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Determination of Cr(VI) in the presence of high excess of a Cr(III) by adsorptive stripping voltammetry

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ABSTRACT

A sensitive and highly selective adsorptive stripping voltammetric procedure for determination of traces of Cr(VI) is presented. Cr(III) interference was minimized due to (a) partial adsorption of this form of chromium from the sample on aluminum oxide and (b) using as a detection method adsorptive stripping voltammetry, which allows for selective determination of Cr(VI) in the presence of a 100-fold excess of Cr(III). The procedure can be used for determination of Cr(VI) even in the presence of a 10,000-fold excess of Cr(III). Conditions of Cr(III) adsorption on aluminum oxide were optimized while conditions of Cr(VI) determination were based on literature data. The calibration graph for Cr(VI) for an accumulation time of 30 s was linear from 1×10^{-9} to 4×10^{-8} mol L^{-1}. The detection limit was 7×10^{-10} mol L^{-1}. The proposed procedure was applied for Cr(VI) determination in a river water sample.

1. Introduction

Chromium occurs in the environment in trivalent and hexavalent oxidation states. Cr(VI) and Cr(III) enter the environment mainly from the discharge of steel, electroplating, tanning and paint production industries [1,2]. Depending on its oxidation state, the physiological effects of chromium on the biological systems are totally opposite. Cr(III) is an essential component having an important role in the glucose, lipid and protein metabolism, whereas Cr(VI) is believed to be toxic and carcinogenic [3]. Taking into account different behavior of both chemical forms of chromium in environmental systems, to assess the toxicity of the sample, determination of chromium species for this purpose is necessary.

Various analytical methods were used for Cr(VI) determination in the presence of Cr(III). The most widely employed procedures for chromium speciation are based on a selective retention of Cr(VI) or Cr(III) using aluminum oxide [4–10], titanium oxide [11–13], ion exchange resins [14–17] or various functionalized and non functionalized adsorbents [18–21]. As detection methods usually atomic spectrometric methods such as ET AAS [9,11,13,16], ICP OES [4,12] or ICP MS [15,17,22] are used. Often to obtain a low detection limit, preconcentration of the determined form was carried out simultaneously with the separation step.

Adsorptive stripping voltammetry (AdSV) is also often used for speciation of chromium. Procedures used for chromium speciation by AdSV are reviewed in [23]. This method offers a low detection limit and allows for direct determination of Cr(VI) [24–32] or both forms of chromium [33]. The low detection limit in AdSV is obtained due to the preconcentration step included in this method. Direct determination of Cr(VI) is possible due to a formation of different complexes with Cr(III) present in the sample and Cr(III) generated as a result of electroreduction of Cr(VI). The most commonly exploited procedure of direct determination of Cr(VI) in the presence of the Cr(III) was described in papers [24,29,30]. In this procedure a decrease of Cr(III) signal with time after the addition of DTPA was observed, while the Cr(VI) signal was stable. The authors attributed such behavior of Cr(III) to the formation at first of active complex of Cr(III)-H_2DTPA which are converted with time to a more stable non-active form Cr(III)-DTPA [30]. Such determinations of Cr(VI) are usually possible only in the presence of a 10–100-fold excess of Cr(III). To obtain better selectivity of Cr(VI) determination, an additional separation step was usually introduced such as precipitation on aluminum hydroxide [34–36], application of masking agents [37–41] or adsorption on Chelex-100 [42].

In this manuscript to obtain a low detection limit and the possibility of determination of Cr(VI) in the presence of a high excess of Cr(III) separation of chromium forms on aluminum oxide was coupled with a species selective adsorptive stripping voltammetric detection method. An additional advantage of the coupling retention of Cr(III) on aluminum oxide and stripping voltammetric detection method is simultaneous adsorption of humic substances on this adsorbent.

