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Journal of Chromatography A, 829 (1998) 351–357

JOURNAL OF  
CHROMATOGRAPHY A

# Capillary zone electrophoresis and ion chromatography in the low $\mu\text{g}/\text{l}$ range applied to the determination of anions in hydrogen peroxide

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Received 7 July 1998; received in revised form 22 September 1998; accepted 25 September 1998

## Abstract

Capillary zone electrophoresis was performed in a 300  $\mu\text{m}$  I.D. column in a closed separation system with a background electrolyte providing resolution of the inorganic anions chloride, sulphate, nitrate, nitrite, fluoride and phosphate. Due to the unusual I.D. of the capillary the sample loadability was such that an injection volume of 350 nl could be injected. Consequently, limits of detection in the low  $\mu\text{g}/\text{l}$  range could be realised with conductivity detection. The method was applied to the determination of trace anionic impurities in hydrogen peroxide of electronic grade. The analysis was characterised by its shortness (5 min) and the direct injection of the hydrogen peroxide. The  $\text{H}_2\text{O}_2$  samples were analysed in parallel by ion chromatography and the results of both methods were compared. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Inorganic anions; Hydrogen peroxide; Capillary zone electrophoresis; Ion chromatography

## 1. Introduction

Hydrogen peroxide is one of the most important chemicals used in the semiconductor industry for cleaning and etching processes.

Hence, there is an increasing demand for the determination of ionic trace impurities, especially due to the fact that ionic contaminants can cause defects and malfunction on the treated microchips.

At present, ion chromatography (IC) has a domi-

nant position among the separation methods used for the determination of inorganic anions [1,2].

As a consequence, an IC method has been developed in order to analyse chloride, nitrate, sulphate and phosphate in industrial hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) samples [3]. This method consists of a matrix elimination and an enrichment step followed by gradient elution. However, organic acids, still present in the  $\text{H}_2\text{O}_2$  samples due to the production process, can interfere with the chloride and sulphate determination.

Capillary zone electrophoresis (CZE) presents a suitable alternative for the determination of the above-mentioned anions. As the separation is based on the effective mobility in an electric field, con-

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ditions should be found in which the interference of organic acid in the determination of inorganic ions should be avoidable.

Unfortunately, a limiting factor in the application of CZE are the attainable limits of detection (LODs) which are about  $10^{-6}$  mol/l [4–6] for 25–75  $\mu\text{m}$  I.D. capillaries and indirect photometric detection.

A straightforward way to lower the LODs is the use of a more sensitive detection method and/or the use of capillaries of greater I.D. linked with an enlarged sample loadability.

Conductivity detection has shown its capability in connection with CZE [7–11] and isotachopheresis (ITP) [12,13].

Although the use of capillaries of greater I.D. is not very common, reports dealing with CZE separations in capillaries of 200–300  $\mu\text{m}$  I.D. clearly show their analytical benefits, especially in terms of attainable LODs [14–17].

Kaniansky et al. [18] showed the determination of inorganic anions in environmental samples, mainly in rain, river and drinking water by the use of 300  $\mu\text{m}$  I.D. capillaries in a closed CZE system.

It is the aim of this paper to extend the application of CZE with capillaries of larger I.D. to industrial matrices, while  $\text{H}_2\text{O}_2$  of electronic grade seems to be a convenient example of a very important chemical product of current interest and high purity requirements.

## 2. Experimental

### 2.1. Instrumentation

An ItaChrom EA 101 (Merck, Darmstadt, Germany) isotachopheresis/electrophoresis instrument was used in the single capillary configuration. The capillary made of fluorinated ethylene–propylene (FEP) copolymer had an I.D. of 300  $\mu\text{m}$  (O.D.=700  $\mu\text{m}$ ). The length was 23 cm (20 cm to the detector). The capillary tube was placed in a compartment made of plexiglas, allowing heat dissipation produced on the passage of current. The samples were injected with the aid of a 350- $\mu\text{l}$  injection valve. For data evaluation and processing the ITP-WIN 2.21 was used.

