Determination of Chromium(VI) in Electronics Materials Using Trioctylamine Modified Carbon Paste Electrode

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A trioctylamine (TOA) modified carbon paste electrode (TOA/CPE) was firstly utilized to determine Cr(VI) in electronics materials. The effects of preconcentration conditions, that is, TOA amount and accumulation time on Cr(VI) accumulation were examined and the optimum experiment conditions for the determination were identified. A sensitive reduction peak in the stripping voltammogram at -0.45 V, a characteristic of trace Cr(VI), was detected when the accumulation time was 10 min. Under optimized conditions, TOA/CPE demonstrated an enhanced sensitivity for Cr(VI), providing a low detection limit ($S/N = 3$) at 3.4×10^{-9} M. Interference studies also displayed high selectivity of the TOA/CPE for Cr(VI); this electrode can accurately determine Cr(VI) in the presence of Cr(III) (600-fold concentration) and other interfering cations.

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Introduction

Cr(VI) was proved to be detrimental to mucous membranes and kidney, and has been classified as a second inorganic contaminant in the environment, although Cr(III) is considered to be biologically essential in mammals for the maintenance of glucose, lipid, and protein metabolism.^{1,2}

Recently, great amounts of Cr(VI) in the form of $\text{Cr}_2\text{O}_7^{2-}$ have been entering into environment via discarded electronics materials, and have led to high toxicity and carcinogenicity to humans as the electronics industry has rapidly grown. On the other hand, Cr(III) and Cr(VI) usually coexists in the electronics materials, which results in a huge inconvenience in the accurate determination of Cr(VI). No effort has been made to develop highly sensitive and selective electrodes for the determination of Cr(VI) in electronics materials.

Many sophisticated analytical techniques, such as UV-visible spectrophotometry,³ diffuse reflectance Fourier-transform infrared spectroscopy,⁴ atomic adsorption spectrophotometry,⁵ inductively coupled plasma-atomic emission spectrometry,⁶ and electrochemical methods⁷⁻¹⁰ have been employed for the determination of trace levels of Cr(VI) in natural water. Among them, the determination of Cr(VI) with the aid of a carbon paste electrode (CPE) and some chemical modifier has been proved to be the most promising alternatives because of their high sensitivity, low detection limit, relative simplicity, low cost of materials, and ability to distinguish Cr(VI) from Cr(III).^{11,12}

The effective preconcentration of Cr(VI) from Cr(VI) and Cr(III) mixture and prevention of the interference of Cr(III) to Cr(VI) are both essential to obtain the best results in determination of Cr(VI). As reported recently, trioctylamine

(TOA) has a strong affinity for Cr(VI), and can effectively extract and concentrate Cr(VI) through a highly selective anion-exchange reaction.¹³ In the present work, TOA was firstly utilized to modify carbon paste electrodes (TOA/CPE) for determination of Cr(VI) in electronics materials.

Experimental

Reagents and chemicals

Trioctylamine (TOA), chloroform, spectroscopic graphite powder, liquid paraffin, potassium dichromate, chromium chloride, copper chloride, iron chloride, potassium chloride, ammonium chloride, sodium chloride, palladium chloride, and cadmium chloride were obtained from the Sinopharm Chemical Reagent Co. (China) and used as received. All other chemicals, unless mentioned otherwise, used in this investigation were of analytical grade (99%). All of the solutions were prepared with Milli-Q (Millipore) A-10 gradient deionized water. Freshly prepared solutions were used in all experiments.

A Cr(VI) stock solution (0.01 M) was prepared by dissolving 2.9418 g potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in a 1-L 0.15 M H_2SO_4 solution. Model solution of Cr(VI) was obtained by diluting a stock solution of Cr(VI) with a 0.15 M H_2SO_4 solution. Working solution of other metals was prepared from their own salts above mentioned with a 0.15 M H_2SO_4 solution.

