

# Application of a single electrode, modified with polydiphenylamine and dodecyl sulfate, for the simultaneous amperometric determination of electro-inactive anions and cations in ion chromatography

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## Abstract

An amperometric sensor with a single working electrode for simultaneous determination of electro-inactive anions and cations, e.g.  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , was designed as a detector in ion chromatography. The modification of its working golden electrode was based on the incorporation of dodecyl sulfate into polydiphenylamine by electropolymerization of diphenylamine in the presence of sodium dodecylsulfate. In ion-exclusion/cation-exchange chromatography, a set of well defined peaks of these anions and cations was obtained at the working potential, +1.35 V (vs. saturated calomel electrode) using a citric acid solution as eluent. The common anions and cations in mineral water samples were determined using this ion-chromatographic system with satisfactory results.

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## 1. Introduction

Ion chromatography can provide a convenient means to separate anions and cations. The simultaneous determination of anions and cations is of particular interest in IC analysis because of its potential simplicity. After Tanaka et al. [1,2] separated common anions and cations ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,

$\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) in rainwater simultaneously using tartaric acid as eluting agent by single column ion-exclusion chromatography/cation-exchange chromatography, this kind of method has been applied to the inorganic components in rain water [3–5] and drinking water [6] with conductivity detection.

Extensive studies on chemically modified electrodes (CMEs) for designing analytical devices have been reported [7] and some of them were directed to the amperometric detection of electro-inactive ions with possible applications in combination to IC [8–

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23]. Since polypyrrole CME [24] and polyaniline CME [25] were reported for the determination of electro-inactive anions in flow injection analysis (FIA), the conductive polymers proved popular in the application of CMEs as analytical sensors to determine electro-inactive anions and cations by IC [8]. Our research group reported an IC method for the simultaneous amperometric detection of electro-inactive anions and cations based on an electrochemical detector with two working electrodes modified with polydiphenylamine (PDPA) and polydiphenylamine dodecyl sulfate (PDPA-DS), respectively, at different working potentials [26]. The PDPA CME was for determining electro-inactive anions, and the PDPA-DS CME was for determining electro-inactive cations. In the same experiments, we also found that when the working potential applied to the PDPA-DS CME was over +1.30 V (vs. saturated calomel electrode, SCE), a set of defined peaks of the common electro-inactive ions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ ) with inverse directions were obtained. Although the baseline was a little unstable, the electrochemical responses against these ions at the PDPA-DS CME were still linear vs. their concentrations.

In this work, we studied this phenomenon and report on an amperometric sensor with a single working electrode for the simultaneous determination of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions in ion-exclusion/cation-exchange chromatography. The modification of the working electrode was as previous reported [26]. At the working potential, +1.35 V (vs. SCE), a set of well-defined peaks of these ions was obtained. The linear ranges between peak height and concentration were two orders of magnitude and the correlation coefficients were all  $>0.987$ . The detection limits calculated using  $3.3\sigma$  criterion ( $\sigma$ =standard deviation of blank solution) were  $12.1 \mu\text{M}$  for  $\text{SO}_4^{2-}$ ,  $11.1 \mu\text{M}$  for  $\text{Cl}^-$ ,  $12.3 \mu\text{M}$  for  $\text{NO}_3^-$ ,  $29.9 \mu\text{M}$  for  $\text{Na}^+$ ,  $32.0 \mu\text{M}$  for  $\text{NH}_4^+$ ,  $28.8 \mu\text{M}$  for  $\text{K}^+$ ,  $57.4 \mu\text{M}$  for  $\text{Mg}^{2+}$  and  $58.6 \mu\text{M}$   $\text{Ca}^{2+}$ . The recoveries by this method were in the range of 92 — 102%. The electrode was stable during the 6-h period of operation with no evidence of chemical and mechanical deterioration. This method was applied to the simultaneous amperometric detection of electro-inactive anions and cations in mineral water samples with satisfactory results.

## 2. Experimental

### 2.1. Chemicals and reagents

All reagents were of analytical grade. Two solutions, 0.50 M diphenylamine (Shanghai Forth Reagent Factory, China) dissolved in acetonitrile and 0.50 M sodium dodecylsulfate (Shanghai Reagent, China), were prepared for the modification of a golden electrode. Stock solutions of cations and anions (10.00 mM) were prepared from the corresponding salts ( $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$  and  $\text{CaCl}_2$ ) purchased from Shanghai First Reagent Factory. Eluent was prepared from methanol and the 0.200 M stock standard solution of citric acid (both from Shanghai Reagent). All reagents were diluted to the desired concentration using deionized and distilled water ( $20 \text{ M}\Omega \text{ cm}^{-1}$ ) just prior to use as routine working solutions. The eluent was filtered through a 0.45- $\mu\text{m}$  nylon-66 membrane filter (Bandao, Shanghai, China) prior to use.

