

# Capillary electrophoresis as a useful tool for the analysis of chemical tracers applied to hydrological systems

V. Martínez<sup>a</sup>, N. García<sup>a</sup>, I. Antigüedad<sup>b</sup>, R.M. Alonso<sup>a,\*</sup>, R.M. Jiménez<sup>a</sup>

<sup>a</sup> *Departamento de Química Analítica, Facultad de Ciencias, Universidad del País Vasco/EHU, Apdo. 664, 48080 Bilbao, Spain*

<sup>b</sup> *Grupo Hidrogeología, Departamento de Geodinámica, Facultad de Ciencias, Universidad del País Vasco/EHU, Apdo. 664, 48080 Bilbao, Spain*

## Abstract

A capillary electrophoretic method was optimised for the separation and determination of iodide used as artificial tracer in hydrology. The influence of the buffer concentration and pH, electroosmotic flow modifier concentration (cetyltrimethylammonium bromide (CTAB)), the injection time and voltage applied, on the electrophoretic separation was studied. A running buffer of 20 mM phosphate (pH 8) containing 1 mM CTAB was found to provide the optimum separation of iodide with respect to resolution, migration time and selectivity. The water samples were injected hydrostatically at 10 cm for 110 s, the voltage applied was  $-20$  kV and a detection wavelength of 214 nm. The influence of the sulphite added to water samples in order to prevent the oxidation of iodide to iodate was also studied. This method can be applied to the determination of iodide free of sulphite interference up to at least a ratio of 1:1000 ( $I^-:SO_3^{2-}$ ). The other inorganic anions, which are present in the water samples (mainly chloride, sulphate, nitrate, carbonate), do not interfere with the determination of iodide. This method allows the simultaneous determination of bromide, nitrite, and nitrate together with iodide. The electrophoretic method showed to be linear from 0.5 to 5 mg l<sup>-1</sup> of iodide (the migration time was 2.6 min) with a quantitation limit of 0.45 mg l<sup>-1</sup> and a intraday repeatability lower than 4% of R.S.D. at different concentration levels.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Water analysis; Iodide; Sulphite; Inorganic anions

## 1. Introduction

In environmental studies, determination of common inorganic anions, such as fluoride, chloride, bromide, nitrite, nitrate and sulphate is a significant component in the characterisation of the quality and extent of pollution in water. It is also a fundamental analytical task required to address many diverse questions in science studies.

Accurate and reliable analytical data of chemical species present in such water samples are essential to understand the physical and chemical processes in water systems. Hydrogeologists promote the use of chemicals as tracers for the quantification of flow and transport processes in hydrological systems.

Potassium iodide (KI) is the iodine-containing compound, most commonly used as tracer in hydrogeology. It shows a solubility of 1.2 kg l<sup>-1</sup> in cold water and it is not toxic at the

concentration used. Its determination is commonly interfere with  $S^{2-}$ ,  $CN^-$ ,  $Br^-$ , and  $Cl^-$  (cited in order of interference strength). Iodide can be chemically and microbiologically converted [1]. Behrens [2] added sulphite to the samples to be investigated to prevent oxidation to iodate. He also described the incorporation of iodide to organisms. Therefore, it follows that iodide is only suitable as tracer for short flow distances. In the literature, 1 g Na<sub>2</sub>SO<sub>3</sub> in 100 ml of water is the concentration recommended [3].

The recovery rates resulting from the few tracing test using KI carried out up to now in the Basque Country, have always been very low. Recovery rates below 30% have been reported in a karstic aquifer whereas other tracers assayed simultaneously, such as LiCl, provided recovery rates above 90%. The improvement in the analytical technique for the separation and determination of iodide should allow a better knowledge of the recovery rates and hence, the identification of the flow and transport processes that occur.

The determination of iodide is very important in a variety of fields, such as food, clinical and biological science [4], industrial [5], and also environmental [6] applications.

\* Corresponding author.

E-mail address: [qapalror@lg.ehu.es](mailto:qapalror@lg.ehu.es) (R.M. Alonso).

