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# Flow injection–capillary electrophoresis coupling to automate on-line sample treatment for the determination of inorganic ions in waters

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## Abstract

An automated interface for coupling flow injection (FI) systems with capillary electrophoresis (CE) has been developed and tested to combine the sample preparation capabilities of FI systems with the separation and determination provided by CE. To demonstrate the usefulness of such integration, two automated methodologies have been developed for on-line multiparametric monitoring of both anionic and cationic species in a water purification plant, to provide continuous control of the quality of the water. The concentration of anions such as chloride, nitrate, nitrite, sulphate and phosphate, of cations such as sodium, potassium, ammonium, calcium, magnesium, iron, and of heavy metals at trace level (e.g., manganese, aluminium, lead, cadmium), preconcentrated in the flow system, is provided in an integral manner by the operational procedure proposed in this paper. The determination limits established by legislation in OECD countries have been achieved demonstrating the potential of CE to be applied to real samples. © 1997 Elsevier Science B.V.

*Keywords:* Flow injection–capillary electrophoresis coupling; Anions; Cations

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## 1. Introduction

Continuous flow systems have great potential for solving a wide variety of analytical problems [1]. These systems offer major advantages for the analysis of liquid (especially water) samples, pretreatment of which is normally quite simple. However, although different alternatives have been proposed to perform multi-analyte determinations, based on the design of specific manifolds [2–5], the main and simpler applications developed are concerned with the determination of a single parameter. For many real applications, this aspect is a limitation, because a

different set of treatments is generally required for a given sample. This is the reason that much attention has been paid recently to the integration of flow systems with chromatographic separation techniques (see e.g. [6–9]).

Capillary electrophoresis (CE) is a simple, highly efficient, analytical separation technique for the analysis of aqueous species. It requires small volume samples with injection volumes in the picolitre to nanolitre range. CE is used in an ever-increasing range of applications (see last “Fundamental Reviews” in Analytical Chemistry, [10]), developing new methods that solve analytical separations and, in some cases, present interesting advantages compared to the corresponding chromatographic techniques.

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Automatic sample introduction in CE by on-line coupling with chromatographic methods [11–13], microdialysis [14] and precolumn reactions [15] is receiving increased attention. These approaches can provide alternatives for coupling CE with other hydrodynamic units for sample preparation.

In this work, an automated mechanical interface has been designed and validated for coupling flow injection (FI) pretreatment systems with CE equipment. This arrangement allows the combination of automatic on-line transportation of samples as well as the sample preparation capabilities of FI systems with the separation and determination possibilities that characterise CE. This assembly has demonstrated its potential usefulness for the on-line monitoring of anionic and cationic species during water treatment in a purification plant. Different CE methods have been reported for the determination of inorganic ions, in particular, those anions [16–19] and cations [20,21] that are of interest in this work. These existing methods needed to be adapted to the legislative requirements of OECD countries for drinking water. There have not been a lot of applications of CE to real samples (for instance, drinking water or sewage water). Consequently, there are a lot of practical problems to be solved, especially in the area of matrix effects or the limit of detection (LOD) required for the legislation. The main purpose of this work was the adaptation of a commercial CE to a FI system by a laboratory-made programmable arm, to automate the filling of CE sample vials and, thus, to achieve an on-line sample pre-treatment process. The final aim was to develop a working scheme that could be applied in water purification plants, which have a wide list of analytes that need to be controlled during the purification process.

## 2. Experimental

### 2.1. Chemicals

Standard and buffer solutions were prepared in purified (18 m $\Omega$ ) water using a Millipore milli-Q water purification system. Anion buffer: 2 mM dichromate potassium and 2 mM diethylene triamine (DETA), pH 7.5. Cation buffer: 4 mM formic acid, 4 mM copper sulphate and 3 mM 18-crown-6 ether,

pH 4.5. Stock standard solutions of 1000 mg/l NaCl, NaNO<sub>2</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, KBrO<sub>3</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, NH<sub>4</sub>Cl, LiCl, AlCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, MnCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub> and Cd(NO<sub>3</sub>)<sub>2</sub>, appropriately standardized, were used to prepare dilute solutions. Solutions of sodium hydroxide (0.1 M), nitric acid (2 M) and ammonium acetate (0.05 M) (all from Merck) were also used. A Chelex-100 cation-exchange resin 100–200 mesh (sodium form) (Sigma) was used. Prior to packing, the Chelex-100 resin was converted into the ammonium form by storing it in a large volumetric excess of 0.05 M ammonium acetate solution for two days, shaking the slurry intermittently, and renewing the solution two–three times each day. Finally, the resin was packed in a minicolumn.