### 2.2. Preparation of the PDPA-DS CME

Prior to the modification, the fresh solution containing 0.20 M diphenylamine and 0.20 M sodium dodecylsulfate used for modification was deaerated with prepurified nitrogen for 15 min. The surface of the gold disc electrode was polished with 0.5- $\mu\text{m}$  alumina on a polishing micro-cloth and rinsed with deionized and distilled water; then it was cleaned thoroughly with acetone, NaOH (50%, w/w),  $\text{HNO}_3$  (1:1, v/v) and deionized and distilled water, respectively. The electrodeposition of the PDPA-DS film was conducted according to the literature [26]. The cleaned gold electrode was cycled in the deaerated solution in the potential range from  $-0.40$  to  $+1.60$  V (vs. SCE) at  $100 \text{ mV s}^{-1}$ . After 15 complete cycles, the PDPA-DS polymer film was electrodeposited onto the gold disc electrode as a purple film. It was washed with acetonitrile to remove the oligomers and the remained monomer, and then stored in a 0.01 M  $\alpha$ -D,L-aminopropionic acid solution.

### 2.3. Instrumentation

Electrochemical experiments were performed on a CHI 720 Electrochemical Analyzer (CH Instruments,

Cordova, USA) in a three-electrode cell with a SCE (Jiangsu Electroanalytical Instruments Works, China) as the reference electrode, a gold flake as the counter electrode and the PDPA–DS CME as the working electrode (1 mm I.D.).

The ion-chromatographic separation was performed on a Shimadzu IC system (Tokyo, Japan) including a LC-10AS eluent delivery pump and an SIL-6B injector equipped with a 25- $\mu$ l sample loop. An TSK gel OA-PAK-A column (300 mm $\times$ 7.8 mm I.D., particle size 5  $\mu$ m) (Tosoh, Japan) was used for the simultaneous separation of anions and cations.

The detector consisted of a CHI potentiostat (Jiangsu Electroanalytical Instruments Works) and a laboratory-made thin-layer cell with an SCE (Jiangsu Electroanalytical Instruments Works) as the reference electrode, a gold flake as the counter electrode and the PDPA–DS CME (1 mm I.D.) as the working electrode. The thin-layer cell size was 30 mm (length) $\times$ 2 mm (width) $\times$ 0.15 mm (height). The recorder was a Dahua x-t recorder (Shanghai, China).

#### 2.4. Chromatographic conditions

The eluent, composed of 6.0 mM citric acid–5.0% methanol–water, was pumped through the column and the laboratory-made detector at a flow-rate of 1.0 ml min<sup>-1</sup>. The column temperature was maintained at 25 °C and equilibrated for 20 min prior to use. The determination was performed in the laboratory-made three-electrode cell detector with an SCE as the reference electrode, a gold flake as the counter electrode and the PDPA–DS CME as the working electrode at a suitable working potential, +1.35 V (vs. SCE). The injection volumes of the standard and sample solutions were 25  $\mu$ l. A blank solution (deionized and distilled water) test was performed before detection.

#### 2.5. Mineral water sample analysis

The mineral water sample was obtained from Shenxing Beverage (Shanghai, China). The water samples were filtered through a 0.45- $\mu$ m nylon-66 membrane filter (Bandao) (soaked in deionized and distilled water for 24 h) prior to analysis. Subsequently, they were analyzed according to the specified chromatographic conditions.

### 3. Results and discussion

#### 3.1. Mechanism of simultaneous amperometric detection ions on the PDPA–DS CME

The most reported methods for amperometric detection of electro-inactive anions and cations are based on the electrochemical transformation of electro-active films that involves the incorporation of an ionic species to counterbalance the electric charge generated in the process of oxidation or reduction. Therefore, by maintaining the electrode potential to a selected value, current will only flow if charge-compensating ions pass the electrode.

