Application of Nafion/Cobalt Hexacyanoferrate Chemically Modified Electrodes for the Determination of Electroinactive Cations by Ion Chromatography

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An amperometric detector based on the chemical modification of Nafion and cobalt(II) hexacyanoferrate(II, III) thin film (Nafion/Co-CN-Fe) onto a glassy carbon (GC) electrode was firstly developed for the determination of electroinactive cations (Li^+, Na^+, K^+, Rb^+, Cs^+ and NH_4^+) in single column ion chromatography. A set of well-defined peaks of electroinactive cation was obtained. The relative standard deviations (RSDs) of chromatographic peak height (nA) for these cations were all below 3.8%. The cations were detected conveniently in the linear concentration range of 6.0×10^{-6}—5.0×10^{-3} mol/L and their correlation coefficients were all above 0.99. The detection limits of the cations were 9.2×10^{-6} mol/L for Li^+, 3.4×10^{-6} mol/L for Na^+, 6.3×10^{-7} mol/L for K^+, 7.8×10^{-7} mol/L for Rb^+, 6.2×10^{-7} mol/L for Cs^+ and 6.2×10^{-6} mol/L for NH_4^+, at a signal-noise ratio of 3. The method was quick, sensitive, simple and was successfully applied to the analysis of rainwater samples. The electrode was stable for a 2 week period of operation with no evidence of chemical or mechanical deterioration.

Keywords   ion chromatography, electrochemical detection, water analysis

Introduction

Ion chromatography (IC) has been recognized as a useful method for the separation of inorganic anions and cations since its introduction by Small et al. in 1975.[1] A significant trend in the development of IC method is search for sensitive and universal detection methods. The main detection techniques in IC include conductivity detection,[2-5] UV-visible absorbance detection,[6,7] fluorescence detection,[8,9] ICP-MS and ICP-AES,[10,11] potentiometric detection[12] and amperometric detection.[13,14] IC combined with electrochemical detection (ECD) appears a very attractive analytical approach for the determination of electroactive ions owing to its sensitivity, selectivity, low cost and ease of fabrication and miniaturization. However, many electroinactive ions (such as Na^+, K^+, NH_4^+, Rb^+, Cs^+, NO_3^-, Cl^-, SO_4^{2-}, etc.) can not be oxidized or reduced easily at a normal electrode. These ions are usually detected by ion chromatography with conductivity detection. Recently, some chemically modified electrodes (CMEs)[15-17] have been used in the amperometric detection of these ions. Martinez et al.[15] incorporated dodecyl sulfate into polypyrrole by electropolymerization of pyrrole to detect Li^+, Na^+ and K^+ in FIA and IC. Sung and Huang[16] have also applied a polyaniline-Nafion composite electrode to the determination of alkali and alkaline earth metal ions in FIA and IC. Barisci et al.[17] reported a chloride-containing polypyrrole film to determine F^-, Cl^-, NO_3^- and PO_4^{3-} by IC.

Since the pioneering work on prussian blue (PB) modified electrodes was firstly reported by Neff,[18] a growing interest has been shown in literature in inorganic polynuclear transition metal cyanometalate coatings over the past few years. PB and its analogues have been used in electrochromic displays, solid-state batteries, ion-selective electrode, and for electrocatalytic or signal enhancement purposes. In this article, an amperometric de-

tector based on the chemical modification of Nafion and cobalt hexacyanoferrate thin film (Nafion /Co-CN-Fe) onto a glassy Carbon (GC) electrode was successfully used for the determination of electroinactive cations (Li^+, Na^+, K^+, Rb^+, Cs^+ and NH_4^+) in ion chromatography.

Experimental

Chemicals and solutions

All the chemicals used were of analytical-grade unless specified otherwise. All solutions were prepared with distilled deionized water. $K_3[Fe(CN)_6]$ (from First Reagent Factory, Shanghai, China), $CoCl_2$ and KCl (from Second Reagent Factory, Shanghai, China) were prepared for the CME. Nitric acid and acetone (from Nanxiang Reagent Co. Shanghai, China) were used aseluent to separate cations. A 5.0% solution of Nafion (from Aldrich) is diluted to 0.2% with methanol. Prior to use, all solutions (except Nafion) were deaerated by degassing with prepurified nitrogen for 15 min.