### 2.2. Apparatus

A Beckman P/ACE 5500 capillary electrophoresis system equipped with a diode array detector and a fused-silica capillary (75  $\mu$ m internal diameter and 67 cm in length) was used for the separation and quantification of the analytes. A Gilson Minipuls-3 peristaltic pump, a Rheodyne 5041 injection valve and three selecting valves were also used. PTFE tubing (0.5 mm I.D.) was used to set up the manifold. The continuous filtration system was developed in our laboratory and tested with different types of microfilters from Millipore (pore sizes of 0.8, 0.45 and 0.22  $\mu$ m). A laboratory-made programmable arm (controlled by a microcomputer through an electronic interface) was used to automate the introduction of the sample to the CE sample vials.

### 2.3. Operating conditions

The running buffer that was used to analyse cations was a mixture of 4 mM CuSO<sub>4</sub>, 4 mM formic acid and 3 mM 18-crown-6 ether, pH 4.5, and it was used with a voltage of 20 KV and a temperature of 20°C. Samples were injected by hydrodynamic injection for 10 s. Electropherograms were recorded at 214 nm. The separation was carried out from the positive to the negative electrode. The running buffer that was used to analyse the anions consisted of 2 mM of both dichromate and DETA, at

pH 7.5, with a voltage of 30 kV and a temperature of 20°C. Samples were injected by hydrodynamic injection for 5 s. Electropherograms were recorded at 265 nm. The separation was carried out from the negative to the positive electrode. In both methods, the capillary was conditioned daily by washing it with ultrapure water (5 min) followed by freshly prepared 0.1 M sodium hydroxide (5 min), ultrapure water (5 min) and fresh buffer (10 min). In order to optimise the migration time and peak shape reproducibility, the capillary was flushed between analyses with 0.1 M sodium hydroxide (1 min), ultrapure water (2 min) and fresh buffer (2 min).

#### 2.4. Flow injection system

The FI manifold is shown in Fig. 1. The selection valve,  $SV_1$ , allowed the sequential introduction of water sample streams from different points of the water purification plant. These samples were continuously filtered before their introduction into the manifold. When preconcentration of the water sample was needed, valve  $IV_1$  was switched to the filling position, allowing the sample to pass through the Chelex-100 minicolumn, where heavy metals were preconcentrated. In this position, an appropriate volume of sample was passed through the column in order to allow amounts of analytes to be retained to obtain sensitive signals in CE afterwards. During this period, determination of the analytes that did not require preconcentration was performed (by the CE equipment). When the preconcentration was com-

plete, a small volume of 2 M  $HNO_3$  was injected through valve  $SV_3$ , in order to elute the analytes from the column, flowing in the opposite direction to the preconcentration step. Thus, a substantial reduction in the dispersion of analytes in the flowing stream was achieved. The fraction containing the eluted analytes was driven to a microvial of the CE sampler via activation of the programmable arm.

The FI system was coupled to the CE equipment via a programmable arm in order to automate the preliminary operations (e.g. preconcentration, filtration and sampling) and the introduction of samples to the autosampler of the CE equipment. An interface was designed between the CE system and the microcomputer that controlled the programmable arm and the peristaltic pump. The software of the commercial CE system also controlled the programmable arm, which has two needles of different lengths. The longer one was for filling the vial and the shorter one was a dispenser drain. The injection needles were connected to the FI system using FI tubes.

