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Electrocatalytic oxidation and ion chromatographic detection of Br^-, I^-, SO_3^{2-}, $S_2O_3^{2-}$ and SCN^- at a platinum particle-based glassy carbon modified electrode

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Abstract

A modified method for dispersing platinum particles on a glassy carbon (GC) electrode was investigated. The ultramicro Pt particle-modified electrode obtained exhibited high catalytic stability and activity towards the oxidation of some halide ions (Br^-, I^-) and inorganic sulfur species ($S_2O_3^{2-}$, SO_3^{2-} and SCN^-). These anions were separated and detected by using ion chromatography and electrochemical detection via this novel dispersed Pt particles–GC working electrode. The detection limits were 20 ng/ml for Br^-, 1.0 ng/ml for I^-, 10 ng/ml for SO_3^{2-} and 4.0 ng/ml for SCN^-. This method was employed for the analysis of industrial and environmental waste waters.

1. Introduction

Ion chromatography (IC) has been an established analytical technique for more than 15 years and its scope has been extended from the determination of simple inorganic anions using ion-exchange separation and conductivity detection to include a diversity of solutes, separation methods and detection methods. The trends in IC have been summarized in a recent book [1]. The combination of ion-exchange separation with conductivity detection accounts for the bulk of publications on IC. Nevertheless, the emergence of alternative detection modes, especially spectroscopic and electrochemical detection methods, is significant [2]. Turning to the areas of application of IC, it is probable that environmental analysis is the most frequent area of application, especially for water samples, such as river waters, ground waters and sea waters. IC offers unrivalled sensitivity and selectivity in many instances.

Ion chromatographic technology via direct conductivity detection can easily separate and determine low concentration levels of halide anions and other anions [3–5]. Consequently, various methods, such as spectrophotometric [6,7], fluorimetric [8,9] and ion-selective electrode methods [10] have been developed for the determination of bromide, iodide, thiosulfate and thiocyanate. An ion-chromatographic system equipped with an amperometric detector makes it possible to determine trace amounts of anions. Amperometric detection via silver [11], gold [12], mercury [13] and glassy carbon (GC) electrodes [14] has been used to determine a series

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of anions. In this paper, the results of placing an anion-exchange column in front of the electrochemical detector are presented. A new type of modified electrode with dispersed ultramicro Pt particles was employed as an electrochemical detector. The electrochemical process for producing this chemically modified electrode (CME) with a modified surface of glassy carbon and a detailed study of the electrooxidation of the chloride complex of platinum(II) at a GC electrode was described previously [15]. This dispersed Pt particle-modified GC exhibits a very high catalytic stability and activity towards the oxidation of some halide ions (Br^-, I^-) and inorganic sulfur species (SO_3^{2-}, $S_2O_3^{2-}$ and SCN^-). These ions can be separated by IC and thus are determined simultaneously. Although bromide and iodide can be determined by IC with conductivity detection, the use of this novel CME as an electrochemical detector results in increased sensitivity and stability.

2. Experimental

2.1. Apparatus

Electrochemical system

A conventional cell with a three-electrode configuration was used throughout. Glassy carbon (electrode area = 0.12 cm^2) was used as a working electrode and was electrochemically activated following the published procedure [15] prior to use. A platinum wire was used as a counter-electrode and a saturated calomel electrode (SCE) as the reference electrode. Electrochemical measurements were performed with an FDH-3204 electrochemical analyser (Fudan University, Shanghai, China) and the potentials were measured and reported with respect to SCE.

Ion chromatographic system

The Gilson Model 715 HPLC system used consisted of the following components: Gilson Model 306 pump; Rheodyne Model 7125 injection valve equipped with a sample loop of 20 μl; ion-exchange column of Spherisorb SAX (200 × 4.0 mm I.D., 5 μm) (Dalian Institute of Chemical Physics, Chinese Academy of Sciences), maintained room temperature; and a Model-400 EC detector with MP 1305 GCE (EG&G PARC) as working electrode. A model 30-286 and Epson LQ-550 and Philips P3348 instruments were used to collect data record data and print out chromatograms, respectively.