Working standard solutions were prepared daily by serial dilution of stock standard solutions of each alkali metal ions and NH_4^+ containing 0.01 mol/L. All standards and samples were stored in acid washed (10% nitric acid) polyethylene bottles.

Instrumentation

Electrochemical experiments were performed on a CHI660 electrochemical analyzer (CH Instruments, Cordova, U.S.A) in a three-compartment cell with a saturated calomel electrode (SCE) (Jiangsu Electroanalytical Instruments Co., China) as the reference electrode, a gold wire as the counter electrode and the Nafion/Co-CN-Fe CME as the working electrode.

The separation of cations was performed on a Shimadzu (Kyoto, Japan) IC system including a LC-AS eluent delivery pump, a SIL-6B injector equipped with a 25 μL sample loop.

The detector consists of a homemade thin-layer cell and a CHI potentiostat (Jiangsu Electroanalytical Instruments Co., China). The recorder is a x-t recorder (Shanghai Dahua Co., China). A shim-pack IC-C1 ion chromatograph column (5.0 mm I.D. × 15 cm stainless) which is filled with a cation exchange resin of a polystyrene-divinylbenzene with a particle size 10 μm as a support incorporating a sulfuric acid base as a functional group.

Electrochemical polymerization

The glassy carbon (GC 3 mm I.D.) disk electrode surface was polished with 0.5 μm alumina slurries on a polishing micro-cloth and rinsed with deionized water. Then, it was subsequently sonicated thoroughly with acetone, NaOH (50%, W/W), HNO_3 (1:1, V/V) and deionized water. In order to pre-activate the GC Surface, the electrode was cycled in the potential range from 0.0 V to 1.0 V (vs. SCE) for 20 cycles at 100 mV/s in a 1.0 mol/L KCl solution. The Nafion/Co-CN-Fe thin film was prepared according to the method reported.[19] First, the pre-activated GC electrode was scanned between 0.1 V and 1.0 V (vs. SCE) in an oxygen-free solution containing $K_3[Fe(CN)_6]$ (0.50 mmol/L), $CoCl_2$(1.0 mmol/L) and KCl (0.50 mmol/L), with a scan rate of 50 mV/s. After 30 cycles, the electrodeposition of Co-CN-Fe thin film was finished. Then, the electrode was removed from the solution and rinsed thoroughly with deionized water to remove loosely adhering substance. The electrode was further modified with a thin film of Nafion by dripping 5 μL of 0.2% (W/V) Nafion/methanol solution onto the electrode surface and allowing to evaporate in the air.

Separation and determination

Chromatographic separation of alkali metals ions and NH_4^+ was performed using HNO_3(3.0 mmol/L)-5%(V/V) acetone as mobile phase at a flow rate of 1.5 mL/min. The column temperature was maintained at 25 ℃ and the column was equilibrated for 30 min, prior to use. The determination was performed in the homemade three-compartment cell detector, with an SCE as the reference electrode, a gold wire electrode as the counter electrode and the Nafion/Co-CN-Fe CME as the working electrode.[13] The detection potential was +0.30 V (vs. SCE), the injection volumes of the standard and sample solutions were all 25 μL and the chromatograms were evaluated by measuring peak heights.

Sample preparation: rainwater samples were collected in Putuo district, which was located in the west of Shanghai. After collection, the samples were stored immediately in a refrigerator (4 ℃), and analyzed within

12 h. All samples were subjected to IC analysis after filtration with a polypropylene-membrane (0.45 μm) filter and they should be diluted with deionized water properly, if the concentrations of analytes were too high.