Fig. 1 shows the cyclic voltammograms for the electrodeposition of PDPA–DS film on a gold disc electrode, which demonstrates that the incorporation of DS in the film was irreversible [19,26]. There were two steady redox states, reduction and oxidation [27]. When an appropriate potential was applied to the PDPA–DS CME, a durative anodic current (background current) appeared because of the present of DS<sup>-</sup> in the CME. The current value increased when anions (e.g. Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) from the eluent passed the electrode, and decreased when cations (e.g. K<sup>+</sup> and Na<sup>+</sup>) passed the electrode. Experiments showed that the background current value also

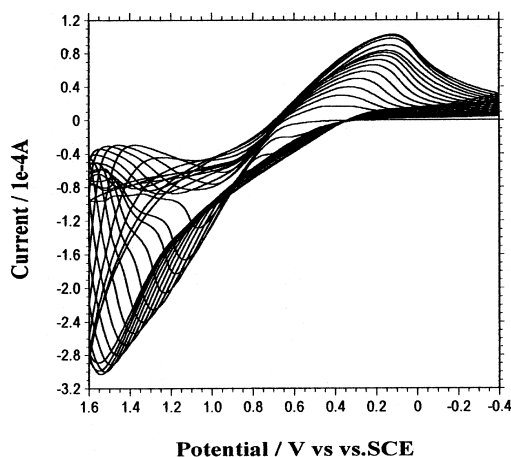


Fig. 1. Cyclic voltammograms of the electrodeposition of PDPA–DS film on a gold disc electrode by consecutive potential cycling in a fresh modification solution containing 0.20 M diphenylamine and 0.20 M sodium dodecylsulfate in the potential range from –0.40 to +1.60 V (vs. SCE) at 100 mV s<sup>-1</sup>.

decreased when divalent cations ( $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) passed this CME; however, their effects were weaker than those of the monovalent cations, because the divalent cations have a large hydrated ionic radius and did not enter the CME film easily.

### 3.2. Selection of eluent

Weak acidic solutions containing methanol were used as eluents for simultaneous separation of anions and cations by ion-exclusion/cation-exchange chromatography, i.e. malonic acid [5], D,L-malic acid [6], citric acid and tartaric acid [1]. In this work, they were tested to determine the electrochemical responses of the anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) at the PDPA–DS CME. Experiments showed that the best responses were obtained and the electrode life span was the longest when a citric acid solution was used as eluent. Therefore, citric acid was chosen.

### 3.3. Hydrodynamic voltammetry

The applied potential was varied from +1.10 to +1.45 V (vs. SCE) in 0.05-V increments and injections of 25  $\mu\text{l}$  of two mixed standard solutions, one contained 0.5 mM  $\text{Na}_2\text{SO}_4$ ,  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$ , the other one contained 2.0 mM  $\text{MgSO}_4$  and  $\text{CaCl}_2$ . The hydrodynamic voltammograms are shown in Fig. 2. When the applied potential was less than +1.20 V (vs. SCE), there were only anionic peaks and essentially no evidence for the cationic peaks. When the applied potential was more than +1.25 V (vs. SCE), both the anionic and cationic peaks appeared. Their heights increased with increasing the applied potential. However, when the potential was more than +1.40 V (vs. SCE), the heights decreased because of the increase of background current; meanwhile, the baseline was too unstable. In this work, +1.35 V (vs. SCE) was chosen as the working potential.

### 3.4. Effects of eluent

To optimize the separation and detection, the effects of citric acid concentration, methanol concentration and flow-rate were investigated.