### 3. Results and discussion

#### 3.1. CE variables

To reduce peak distortion, the buffer chosen for anions consisted of 2 mM DETA and 2 mM dichromate, which presented an ionic equivalent conductivity that was close to that of chloride, nitrite and nitrate anions [16]. DETA was used in the buffer to

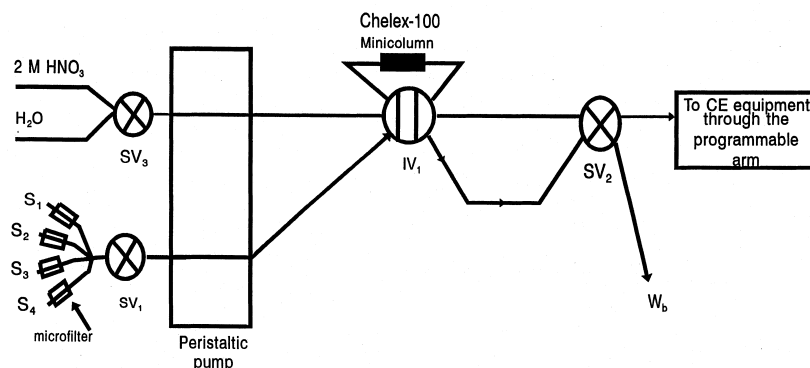


Fig. 1. Single FI system used for sample preparation/introduction in the CE system. IV=injection valve; SV=selecting valve; w=waste. (For details, see text)

reverse electro-osmotic flow. To separate the cations, the buffer chosen was a mixture of 4 mM CuSO<sub>4</sub>, 4 mM formic acid and 3 mM 18-crown-6 ether, pH 4.5. Because the electrophoretic mobilities of the cations studied are similar, the use of at least one chelating agent was required to increase the resolution. Because only a few inorganic ions can be detected by direct UV absorbance, indirect detection is widely employed in CE [17], and dichromate and CuSO<sub>4</sub> were used for this purpose. The pH of the buffer solution used for the separation can have a large effect on the separation of ions using capillary electrophoresis. The optimum pH values obtained for a good separation were 4.5 for cations and 7.5 for anions.

Values of 20 and 30 kV were chosen for cations and anions, respectively; a lower voltage provided no advantages in selectivity, sensitivity and analysis time. Hydrostatic injection was used as it showed better reproducibility in comparison to electromigration. An injection time of 5 s was sufficient for concentrations greater than 0.5 µg ml<sup>-1</sup> and 10 s were required for species that required lower detection limits. The optimum temperature was 20°C for both cations and anions. The same capillary was used to analyze cations and anions. The most appropriate wavelengths for quantification purposes were 214 nm (cations) and 265 nm (anions), which were the values finally selected.

### 3.2. FI variables

A sample volume of 25 ml was enough to achieve the sensitivity required for the cations that needed to be preconcentrated (Mn<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> and Al<sup>3+</sup>). Elution was performed with 200 µl of 2 M HNO<sub>3</sub>, flowing at 4 ml min<sup>-1</sup>. The exchange minicolumn containing Chelex-100 chelating resin in ammonium form was 70 mm long and 2 mm I.D. Under these conditions, the preconcentration time was 6 min, whereas a time of 20 s was needed for the eluting step. During this time, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and Fe<sup>2+</sup> were electrophoretically determined in the CE system, as no preconcentration was needed for these ions.

### 3.3. Calibration curves

First, the usefulness of the methods for the quan-

titative monitoring of both anions and cations in water samples was evaluated by means of calibration and reproducibility experiments. As shown in Table 1, valid calibration plots could be obtained for all anions and cations that were electrophoretically separated. Standard deviation of residuals ( $S_{y/x}$ ) and the curve-fitting level (in percent,  $R^2$ ), were obtained by ANOVA, for validation of the model. Values lower than ±0.15 were obtained for  $S_{y/x}$  in all cases, whereas  $R^2$  was always higher than 99.3% for the analytes determined. Detection limits of 0.05 µg ml<sup>-1</sup> were the objective for the parameters that needed preconcentration and 0.1 µg ml<sup>-1</sup> for the analytes that were determined directly in water. The limit of detection (LOD) was calculated from the blank value plus three times its standard deviation, whereas the limit of quantification (LOQ) was calculated from the blank value plus ten times its standard deviation. The maximum values tolerated by the legislation [22] are above the limit of detection for all anions and cations considered in this paper. The general determination range obtained for the anions and cations using hydrodynamic injection was 0.1 to 80 µg ml<sup>-1</sup>. By using the preconcentration step in the FI system, a generally more sensitive range can be obtained, i.e., 0.005 to 10 µg ml<sup>-1</sup>. For qualitative purposes, the addition of an internal standard becomes necessary to compensate for experimental fluctuations in the injection and separation processes. A number of ions were tested as internal standards. Among these ions, all of which are not expected to be found in water samples (at concentrations of above 0.1 ppm), lithium was chosen for the cation method and bromate for the anion method. For quantitative purposes, these internal standards were not used because no significant advantage was observed with respect to the external calibration method.