Results and discussion

Electrodeposition of the Co-CN-Fe thin film by cyclic voltammetry

Fig. 1 shows the electrodeposition of Co-CN-Fe film on a GC electrode by 30 consecutive potential cycles in the solution containing $K_3[Fe(CN)_6]$ (0.50 mmol/L), $CoCl_2$(1.0 mmol/L) and KCl (0.50 mmol/L).
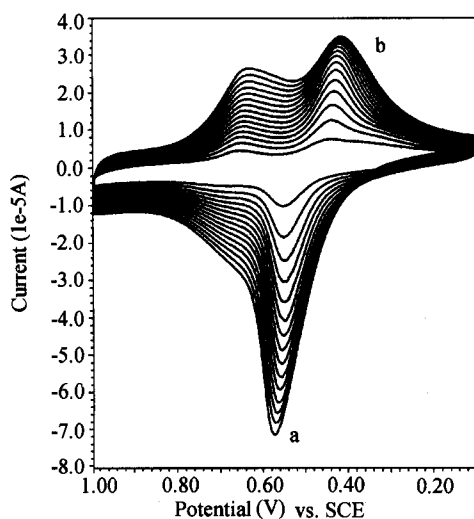
Fig. 1 Cyclic voltammograms of the electrodeposition of Co-CN-Fe film on a GC electrode by consecutive potential cycling in a fresh modifier solution containing $K_3[Fe(CN)_6]$ (0.50 mmol/L), $CoCl_2$(1.0 mmol/L) and KCl (0.50 mmol/L). Scan rate: 50 mV/s.

The increase in peak currents is consistent with the growth of Co-CN-Fe film on the GC disc electrode substrate. Initially there are two sets of redox peaks, but as the film grows, peaks in the positive sweep direction merge into one. The pair of peaks at 0.56 V, 0.44 V (a and b), can be ascribed to the $KCo^{II}Fe^{III}(CN)_6/K_2Co^{II}Fe^{II}(CN)_6$ couple. The electrodeposition reaction is thought to proceed as follow:[20]

$$Fe^{II}(CN)_6^{4-} + Co^{2+} + 2K^+ = K_2Co^{II}Fe^{II}(CN)_6$$

$$K_2Co^{II}Fe^{II}(CN)_6 = KCo^{II}Fe^{III}(CN)_6 + K^+ + e$$
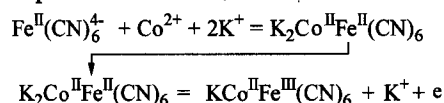
After washed thoroughly with deionized water and kept in 3 mmol/L nitric acid solution, the CoHCF CME yielded stable CV responses.

### Voltammetric response of NH_4^+ and alkali metal ions at the Nafion/Co-CN-Fe CME

To our knowledge, redox transitions in zeolitic inorganic polymer electrodes must be accompanied by a flux of cation electrolyte to maintain electric neutrality during the redox process. It is well known that alkali and some alkali earth metal cations can move into or out of PB and its analogue thin films to maintain charge balance. Fig. 2 shows the cyclic voltammograms of solutions of different cations at the Nafion/Co-CN-Fe CME using nitric acid (3.0×10^{-3} mol/L) as the supporting electrolyte. According to Fig. 2, alkali metal ions and NH_4^+ have good electrochemical responses at Nafion/Co-CN-Fe.

Hydrodynamic voltammetry

The applied potential was varied from +0.10 V to +0.60 V (vs. SCE) (each increment is 0.05 V), and injections of 25 μL of a mixed standard solution containing 5.0×10^{-4} mol/L Li^+, Na^+, K^+, Rb^+, Cs^+ and NH_4^+. Hydrodynamic voltammograms are shown in Fig. 3. From Fig. 3, Li^+, Na^+, NH_4^+ and Cs^+ have the biggest current response at +0.30 V, while K^+ and Rb^+ at about +0.25 V and +0.35 V, respectively. In this experiment, +0.30 V (vs. SCE) was choosen as the optimum working potential.
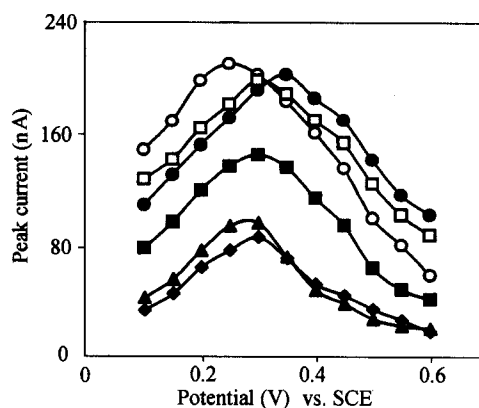
Effect of eluent concentration and flow rate

