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Conductivity detection cell for capillary zone electrophoresis with a solution mediated contact of the separated constituents with the detection electrodes

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Abstract

A contact conductivity detection cell for capillary zone electrophoresis (CZE) with an electrolyte solution mediated contact of the separated constituents with the detection electrodes (ESMC cell) was developed in this work. This new approach to the conductivity sensing in CZE is intended to eliminate detection disturbances due to electrode reactions and adsorption of the separated constituents when these are coming into direct contact with the detection electrodes. An optimum detection performance of the cell was achieved when the carrier electrolyte solution mediated the electric contact of the detection electrodes with the separated constituents. Different compositions of the mediator and carrier electrolyte solutions led to large drifts of the detection signals. Isotachophoresis experiments performed in this context with the ESMC cell revealed that origins of these drifts are in transport processes (diffusion and electromigration) between the detection compartment and the detection electrodes in the cell. These processes affected, to some extent, other analytically relevant performance parameters of the ESMC cell of the present construction as well [e.g., concentration limits of detection (LODs), a contribution of the cell to the band broadening]. For example, the ESMC cell gave, under optimum operating conditions, 3–4 times higher concentration LODs for the test analytes than a current on-column conductivity cell employed under identical working conditions. On the other hand, these LOD values (25–150 nmol/l) were still 20–25 times lower than those estimated from reference experiments for a contactless conductivity detector. CZE experiments with iodide, carried out under working conditions leading to electrochemical reactions of this anion on the detection electrodes of current conductivity cells, did not occur in the ESMC cell. In addition, this cell, contrary to a reference contact conductivity cell, required no special care (e.g., cleaning of the surfaces of the detection electrodes by chemical or electrochemical means) to maintain its reliable long-term performance. Anionic CZE analyses of tap and mineral water samples monitored by the conductivity detector provided with the ESMC cell demonstrated a practical applicability and certain limitations of this detection approach in the analysis of ionic constituents present in high ionic strength sample matrices.

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

1. Introduction

An interest in the use of conductivity detection in capillary zone electrophoresis (CZE) dates back to some of the CZE pioneering works [1–3]. At present, analytical potentialities and limitations of this

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detection technique in CZE are known [2,4] and its use is, mainly, linked with the detection of inorganic ions (see, e.g., Refs. [3,5–18]) and low-molecular-mass organic ions [19–24]. Providing approximately 10-fold higher sensitivity than indirect UV detection [11], the conductivity detection can be considered as a general alternative to this, currently preferred, technique in the detection of ions that lack suitable chromophores [25].

From research linked with the developments of contact conductivity detectors for capillary isotachophoresis (ITP) it is known that reactions of some electrochemically active analytes on the detection electrodes and/or accompanying changes of the electrode surfaces may impair performances of the contact conductivity detectors significantly [26–28]. Samples containing constituents exhibiting strong adsorptivities on the electrode surfaces may be sources of various problems as well [27,28]. These disturbing phenomena occur also in CZE with the contact conductivity detection (see, e.g., Ref. [29], p. 150). Here, their impacts on the analytical data may be even more serious as in CZE often very small conductance changes due to the zones of the separated constituents are to be measured on a high conductance background of the carrier electrolyte. The use of the contactless conductivity detection solves these problems in ITP [30–33]. For the same reasons, this detection approach is a subject of recent research in CZE [34–36]. So far, however, current contact conductivity detectors provide, under comparable CZE working conditions, significantly higher detection sensitivities than their contactless counterparts (see, e.g., Ref. [36]). Although a high operational robustness of the contactless detection may in some instances more than compensate for these disadvantages [18,36] a need for a high sensitivity and at the same time robust CZE conductivity detector still remains.

A lack of an operational robustness of the contact conductivity detection in CE can be apparently attributed to a direct contact of the separated constituents with the detection electrodes (see, e.g., Refs. [26–36]). Therefore, it seems reasonable to expect that by mediating this contact via an appropriately chosen electrolyte solution an improved robustness of the detector can be achieved. Following this general idea, an electrolyte solution mediated contact conductivity cell (ESMC cell) for CZE was developed in this work. Performance parameters of the conductivity detector provided with this detection cell were evaluated and compared with those characterizing a current contact conductivity detector [37] and a high-frequency contactless detector [30–33,36]. Its utility in the analysis of practical samples was also assessed.