### 3.4. Analytical applications

First, electrophoretic methods had to be developed for the separation and quantification of both sets of analytes (anionic and cationic species in water samples). Some references can be found in the literature [16,17,20,23,24], but the final methods selected had to be adapted and optimized in order to cover the legal requirements for this kind of control.

Table 1  
Optimum conditions for the determination of cationic and anionic species by CE methods

Species	Equation	LOD	LOQ	Regulatory limit <sup>c</sup>
	( $y = a + bx$ )			
Fe <sup>3+</sup>	$a = 2.1E-3 \pm 9.0E-3$ $b = 0.25 \pm 1.8E-3$	0.1	0.36	0.2
NH <sub>4</sub> <sup>+</sup>	$a = 0.038 \pm 0.051$ $b = 0.966 \pm 0.022$	0.15	0.52	0.5
K <sup>+</sup>	$a = 0.03 \pm 0.03$ $b = 0.86 \pm 0.013$	0.1	0.34	12
Na <sup>+</sup>	$a = 0.021 \pm 0.03$ $b = 0.92 \pm 0.013$	0.09	0.32	150
Ca <sup>2+</sup>	$a = 0.015 \pm 0.022$ $b = 0.81 \pm 9.8E-3$	0.08	0.27	–
Mg <sup>2+</sup>	$a = -0.01 \pm 0.013$ $b = 1.18 \pm 5.7E-3$	0.03	0.1	50
Mn <sup>2+</sup>	$a = -5.48E-3 \pm 8.87E-3$ $b = 0.48 \pm 0.015$	0.05	0.18	0.05
Cd <sup>2+</sup>	$a = 7.04E-4 \pm 1.51E-3$ $b = 0.34 \pm 2.69E-3$	0.01	0.04	0.05
Pb <sup>2+</sup>	$a = -3.16E-3 \pm 5.7E-3$ $b = 0.81 \pm 0.01$	0.02	0.07	0.05
Al <sup>3+</sup>	$a = -8.42E-3 \pm 8.35E-3$ $b = 0.87 \pm 0.014$	0.02	0.095	0.2
Cl <sup>-</sup>	$a = -3.4E-3 \pm 0.03$ $b = 1.17 \pm 0.013$	0.07	0.25	–
NO <sub>2</sub> <sup>-</sup>	$a = 2.7E-3 \pm 0.011$ $b = 0.34 \pm 2.27E-3$	0.09	0.3	0.1
NO <sub>3</sub> <sup>-</sup>	$a = 8.8E-3 \pm 0.014$ $b = 0.28 \pm 2.8E-3$	0.15	0.5	50
SO <sub>4</sub> <sup>2-</sup>	$a = -2.78 \pm 0.019$ $b = 0.78 \pm 8.6E-3$	0.07	0.24	250
HPO <sub>4</sub> <sup>2-</sup>	$a = 0.023 \pm 0.03$ $b = 0.87 \pm 0.026$	0.1	0.34	–

$a$ =Intercept;  $b$ =slope; LOD=limit of detection; LOQ=limit of quantification; Concentrations, LOD and LOQ are expressed in  $\mu\text{g ml}^{-1}$ .  
<sup>c</sup> Maximum value allowed in Spanish legislation.

Using experimental conditions, separation and quantification could be obtained for six anions and ten cations without any pre-treatment. Fig. 2a and b show the analytical capabilities of such adapted methods. From the migration times of the anions, it is clear that their determination may be problematic with samples of extreme composition (e.g. sea water or drinking water with high levels of nitrate), but this was not the case for the samples analyzed in this paper (from a water purification plant).