Mobile phase

The mobile phase was prepared daily as 20 mmol/l $NaNO_3$–10 mmol/l NaH_2BO_3 (prepared from 10 mmol/l H_3BO_3 and NaOH), adjusting to pH 7.0. The mobile phase was filtered through filter-paper and briefly degassed in an ultrasonic bath before use. The experiments were carried out at room temperature.

2.2. Reagents

All chemicals were of guaranteed-reagent grade. All solutions were prepared with doubly distilled water. Analytical-reagent grade K_2SO_4, H_2SO_4 and K_2PtCl_4 (Shanghai Chemical Reagent Factory) were used as received. K_2PtCl_4 solution was freshly prepared.

Stock standard bromide and iodide solutions (ca. 100 μg/ml) were prepared daily by dissolving ca. 0.25 g of commercially available sodium bromide and sodium iodide in 250 ml of water. Working standard solutions were prepared by dilution with water as required.

Stock standard sulfite, thiosulfate and thiocyanate solutions (ca. 100 μg/ml) were prepared daily by dissolving sodium hydrogensulfite sodium thiosulfate and sodium thiocyanate in 250 ml of water. Working standard solutions were prepared by dilution with water as required.

Samples of natural water (lake) were kept at 4°C in polypropylene bottles before and after analysis.

3. Results and discussion

3.1. Electrochemical process for preparing Pt particle-modified working electrode

Prior to preparing the Pt particles–GC, the glassy carbon electrode was pretreated to be

electroactive by cycling it in 0.1 mol/l H_2SO_4 with a scan voltage range from −0.3 to +0.8 V for 10 min. Then the polished GC was scanned in $2.5 \cdot 10^{-3}$ mol/l K_2PtCl_4 in the potential range from +0.3 to −1.3 V for 10 min at a scan rate of 100 mV/s. It was very interesting that the anodic peaks for the oxidation of the $PtCl_4^{2-}$ complex decrease gradually from cycle to cycle and finally, on reaching the steady state, no distinct anodic peaks could be seen. Considering the oxide functional groups of an electrochemically activated GC electrode, it is reasonable to suggest that the oxygen atom of the functional group served as one of the two axial ligands when the planar complex of Pt(II) was oxidized to form the octahedral complex of Pt(IV). The surface complex hindered the electrooxidation of the Pt(II) complex by occupying active sites in the compact double layer, thus decreasing the apparent electrode area.

After the GC electrode had reached the steady state, the electrode was electrochemically activated by cycling it between −0.25 and +1.65 V in 0.1 *M* H_2SO_4. The surface complex on electrode can be transferred to platinum particles on cathodization. As shown in Fig. 1, the morphology of the cyclic voltammogram changed from cycle to cycle. The cathodic current, around a potential of −0.1 V on the initial cycles (curve a), was attributed to the reduction of Pt(IV) complex of electrode surface. At the same time, an anodic peak appeared at a potential of +1.05 V, where $PtCl_4^{2-}$ was oxidized. It is concluded that the Pt(IV) complex on the surface of GC can be reduced to Pt^0 or Pt(II) complex on the cathodic scan. Finally, the anodic peak at +1.05 V in Fig. 1 decreased as more and more platinum complexes were transformed in to platinum particles. After potential cycling for about 5 min between the fixed potentials in H_2SO_4 solution, a typical steady state for the activated Pt–GC electrode was achieved as curve b in Fig. 1.