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2. Experimental

2.1. Apparatus

The measurements were performed using a μAutolab analyser made by Eco Chemie, the Netherlands and a HMDE (MTM-ANKO, Poland). The three-electrode water jacketed voltammetric cell of volume 10 mL consisted of an Hg electrode, a Pt electrode and an Ag/AgCl reference electrode was used. The Hg drop area was 0.86 mm^2. The temperature of measurements was controlled using a thermostat (PolyScience, USA). Microshaker326m made by Premed, Poland was used for mixing sample solutions with Al_2O_3. For centrifuging of the Al_2O_3 from the solution, the laboratory centrifuge MPW-250, Poland was applied.

2.2. Reagents

CH_3COOH, KNO_3 and Suprapure NaOH were obtained from Merck. KNO_3 was additionally purified by recrystallization from its saturated solution acidified to pH about 2 using concentrated HNO_3. Crystallization was repeated twice. $(NH_4)_2SO_4 + NH_4OH$ buffers (pH: 8.3, 8.8, 9.0, 9.3 and 10.0) were prepared from Suprapure reagents, Merck. Morpholinoethanesulfonic acid (MES) was obtained from Fluka. Suprapure NaOH was used to adjust pH of acetate and MES buffers. Diethylenetriaminepentaacetic acid (DTPA) was obtained from Sigma. Aluminum oxide, nanopowder <50 nm particle size was obtained from Aldrich. It was additionally purified by shaking 0.25 mol L^{-1} KNO_3 + 0.005 mol L^{-1} DTPA + 0.05 mol L^{-1} acetate buffer (pH 6.1), sedimentation and drying at 50 °C. Presence of KNO_3 in the solution lead to faster purification of Al_2O_3. A standard solutions of Cr(VI) and Cr(III) at concentration 1 g L^{-1} were obtained from Fluka. Working solutions of Cr(III) and Cr(VI) were prepared by dilution of standard solutions with 0.02 mol L^{-1} HCl and water, respectively. River fulvic acid was a standard sample obtained from the Suwannee River and purchased from the International Humic Substances Society. Humic acid sodium salt was obtained from Aldrich. Water used to prepare all solutions was purified in the Millipore system.

2.3. Standard procedure of sample preparation

10 mL of the analyzed sample solution alkalized using ammonia buffer was pippeted into a centrifuge tube and 200 mg of Al_2O_3 as a dry powder was added. Then the sample was shaken for 45 s using a microshaker and Al_2O_3 was separated by rotating at 10,000 rpm for 5 min.

2.4. Standard procedure of measurement

Determination of Cr(VI) in the sample prepared as described above was carried out according to the procedure described in [29]. 5 mL of the sample was pippeted into the electrochemical cell thermostated to 40 °C and the following reagents were added: 1.5 mL 3 mol L^{-1} KNO_3 + 0.5 mL 0.2 mol L^{-1} DTPA + 2 mL 0.5 mol L^{-1} MES buffer (pH 6.1). The sample was adjusted to 10 mL with water. Oxygen was removed by passing nitrogen for 5 min. The accumulation step was carried out at −1.0 V for 30 s from the stirred solution. Stirring was performed using a magnetic stirring bar. Then, after a rest period of 10 s a differential pulse voltammogram was recorded, while the potential was changed from −1.0 to −1.375 V. The amplitude and potential step were 50 and 4 mV, respectively.

3. Results and discussion

Although reports on Cr(VI) determination by AdSV at mercury [24–31] and other electrodes [43] can be found in the literature, in most procedures only a 10–100-fold excess of Cr(III) is permissible without its interference. The preliminary experiments performed with the application of adsorption of Cr(III) on Al_2O_3 show that the commonly used method of chromium determination in the presence of DTPA and nitrates [29] allows for selective determination of Cr(VI) at least in the presence of a 1000-fold excess of Cr(III), so the optimization of conditions of Cr(III) separation and Cr(VI) determination were performed.