Metal ions such as Mn<sup>2+</sup>, Al<sup>3+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> needed a preconcentration step to achieve the levels reported in the legislation. Thus, these cations were retained in the chelating column by passing an appropriate volume of sample through the column,

after which, they were eluted using a 2 M HNO<sub>3</sub> solution. The electropherogram of this eluted solution shows narrow peaks corresponding to these cations, whereas a wide peak was obtained for the HNO<sub>3</sub> solution used for the elution (see Fig. 2c). This wide peak interferes with the alkaline-earth metals, which were also retained in the resin, but it did not affect to the peaks of Mn<sup>2+</sup>, Al<sup>3+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup>.

To demonstrate the applicability of the proposed methods, they were first applied to the determination of anions and cations in synthetic water samples. The results can be seen in Table 2 (anions) and Table 3 (cations). These results were considered to be adequate for our purposes, although, as can be

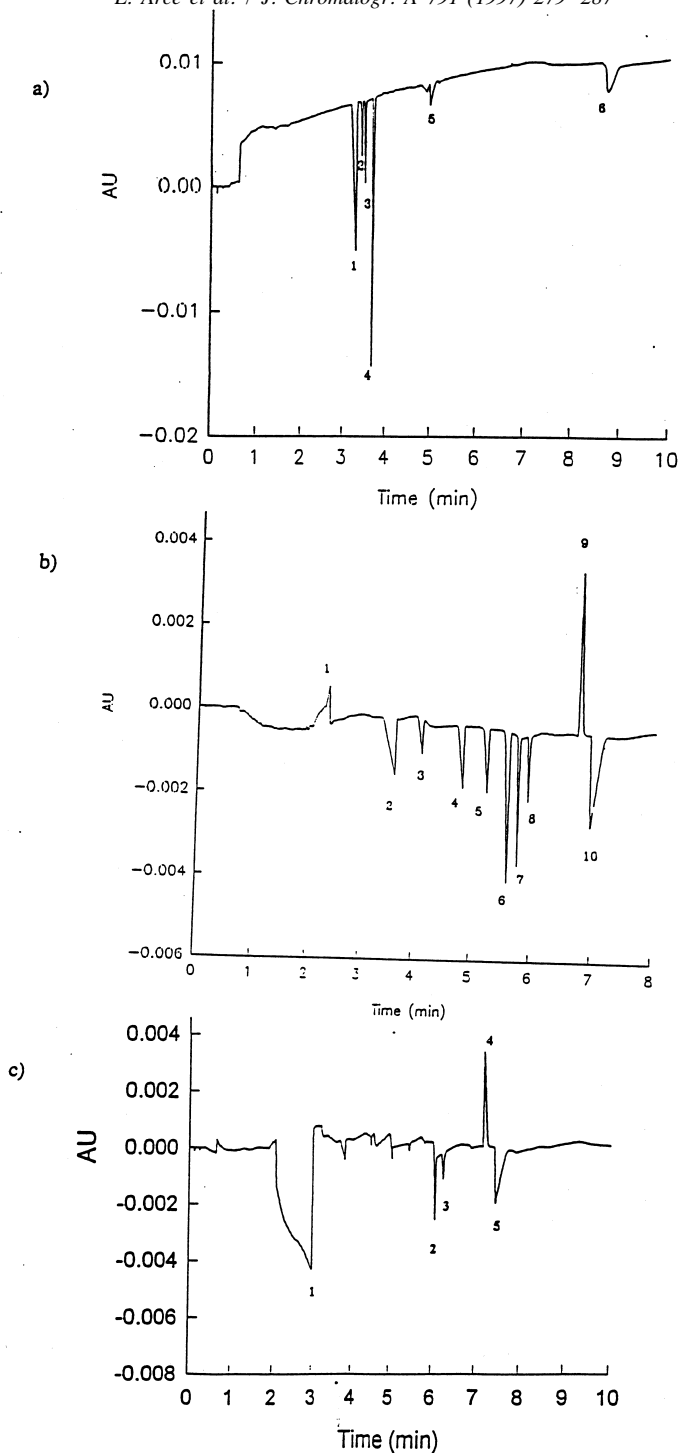


Fig. 2. (a) Electropherogram of a standard mixture of anions. 1=Chloride; 2=nitrite; 3=nitrate; 4=sulfate; 5=bromate and 6=phosphate (10  $\mu\text{g}/\text{ml}$  each). (b) Electropherogram of a standard mixture of cations. 1=Iron; 2=ammonium; 3=potassium; 4=sodium; 5=calcium; 6=magnesium; 7=manganese; 8=cadmium; 9=lead and 10=aluminium (10  $\mu\text{g}/\text{ml}$  each). (c) Electropherogram of a preconcentration standard mixture. 1=Eluent nitric solution; 2=manganese; 3=cadmium; 4=lead and 5=aluminium (0.1  $\mu\text{g}/\text{ml}$  each).