IC experiments were carried out with a DX 500 IC

system (Dionex, Idstein, Germany) consisting of a chromatographic module a gradient pump and a conductivity detector. The separation column was an IonPac AS12A 4 mm anion-exchange column. The respective guard column was an IonPac AG12A 4 mm. A TAC-2 column was used for concentration of the hydrogen peroxide samples. Conductivity detection was performed with an anion self regenerating suppressor (ASRS-II 4 mm) in the recycle mode.

Data collection and processing were carried out by a chromatographic data system (PeakNet 4.3, Dionex).

### 2.2. Chemicals

The following chemicals were used: succinic acid, sodium hydrogencarbonate, sodium carbonate, all analytical-reagent grade, from Merck; 1,3-bis-[tris(hydroxymethyl)methylamino]propane (BTP) (BioChemika) from Fluka (Buchs, Switzerland); polyvinylpyrrolidone (PVP) K90 from Serva (Heidelberg, Germany); purified methylhydroxyethylcellulose (MHEC) 1% stock solution from Laboratory of Environmental Analysis and Services, Comenius University, (Bratislava, Slovak Republic). Anion standard solutions of chloride, nitrate, sulphate, fluoride and phosphate of 1000 mg/l were obtained from Merck. All solutions, electrolytes, eluents and standards were produced using ultra-pure water from a Seral PRO 90 C system (Seral, Ransbach-Baumbach, Germany) with a conductivity of less than 0.1  $\mu\text{S}/\text{cm}$ .

## 3. Results and discussion

### 3.1. CZE separation

The absolute mobilities of the analytes are very close, showing only small mobility differences [19]. Therefore, a CZE separation by the optimisation of the pH value is not practicable. To enhance the resolution of the analytes different additives in the background electrolyte (BGE) are necessary. In connection with these additives we followed the suggestions made by Kaniansky et al. [18] who proposed PVP and BTP to be added to the electrolyte system. Only slight modifications in the concen-

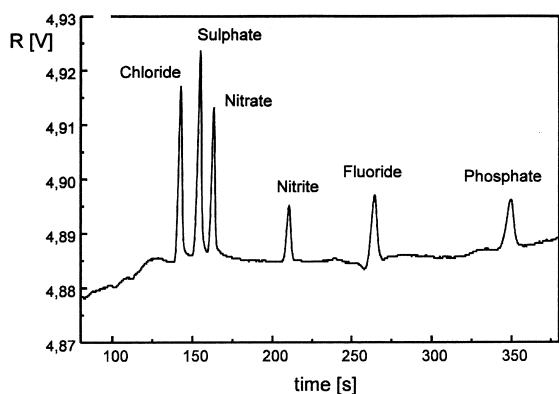


Fig. 1. CZE separation of inorganic anions at pH=3.4. The electrolyte system consisted of 7 mmol/l succinic acid with BTP as counterion, 0.1% MHEC and 5% PVP. A current of 20  $\mu$ A was used. Chloride (177  $\mu$ g/l), sulphate (480  $\mu$ g/l), nitrate (310  $\mu$ g/l), nitrite (230  $\mu$ g/l), fluoride (95  $\mu$ g/l), phosphate (475  $\mu$ g/l). R=Resistance.

tration of some of the additives lead to the electrolyte system used in our investigations. The electrolyte system consisted of 7 mmol/l succinic acid with BTP as counterion, 0.1% MHEC and 5% PVP. The pH value of the system was 3.4. With regard to the potential interferences in the determination of the inorganic anions due to organic compounds present in the  $H_2O_2$  samples, a low pH value was preferred. Through the low pH value in the BGE the degree of dissociation of organic species can be decreased, generating in this way sufficient mobility differences between the analytes and organic constituents. In addition, PVP is known for its property to decrease the effective mobility of some organic compounds which need to be considered [20]. Fig. 1 shows the

separation of the analytes of interest. Table 1 summarises some performance parameters of the CZE separation. It is obvious that the system provided reproducible migration times with typical values for the relative standard deviation (R.S.D.) in the range from 0.23–2.60%. The values for the peak areas fluctuated around 5%. A possible reason for the high R.S.D.s may originate from a possible decomposition of the hydrogen peroxide during the time needed for the CZE separation.