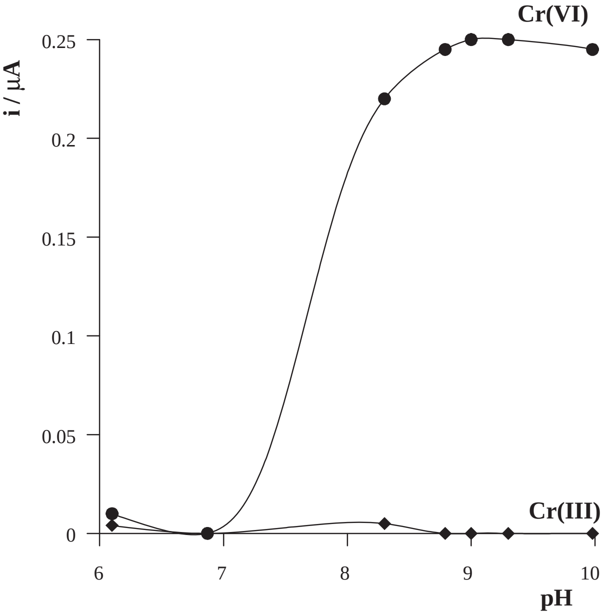

Fig. 1. Influence of pH of the sample solution on the Cr(VI) and Cr(III) peak current after shaking the sample with Al_2O_3. Shaking time 300 s. Concentrations of Cr(VI) and Cr(III) were 1×10^{-8} and 2×10^{-5} mol L^{-1}, respectively.

3.1. Cr(III) adsorption conditions

It is known that Cr(III) is adsorbed on Al_2O_3 from mild alkaline solutions [4–10], so a $(NH_4)_2SO_4 + NH_4OH$ buffer was used for alkalization of sample solutions. The optimization experiments were carried out separately for Cr(VI) and Cr(III). Cr(VI) and Cr(III) concentrations were equal to 1×10^{-8} and 2×10^{-5} mol L^{-1}, respectively. The concentrations of Cr(VI) and Cr(III) reported in this paper are in the samples taken for their preparation for analysis. The concentrations in the voltammetric cell were two times lower. Voltammetric determinations of chromium were carried out at pH 6.1. To better stabilize pH in the voltammetric cell, the routinely used acetate buffer was replaced by the MES buffer. The MES buffer has a higher capacity at pH 6.1.

The pH of the sample solution was changed from 6.1 to 10.0. The obtained results are presented in Fig. 1. For further study a pH 9.0 was chosen.

The concentration of the ammonia buffer was changed from 0.01 to 0.1 mol L^{-1}. The obtained results are presented in Fig. 2. For further study a concentration of the ammonia buffer 0.02 mol L^{-1} was chosen.

The mass of Al_2O_3 added to the sample was changed from 0 to 500 mg. The effect of the mass of Al_2O_3 on the Cr(VI) and Cr(III) peak currents is presented in Fig. 3. For further study a mass of added Al_2O_3 equal to 200 mg was chosen.

The effect of the shaking time of the sample with Al_2O_3 was studied in the range from 0 to 600 s. It was observed that adsorption time of 30 s is sufficient for satisfactory removing of Cr(III) from the sample. Prolongation of the shaking time did not increase the

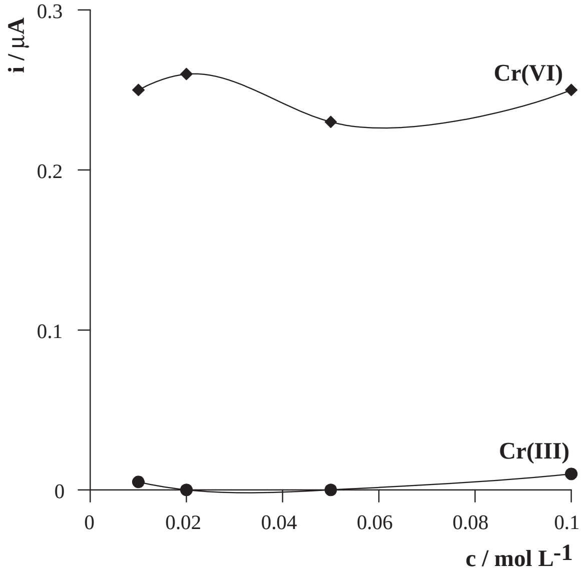

Fig. 2. Influence of concentration of ammonia buffer added to the sample on the Cr(VI) and Cr(III) peak current after shaking the sample with Al_2O_3. Other conditions as in Fig. 1.