A variety of analytical techniques have been used for the determination of iodide, including atomic absorption spectroscopy [7], ion chromatography [8], potentiometry [9,10], inductively coupled plasma-atomic emission spectrometry [11] and voltammetry [12,13]. The main disadvantage of some methods is that a two-step procedure (chemical reactions and determination) should be used. These procedures do not satisfy all requirements for routine analysis because of their complicated process design or the need of expensive instruments.

During recent years, capillary electrophoresis (CE) has become established as a powerful technique for the separation and determination of inorganic anions since it offers efficient and rapid separations for these ions. Iodide also has been determined by capillary zone electrophoresis in standard solutions [14], commercial antiseptics [4], and artificial seawater [15].

Alkylammonium surfactants, such as cetyltrimethylammonium bromide (CTAB) or tetradecyltrimethylammonium bromide (TTAB) are commonly added to the electrolyte to reverse the electroosmotic flow (EOF) for anion separation [16]. In addition to acting as flow modifiers, it was noted that the concentration of alkylammonium surfactants affects the migration times of some inorganic anions through ion pairing interactions [17,18]. Also, varying the electrolyte concentration and pH of the background buffer can change the degree to which the analyte interacts with the surfactant and its resultant migration time [14].

The aim of this work is the development of a simple capillary electrophoretic method for the separation and determination of iodide used as artificial tracer in hydrology. So, an optimisation study of the technique variables: pH and buffer concentration (phosphate buffer), electroosmotic flow modifier concentration (CTAB), the injection time and voltage applied were carried out.

## 2. Experimental

### 2.1. Apparatus

This work was performed on Waters Quanta 4000E capillary electrophoretic system (Milford, MA, USA). Electropherograms were collected and data treated using the Millennium 32 Chromatography Manager software (Waters Chromatography Division, Barcelona, Spain).

This method uses a 58 cm  $\times$  75  $\mu\text{m}$  i.d.  $\times$  375  $\mu\text{m}$  o.d. fused-silica capillary (Composite Metal Services, Worcester, UK) with a portion of the capillary's outer coating removed to act as the detection window. The effective separation length up to the detection window was 50 cm.

All pH values were measured with a Crison GLP 22 pH-meter (Barcelona, Spain), calibrated immediately prior to use, employing a Crison glass-combined electrode model 52-01 equipped with a reference system Ag/AgCl and electrolyte 3 M KCl saturated in AgCl.

### 2.2. Electrophoretic conditions

A buffered aqueous electrolyte solution containing electroosmotic flow modifier was used. The running buffer of 20 mM phosphate (pH 8) containing 1 mM CTAB was found to provide the optimum separation of iodide with respect to resolution, migration time and selectivity.

An electric field was generated by applying  $-20$  kV of voltage using a negative power supply (current 58  $\mu\text{A}$ ). This defines the detector end of the capillary as the anode. UV detection was achieved at the anodic end of the capillary with a mercury lamp using a 214 nm optical filter.

Samples were injected hydrostatically at the cathodic end of the capillary for 110 s at 10 cm. The capillary temperature was kept at  $30.0 \pm 0.1^\circ\text{C}$ . Prior to the first analysis, the capillary was rinsed for 5 min with 0.1 M sodium hydroxide, 5 min with deionized water and 5 min with the running electrolyte. All analysis was preceded by a 2 min purging time with the carrier electrolyte to clean the capillary.

### 2.3. Chemical reagents

All of the chemicals used were of analytical reagent grade and were used without further purification. Dipotassium hydrogenphosphate, potassium dihydrogenphosphate anhydrous, sodium hydroxide, and potassium iodide were obtained from Merck (Bilbao, Spain). Sodium sulphite was obtained from Probus (Bilbao, Spain).

Cetyltrimethylammonium bromide (Sigma-Aldrich, Bilbao, Spain) was used as electrophoretic modifier. Anion standard solutions of each ion containing 1000  $\text{mg l}^{-1}$  of nitrite, nitrate, bromide, chloride, and sulphate were purchased from Merck.