The separation efficiencies, expressed in numbers of theoretical plates per meter, were somewhat unexpected in consideration of the I.D. of the capillary but understandable bearing in mind the low concentration of the BGE.

### 3.2. IC analysis of hydrogen peroxide

A modified approach was performed in our experiments; in contrast to Ref. [3] an isocratic system with a different eluent and different ion-exchange columns were used. The reasons for using an isocratic technique are founded in a better long-term stability and reproducibility compared to the NaOH gradient elution. The routine analysis using NaOH is impaired due to absorption of  $CO_2$  leading to carbonate signals and concentration changes in the eluent. Moreover, in a strong alkaline solution chemical reactions of the  $H_2O_2$  may occur.

The IC method combined a matrix elimination and a concentration step followed by the chromatographic separation. The sample loop volume of 750  $\mu$ l was first passed through the concentrator column TAC-2 against the flow direction. In this way the containing anionic impurities were retained and the  $H_2O_2$  was

Table 1  
Separation efficiency and reproducibilities in the CZE separation

Anion	Separation efficiency, $l = 20 \mu$ A	R.S.D. migration time (%)	R.S.D. peak area (%)
Chloride	113 580	0.25	5.8
Sulphate	127 255	0.72	4.3
Nitrate	139 405	0.23	4.5
Nitrite	141 015	2.06	6.5
Fluoride	135 435	2.70	4.8
Phosphate	144 780	0.41	5.0

The data were obtained from six runs.

The separation efficiency is expressed in theoretical plates per meter.

brought into the waste. The column was then flushed with eluent in order to elute the retained anions towards the IonPac AG12A 4 mm and the IonPac AS12A 4 mm separation column, where the retained anions were separated.

Fig. 2 (top) shows a chromatogram of the ions of interest, demonstrating that the analytes elute within 20 min. In Fig. 2 (bottom) the application of the IC method to  $H_2O_2$  of electronic grade is illustrated. The problems in the determination of chloride and sulphate are obvious. The chloride peak is not baseline resolved from the predominate peak, probably assigned to short chain acids such as formic and acetic acid. The sulphate peak with a retention time of 18 min is broadened due to dispersion effects.