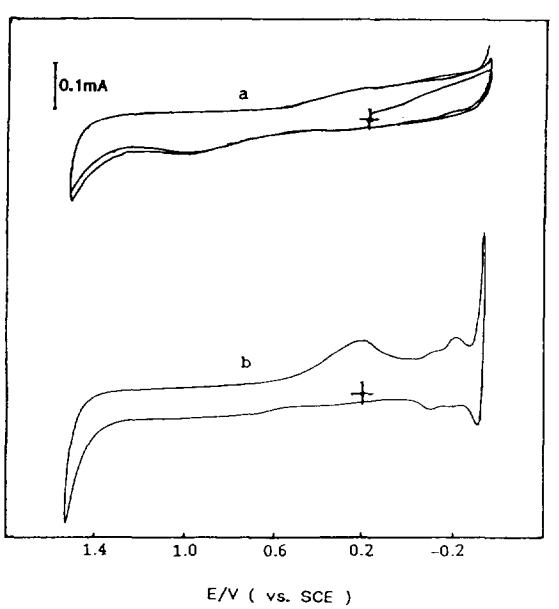

Fig. 1. Cyclic voltammograms of a completely deactivated GC electrode in 0.1 *M* H_2SO_4 Solution. (a) First two potential cycles; (b) steady-state after cycling for 5 min. Scan rate, 500 mV/s.

The above procedure was employed as a unique method to disperse ultramicro Pt particles on the surface of the GC electrode. This method was different from the common deposition technique, which employed the electroreduction of platinum salt from solution.

3.2. *Electrocatalytic behaviour of the CME for* I^- Br^- SO_3^{2-} *and* SCN^-

Cyclic voltammetric (CV) experiments, carried out in a conventional three-electrode voltammetric cell, were recorded in an electrolyte of 0.02 mol/l $NaNO_3$–0.01 mol/l NaH_2BO_3 (pH 7.0), in the potential range between 0.0 and +1.2 V (vs. Ag/AgCl). Fig. 2 shows the cyclic voltammograms of Br^-, I^-, SO_3^{2-} and SCN^- on the Pt particle-modified GC electrode. Well defined oxidation responses for these ions were obtained at +0.9 to +1.2 V. Compared with the results obtained at the GC electrode, the oxidation peak potential shifted 300–500 mV negatively (for I^-, 1200 mV at the bare GC and 900 mV at the CME) and the peak current increased significantly, indicating a great improvement in the oxidation of these ions in the electrode process. These phenomena show that Pt particles have an electrocatalytic oxidation effect with halide ions and inorganic sulfur anions. It was indicated from the cyclic voltammograms for iodide on the Pt particle CME in an electrolyte of 0.02 mol/l $NaNO_3$–0.01 mol/l NaH_2BO_3 (pH

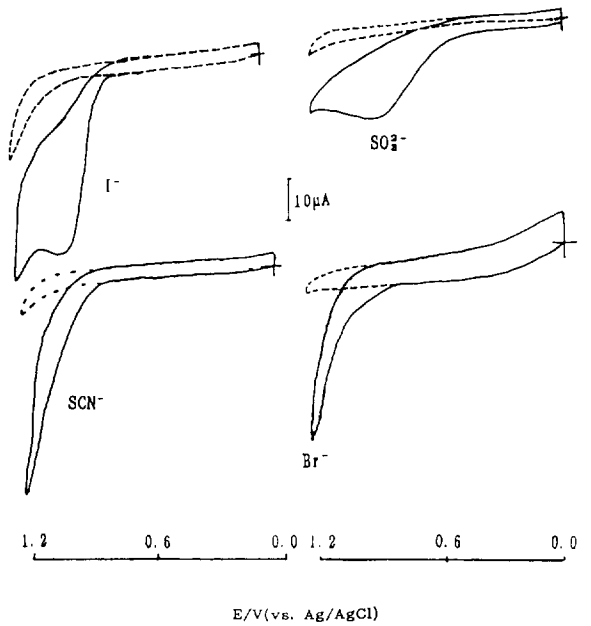

Fig. 2. Steady-state cyclic voltammograms of $1.0 \cdot 10^{-3}$ mol/l SO_3^{2-}, Br^-, I^- and SCN^- at the Pt particle-modified electrode. Electrolyte: 0.02 mol/l $NaNO_3$ + 0.01 mol/l NaH_2BO_3 (pH 7.0). Dashed curves, electrolyte; solid curves, analysed anions. Applied potential range, 0.0–1.2 V (vs. Ag/AgCl); scan rate, 100 mV/s.