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 using the following modules: (1) a CZE injection valve with a 200-nl internal sample loop (Villa-Labeco); (2) one of the columns provided with the following detection sensors: (i) an ESMC cell developed in this work (see Fig. 2), connected to a 300-μm I.D.×500-μm O.D. capillary tube made of PTFE of a 250-mm length to the cell; (ii) an on-column contact conductivity detection cell (Villa-Labeco), connected to a 300-μm I.D.×650-μm O.D. capillary tube made of PTFE of a 160-mm length to the cell; (iii) a four-electrode, on-column contactless conductivity detection cell (Villa-Labeco), connected to a 300-μm I.D.×430-μm O.D. capillary tube made of fused-silica of a 130-mm length to the cell; (3) counter-electrode compartment with a hydrodynamically (membrane) closed connecting channel to the separation compartment (Villa-Labeco).

The signal from the conductivity detector was led to a Pentium personal computer via a Unilab data acquisition unit (Fitek, Šala, Slovak Republic). ITP Win software (version 2.31) obtained from Kascomp (Bratislava, Slovak Republic) was used for the acquisition and processing of the detection data.

2.2. Electrolyte solutions and samples

The solutions of the carrier electrolytes were prepared in water demineralized by a Pro-PS water purification system (Labconco, Kansas City, KS, USA). Methylhydroxyethylcellulose 30 000 (m-

HEC) added to the carrier electrolyte solutions served as a suppressor of the electroosmotic flow. The solutions were filtered through disposable membrane filters (a 1.2-μm pore size) before the use.

Stock solutions containing the salts of inorganic acids at 10 m*M* concentrations were used for the preparations of the model samples. The model samples were prepared always fresh before a series of the analyses by appropriately diluting the stock solutions with demineralized water.

Mineral water (Budiš, Slovak Republic), bought in a local supermarket, was sonicated for 5 min to remove free CO_2. Tap water samples were collected in the laboratory into polyethylene sample containers. They were appropriately diluted with demineralized water or injected directly into the CZE equipment without any sample preparation.

3. Results and discussion

3.1. Design of the detection cell

Schemes providing generalized views of the arrangements of the detection electrodes in contact conductivity detection cells as used in CZE are given in Fig. 1. The one proposed in this work (Fig. 1c) introduces an electrolyte solution mediated contact of the separated constituents with the detection electrodes. As already mentioned in Section 1 such a solution is assumed to eliminate or, at least, reduce disturbances that originate in adsorption and/or electrode reactions of the separated constituents on the detection electrodes. A schematic drawing in Fig. 2 shows an actual arrangement of the detection cell based on this approach as developed in this work. Here, the detection electrodes (Fig. 2c) are placed into channels (Fig. 2d) outside the separation capillary. The electrolyte solution filling these electrode channels mediates the electrical contact of the electrodes with the constituents migrating through the detection compartment of the cell (Fig. 2e). Electrode channels of 1.5-mm I.D. and with steeply tapered connections to the detection compartment were chosen to minimize contributions of the electrolyte solution in these channels to the measured resistance. Placement of the detection electrodes outside the capillary reduces voltage drops on the

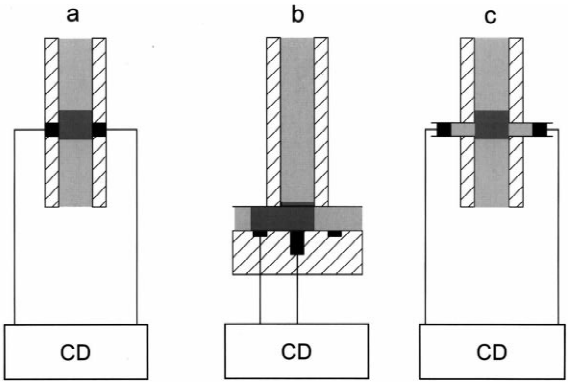

Fig. 1. General schemes of the arrangements of the detection electrodes in contact conductivity detection cells for CZE. (a) An in-column placement of the detection electrodes exposed to direct contacts with the separated constituents; (b) a post-column placement of the detection electrodes exposed to direct contacts with the separated constituents; (c) an on-column placement of the detection electrodes with an electrolyte solution mediated contact with the detection compartment of the cell. CD, measuring circuitry of the detector.