Diluted standard and buffer solutions were prepared with ultrapure water produced from a Milli-RO, Milli-Q water purification system ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) (Millipore, Bedford, MA, USA). Water samples were obtained from the Alegria River in Vitoria-Gasteiz (Spain) and stored in dark at  $4^\circ\text{C}$ .

### 2.4. Standards solutions and buffer preparation

The 1000  $\text{mg l}^{-1}$  iodide stock solution was prepared by dissolving potassium iodide in deionized water and stored in the dark at  $4^\circ\text{C}$ . Fresh stock solution was daily prepared. Dilutions of this stock solution were performed at the appropriate analyte concentration.

The different separation electrolyte solutions were prepared by mixing the adequate volumes of the stock solutions of 0.1 M phosphate buffer and 5 mM electroosmotic flow modifier, to give the desired pH and concentration of the electrolyte. The pH of the phosphate buffer was adjusted before the addition of the electroosmotic flow modifier. Fresh working electrolyte was daily prepared.

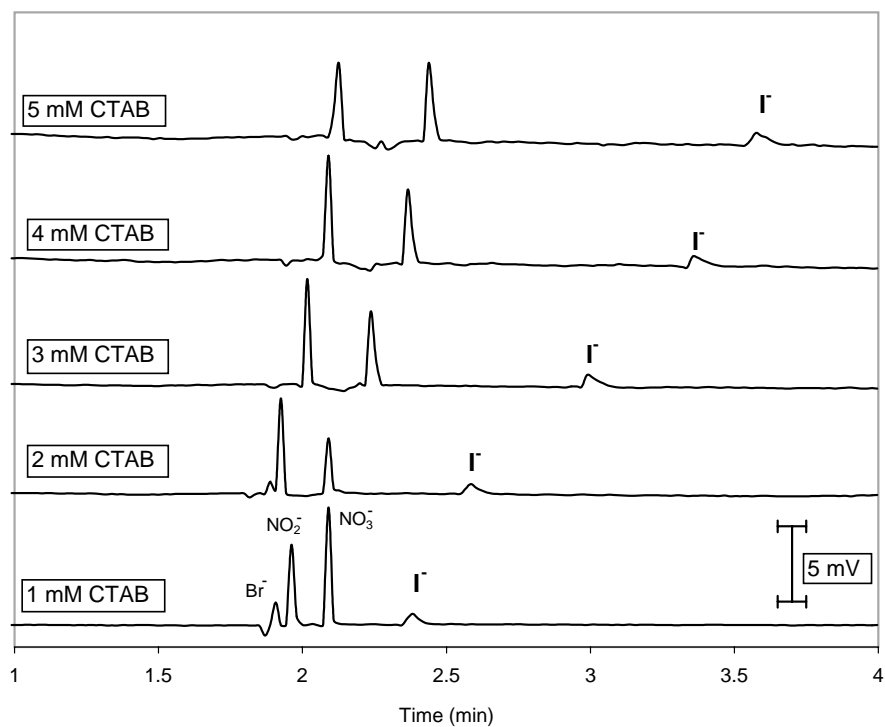


Fig. 1. Influence of the CTAB concentration on the resolution of inorganic anions: bromide, nitrite, nitrate and iodide ( $10 \text{ mg l}^{-1}$  each). Electrophoretic conditions: 20 mM phosphate buffer (pH 8);  $V = -20 \text{ kV}$ ;  $\lambda = 214 \text{ nm}$ ;  $t_{\text{inj}} = 30 \text{ s}$ .