Table 2

Errors obtained in the analysis of synthetic samples (anions) by the proposed method

<i>Chloride:</i>					
Amount added:	10	20	25	30	
Error (%):	-2.0	0.0	1.6	1.0	
<i>Sulfate:</i>					
Amount added:	5	20	25	40	50
Error (%):	2.0	0.0	2.0	2.5	0.4
<i>Phosphate:</i>					
Amount added:	3	5	7	10	20
Error (%):	10	0.0	1.4	1.0	-1.5
<i>Nitrate:</i>					
Amount added:	0.1	0.5	4	10	
Error (%):	-4.0	-2.0	-5.0	0.0	
<i>Nitrite:</i>					
Amount added:	0.4	0.75	2.5	5	10
Error (%):	5.0	-1.3	8.0	-6.0	0.0

Concentrations are given in  $\mu\text{g ml}^{-1}$ .

expected, the errors increased at lower concentrations of the analytes. Afterwards, the methods were also applied to the analysis of real samples (drinking and natural waters). Some of these samples were provided by EMACSA (the water purification plant of Córdoba), from different parts of the plant. The main advantage of the proposed method was the possibility of monitoring changes in concentrations with time in a water purification plant. In this case, water from a reservoir arrives and needs to be treated to make it suitable for human consumption. CE–FI could be a useful technique for monitoring all of these parameters because of the on-line transport of the samples from the different parts of the plant and the easy automation of the sampling treatment and introduction into the CE system. The consumption of reagents and the storing of samples are avoided by using the CE–FI method. The results obtained by the proposed methods and the reference methods [25] are listed in Table 4 (anions) and Table 5 (cations). The results are in agreement with those found by the reference methods (extracted from Ref. [25]): chloride by titration; nitrite, nitrate, sulfate, phosphate and ammonium by molecular absorption UV–Vis spectrometry; iron, potassium, sodium, calcium, magnesium, manganese, cadmium, lead and aluminium by atomic absorption spectroscopy.

Table 3

Errors obtained in the analysis of synthetic samples (cations) by the proposed method

<i>Sodium:</i>					
Amount added:	5	7	15	30	40
Error (%):	0.0	-5.7	-1.3	1.0	0.5
<i>Potassium:</i>					
Amount added:	1	5	10	20	30
Error (%):	-3.0	-2.0	-8.6	1.5	6.6
<i>Calcium:</i>					
Amount added:	5	10	20	30	40
Error (%):	2.0	2.5	-1.0	-1.0	-0.7
<i>Magnesium:</i>					
Amount added:	5	15	20	30	50
Error (%):	4.0	5.3	5.0	5.6	2.2
<i>Ammonium:</i>					
Amount added:	0.4	0.5	2	5	10
Error (%):	-2.5	-4.0	10	-1.4	-0.8
<i>Iron:</i>					
Amount added:	0.2	0.5	1	3	5
Error (%):	10	6.0	-4.0	0.0	2.0
<i>Aluminium:</i>					
Amount added:	0.05	0.07	0.1	0.3	0.5
Error (%):	6.0	4.3	-7.0	-10	2.0
<i>Manganese:</i>					
Amount added:	0.05	0.1	0.2	0.5	0.75
Error (%):	4.0	-10	15	2.0	-2.6
<i>Lead:</i>					
Amount added:	0.05	0.15	0.2	0.5	1
Error (%):	14	0.0	15	-12	3.0
<i>Cadmium:</i>					
Amount added:	0.08	0.1	0.2	0.3	0.5
Error (%):	25	10	-5	10	-4

Concentrations are given in  $\mu\text{g ml}^{-1}$ .