electrodes due to the driving electric field [26]. This gave us a possibility to use detection electrodes of large surface area (Pt wires of 0.3 mm diameter) in the present cell. In this way, we reduced densities of the leakage currents flowing through them to the ground potential of the measuring system (10–20-pA leakage currents were typical for the present detection cell when it operated at a 5-kV potential) and,

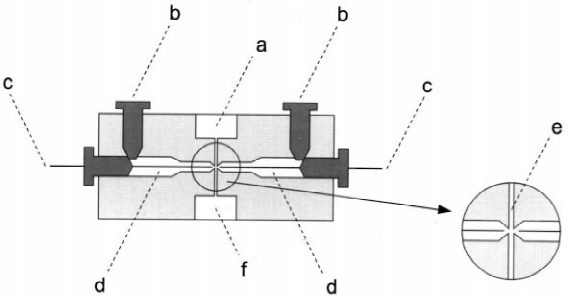

Fig. 2. A schematic drawing of the conductivity detection cell with an electrolyte solution mediated contact of the separated constituents with the detection electrodes. (a) a connection of the cell to the separation capillary; (b) holes with screw plugs for filling the electrode channels (d) with the detection electrodes (c); (e) the detection compartment; (f) a connection of the cell to the counter-electrode compartment. A body of the cell was made of poly(methyl methacrylate).

consequently, kept at a minimum disturbances due to electrode reactions associated with the leakage currents (see Ref. [28], p. 188).

3.2. Choice of the electric contact mediating solution

A series of CZE experiments with identical and different mediator and carrier electrolyte solutions was carried out to investigate roles of their compositions on the response of the detector provided with the ESMC cell. From typical electropherograms as obtained in these experiments (Fig. 3) we can see that the use of identical electrolyte solutions led to the best results (Fig. 3b) while the solutions of differing compositions characterized large baseline drifts of the detection signals (Fig. 3a,c). These drifts, apparently linked with electric conductance changes in the detection cell during the run, can be attributed, for example, to diffusion driven mixing of the carrier electrolyte and mediator solutions in the cell.

To identify places and mechanisms of these conductance changes in the detection cell ITP separations of a model anionic mixture (Fig. 4) spiked with traces of anionic dyes (SPADNS and bromphenol blue) were monitored by the ESMC cell. Here, the ITP stack of the model analytes provided a well-defined contiguous series of concentration pulses of different constituents that sequentially contacted the mediator solution (the leading electrolyte solution) present in the electrode channels (see Fig. 2). The dyes, focused into very narrow bands in the stack, visualized processes occurring on these contacts. Each of the dyes passed in front of the connecting holes to the electrode channels in about 1 s under working conditions employed in our experiments (Fig. 4). We observed that during these contact times minute parts of their bands entered the electrode channels and moved very slowly, in a diffuse stack, in the direction to the detection electrodes. This movement of the stack stopped after the driving voltage was switched off. Subsequently, the stack vanished by a diffusion-driven mixing. These facts indicate that besides diffusion also electromigration of the constituents from the detection compartment, associated with leakage currents through the electrode channels, significantly contributed to changes in the composition of the mediator solution in the electrode channels. Relatively low rates of these changes caused that the plateau values of the detection signal for the ITP zones could be reached only very slowly (Fig. 4) in comparison to what is typical in ITP when the cells corresponding to a general scheme in Fig. 1a are used [28,38].