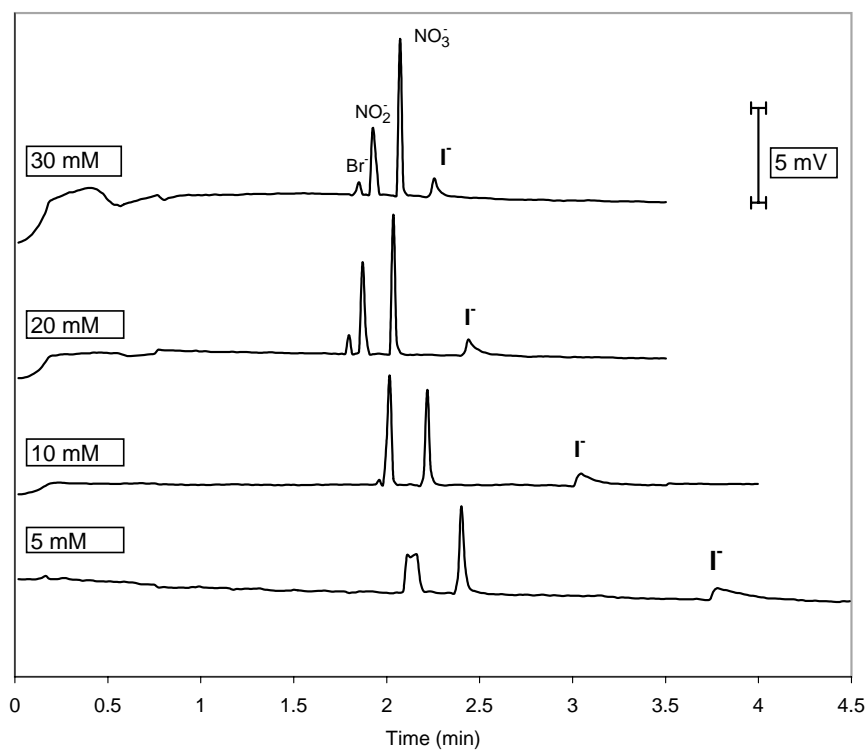


Fig. 2. Influence of the phosphate buffer concentration on the resolution of inorganic anions: bromide, nitrite, nitrate and iodide ( $10 \text{ mg l}^{-1}$  each). Electrophoretic conditions: 1 mM CTAB; phosphate buffer (pH 8);  $V = -20 \text{ kV}$ ;  $\lambda = 214 \text{ nm}$ ;  $t_{\text{inj}} = 30 \text{ s}$ .

### 3. Results and discussion

#### 3.1. Optimisation of the electrophoretic conditions

Initially, the conditions used for the optimisation study were 20 mM phosphate buffer (pH 8) containing 2 mM CTAB. An electric field of  $-20$  kV was applied, UV detection was set at 214 nm and samples were injected hydrostatically for 30 s at 10 cm.

In the above experimental conditions, the following inorganic anions were assayed: chloride, bromide, nitrite, nitrate, sulphate and iodide. The major anions present in water (mainly chloride, nitrate, sulphate and carbonate) do not interfere with iodide determination since chloride, sulphate and carbonate are not absorbent at 214 nm. So, only bromide, nitrite and nitrate could be quantified together with iodide.

In an attempt to achieve a better resolution in the separation of these anions, the effect of the concentration of the cetyltrimethylammonium bromide as electroosmotic flow modifier (1–5 mM) was studied. The increment of CTAB concentration gives rise to higher migration times, the overlapping of bromide and nitrite peaks and a greater difference between nitrite and nitrate migration times (Fig. 1). The electrophoretic mobility of the bromide, nitrite and nitrate peaks, shows slight decrease, as the surfactant concentration is increased and the iodide mobility shows a sharp

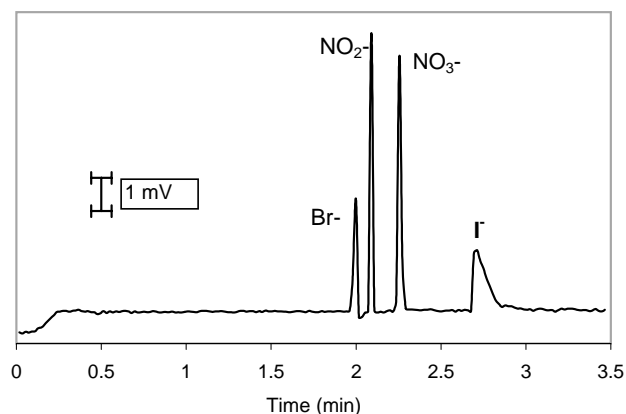


Fig. 4. Electropherogram of a standard solution of bromide ( $5 \text{ mg l}^{-1}$ ), nitrite ( $1 \text{ mg l}^{-1}$ ), nitrate ( $1 \text{ mg l}^{-1}$ ) and iodide ( $5 \text{ mg l}^{-1}$ ). Electrophoretic conditions: 1 mM CTAB; 20 mM phosphate buffer (pH 8);  $V = -20$  kV;  $\lambda = 214$  nm;  $t_{\text{inj}} = 110$  s.

decrease due to stronger interactions with the surfactant. A CTAB concentration of 1 mM was chosen as optimum.