Apparatus

Electrochemical measurements were performed using TOA/CPE as a working electrode, Pt wire as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The Cr(VI) concentration was determined by making a stripping voltammogram at a computer-controlled CHI660 electrochemical analyzer in the range of -1.0 to 0.6 V with different scan rates. Dissolved oxygen was removed by purging

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nitrogen, and the experimental temperature was kept at $25 \pm 1^\circ\text{C}$. For pH measurements, a Metrohm 691 pH meter was used. The UV-vis absorption spectra of Cr(VI) were determined using a 1240 UV-visible spectrophotometer (Japan).

Procedure

Preparation of TOA/CPE. Different amounts of TOA (0.05 – 0.20 g) were sufficiently commixed with 1.9 g chloroform, followed by the addition of 0.667 g spectroscopic graphite powder and complete blend. After evaporating the chloroform, 0.20 ml liquid paraffin (0.1668 g) was added and TOA modified carbon paste was prepared by intimately homogenizing. The ready-made paste with an ohmic resistance of about $5\ \Omega$ was then packed into a piston-driven carbon-paste holder. The electrode surface was renewed by the extrusion of approximately 0.5 mm carbon paste from the holder and smoothing with a filter paper. Typically, such a mechanical renewal of a carbon-paste surface is done when starting a new series of measurements (e.g. prior to the analysis of each sample).

Analysis of model solution. After preparing a Cr(VI) model solution to be analyzed and purging with N_2 for ca. 5 min, measurements were carried out in the cathodic stripping voltammetric mode. A typical experiment consisted of three consecutive steps with the following experimental conditions: a preconcentration step for 1 – 20 min under a stirring condition, a washing step three times, and a stripping step run from +0.6 to –1.0 V by applying different scan rates. For a comparison, nude CPE was directly inserted in the Cr(VI) model solution under the same condition. A mixture solution composed of 0.15 M K_2SO_4 and 0.15 M H_2SO_4 was used as electrolyte.

Analysis of real sample. Electronic material scraps were pretreated using a wet nitration method.^{14–16} Then 0.5 g electronic material scraps were dissolved into a mixture solution of 2 mL HCl and HNO_3 (15 wt%). Fe and Cu elements were completely precipitated by adjusting the pH value to 9.5 and 11, respectively. After boiling for 2 – 3 min and then cooling to room temperature, the above-mentioned solution was filtered, diluted to 10 mL using deionized water and used as a real sample solution. The analysis procedure for a real sample solution was in accordance with that for a model solution.

The Cr(VI) concentration in a real sample was also determined by UV-visible spectrophotometry. The sample pretreatment process was identical to that by stripping voltammetry. According to literature reports,¹⁷ the detection wavelength was set at 372 nm.

Results and Discussion

Principles of the preconcentration process

In acid surroundings, TOA can preconcentrate Cr(VI) in the form of $\text{Cr}_2\text{O}_7^{2-}$ through an anion-exchange course.^{18,19} Firstly, TOA (represented as R_3N) can be protonated according to Eq. (1):

Then $\text{Cr}_2\text{O}_7^{2-}$ can be preconcentrated by R_3NH^+ by the anion-exchange procedure according to Eq. (2):

Determination of Cr(VI) in model solution and real sample using TOA/CPE

Figure 1 presents stripping voltammograms of TOA/CPE and

Fig. 1 Comparison of the reduction response for Cr(VI) at TOA/CPE (a, c) and nude CPE (b) before (c) and after (a, b) the preconcentration process. Electrolyte, 0.15 M K_2SO_4 – H_2SO_4 ; scan rate, 20 mV/s; Cr(VI), 1.0×10^{-7} M.