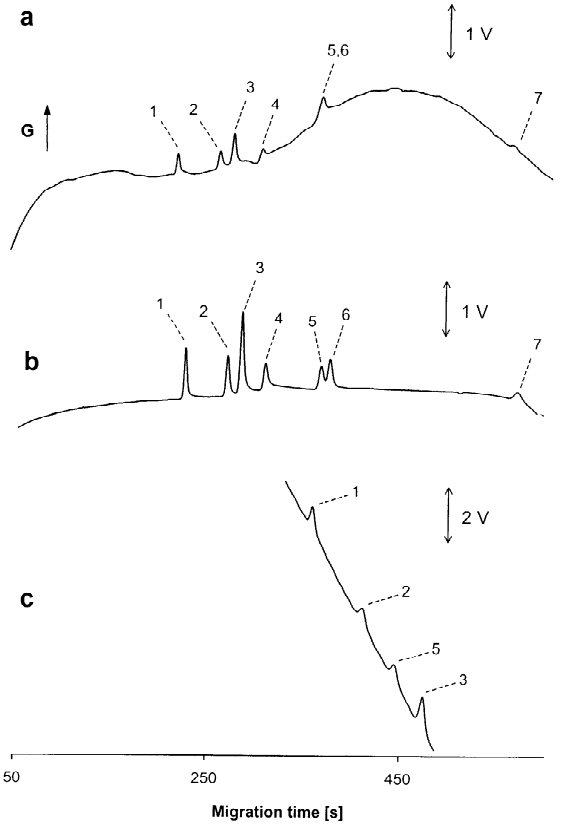

Fig. 3. A role of the composition of the mediator and carrier electrolyte solutions in the ESMC cell on the response of the conductivity detector in CZE separations. The compositions of the solutions were: (a) the carrier electrolyte solution ES 1 (Table 1), the mediator solution ES 2; (b) the carrier electrolyte solution ES 1, the mediator solution ES 1; (c) the carrier electrolyte solution ES 2, the mediator solution ES 1. The concentrations of the analytes in the injected sample were 20 μmol/l. Peak assignments: (1) chloride, (2) nitrate, (3) sulfate, (4) nitrite, (5) iodide, (6) fluoride, (7) phosphate. The separations were carried out with a 50-μA driving current.

Undoubtedly, the same transport processes were effective in the above CZE separations and, therefore, changes in the compositions of the mediator

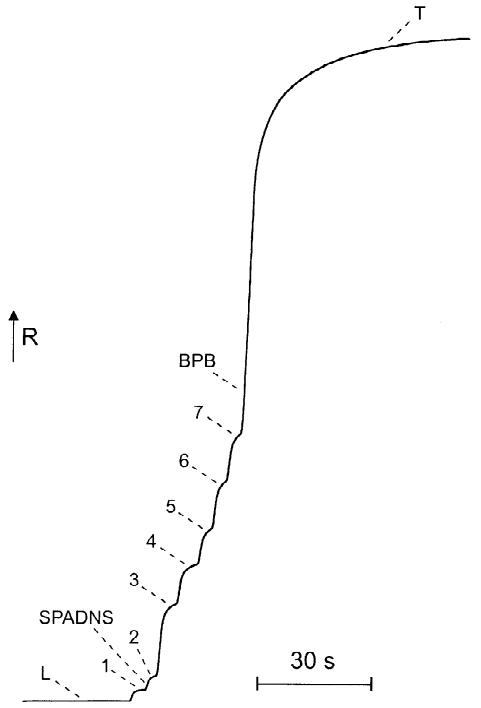

Fig. 4. An isotachopherogram from the separation of anions as obtained by an electrolyte solution mediated contact detection cell. The zone assignments: (1) sulfate, (2) chlorate, (3) succinate, (4) adipate, (5) acetate, (6) lactate, (7) benzoate, SPADNS, 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonic acid; BPB, bromophenol blue (3′,3″,5′,5″-tetrabromophenolsulfonephthalein). The concentrations of the anions in the injected sample (200 nl) were 5 m*M* while the concentrations of the anionic dyes (SPADNS and BPB) were 100-fold lower. The leading electrolyte: 10 m*M* hydrochloric acid buffered to pH 6.0 with histidine [methylhydroxyethylcellulose present in the leading electrolyte solution at a 0.2% (w/v) concentration served as a suppressor of the electroosmotic flow]; the terminating electrolyte: 7 m*M* 2-(*N*-morpholino)ethanesulfonic acid buffered to pH 6.0 with histidine. The separation was carried out with a 50-μA driving current.

solutions in the electrode channels explain large baseline drifts on the electropherograms in Fig. 3a,c. In the light of these facts we can conclude that identical compositions of the mediator and carrier electrolyte solutions a priori lead to favorable detection conditions in the CZE separations. This is understandable as under such electrolyte conditions there is no driving force for diffusion and no change in the composition of the mediator solution accompany the electromigration transport of the constituents through the electrode channels. Obviously, the CZE migration of the separated constituents through the detection compartment introduces certain disturbances into this state.