amount of adsorbed Cr(III) so for further study a shaking time of 45 s was chosen.

3.2. Effect of Cr(VI) and Cr(III) concentration on their peak currents

To assess the effectiveness of Cr(III) adsorption on Al_2O_3 and so minimization of Cr(III) interference on the Cr(VI) signal and selectivity of the method of Cr(VI) determination by AdSV, the influence of Cr(III) concentration on its peak current with and without the application of Al_2O_3 was studied. Additionally, the influence of Cr(VI) concentration on the peak current in the presence of aluminum oxide was studied. The results obtained are presented in Fig. 4. The results show that Cr(VI) at concentrations of the order of 10^{-9} mol L^{-1} can be determined without significant interference from Cr(III) at concentration 1×10^{-5} mol L^{-1}.

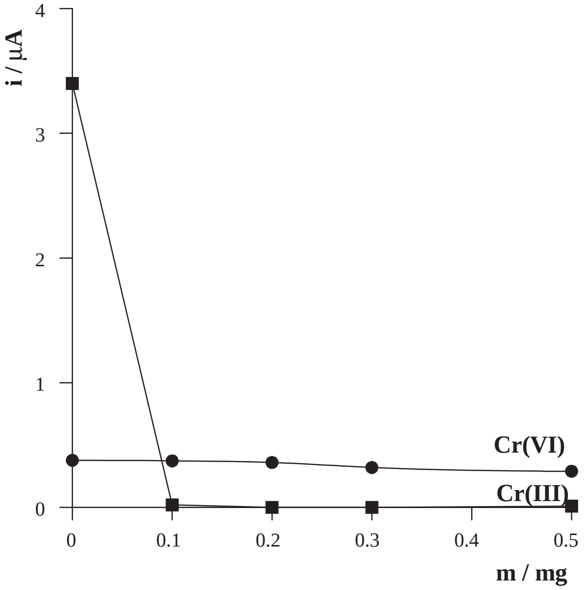

Fig. 3. Influence of the mass of Al_2O_3 added to the sample on the Cr(VI) and Cr(III) peak current. Other conditions as in Fig. 2.

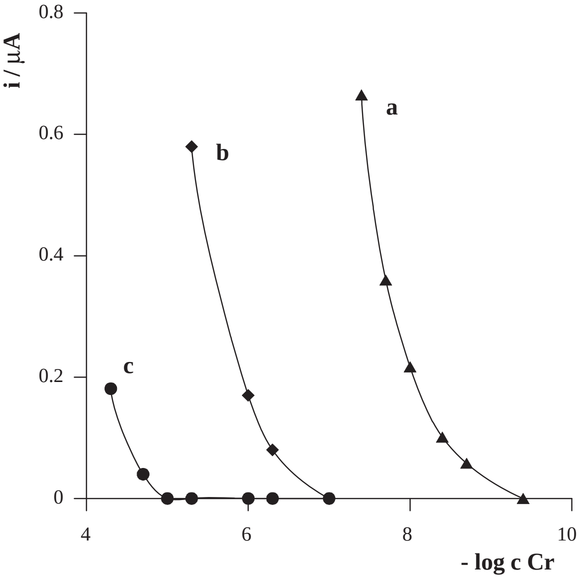

Fig. 4. Effect of chromium concentration on their peak currents: (a) Cr(VI) after shaking with Al_2O_3; (b) Cr(III) without shaking with Al_2O_3; (c) Cr(III) after shaking with Al_2O_3. Mass of Al_2O_3 was equal to 200 mg. Shaking time 45 s.