7.0) at different scan rates that the peak current–scan rate dependence was linear over the range of scan rates studied (Fig. 3A). The catalytic oxidation response was long-lived and the catalytic oxidation current was directly proportional to the iodide concentration (Fig. 3B), which was characteristic of a surface-controlled detection mechanism and the analytical signal concurred with the result from the electrocatalytic oxidation of adsorbed analyte simultaneously with anodic formation of surface oxide. Considering the high catalytic activity of the Pt particle-modified electrode, this is due to the fact that dispersed Pt particles possess an extended apparent electrode area and the number of Pt atoms at the edges and corners is greatly increased. Hence the catalytic species are increased and the reaction rate is increased, indicating a great improvement in the electrode oxidation process of these ions.

The mechanism for the oxidation of these anions on the Pt particle CME is consistent with the results on Pt metal electrodes reported previously [16]. This anodic electrocatalytic phenomenon is associated with the formation of a hydroxide film on the GC base electrode. Anodic formation of hydroxide at the platinum particle-modified electrode was concluded to involve a quasi-reversible discharge of H_2O to produce adsorbed hydroxyl radicals by the reaction $Pt + H_2O \rightleftharpoons PtOH + H^+ + e^-$ [17]. The oxidation reactions of these anions on the CME correspond to the increase in oxygen content of these reaction products, e.g., $SO_3^{2-} \rightarrow SO_4^{2-}$, $I^- \rightarrow IO_3^-$ and $Br^- \rightarrow BrO_3^-$ [18]. This hydroxide film on the Pt particles was concluded to function as an oxygen-transfer catalyst and the adsorbed hydroxyl radial (PtOH) was the active hydroxide catalytic species, based on the observation of the greatest catalytic activity towards these small inorganic anions.

The stability of the CME was investigated with regard to its catalytic behaviour in various electrolyte buffer systems ranging from pH 4.5 for acetate buffer to pH 10.0 for carbonate buffer. For example, using acetate buffer (pH 4.5) and carbonate buffer (pH 10.0) as electrolyte in CV experiments, after the catalytic oxidation currents had reached their steady state, during more than 50 cycles of potential scan, there was no obvious decrease in the anodic peak currents. Further, the CME appeared to possess excellent mechanical and chemical stability. Immersing the electrode in an ultrasonic bath for 5 min and immersing it in 1.0 *M* H_2SO_4 and 1.0 *M* KOH for 2 min had no effect on the magnitude or longevity of the catalytic oxidation response for these ions. The high stability of the CME might be due to the unique electrodeposition process; the electroreduction of platinum salt from the platinum complex solution could produce Pt^0 in the inner surface of the glassy carbon electrode. This excellent mechanical and chemical stability was very favourable for its application in flow systems.