3.3. Evaluation of some performance parameters of the detection cell

CZE experiments with model analytes, monitored by the present ESMC cell, were performed to obtain data characterizing its detection performance. Here, for obvious reasons, the carrier electrolyte solution (Table 1) used in a particular experiment served at the same time as the mediator solution in the electrode channels of the detection cell. Analogous data (Table 2), as obtained for the same CZE experiments monitored by a contactless conductivity detector [36] and a contact detection cell with the arrangement of the detection electrodes as given in Fig. 1a [37], served as references reflecting a current status in the conductivity detection in CZE.

Electropherograms in Fig. 5 illustrate detectabilities of the model analytes by the detection systems employed in our performance tests (the concentrations of the analytes in CZE runs monitored by the contactless detector in the sample were higher to reflect a lower sensitivity of this detector). From these electropherograms we can see that the drift of

Table 1
Electrolyte systems[a]

Parameter	ES 1	ES 2
Solvent	Water	Water
Carrier ion	L-Aspartate	PEG–DC
Concentration (m*M*)	10	14
Counter-ion	BTP	BTP
Concentration (m*M*)	2.6	4.5
pH	4.0	3.6
Additive	m-HEC	m-HEC
Concentration (%, w/v)	0.2	0.1
Complexing additive	α-CD	PVP K15
Concentration	70 m*M*	5.1% (w/v)

[a] BTP, 1,3-bis[tris(hydroxymethyl)methylamino]propane; m-HEC, methylhydroxyethylcellulose; α-CD, α-cyclodextrin; PEG-DC, polyethyleneglycol dicarboxylic acid; PVP, polyvinylpyrrolidone.

Table 2
Some performance parameters of the ESMC and reference detection cells

Anion	Peak area[a], RSD (%)	LOD (nmol/l)			Separation efficiency (N/m)		
		ESMC cell	Reference contact	Contactless	ESMC cell	Reference contact	Contactless
Chloride	3.1	38	9	1060	118 000	186 000	168 000
Sulfate	2.9	26	5	540	123 000	211 000	165 000
Nitrate	3.2	45	10	1200	143 000	294 000	210 000
Nitrite	3.1	97	20	2580	87 000	191 000	172 000
Iodide	3.9	63	19	1700	126 000	234 000	167 000
Fluoride	4.9	75	17	2230	123 000	187 000	147 000
Phosphate	4.4	155	34	3750	117 000	229 000	156 000

[a] Calculated from 10 parallel determinations of a model sample, containing the anions at 10 μmol/l concentrations, in the electrolyte system ES 1 (Table 1) with a 50-μA driving current. The concentration limits of detection were estimated in the way as described in the text; N/m, the number of theoretical plates per metre, calculated from the data obtained for 10 μmol/l concentrations of the anions in the electrolyte system ES 1 using a 50-μA driving current (the data for the contactless detector were obtained with 30 μmol/l concentration of the anions).

the baseline of the detection signal characteristic for the present ESMC cell was comparable to the drifts of the reference detection systems when identical mediator and carrier electrolyte solutions were used. A small drift, probably due to slow conductance fluctuations of the electrolyte solution in the separation compartment, did not impair evaluations of the detection data also for sub-μmol/l concentrations of the analytes.

Limits of detection (LODs) for the test anions were estimated in the way used previously [10] with the aid of the relationship:

$$\mathrm{LOD} = 3\,N_{\mathrm{p-p}}/5S \qquad (1)$$

where $N_{\mathrm{p-p}}$ is the peak-to-peak noise of the detector in a particular electrolyte system (see Table 2). S is the slope of the dependence of the peak height on the concentration of the analyte for a 200-nl injection volume and a 50-μA driving current (obtained for the contact detectors for concentrations of the analytes in the range of 50–500 nmol/l and for 20 times higher concentrations for the contactless detector). A comparison of the LOD data for the contact conductivity detection cells, obtained with the same CE equipment (see Section 2), shows (Table 2) that the ESMC cell provided 3–4 times higher LOD values than the one serving as a reference. As the noise parameters of the conductivity detector in both instances were almost identical this difference apparently indicate a lower sensitivity of the present ESMC cell (lower peak heights linked with longer migration times of the test analytes in the column provided with this cell can explain [29,39] these differences only partially). Dispersive disturbances linked with the transport processes in the cell as discussed above appear to be responsible for this. On the other hand, the LOD values of the present detector were 20–25 times lower than those attainable under identical working conditions by the contactless conductivity detector. This indicates that an elimination of the contact of the separated constituents with the detection electrodes via an electrically conductive mediator offers a competitive alternative to the contactless detection as far as the detectability is concerned.