3.3. Calibration measurements and limit of detection

The calibration graph for Cr(VI) in the presence of 1×10^{-5} mol L^{-1} Cr(III) was linear from 1×10^{-9} to 4×10^{-8} mol L^{-1} and obeyed the equation $y = 18x + 4$, where y and x are the peak current (nA) and Cr(VI) concentration (nmol L^{-1}), respectively. The correlation coefficient r was 0.996. The relative standard deviation for Cr(VI) determination at a concentration 1×10^{-8} mol L^{-1} was 4.6% ($n = 5$). The detection limit calculated as $3 \times$ standard deviation for the lowest studied concentration of Cr(VI) was 7×10^{-10} mol L^{-1}. The voltammograms obtained for different concentrations of Cr(VI) in the presence of 1×10^{-5} mol L^{-1} Cr(III) are presented in Fig. 5.

3.4. Influence of humic substances

Natural waters as well as extracts from soil and sediment samples contain humic substances which can interfere in Cr(VI) determination using electrochemical [25] and other methods

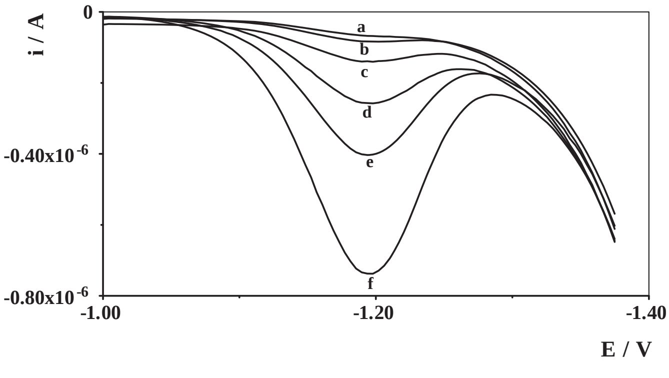

Fig. 5. Differential pulse voltammograms obtained for various concentrations of Cr(VI) in the presence of 1×10^{-5} mol L^{-1} following accumulation for 30 s. Concentrations of Cr(VI): (a) 0; (b) 1×10^{-9}; (c) 4×10^{-9}; (d) 1×10^{-8}; (e) 2×10^{-8}; (f) 4×10^{-8} mol L^{-1}. Accumulation time 30 s.

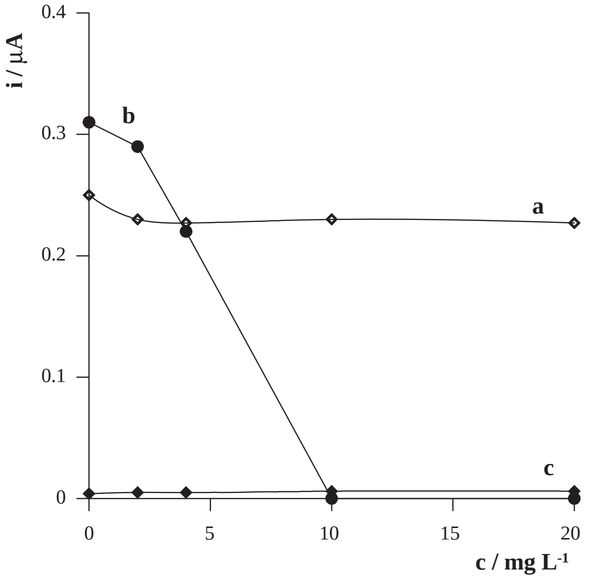

Fig. 6. Effect of humic acid concentration on chromium peak currents: (a) Cr(VI) after shaking with Al_2O_3; (b) Cr(VI) without shaking with Al_2O_3; (c) Cr(III) after shaking with Al_2O_3. Mass of Al_2O_3 equal to 200 mg. Shaking time 45 s.

