the contact conductivity detector [25], only one of the microconstituents (fluoride) could be detected with the present

contactless detector in the same volume of injected sample. Undoubtedly, this is a consequence of the current status of the detection performance of the latter detector (see Table 3).

The repeatability of the CZE determination of chloride, nitrate and sulfate in an aqueous extract of a soil sample with a high content of humic material (see Section 2.3) was evaluated to test the robustness of the present detector. This sample type was chosen for the test as it was found to adversely affect the performance of the contact conductivity detector (coating of the detection electrodes responsible for changes in the detection sensitivity of the contact conductivity detector [8,32]). The series of elec-

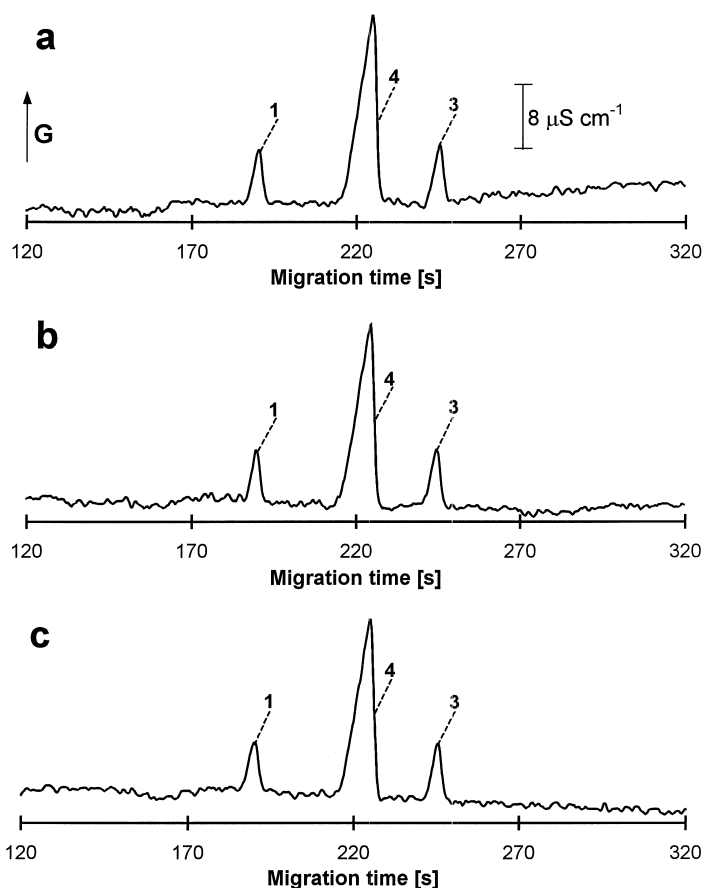


Fig. 6. Repeatability of the CZE separation of inorganic anions in an aqueous soil extract. (a, b and c) The first, twenty-fifth and fiftieth runs in a consecutive series of 50 CZE runs, respectively. Peaks: chloride (1), sulfate (3) and nitrate (4). The soil extract was obtained in the way described in Experimental. The separations were carried out in the PTFE column with the best detection performance (PTFE “3” in Table 2) in electrolyte system No. 1 (Table 1). The driving current was stabilized at 30  $\mu\text{A}$ . The inner wall of the capillary tube was coated with methylhydroxyethylcellulose to suppress the electroosmotic flow.

tropherograms shown in Fig. 6 serves as an illustration of the repeatability that can be attained for this matrix. The robustness of the present detector is manifested by the following facts: (i) The peak areas of the anions from a series of 50 consecutive CZE runs agreed within 1–3%; (ii) the response characteristics of the detector before and after the series of experiments were identical; (iii) precipitation of the sample matrix in the capillary tube had no impact on the performance of the detector.

The results obtained in this work and in work dealing with milk samples [38] clearly indicate that the present contactless detector offers very favourable detection conditions for common inorganic anions in situations where the sample matrices may have a negative impact on the performances of the contact detectors. Obviously, less favourable LOD values (see Table 3) must be acceptable in such instances.

The results presented in this work reflect a primary performance status of the contactless conductivity detection system in CZE separations and, as such, they cannot be taken as conclusive. It is clear that the roles of various parameters responsible for current performance limits of the high-frequency contactless detection system still need to be investigated, especially for improving its noise/sensitivity ratio, as this can significantly enhance its overall versatility in CZE. The use of a different detection principle, as described recently in the work by Zemmann et al. [37], may offer another alternative in achieving such a goal.

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