The study of the pH effect on the electrophoretic separation was made using 1 mM CTAB in 20 mM phosphate buffer. The pH was varied from 6 to 9. An increase of the pH value provides a better resolution of the electrophoretic peaks. Although the EOF increases, the migration times of bromide, nitrite and nitrate are very similar. Only the

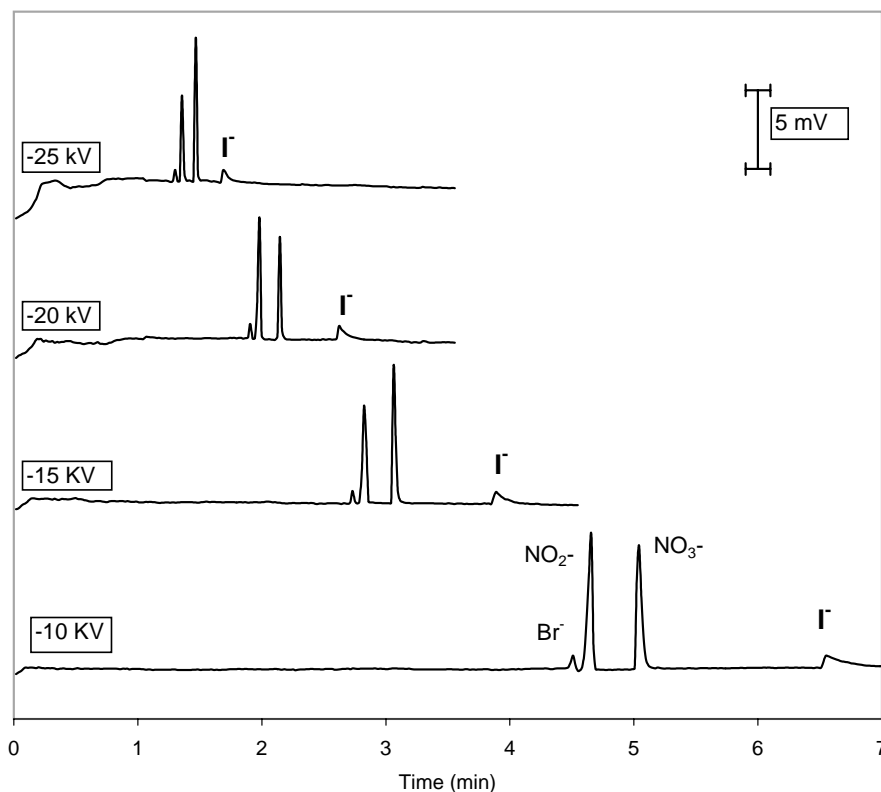


Fig. 3. Effect of the voltage applied on the separation of inorganic anions: bromide, nitrite, nitrate and iodide ( $10 \text{ mg l}^{-1}$  each). Electrophoretic conditions: 1 mM CTAB; 20 mM phosphate buffer (pH 8);  $\lambda = 214$  nm;  $t_{\text{inj}} = 30$  s.