When nitric acid concentration varied from 1×10^{-3} mol/L to 6.0×10^{-3} mol/L, there is no obvious effect on the peak current of the alkali metal ions and NH_4^+. However, with the increasing of nitric acid concentration, the peak resolution decreases (Fig. 4). When the nitric acid concentration is 3.0×10^{-3} mol/L, all these cations can be separated effectively. With the eluent flow rate increasing, the retention time of the cations decreases. However, the baseline is unstable if the flow rate is too fast. Thus the appropriate flow rate is 1.5 mL/min.
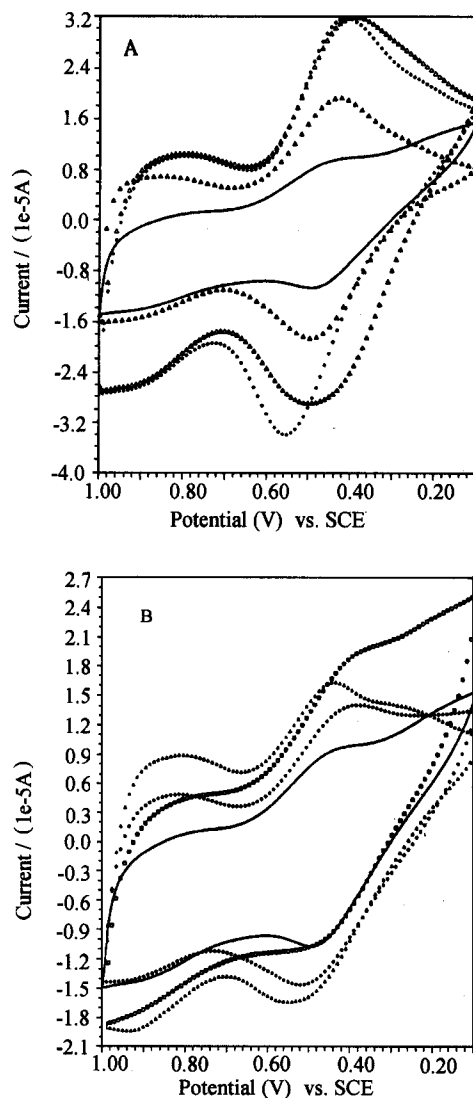
Fig. 2 Cyclic voltammograms of solution of different cations at the Nafion/Co-CN-Fe CME using 3.0×10^{-3} mol/L nitric acid as the supporting electrolyte. The concentrations of cations are all 1.0×10^{-3} mol/L. Scan rate: 100 mV/s. (A) $\triangle$—Na^+, $\blacktriangle$—NH_4^+, $\blacklozenge$—K^+, — — blank solution. (B) $\square$—Cs^+, $\blacklozenge$—Li^+, $\triangle$—Rb^+, — —blank solution.