Reproducibilities of the determination of the analytes using the present ESMC cell, expressed via the RSD values, spanned from 2.9 to 4.4% for 10 μmol/l concentrations of the analytes in the injected sample (Table 2) and agreed well with those obtained by the reference contact detection system. This suggests that minute losses of the analytes accompanying transport processes in the detection cell (see above) did not introduce significant random errors into their quantitations. Here, it seems reasonable to assume that these transport processes can be considered as sources of (hardly identifiable) proportional errors in the quantitation.

Lower separation efficiencies for the test analytes were typical for the present ESMC cell when related

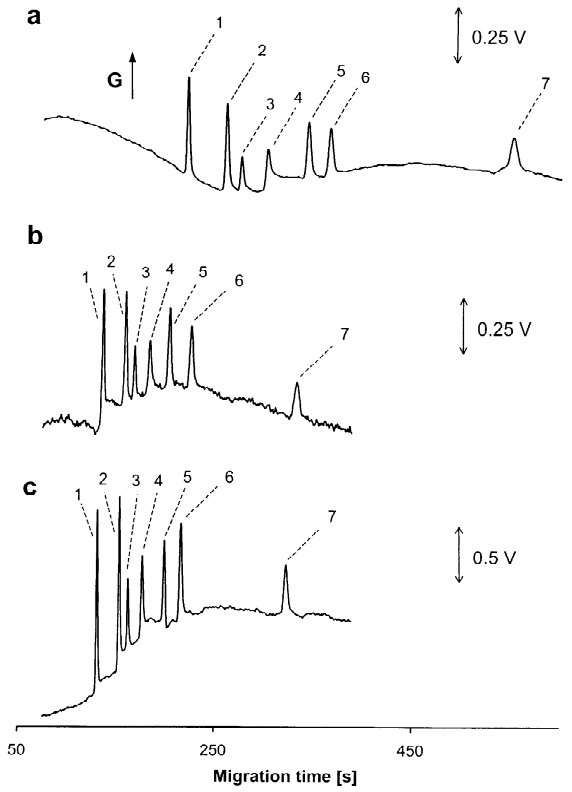

Fig. 5. Detectabilities of the test analytes with the aid of the ESMC cell (a), contactless (b) and reference contact (c) detection cells. Peak assignments: (1) chloride, (2) nitrate, (3) sulfate, (4) nitrite, (5) iodide, (6) fluoride, (7) phosphate. The concentrations of the anions in the injected samples in the CZE runs (a) and (c) were 10 μmol/l (the concentration of sulfate was 2 μmol/l). Their concentrations in the CZE run (b) were 40 μmol/l (the concentration of sulfate was 8 μmol/l). The separations were carried out in the carrier electrolyte ES 1 (Table 1). In the run (a) ES 1 served also as the mediator solution. The driving current was stabilized at 50 μA.

to those characterizing the reference cells (Table 2). About 10 times larger nominal volume of the cell, in comparison to the volumes of the reference cells, offers a partial explanation of this fact [29,39]. Undoubtedly, a major role in this respect can be ascribed to the rates of the transport processes in the cell as discussed above. Here, we should note that the efficiency data characterizing the reference contact cell (obtained with the same instrumentation and under identical working conditions), in fact, outline limits attainable by the ESMC cell when its design approaches to an optimum (e.g., geometrical dimensions and shapes of the electrode channels). However, a detail design and performance evaluation study is essential to reach this goal.

Parameters of the regression equations of the calibration graphs as obtained with the present cell for the model anions in two series of calibration experiments are given in Table 3. Relative differences in the numerical values of the slopes (analytical sensitivities) indicate a good long-term stability of the response of the detection cell (detection sensitivity) as these differences include, in addition to the fluctuations in the detection sensitivity, at least, small deviations in the compositions of the carrier electrolyte solutions in which the calibration data were obtained and small differences in the compositions of the calibration solutions.