Fig. 2 Effect of the TOA amount on the reduction peak current of Cr(VI). Cr(VI), 1.0×10^{-7} M.

nude CPE before and after they were placed in a Cr(VI) model solution for 10 min. The accumulation of Cr(VI) and its subsequent reduction at the TOA/CPE gave rise to an apparent reduction peak at –0.45 V (curve a) compared to that obtained with nude CPE under otherwise identical conditions (curve b). Yet no reduction peak appeared before the TOA/CPE was treated with the preconcentration procedure (curve c). Similar results were obtained after TOA/CPE and nude CPE were placed in a real sample solution (curves not shown here). These above results proved that Cr(VI) could be effectively preconcentrated by TOA, which highly increased the electrochemical response of TOA/CPE to Cr(VI). On the other hand, the cathodic current for the TOA-free CPE is much larger than that for TOA/CPE before the preconcentration process, indicating that TOA helps to decrease the background current of CPE.

Influences of different operational parameters

Effect of the TOA amount on Cr(VI) accumulation. The role of TOA in our work was to preconcentrate Cr(VI) from the model or real solution, its amount greatly influenced the accumulated amount of Cr(VI), which shows that a condign amount of Cr(VI) is needed in the course of electrode preparation. Figure 2 shows the relationship of the reduction peak current with the amount of TOA when the weight ratio of graphite and paraffin is set at 1:0.25.²⁰ With an increase in the TOA amount, the peak current

Fig. 3 Effect of the accumulation time on the reduction peak current of Cr(VI). Cr(VI), 1.0×10^{-7} M.

Fig. 4 Stripping voltammograms of Cr(VI) at TOA/CPE in 0.15 M HNO₃-KNO₃ (a), H₂SO₄-K₂SO₄ (b) and HCl-KCl (c) solutions, respectively.

goes up initially, culminates when the TOA amount is 0.125 g and remains stable even if the TOA amount increases afterwards, which means that the optimal weight ratio of the graphite/paraffin/TOA is *ca.* 1:0.25:0.19.

Influence of time on Cr(VI) accumulation. Figure 3 presents the reduction peak current value after TOA/CPE was placed in the model solution for different time. The reduction peak currents increased along with the accumulation time from 3 to 10 min, and remained invariable up to 30 min, which illuminates that 10 min is adequate for Cr(VI) accumulation. The reason why the cathodic response for Cr(VI) reaches a plateau is that all the TOA molecules are combined with Cr(VI) and the amount of the accumulated Cr(IV) culminates when the TOA/CPE is placed in a Cr(VI) solution for 10 min.

Influence of electrolyte on Cr(VI) determination. Figure 4 illustrates stripping voltammograms of TOA/CPE in a 0.15 M H₂SO₄-K₂SO₄, a HCl-KCl and a HNO₃-KNO₃ solution, respectively. No reduction peak exists when Cr(VI) is determined in HNO₃-KNO₃ solution (curve a), while obvious reduction peak appears when Cr(VI) is determined in H₂SO₄-K₂SO₄ or HCl-KCl solution. Moreover, the reduction peak current in H₂SO₄-K₂SO₄ solution (curve b) is higher than that in HCl-KCl solution (curve c), indicating that the electrochemical response of Cr(VI) obtained in the SO₄²⁻ system was better than that obtained in the Cl⁻ system.

Fig. 5 Absorption spectra of a 0.01 mM Cr(VI) solution before (a) and after adding 0.30 mM KCl (b), K₂SO₄ (c) and KNO₃ (d).

Table 1 Interferences of various cations on the determination of 1.5×10^{-5} M Cr(VI)

Cation	Acceptable maximum concentration/mM
K ⁺ , Na ⁺ , NH ₄ ⁺	10
Cr ³⁺	9
Fe ³⁺	3
Cu ²⁺ , Pd ²⁺ , Cd ²⁺	2

To illuminate the effect of different anions on Cr(VI) determination, UV-visible spectra of the Cr(VI) solution were measured after 0.30 M KCl, K₂SO₄ or KNO₃ were added, as depicted in Fig. 5. Cl⁻ and SO₄²⁻ had no influence on the absorption curves of Cr(VI), while the absorption peak position changed after NO₃⁻ was added, which may be due to that NO₃⁻ can fleetly complex with Cr(VI). Based on these results, a H₂SO₄-K₂SO₄ solution was chosen as an electrolyte to determinate Cr(VI) in our work.