Fig. 3 Hydrodynamic voltammograms of cations. Column, Shimadzu shim-pack IC-C1 (5.0 mm I.D. × 15 cm); injection volume, 25 μL; eluent, 3.0×10^{-3} mol/L nitric acid-5% acetone; flow rate, 1.5 mL/min; column temperature, 25 ℃. $\blacklozenge$—Li^+, $\blacksquare$—Na^+, $\blacktriangle$—NH_4^+, $\bigcirc$—K^+, $\bullet$—Rb^+, $\square$—Cs^+.
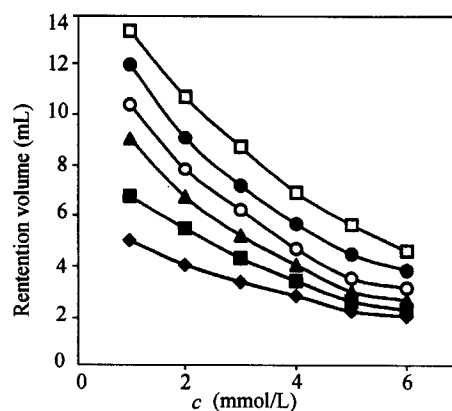
Fig. 4 Effect of eluent concentration on the retention volume in IC-ECD of the cations: $\blacklozenge$—Li^+, $\blacksquare$—Na^+, $\blacktriangle$—NH_4^+, $\bigcirc$—K^+, $\bullet$—Rb^+, $\square$—Cs^+. Their concentrations are all 5.0×10^{-4} mol/L. Applied potential: + 0.30 V (vs. SCE); injection volume, 25 μL; flow rate: 1.5 mL/min.

Effect of organic solvent

Zhao *et al.*[21] have reported that organic solvents have swelling capacity to Co-CN-Fe thin film, and they tended to alter the membrane permeability. In this experiment, We tried to find the effect of organic solvent (such as acetone, acetonitrile, ethanol and methanol) on the peak current. The result follows the sequence: acetone >

acetonitrile > H_2O > ethanol > methanol. When the concentration of acetone is less than 5%, the peak current increase with the enhancement of concentration, but when the concentration of acetone is more than 5%, the variation of peak current decreases gradually. So, in this experiment, 3 mmol/L nitric acid-5% acetone solution was choosen as eluent. Fig. 5 shows the trend of K^+ peak current varies with the concentration of acetone. The effects of acetone concentration on other cations are similar to K^+.
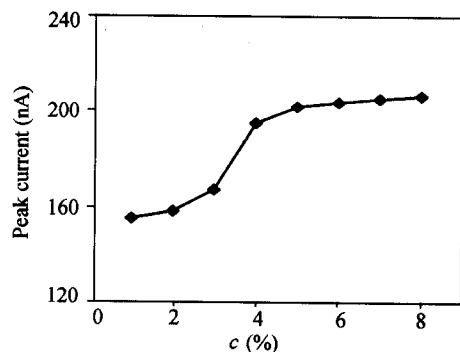
Fig. 5 Effect of acetone concentration on K^+ peak current.

Effect of Nafion

Nafion is a cation exchanger, in the presence of immobilized sulphonate groups the movement of anions into the thin film will be hindered, while the movement of cations becomes necessary to accomplish the redox process of polymers.[16] In this experiment, it was found that the peak current of alkali metal cations and NH_4^+ at the Nafion/Co-CN-Fe CME were higher than at Co-CN-Fe CME without Nafion (Figs. 6A and 6B).

Linearity and detection limits

In order to test the linearity for the alkali metals ions and NH_4^+ at the Nafion/Co-CN-Fe CME with electrochemical detection, a series of mixed standard solutions of these cations ranging from 1.0×10^{-5} mol/L to 5.0×10^{-3} mol/L were tested. The ranges of linear relationships observed between currents and concentrations were over two orders of magnitude and correlation coefficients were all more than 0.99. The detection limits of the cations are 9.2×10^{-6} mol/L for Li^+, 3.4×10^{-6} mol/L for Na^+, 6.3×10^{-7} mol/L for K^+, 7.8×10^{-7} mol/L for Rb^+, 6.2×10^{-7} mol/L for Cs^+ and 6.2×10^{-6} mol/L for NH_4^+ at a signal to noise ratio of 3.