We found that the detection of iodide in the electrolyte system containing PVP (ES 2, in Table 1) is disturbed by its electrode reaction (see Fig. 6b) on the detection electrodes exposed to direct contacts with the separated constituents (Fig. 1a). This reaction started to occur after several CZE runs with

Table 3
Parameters of the regression equations ($y=a+bx$) for the calibration graphs of the test anions for 5–50 μmol/l concentrations[a]

Anion	*a* (mV s)	*b* (mV s/μmol/l)	*r*
Chloride	−32.5[b]	100.6[b]	0.9967[b]
	146.9[c]	113.5[c]	0.9985[c]
Nitrate	−25.9[b]	95.2[b]	0.9985[b]
	33.1[c]	107.8[c]	0.9980[c]
Iodide	−5.3[b]	92.6[b]	0.9981[b]
	76.8[c]	100.8[c]	0.9989[c]
Sulfate	−97.8[b]	186.9[b]	0.9986[b]
	78.9[c]	202.0[c]	0.9995[c]
Nitrite	−52.0[b]	91.5[b]	0.9935[b]
	70.3[c]	94.0[c]	0.9962[c]
Fluoride	−112.3[b]	83.0[b]	0.9987[b]
	−72.3[c]	97.8[c]	0.9970[c]
Phosphate	−103.6[b]	74.5[b]	0.9937[b]
	−5.5[c]	66.9[c]	0.9951[c]

[a] *y*, peak area; *x*, concentration of the test anion in the injected sample (μmol/l); *a*, intercept; *b*, slope; *n*, number of data points; *r*, correlation coefficient.

[b] Data based on initial calibration experiments ($n=15$).

[c] Calibration experiments after a 1-month use of the cell ($n=15$).

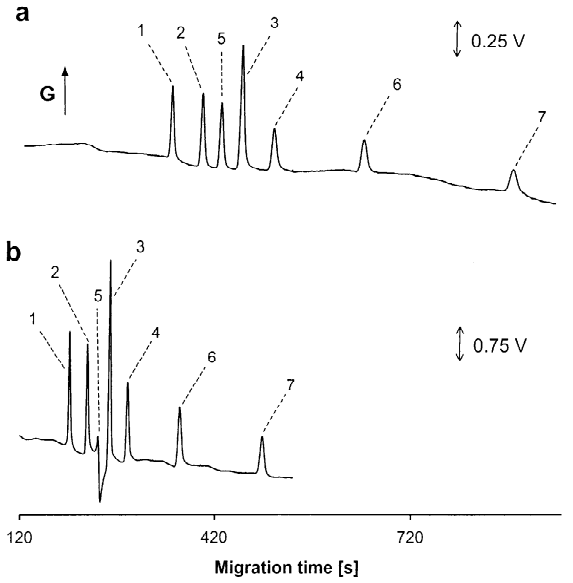

Fig. 6. A comparison of the detection of iodide with the aid of the present ESMC (a) and reference contact (b) detection cells. Peak assignments: (1) chloride, (2) nitrate, (3) sulfate, (4) nitrite, (5) iodide, (6) fluoride, (7) phosphate. The concentrations of the anions in the injected samples were 30 μmol/l. The separations were carried out in the carrier electrolyte ES 2 (Table 1). The carrier electrolyte served also as the mediator solution in the run (a). The driving current was stabilized at 50 μA.

iodide containing samples when the carrier electrolyte solution in the capillary was not replenished between the runs. As expected, such disturbances did not appear in any of the comparative experiments performed with the ESMC cell (see a typical electropherogram in Fig. 6a obtained under identical working conditions). These results, undoubtedly, indicate a positive role of the mediated contact of the analytes with the detection electrodes in enhancing an operational robustness of the contact detection.

3.4. The use of the detection cell in the analysis of practical samples

A practical utility of the present ESMC cell was assessed in experiments carried out with tap and mineral water samples (see Section 2). The separations were performed in the carrier electrolyte solution ES 2 (Table1) as this was shown to provide favorable sample loadabilities in the analysis of water and soil samples monitored by a contactless conductivity detector [36]. Here, the detections of anionic macro- and microconstituents were of our interest. An electropherogram as obtained from the analysis of an undiluted sample of tap water (Fig. 7a) shows that under the preferred separating conditions the detector was sensitive enough to detect not only the macroconstituents (chloride, sulfate and nitrate) but also fluoride (present in the sample at about 4 μmol/l concentration). Although other anionic microconstituents to be expected in water samples [10] were also resolved from the macroconstituents (Fig. 7b) their concentrations in the actual sample were too low to be detectable by the conductivity detector under the employed electrolyte conditions. Electropherograms in Fig. 7c,d, obtained from the analysis of mineral water, illustrate detection capabilities of the ESMC cell in situations when high ionic strength samples (an actual sample contained the anionic macroconstituents at a total concentration