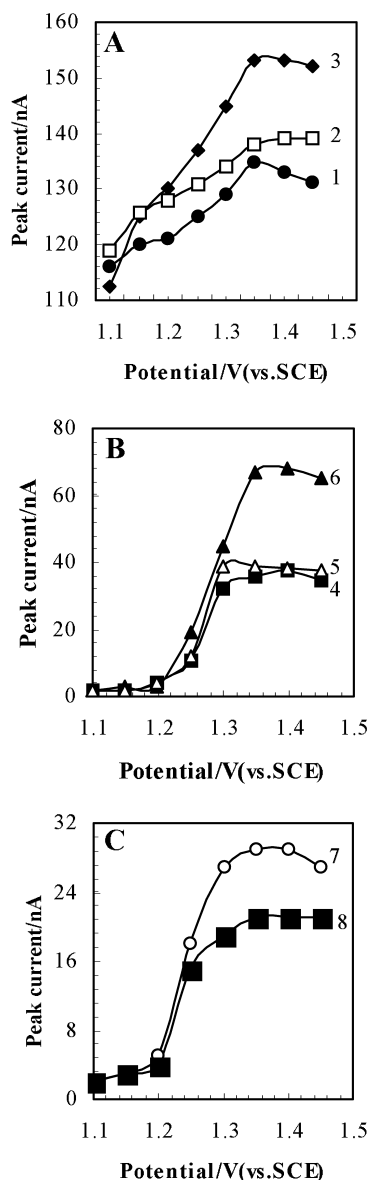


Fig. 2. Hydrodynamic voltammograms of anions and cations. 1 =  $\text{SO}_4^{2-}$ , 2 =  $\text{NO}_3^-$ , 3 =  $\text{Cl}^-$ , 4 =  $\text{K}^+$ , 5 =  $\text{NH}_4^+$ , 6 =  $\text{Na}^+$ , 7 =  $\text{Mg}^{2+}$ , 8 =  $\text{Ca}^{2+}$ . Column, Tosoh TSK gel OA-PAK-A; standard mixture solutions, (A) and (B) 0.5 mM  $\text{Na}_2\text{SO}_4$ ,  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$ , (C) 2.0 mM  $\text{MgSO}_4$  and  $\text{CaCl}_2$ ; injection volume, 25  $\mu\text{l}$ ; eluent, 6.0 mM citric acid–5.0% methanol–water; flow-rate, 1.0 ml  $\text{min}^{-1}$ ; column temperature, 25 °C.

Experiments showed that the retention time ( $t_R$ ) of cations decreased and that of anions increased with increasing the citric acid concentration from 1.0 mM

to 5.0 mM in the eluent. When citric acid concentration was over 6.0 mM, the changes leveled off. The peak currents of anions and cations at the PDPA–DS CME showed no obvious changes when citric acid concentration increased from 1.0 mM to 6.0 mM. Therefore, 6.0 mM citric acid was chosen as optimum.

It was necessary to maintain a certain amount of methanol in the eluent to improve the peak resolution of ions [1–4,28]. Experiments showed that with increasing methanol concentration, the retention times of anions had only small changes, those of the monovalent cations increased and those of the divalent cations decreased; meanwhile, the peak current values of anions and cations all decreased. Therefore, ~5.0% was chosen as a compromise.

Flow-rate was also important for the separation and detection. It affected retention time, response, resolution and column pressure. Experiment results showed that with increasing flow-rate, the retention time, resolution and responses of these anions and cations all decreased, however, the column back-pressure increased dramatically. Hence, the flow-rate was chosen as 1.0 ml min<sup>-1</sup>, which not only gave satisfactory separation and sensitivity for analysis, but also had a relatively low column backpressure.

### 3.5. Analytical characteristics

The reproducibility was estimated by making replicate injections ( $n=5$ ) of a mixture of mineral water sample and a standard solution containing  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions. The relative standard deviations (RSDs) of the peak heights of anions and cations were all <5.0%. The electrode-to-electrode ( $n=7$ ) reproducibility of the CME was estimated by detecting a mixed standard solution of  $\text{NO}_3^-$  and  $\text{K}^+$  five times. The RSDs of the peak height were both <3.4%. The response of anions and cations at the PDPA–DDS CME maintained over 94 and 91% of the original

value after continuous potential applied to +1.35 V (vs. SCE) for 6 h, respectively, and there was no evidence of baseline drift and chemical and mechanical deterioration during the 6-h period of consecutive operation. It was tested by injecting a mixed standard solution containing  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions ( $n=7$ ). The short life span could be attributed to the applied high working potential. As a comparison, its life span was about 1 week when the applied potential was +0.15 V (vs. SCE) [26].

To determine the linearity for  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions by this method, a series of standard solutions of these ions ranging from 0.01 mM to 10 mM were tested. The linear ranges observed between peak heights and concentrations were from 0.02 to 1.00 mM for anions and divalent cations, and from 0.08 to 1.50 mM for divalent cations. Their correlation coefficients were all >0.987. The detection limits were calculated using 3.3 $\sigma$  criterion, where  $\sigma$  represents the standard deviation of a blank solution ( $n=7$ ). The results are summarized in Table 1.

### 3.6. Application

The method was applied to the determination of the common inorganic anions and cations in mineral water sample. Typical chromatograms are shown in Fig. 3. Here, the unusual peak shape of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  could be attributed to the slower responses on the CME because of their large hydrated ionic radius. The recoveries with this method were tested by analysis of a spiked mineral water sample and replicate injections ( $n=7$ ). Comparing the results detected using this chemical sensor and using conductivity detection, the data were consistent—demonstrating that the proposed method was reliable for determining the common anions and cations in real water samples. Results are given in Table 2.