3.3. Application of Pt particles–GC electrode in IC analysis

The separation of two groups, I^-, Br^-, SCN^-

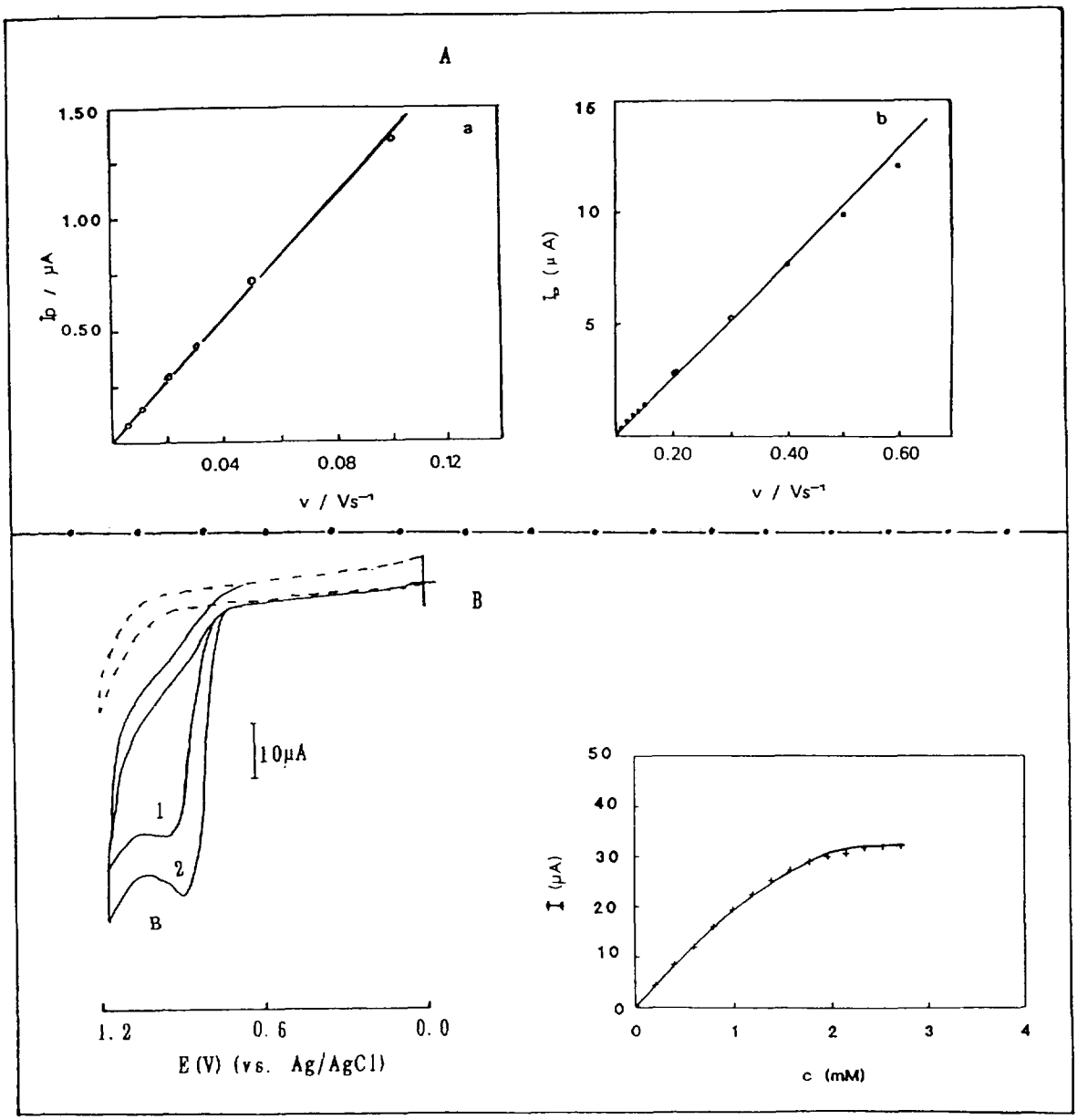

Fig. 3. (A) Linear dependence of current of iodide at Pt particle CME on scan rate. (B) Steady-state cyclic voltammograms of iodide at the CME [(1) $C_{I^-} = 1.0 \cdot 10^{-3}$ mol/l; (2) $C_{I^-} = 2.0 \cdot 10^{-3}$ mol/l] and plot of the electrocatalytic oxidation current vs. I^- concentration for CV. Other conditions as in Fig. 2.

and SO_3^{2-}, $S_2O_3^{2-}$, SCN^-, was achieved by using a Spherisorb SAX anion column. A typical chromatogram is shown in Fig. 4. These anions were eluted by two group separation modes in the orders Br^-, I^-, SCN^- and SO_3^{2-}, $S_2O_3^{2-}$, SCN^-.