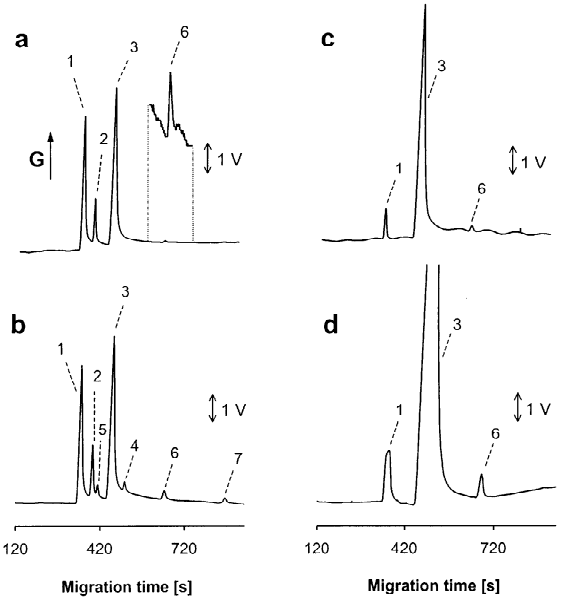

Fig. 7. Electropherograms from the analyses of water samples using the ESMC cell. (a) CZE run with an undiluted tap water sample; (b) the same sample as in (a) spiked with the test anions at 30 μmol/l concentrations; (c) mineral water "Budiš " 5 times diluted with demineralized water; (d) the same as in (c) only the undiluted sample was injected. Peak assignments: (1) chloride, (2) nitrate, (3) sulfate, (4) nitrite, (5) iodide, (6) fluoride, (7) phosphate. The separations were carried out using the carrier and mediator electrolyte solutions ES 2 (Table 1). The driving current was stabilized at 50 μA.

about 10 times higher than the tap water sample) were loaded onto the CZE column. Here, besides the macroconstituents (chloride and sulfate) also fluoride (the only anionic microconstituent listed on the label of the bottled mineral water) could be reliably detected.

Tailings of the macroconstituent peaks are typical features of the electropherograms in Fig. 7. Origins of these disturbances were apparently in conductivity changes due to significant differences in the compositions of the electrolyte solutions in the detection compartment and the electrode channels of the cell in the presence of the macroconstituent zones as discussed above. These results imply practical limits of the present ESMC cell in the analysis of samples containing ionic constituents at high concentrations.

4. Conclusions

This work showed that the contact conductivity detection with an electrolyte solution mediated contact of the separated constituents with the detection electrodes is feasible and offers a practically applicable detection approach for CZE. Our experiments with the detection cell based on this principle revealed that the use of identical mediator and carrier electrolyte solutions is essential when an acceptable performance of the detector is to be attained. However, such a restriction has probably only a limited impact on a practical utility of the detector.

CZE experiments with iodide containing samples demonstrated (see Fig. 6) a key benefit offered by the present detection approach, viz., an enhanced robustness with respect to disturbances originating in a direct contact of the separated constituents with the detection electrodes. Obviously, appropriately chosen experiments with different CE analytes known to adversely affect the response of the contact conductivity detectors are needed to make a certain generalization in this respect justified. In this context, we should note that the present ESMC cell, contrary to the one used as a reference contact cell in our experiments, required no special maintenance (e.g., cleaning of the surfaces of the detection electrodes by effective chemical or electrochemical means [37]) to reach a reliable long-term performance.

Our results indicate that transport processes (diffusion and electromigration) between the electrode channels and the detection compartment of the ESMC cell, due to changes in the composition of the electrolyte solution in the detection compartment during the separation, set limits for some analytically relevant performance parameters of the detector. Therefore, improved LOD for the CZE analytes and reduced band broadening in the cell can be expected, mainly via an improved construction of the ESMC cell. Although mechanisms of the processes responsible for these disturbances seem clear a time consuming design and testing cannot be excluded before such a goal is reached.

ITP experiments performed in this work imply only limited possibilities of the ESMC cell to monitor the ITP separations (see Fig. 4). Here, low rates of the transport processes in the electrode channels and stepwise changes in the composition of the solution in the detection compartment (inherent to the ITP stack) seem to restrict its use in this CE technique.

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