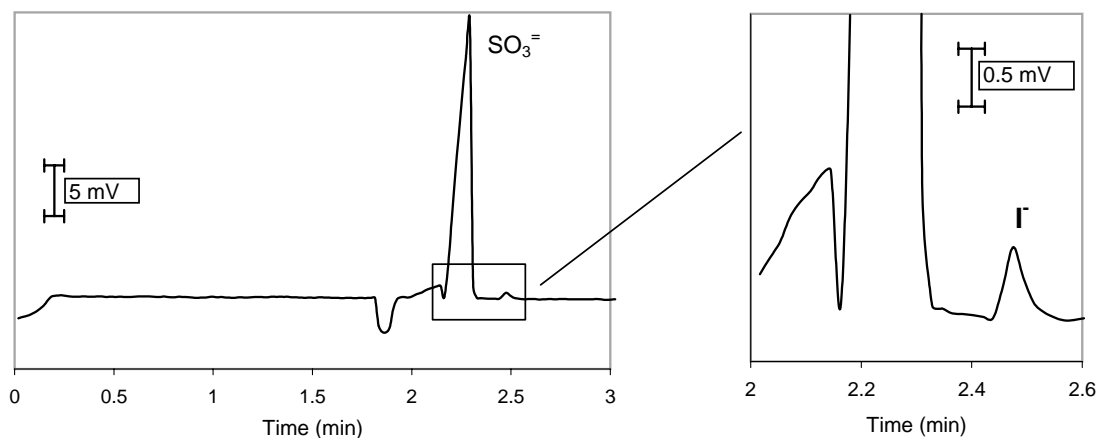


Fig. 5. Electropherogram of a standard solution of sulphite ( $1000 \text{ mg l}^{-1}$ ) and iodide ( $1 \text{ mg l}^{-1}$ ). Electrophoretic conditions:  $1 \text{ mM CTAB}$ ;  $20 \text{ mM phosphate buffer (pH 8)}$ ;  $V = -20 \text{ kV}$ ;  $\lambda = 214 \text{ nm}$ ;  $t_{\text{inj}} = 110 \text{ s}$ .

electrophoretic mobility of iodide enhances, as the pH value becomes higher. At pH 6, the overlapping of nitrite and bromide occurs. Despite of pH 8 is considered as the most adequate with respect to resolution and migration time, a wide range of pH values (7–9) can be used for the separation and determination of bromide, nitrite, nitrate and iodide.

The influence of the phosphate buffer concentration (5–30 mM) on the electropherograms of the anions is shown in Fig. 2. An increase of the concentration produces a decrease of the migration times of bromide, nitrite and nitrate and an improvement of the resolution of the electrophoretic peaks. Again, this effect is greater for iodide; its electrophoretic mobility shows a sharp decrease as the phosphate buffer concentration increases and leads to shorter migration times. Phosphate buffer (20 mM) was used throughout the work since an overlapping of nitrate with iodide peaks would occur at high anion concentrations if a greater concentration of buffer is used.

In order to determine the optimum voltage applied, electropherograms were obtained at different voltage from  $-10$  to  $-25 \text{ kV}$ . As can be seen in Fig. 3, the whole voltage range studied can be used for the separation and determination of bromide, nitrite, nitrate and iodide. A voltage of  $-20 \text{ kV}$  was chosen as optimum since gave rise to adequate resolution and migration times.

Finally, the influence of the injection time was studied (30–120 s). An optimal injection time of 110 s was selected since peak-height saturation occurs above this value for iodide.

### 3.2. Analytical applications

In Fig. 4, the electropherogram for a standard solution of bromide, nitrite, nitrate and iodide in the optimum conditions is shown. The migration times for bromide, nitrite, nitrate and iodide are 1.99, 2.08, 2.23 and 2.60 min, respectively.

The influence of the sulphite added to water samples on the iodide determination was studied. This method allows

the determination of iodide free of sulphite interference up to at least a ratio of 1:1000 ( $\text{I}^-:\text{SO}_3^{2-}$ ) as can be seen in Fig. 5. This sulphite concentration makes not possible the determination of bromide, nitrite and nitrate together with iodide.