Reproducibility and stability

The reproducibility was estimated by making repetitive injection ($n = 7$) of a standard solution containing alkali metal ions and NH_4^+. According to the experiment, the relative standard deviations (RSDs) of chromatographic peak height (nA) of cations were all less than 3.8%. There was no evidence of baseline drift during a 5 h period of consecutive operation, which indicated that the ana-

lytical system had good stability. The electrode was stable during a 2 week operation period with no evidence of chemical or mechanical deterioration.
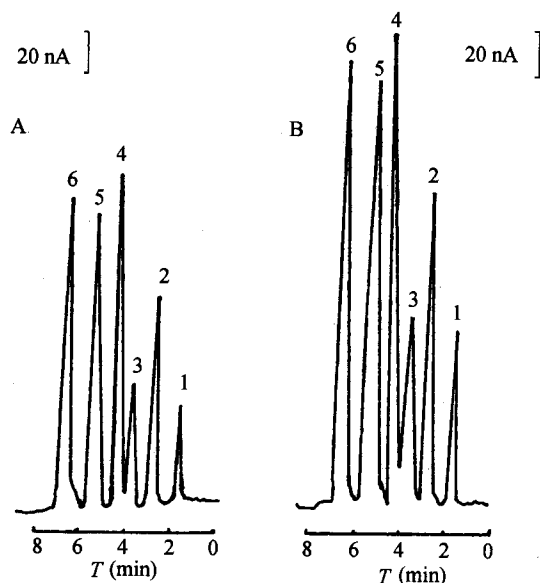

Fig. 6 Chromatograms of mixed standard solution of 1—Li^+, 2—Na^+, 3—NH_4^+, 4—K^+, 5—Rb^+ and 6—Cs^+. A: Co-CN-Fe CME; B: Nafion/Co-CN-Fe CME. Column, Shimadzu shim-pack IC-C1 (5.0 mm I.D. × 15 cm). Other conditions are as in Fig. 4.
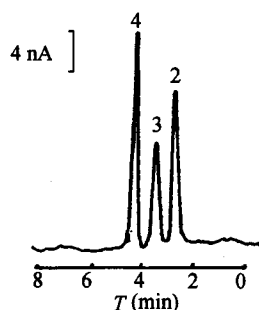
Application

Rainwater analysis: acid rain is a widespread environmental pollution problem. In order to analyze and evaluate the effects of acid precipitation in nature and artificial environments caused by acid rain, it is necessary to monitor the ionic components of rainwater. Na^+, K^+ and NH_4^+ are the major cation components of rainwater. They act as important role in the acid-base equilibrium of rainwater. The proposed method was applied to the analysis of rainwater (Fig. 7). The analysis was performed according to the specified procedure. The recoveries with this method were tested by the analysis of a spiked rainwater sample and replicated injections ($n = 7$). The results are given in Table 1. The results obtained by electrochemical detection (ECD) method are consistent with results obtained by conductivity detection (CD) method in IC. The data demonstrate that the proposed IC method is reliable for determining these cations in rainwater samples.

Table 1 Results of the alkali cations and NH_4^+ in rainwater sample detected by IC-ECD and IC-CD ($n = 7$)

Ions	Detection by ECD					Detection by CD	
	Mean (10^{-5} mol/L)	RSD (%)	Added (10^{-5} mol/L)	Found (10^{-5} mol/L)	Recovery (%)	Mean (10^{-5} mol/L)	RSD (%)
Na^+	6.15	3.40	10.00	10.32	103	6.21	3.83
NH_4^+	7.83	4.60	10.00	10.41	104	7.54	4.42
K^+	3.14	2.62	10.00	10.24	102	3.25	2.38
Rb^+	n.d.[a]		10.00	9.88	98.8	n.d.	
Cs^+	n.d.		10.00	9.78	97.8	n.d.	
Li^+	n.d.		10.00	10.34	103	n.d.	

[a] Not detected.

Fig. 7 Chromatograms of rainwater sample, 2—Na^+, 3—NH_4^+, 4—K^+. Other conditions are as in Fig. 4.

Conclusion

In this article, we successfully applied Nafion/Co-CN-Fe chemically modified electrode to detect electroinactive cation ions. The results of the experiment show that the method is very rapid, simple and highly sensitive for the detection of alkali metals and NH_4^+. Compared with conductivity detection, amperometric detection has the advantages of quick response, low cost, low detection limit, easy fabrication and miniaturization. The proposed method was successfully applied to the detection of the common cations in real water samples.

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