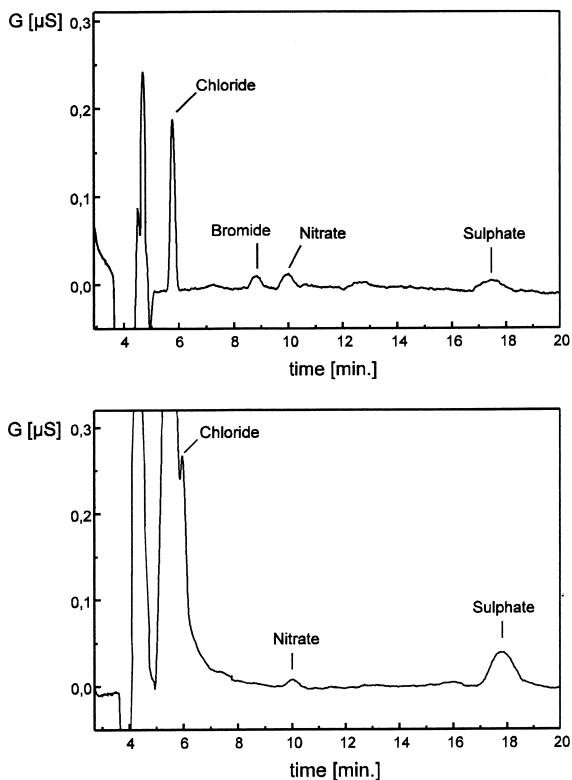


Fig. 2. Chromatograms of an anion standard with a concentration of  $5 \mu\text{g/l}$  (top) and a 31% electronic grade hydrogen peroxide sample (below). Both separations were performed with the following conditions; eluent:  $1.3 \text{ mM NaHCO}_3$  and  $1.4 \text{ mM Na}_2\text{CO}_3$ , columns: TAC-2, AG12A, AS12A, eluent flow-rate:  $1.8 \text{ ml/min}$ , detection: CD20 with suppression, sample loop:  $750 \mu\text{l}$ . G=Conductivity.

Furthermore it is known that close to the retention time of sulphate other organic compounds, mainly divalent organic acids, can be detected [3]. Therefore it is sometimes uncertain whether the sulphate peak consist of sulphate on its own or not.

The purity requirements for the hydrogen peroxide of electronic grade were defined as follows: chloride:  $<10 \mu\text{g/l}$ , sulphate:  $<20 \mu\text{g/l}$ , nitrate:  $<50 \mu\text{g/l}$ .

By comparing the separation of the anion standard with the  $H_2O_2$  sample it can be seen that the above requirement was fulfilled.

The quantification of the analytes was executed by using the average peak areas of three measurements of anion model standards with a concentration of  $5 \mu\text{g/l}$  as a reference (Fig. 2). These three standards were recorded each time prior to the analysis of the peroxide samples.

### 3.3. CZE analysis of hydrogen peroxide

With regard to the potential problems in the determination of chloride and sulphate in IC it was our aim to develop a CZE separation providing an alternative method for the analysis of anionic contaminants in  $H_2O_2$ . For obvious reasons we focused our investigations on the ions chloride, sulphate and nitrate, which were the analytes of interest, despite the necessity of ensuring that the CZE determination was able to work in the low  $\mu\text{g/l}$  range.

Recording calibrations lines offers a convenient way to verify the desired working range. We followed this approach by decreasing the concentration of the analytes successively.

Table 2 shows the measured calibration lines illustrating the working range as being in the low  $\mu\text{g/l}$  range and thus covering the purity demands of the  $H_2O_2$ . Furthermore, as can be seen a good linearity with four (chloride) and/or five (sulphate and nitrate) calibration levels was obtained.

The peroxide samples were stored and handled in polyethylene vessels in order to avoid contamination, adsorption and desorption processes, respectively. If glassware was used the flasks were filled with ultra pure water and treated in the ultrasonic bath for 2 min before use. This precautions were taken due to the ubiquitous presence of the anionic analytes, especially in the concentration range we had to deal with.

Table 2  
Calibration equation, parameters and LODs of the respective anions

Anion	Calibration equation	Range ( $\mu\text{g/l}$ )	$r$	$n$	LOD ( $\mu\text{g/l}$ )
Chloride	$y=4.305+1.794x$	5–100	0.9998	7	3
Sulphate	$y=4.443+1.055x$	5–100	0.9993	8	4
Nitrate	$y=0.941+0.334x$	10–100	0.9979	8	5

$r$  = Correlation coefficient.

$n$  = Number of calibration points.

The  $\text{H}_2\text{O}_2$  was injected directly by means of a CZE injection valve. Fig. 3 shows an electropherogram of  $\text{H}_2\text{O}_2$  of electronic grade (top) and a  $10 \mu\text{g/l}$  anion standard (below). A drift in the baseline in this low  $\mu\text{g/l}$  range was unavoidable.

By comparing both signals it is apparent that the peroxide sample fulfilled the above-mentioned purity requirements. Furthermore it can be seen that no organic compound (peak with a retention time about 5 min in Fig. 2) migrates in the CZE time window. This fact demonstrates the above-mentioned claims concerning the conditions of the CZE separation.

Quantification was performed with the aid of the calibration lines (Table 2), already recorded; three independent measurements were used for the calculation. As a result the sample plotted in Fig. 3 contained  $6.7 \mu\text{g/l}$  chloride,  $7.1 \mu\text{g/l}$  sulphate and  $8 \mu\text{g/l}$  nitrate.