3.4. Applied potential

As the potential was increased, the peak also generally increased, hence this CMA can be used as a sensitive amperometric detector to detect halide ions and sulfur compounds. When an

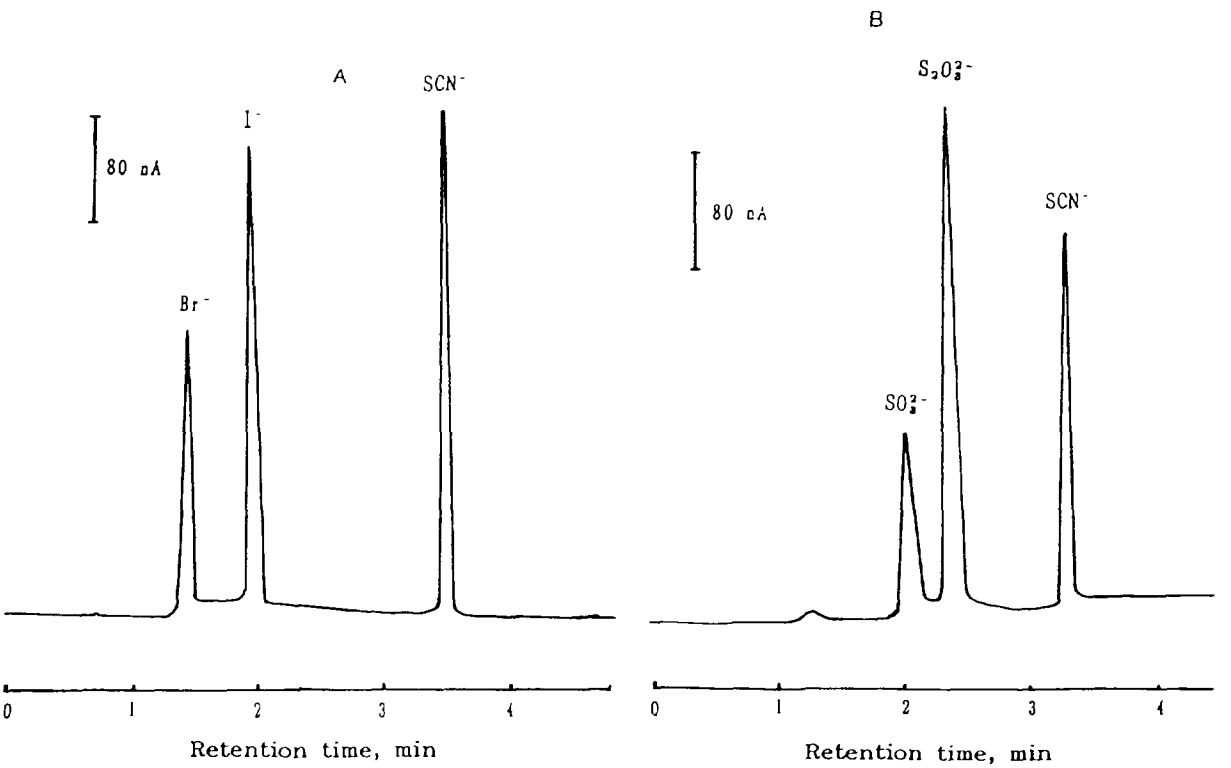

Fig. 4. Typical ion chromatographic detection obtained by using the Pt particle CME. Mobile phase, 0.02 mol/l $NaNO_3$ + 0.01 mol/l NaH_2BO_3 (pH 7.0); flow-rate, 1.0 ml/min; E_{app} = +1.0 V (vs. SCE); Column, Spherisorb SAX (5 μm); column temperature, 22 ± 2°C (A) 7.0 μg/ml Br^-, 5.0 μg/ml I^- and 7.5 μg/ml SCN^-; (B) 7.0 μg/ml SO_3^{2-}, 4.0 μg/ml $S_2O_3^{2-}$ and 5.0 μg/ml SCN^-.

applied potential of more than 1100 mV was employed, the peak heights of the determined anions increased rapidly. However, at an applied potential as high as 1200 mV, the baseline on the chromatogram was much more subject to the influence of the pulsatory motion of the pump. Further, the reproducibility of the peak heights was poor. An applied potential of 1000 mV was therefore adopted.