#### 4. Conclusions

The aim of this paper was to evaluate the coupling of FI with CE to automate sample transportation and simplify sample pretreatment. This interface can be considered as a general approach to make discrete analytical equipment (which they commonly use sample turntables) compatible with continuous flow systems. The applicability of this arrangement has been demonstrated by providing continuous control of the quality of samples in a water purification plant. The electrophoretic methods separate a wide variety of common inorganic ions in less than 15

Table 4  
Analysis of real samples of water (anions), from different places of the water purification plant of Córdoba (EMACSA)

	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HPO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>
Guadalmellato	10.4±0.4 (9.7±0.3)	9.2±0.3 (9.8±0.4)	0.26±0.05 (0.27±0.03)	11.1±0.5 (10.9±0.1)	(0.16±0.01)
Settling pool	10.3±0.4 (10.1±0.5)	22.2±1.0 (21.5±0.5)	0.23±0.04 (0.25±0.01)	11.1±0.3 (11.2±0.4)	— (—)
Filter	9.1±0.2 (9.06±0.3)	28.7±0.3 (29.1±0.8)	— (—)	11.1±0.3 (9.9±0.6)	— (—)
Deposit	11.8±0.7 (11.1±0.9)	30.1±0.2 (30.9±0.8)	— (—)	12.8±0.6 (14.0±0.2)	— (—)
Guadalnuño (reservoir)	10.2±0.6 (10.0±0.6)	9.9±0.2 (9.2±0.2)	0.57±0.02 (0.54±0.04)	10.9±0.4 (11.0±0.3)	0.19±0.04 (0.13±0.2)
Mineral water	137.5±0.5 (148.4±0.8)	33.9±0.1 (32.9±0.8)	— (—)	0.32±0.02 (—)	— (—)

Concentrations are given in µg ml<sup>-1</sup>.

Values in brackets correspond to reference methods.

Table 5  
Analysis of real samples of water (cations), from different places in the water purification plant of Córdoba (EMACSA)

	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Fe <sup>3+</sup>	Pb <sup>2+</sup>	Al <sup>3+</sup>	Cd <sup>2+</sup>	Mn <sup>2+</sup>
Guadalmellato (reservoir)	9.2±0.3 (8.5±0.2)	1.3±0.2 (1.4±0.1)	22.4±0.9 (18.6±0.5)	5.0±0.8 (6.1±0.7)	0.60±0.07 (0.49±0.06)	0.21±0.03 0.178±0.003	0.09±0.02 (0.06±0.05)	0.4±0.05 (0.35±0.09)	0.08±0.03 (0.09±0.02)	0.1±0.05 (0.08±0.02)
Settling pool	3.8±0.25 (4.3±0.35)	— (—)	12.2±0.7 (13.2±0.7)	5.0±0.3 (4.7±0.4)	— (—)	— (—)	0.08±0.03 (0.07±0.05)	0.35±0.05 (0.38±0.03)	0.08±0.04 0.08±0.05	0.08±0.03 (0.07±0.01)
Filter	4.45±0.47 4.1±0.3	— (—)	12.1±0.3 (11.1±0.7)	4.8±0.5 (4.9±0.3)	— (—)	— (—)	— (0.07±0.03)	0.06±0.02 (0.42±0.04)	0.39±0.09 (—)	— (—)
Deposit	3.8±0.3 (3.8±0.59)	— (—)	13.6±0.5 (14.0±0.5)	4.4±0.5 (5.3±0.3)	— (—)	— (—)	— (—)	0.1±0.08 (0.15±0.07)	— (—)	— (—)
Guadalnuño (reservoir)	11.8±0.9 (11.2±0.7)	1.58±0.29 (1.24±0.21)	12.6±0.9 (11.5±0.4)	6.9±0.2 (5.6±0.3)	0.21±0.04 (0.16±0.01)	0.21±0.04 (0.17±0.02)	— (—)	— (—)	0.005±0.002 (0.004±0.002)	(—) (—)
Mineral water	88.0±0.04 (89.0±0.6)	1.86±0.15 (1.8±0.1)	69.1±0.7 (72.6±0.5)	15.5±0.5 (16.6±0.2)	— (—)	— (—)	— (—)	— (—)	— (—)	— (—)

Concentrations are given in µg ml<sup>-1</sup>.

Values in brackets correspond to reference methods.

min, with high peak efficiency. The advantages of the use of Chelex-100 resin for the preconcentration of metals has been demonstrated, achieving the appropriate sensitivity and selectivity in an on-line system.

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