The LODs for the ions of interest were estimated in the classical way based on the work of Hubaux

and Vos [21] and Kaiser et al. [22,23], we used a factor 5 instead of 3.

$$\text{LOD} = x_{\text{bl}} + 5\sigma_{\text{bl}} \quad (1)$$

where  $\sigma$  = standard deviation of the blank value and  $x_{\text{bl}}$  = blank value.

Under our working conditions, using 350 nl injection and a  $20 \mu\text{A}$  driving current, the LODs in Table 2 clearly confirm that the CZE with enlarged sample loadability is a powerful tool.

Comparing the LODs with the data of conventional CZE with narrow bore capillaries, as referred to in the introduction, a significant improvement can be observed.

### 3.4. Comparison of the IC and CZE determination

In order to compare both methods four hydrogen peroxide samples were analysed by IC and CZE simultaneously (Fig. 4).

We did not consider a non quantitative elution from the TAC-2 column in the IC method as being a possible source of error.

The following conclusion can be drawn from Fig. 3: significantly higher values for the ions chloride and nitrate ions and slightly lower values for sulphate were found by the CZE method.

As it is shown in the IC determination (Fig. 2), the chloride peak is a shoulder of the large peak consisting of monovalent organic acids. Due to this overlapping the interpretation of the chloride peak is hindered. The lower values for chloride in the IC are therefore explainable by the non-existing baseline resolution.

With regard to the sulphate content measured by ion chromatography the remarks made in the introduction should be considered. Because of the slightly

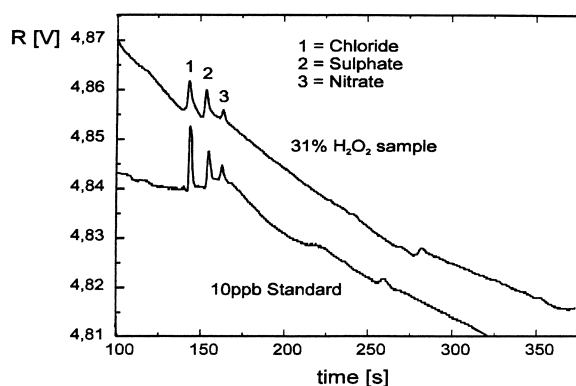


Fig. 3. Electropherogram of a 31%  $\text{H}_2\text{O}_2$  sample (top) and a  $10 \mu\text{g/l}$  anion standard (below). Conditions as in Fig. 1. 1 = Chloride ( $6.7 \mu\text{g/l}$ ), 2 = sulphate ( $7.1 \mu\text{g/l}$ ), 3 = nitrate ( $8 \mu\text{g/l}$ ). R = Resistance.