3.5. Effect of the pH of the mobile phase

As the pH of the mobile phase was raised (pH > 7.0), the retention times of the anions decreased and the peak heights increased. Although a higher pH of the mobile phase gave a sensitive method for the determination for those ions, overlapping became serious. At pH > 8.0, the peaks of bromide and iodide overlapped. Accordingly, in subsequent work, a mobile phase of pH 7.0 was used for the determination of the anions. Regarding the influence of the electrolyte strength on separation, the peak heights of these ions decreased with increasing concentration of $NaNO_3$ and the retention times also became shorter. From these results, we considered a suitable concentration of $NaNO_3$ to be 0.02 mol/l.

3.6. Calibration, dynamic linear and detection limit

A calibration graph was obtained for iodide with a linear range up to 60 μg/ml, the correlation coefficient was 0.9986 and the detection limit was 1.0 ng/ml. For concentrations lower than 1.0 ng/ml, the detector became insensitive to iodide. Further, the relative standard deviation of ten measurements was 2.5% for 10 ng/ml iodide. The dynamic linear range and detection

Table 1
Dynamic linear range, regression equation and detection limit

Anion	Dynamic linear range (μg/ml)	Detection limit (ng/ml)	R.S.D. (%) (n = 10)
Br^-	0–35	20	2.8
I^-	0–60	1	2.5
SCN^-	0–70	4	4.4
SO_3^{2-}	0–50	10	3.4
$S_2O_3^{2-}$	0–60	6	6.9

Conditions: mobile phase, 0.02 mol/l $NaNO_3$ + 0.01 mol/l NaH_2BO_3 (pH 7.0); flow-rate, 1.0 ml/min; E_{app} = +1.0 V (vs. SCE); column, Spherisorb SAX (5 μm); column temperature, 22 ± 2°C.

limit (signal-to-noise ratio = 3) of these ions are given in Table 1.

3.7. Determination of ions in environmental water samples

Samples of 0.05 μl of environmental water from South Lake were analysed by the procedure after filtration through a membrane filter of 0.2-μm pore size. The accuracy of the proposed method was checked by adding known amounts of iodide and bromide to the water sample. The results obtained are given in Table 2 and indicate that ion chromatography with Pt–GC electrochemical detection is comparable to ion-pair RP-HPLC with indirect UV detection [19]. Examples of chromatograms obtained for lake water sample with I^- and Br^- added are illustrated in Fig. 5, demonstrating the applicability of the proposed method to the accurate determination of these anions in water at low concentrations.

4. Conclusions

Irreversible oxidation of K_2PtCl_4 on GC can be obtained in the absence of chloride ions. The oxygen atom of the oxide functional group on GC may serve as one or two axial ligands to form an octahedral Pt(IV) complex, which results in the formation of a Pt(IV) complex on the

Table 2
Analytical results for determination of I^- and Br^- in lake water

Anion	Proposed method[a]				Found (UV)[b] (μg/ml)
	Added (μg/ml)	Found (mean ± S.D., n = 6) (μg/ml)	R.S.D. (%) (n = 6)	Recovery (%)	
Br^-	–	0.11 ± 0.05	3.4	–	0.12
	0.5	0.61 ± 0.01	4.1	99.6 ± 1.2	0.62
	1.25	1.37 ± 0.01	0.87	102.6 ± 1.0	1.3
	2.0	2.1 ± 0.03	1.3	114.0 ± 1.4	2.1
	3.0	3.1 ± 0.003	2.8	97.4 ± 0.1	3.2
	5.0	5.1 ± 0.02	5.1	108.8 ± 0.36	5.2
I^-	–	N.D.[c]	–	–	N.D.[c]
	0.125	0.13 ± 0.001	0.89	103.2 ± 0.96	0.13
	0.25	0.27 ± 0.004	1.6	106.0 ± 1.7	0.26
	0.5	0.49 ± 0.009	1.7	97.4 ± 1.8	0.47
	0.35	0.34 ± 0.007	2.0	97.7 ± 2.0	0.37
	1.25	1.24 ± 0.003	0.21	99.2 ± 0.24	1.3

Water sample collected from South Lake (Changchun, China) and analysed in September 1994.
[a] Sample dilution factor = 100.
[b] UV detection conditions as in Fig. 5.
[c] N.D. = not detectable.