[14,44]. In electrochemical methods the interference from humic substances is ascribed to competitive adsorption between humic substances and the complex of interest or to the reduction of Cr(VI) by humic substances [25]. In other methods, the presence of humic substances usually influences the separation step [14]. Taking into account the possible interference from humic substances, the influence of humic and fulvic acids on the Cr(VI) and Cr(III) signals was studied. The results obtained are presented in Figs. 6 and 7. The results show that in the presence in the sample 10 mg L^{-1} humic acids Cr(VI) peak is not observed on the voltammogram, while with application of Al_2O_3 even in the presence of 20 mg L^{-1} of humic acids the Cr(VI) peak current is practically not changed. The influence of the concentration of fulvic acids on the Cr(VI) signal was less pronounced than in the presence of humic acids, however, with the application of Al_2O_3 the peak current of Cr(VI) is practically not changed even in the presence of 20 mg L^{-1} of fulvic acids.

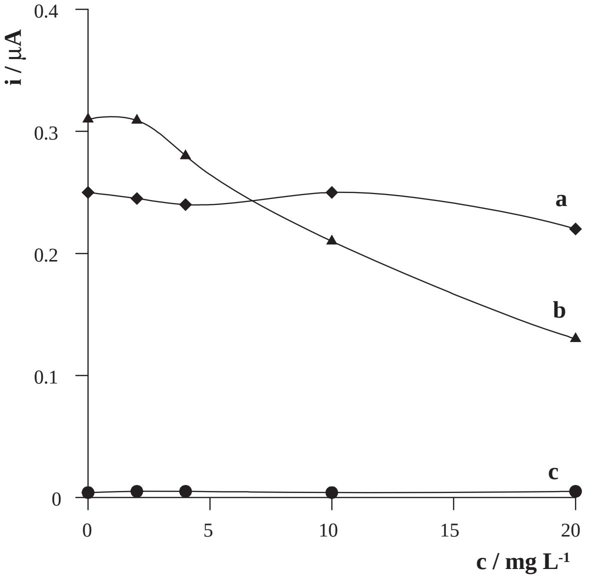

Fig. 7. Effect of fulvic acid concentration on chromium peak currents: (a) Cr(VI) after shaking with Al_2O_3; (b) Cr(VI) without shaking with Al_2O_3; (c) Cr(III) after shaking with Al_2O_3. Mass of Al_2O_3 was equal to 200 mg. Shaking time 45 s.

3.5. Analysis of river water sample

The method was applied to determine Cr(VI) in river water sample from the Bystrzyca (Lublin). Because the Cr(VI) content in the river water sample was below the detection limit of the method, the recoveries of the added Cr(VI) were studied. The obtained recoveries of Cr(VI) added in concentrations of 5 and 10 nmol L^{-1} were 94% and 98% with RSD from 3.8% to 5.2%, respectively. It should be noted that during the analysis of river water samples spiked with Cr(VI) with the application of Al_2O_3 a depression of the Cr(VI) peak was not observed, while in direct analysis by AdSV omitting the adsorption on Al_2O_3 the peak of Cr(VI) at concentration 5 nmol L^{-1} was completely depressed. It means that organic substances present in natural water were adsorbed on Al_2O_3.

4. Conclusions

The coupling adsorption of Cr(III) on Al_2O_3 in the course of preparation of the sample for AdSV determination of Cr(VI) using species selective DTPA method [29] it is possible to determine Cr(VI) even in the presence of a 10,000-fold excess of Cr(III). It was shown that simultaneously with the adsorption of Cr(III), humic substances are adsorbed on Al_2O_3 and their influence on the Cr(VI) signal is minimized. An additional advantage of the procedure is the fact that the sample solution need not be acidified to a low pH, because according to the literature data [45,46] at the pH used Cr(VI) is not reduced by organics present in the sample.

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