Table 1

Detection limits for ions in ion-exclusion/cation-exchange chromatography by electrochemical detection (mean values of seven determinations)

Ions	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
Detection limits ( $\mu\text{M}$ )	12.1	11.1	12.3	29.9	32.0	28.8	57.4	58.6

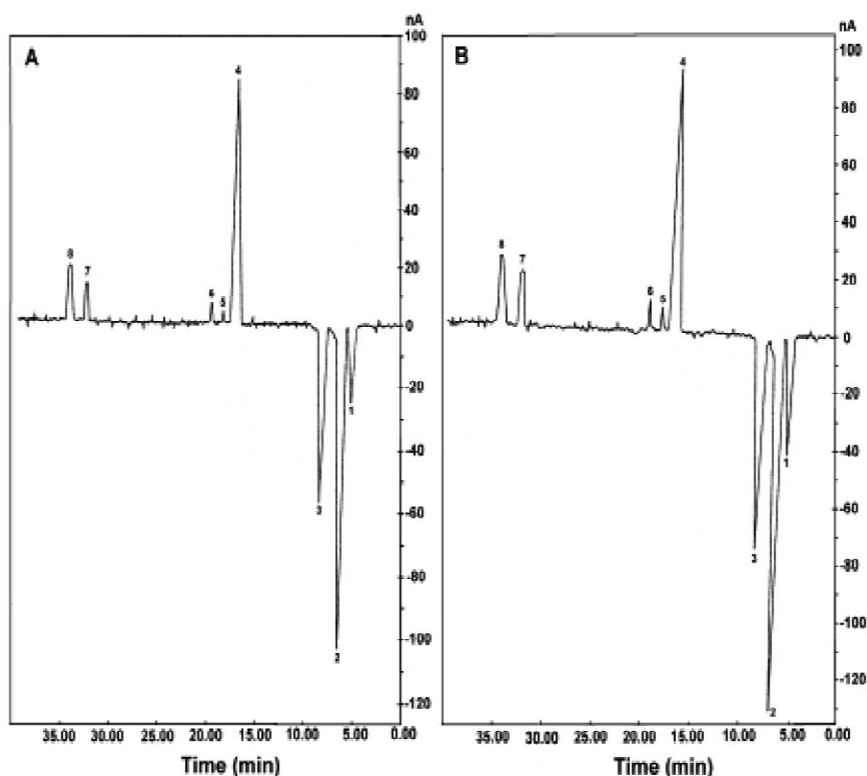


Fig. 3. Chromatograms of (A) mineral water sample, (B) (A)+standard mixture solution ( $50 \mu\text{M}$   $\text{Na}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{MgSO}_4$  and  $\text{CaCl}_2$ ). 1= $\text{SO}_4^{2-}$ , 2= $\text{Cl}^-$ , 3= $\text{NO}_3^-$ , 4= $\text{Na}^+$ , 5= $\text{NH}_4^+$ , 6= $\text{K}^+$ , 7= $\text{Mg}^{2+}$ , 8= $\text{Ca}^{2+}$ . Applied potential, +1.35 V (vs. SCE); other chromatographic conditions as in Fig. 2.

#### 4. Conclusions

This work has described for the simultaneous amperometric detection of electro-inactive anions

and cations in real water sample using an electrochemical sensor with single working electrode by ion chromatography. The proposed approach is simple and quick. However, the detection limits of the

Table 2

Content of the anions and cations in mineral water by electrochemical detection (ED) and conductimetric detection (CD) (mean values of seven determinations)

Ion	Detection by ED			Detection by CD			Labeled (mM)	
	Mean (mM)	RSD (%)	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	Mean (mM)		RSD (%)
$\text{SO}_4^{2-}$	0.19	1.83	100	97.8	97.8	0.18	1.77	0.17
$\text{Cl}^-$	0.74	2.41	100	97.1	97.1	0.75	1.92	0.72
$\text{NO}_3^-$	0.43	2.39	100	102	102	0.42	1.79	0.43
$\text{Na}^+$	1.14	3.21	100	97.8	97.8	1.14	2.24	1.16
$\text{NH}_4^+$	0.04	3.53	50.0	47.5	95.0	0.04	2.26	0.04
$\text{K}^+$	0.07	3.48	50.0	48.1	96.2	0.07	2.49	0.06
$\text{Mg}^{2+}$	1.31	3.62	50.0	46.5	93.5	1.32	2.54	1.35
$\text{Ca}^{2+}$	2.16	3.29	50.0	46.2	92.4	2.12	2.51	2.12

method and the operational life span of the CME need to be improved in the future.

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