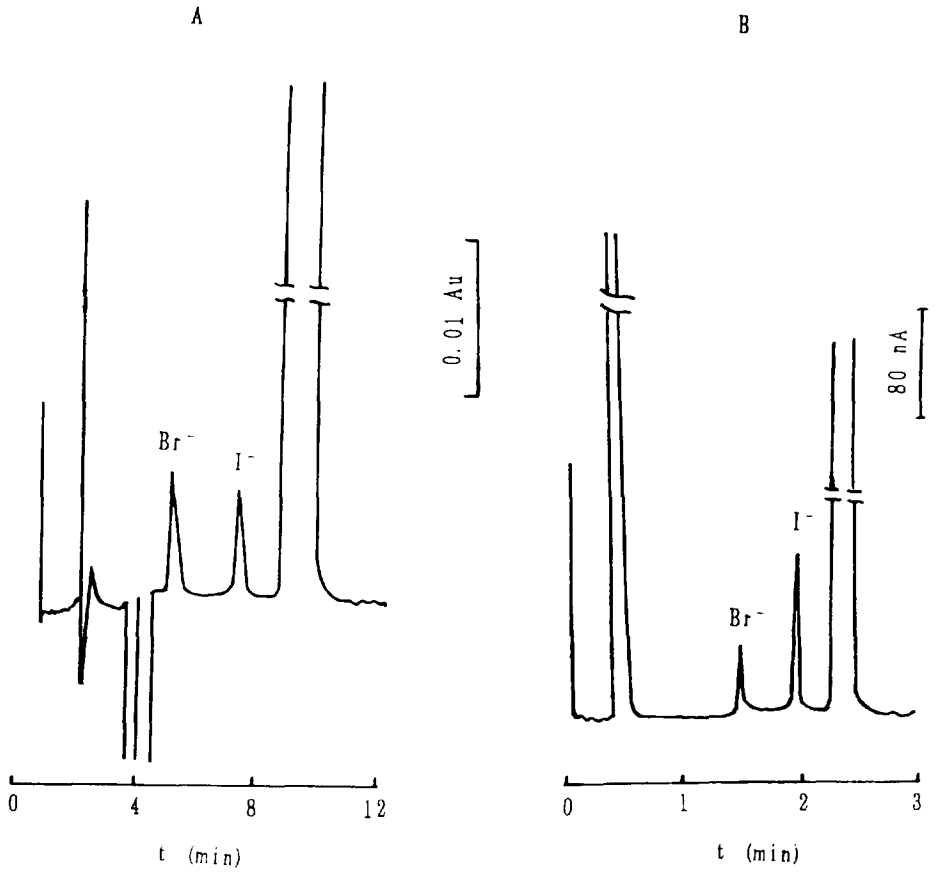

Fig. 5. Chromatograms of a water sample with 1.0 μg/ml I^- and 10 μg/ml Br^- added. (A) RPLC with UV detection, optimum conditions according to Ref. [19]: mobile phase, 35% CH_3OH–2.5 mmol/l. TBAOH–0.5 mol/l toluene-*p*-sulfonic acid (pH 5.5); flow-rate, 1.0 ml/min; detection wavelength, 254 nm, column, Nucleosil C_{18} (5 μm) (200 mm × 4.0 mm I.D.). (B) Electrochemical detection via Pt particle-modified GC electrode. Ion chromatographic conditions as in Fig. 4.

surface of the GC electrode and, in turn, deactivates the working electrode by occupying the active sites. The surface complex can be reduced to form platinum ultramicro particles cathodization. The Pt particle-modified electrode obtained exhibited a high catalytic effect for halide ions and inorganic sulfur compounds. At good detection limit for the separation of these ions was obtained by ion chromatography with electrochemical detection using the Pt particle-modified working electrode. Such small inorganic anions can be determined by this CME.

Acknowledgement

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