Effect of the scan rate on the Cr(VI) determination. The change in the electrochemical reduction current with the scan rate was investigated, and it was found that the reduction peak current linearly increased with the scan rate; the linear equation is $i_p = 6.1218v + 0.1471$ in the range of 20 – 200 mV/s, indicating that this electrochemical course is mainly controlled by an adsorption process.²¹

Maximum acceptable concentration of interfering cations

The interfering effect of some cations on the analysis of 1.5×10^{-5} M Cr(VI) was studied. Table 1 presents the maximum acceptable concentration of various interfering cations when the test error of Cr(VI) was set at 5%. The determinations of Cr(VI) could be carried out in the presence of 600-fold excess of Cr(III), and the presence of high concentrations of K⁺, Na⁺, NH₄⁺, Fe³⁺, Cu²⁺, Pd²⁺ and Cd²⁺ did not have any significant effect on the Cr(VI) signal. In a comparison with other reported methods,²² the interference effect of Cr(III) was greatly lowered.

Calibration curve of Cr(IV) under the optimum conditions

Figure 6 shows a calibration curve of Cr(VI) at the TOA/CPE after being treated with the above-mentioned optimum preconcentration procedure. The response current of Cr(VI) in the model solution showed a linear relationship with the concentration of Cr(VI) over the range of 5.0×10^{-7} – 1.0×10^{-3} M. The equation and the correlation coefficient (*r*) were $I = 0.0292C + 0.7138$ (*I*, mA; *C*, μM) and 0.9898, respectively. Based on the above equation and the determined reduction

Fig. 6 Calibration curve of Cr(VI) at the TOA/CPE after being treated with the preconcentration procedure. Experimental conditions: TOA amount, 0.125 g; accumulation time, 10 min.

Table 2 Comparison of the concentration of Cr(VI) in electronic equipment scraps determined by stripping voltammetry or spectrophotometry

Sample	Concentration of Cr(VI) in real samples/mM	
	Stripping voltammetry	Spectrophotometry
1#	0.0531	0.0522
2#	0.0133	0.0141
3#	0.021	0.022
4#	0.989	1.012

Samples 1# to 4# are electronic material scraps from different electronics products.

current, the concentration of Cr(VI) in a real sample solution could be easily and accurately calculated.

Merits of TOA/CPE in an analytical process: reproducibility and detection limit of the method

Under the optimum experimental conditions, the detection limit was obtained as 3.4×10^{-9} M ($S/N = 3$). The reproducibility in the preparation of different TOA/CPE for determining Cr(VI) is excellent in terms of the experimental results. The relative standard deviation (RSD, %) for eight measurements was less than 3%. Furthermore, TOA/CPE had a stable response to Cr(VI) for the following six months. The above results prove that TOA/CPE has good reproducibility and stability, and a low detection limit.

Analysis of real sample

Four kinds of electronic material scraps were pretreated; the obtained determination results from stripping voltammograms are given in Table 2. For a comparison, Cr(VI) concentrations in electronic material scraps have also been determined by UV-visible spectrophotometry. The determined results of these two methods were close, which means that the accuracy of the electrochemical method was satisfactory. As can be seen, the TOA/CPE could be successfully applied to the determination of trace amounts of Cr(VI) in electronic material scraps.

Conclusion

In this work, TOA/CPE was successfully utilized to determine

Cr(VI) in electronic material scraps. This method can accurately determine Cr(VI) in the presence of Cr(III) (600-fold concentration); the detection limit is 3.4×10^{-9} M, which proves that this method has both high selectivity and sensitivity. Furthermore, this method is convenient and inexpensive, and the precision, reproducibility and stability of the method were satisfactory.

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