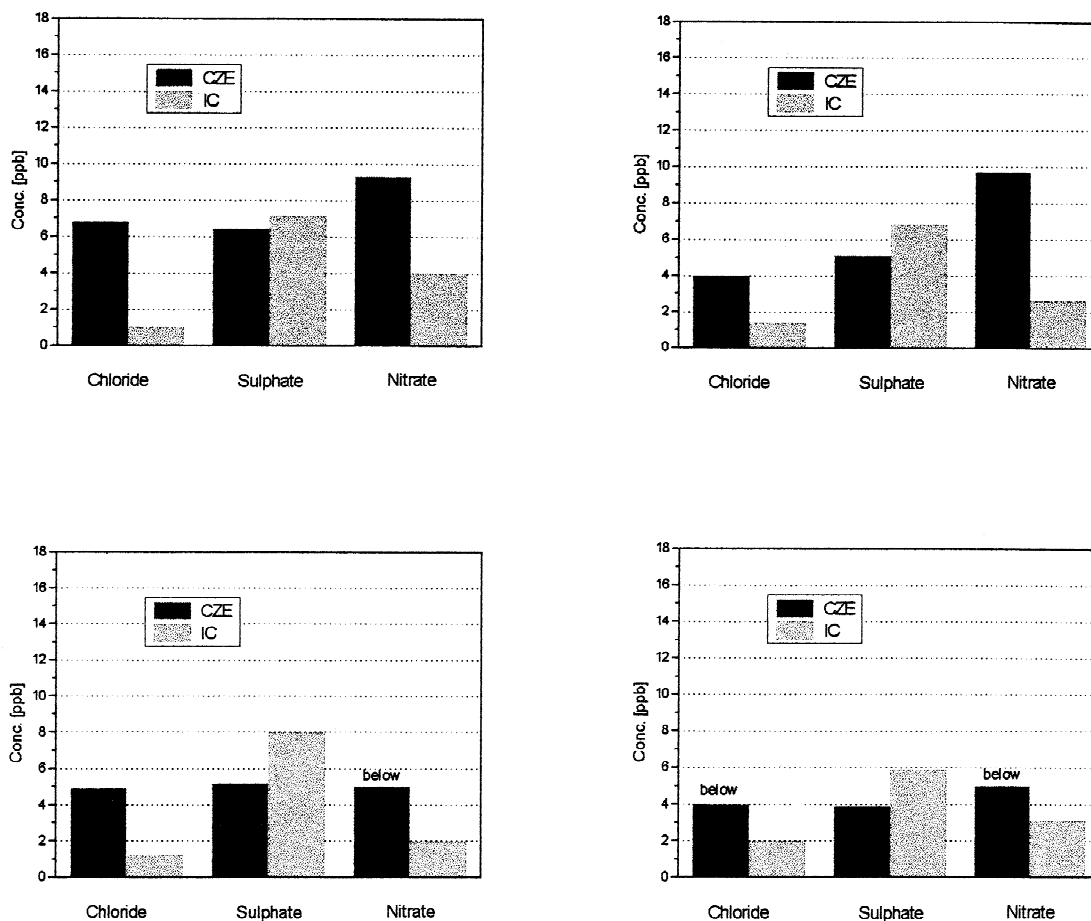


Fig. 4. Comparison of the IC and CZE determination of anions in hydrogen peroxide. The concentration values found by the IC and CZE method are shown. Conditions as in Fig. 1 for the CZE determination and as in Fig. 2 for the IC separation were applied for the determination of the respective ions.

higher values found in IC, it seems to be that organic compounds may coelute with the sulphate peak.

In the case of the nitrate ion, it must be stated that the difference between IC and CZE may have originated from the CZE method. As can be seen in Fig. 3 the nitrate peak is only small; therefore slight changes in peak areas resulted in relatively large fluctuations of concentration.

Of course, the higher values of chloride and nitrate could be explained by contamination. However, we would like to exclude this source of error due to the fact that the samples were strictly handled in polyethylene vessels and one-way syringes. Additionally, a CZE injection valve made of PTFE was used.

Taking into consideration the analysis time of only 6 min for CZE (as compared to 20 min for IC) the additional advantage of potential time and personnel savings with the CZE method are evident.

#### 4. Conclusions

It has been shown that CZE provides a promising alternative to the determination of inorganic anions. Due to the enhanced sample loadability of capillaries with greater I.D. the working range could be extended to the low  $\mu\text{g/l}$  range without pre-concentration and/or sample pre-treatment. Hence, hydrogen

peroxide of electronic grade could be checked for the content of anionic impurities. By using a low pH of the BGE, potential interferences caused by organic compounds in the IC method could be excluded.

The advantage of the CZE include short analysis time and ease of operation.

A further improvement linked with larger sample volumes can be expected; our prospective investigations will deal with this opportunity.

### Acknowledgements

The authors wish to thank Mrs. A. Gruber (Merck, Germany) for the ion chromatographic measurements and Professor Dr. Kaniansky (Comenius University, Bratislava, Slovak Republic) for the helpful discussions and suggestions.

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