Once the optimum electrophoretic conditions had been established, a quantitative method for the determination of iodide was developed. Calibration curve was constructed by plotting electrophoretic peak area against iodide concentration and was fitted to the linear regression equation:  $y = a + bx$ . The electrophoretic method showed a linear relationship from  $0.5$  to  $5 \text{ mg l}^{-1}$  of the tracer in presence of bromide, nitrite and nitrate:  $y = (83 \pm 101) + (1225 \pm 76)x$  (the regression coefficient was 0.996). The within-day repeatability was determined by injecting six replicate samples of iodide, and R.S.D. values of 2.66% at  $1 \text{ mg l}^{-1}$  and 3.47% at  $5 \text{ mg l}^{-1}$  level concentration were obtained. The experimental quantitation limit, defined as the lowest concentration of iodide in a spiked water sample (obtained from the Alegria River in Vitoria-Gasteiz, Spain) which gives rise to a signal able to be quantified with a R.S.D. below 5% ( $n = 5$ ) was  $0.45 \text{ mg l}^{-1}$ .

## 4. Conclusions

The described capillary electrophoretic method has proved to be fast, simple and a useful tool for the separation and determination of iodide in water samples. The other anions which are present in the sample (mainly chloride, nitrate, sulphate and carbonate) do not interfere its determination. This method also allows the determination of bromide, nitrite and nitrate together with iodide. Complete separation of the four inorganic anions was reached in less than 3 min.

Sulphite added to prevent the oxidation of iodide to iodate does not interfere the determination of iodide, up to a ratio of 1:1000 ( $\text{I}^-:\text{SO}_3^{2-}$ ), but it does not allow the simultaneous analysis of bromide, nitrite and nitrate.

The developed method is the basis for the assay of iodide as a tracer in a hydrological system. This electrophoretic method will be applied to the determination of iodide in the effluents of the sewage treatment plant in a karstic swallow hole in order to identify the flow and transport processes of the Hydrological Unit of Ereñozar (Spain).

### Acknowledgements

This work was included as a part of the project REN2002-01705 (MCYT, Spanish Government).

### References

- [1] W. Käss, *Tracing Technique in Geohydrology*, Balkema, 1998, p. 581.
- [2] H. Behrens, *Steir. Beitr. Hydrogeol.* (1966/1967) 79.
- [3] A. Parriaux, M. Liskay, I. Müller, G. Della Valle, *Guide Pratique pour l'Usage des Tracers Artificiels en Hydrogéologie*, Groupe des Hydrogéologues, Société Géologique Suisse, 1988, p. 27.
- [4] V. Paliulionyte, A. Padaruskas, *Anal. Chim. Acta* 466 (2002) 133.
- [5] J.L. Fernández, J.F. Llorens, M. Carnicero, F. Valero, *Quim. Anal.* 19 (2000) 217.
- [6] K.A. Anderson, B. Casey, E. Diaz, P. Markowski, B. Wright, *J. AOAC Int.* 79 (1996) 751.
- [7] M.C. Yebra, R.M. Cespón, *Anal. Chim. Acta* 405 (2000) 191.
- [8] H.L. Tucker, R.W. Flack, *J. Chromatogr. A* 804 (1998) 131.
- [9] Y. Ni, A. Wu, *Anal. Chim. Acta* 390 (1999) 117.
- [10] T. Poursaberi, M. Hosseini, M. Taghizadeh, H. Pirelahi, M. Shamsipur, M.R. Ganjali, *Microchem. J.* 72 (2002) 77.
- [11] A. Dudoit, S.A. Pergantis, *J. Anal. At. Spectrom.* 16 (2001) 575.
- [12] I. Svancara, J. Konvalina, K. Schachl, K. Kalcher, K. Vytras, *Electroanalysis* 10 (1998) 435.
- [13] A. Walcarius, G. Lefevre, J.P. Rapin, G. Renaudin, M. Francois, *Electroanalysis* 13 (2001) 313.
- [14] J. Li, W. Ding, J.S. Fritz, *J. Chromatogr. A* 879 (2000) 245.
- [15] A. Lucy, M.A. Woodland, *Analyst* 126 (2001) 28.
- [16] W.R. Jones, P. Jandik, *J. Chromatogr.* 546 (1991) 445.
- [17] A.H. Harakuwe, P.R. Haddad, W. Buchbeger, *J. Chromatogr. A* 685 (1994) 161.
- [18] T. Kaneta, S. Tanaka, M. Taga, H. Yoshida, *Anal. Chem.* 64 (1992) 798.