

**Catalytic adsorptive stripping voltammetric
determination of Cr(VI) in the presence of cupferron
following its deposition to the metallic state**

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A sensitive and very selective procedure for voltammetric determination of traces of Cr(VI) in the flow system is presented. The calibration graph is linear from 1×10^{-9} to 5×10^{-9} and from 5×10^{-10} to 2.5×10^{-9} mol·l⁻¹ for deposition times 60 and 120 s, respectively. The relative standard deviation for 3×10^{-9} mol·l⁻¹ Cr(VI) is 5.7 % (n = 5). The detection limit estimated from 3σ for low concentration of Cr(VI) and the deposition time 120 s is 2×10^{-10} mol·l⁻¹. The method is free from the interference of surface active compounds at the concentration typically present in natural water samples. The influence of common foreign ions is also presented. The validation of the method was made by comparative analyses of tap and river water samples by means of another well established voltammetric procedure.

1. INTRODUCTION

The determination of trace concentrations of Cr(VI) has recently received much attention owing to environmental concerns. The toxicity of Cr(VI) is about 100-1000 times higher than Cr(III) [1], so the methods for its quantification at trace level are valuable. Electrochemical methods offer a low detection limit and usually do not require additional separation and/or a preconcentration before the electrochemical measurements. Several voltammetric procedures have been described for determination of Cr(VI) using mercury [2-13] and stable modified electrodes [14, 15]. The voltammetric

procedures of Cr(VI) determination offer a low detection limit, however, interference from surface active compounds in most of the procedures is observed. The interference causes a significant decrease in sensitivity when natural water samples are analysed. Only in procedures [11-13] was the interference of surface active compounds minimised.

This paper presents a voltammetric procedure which allows for Cr(VI) determination in the presence of surface active substances without serious interference. The proposed procedure is based on a combination of a selective method of deposition of Cr(VI) reduction product in the form of metal on HMDE and a very sensitive method of total chromium determination in the presence of cupferron [16].

2. EXPERIMENTAL

Reagents. $0.75 \text{ mol}\cdot\text{l}^{-1}$ ammonium buffer solution (pH 8.5) was prepared from Suprapure HCl (Merck) and reagent grade ammonium hydroxide. Piperazine-1,4-bis(ethanesulfonic acid) (PIPES) was obtained from Fluka. Cupferron and other reagents were obtained from Merck and used as received. The $0.1 \text{ mol}\cdot\text{l}^{-1}$ solution of cupferron was prepared daily. All solutions were made using doubly distilled water. Standard solutions of Cr(VI) and Cr(III) were made by dissolution of K_2CrO_4 and $\text{CrCl}_3 \times 6\text{H}_2\text{O}$ in water and $0.5 \text{ mol}\cdot\text{l}^{-1}$ HCl, respectively.

Instrumentation. The measurements were performed using the EA9 electrochemical analyzer and a static mercury drop electrode (SMDE), both made by MTM Poland. The three-electrode flow cell consisting of an Hg electrode, a Pt electrode, and Ag/AgCl reference electrode as presented in Figure 1 was used. The Hg drop area was 1.4 mm^2 . The solutions were delivered from a constant headspace reservoirs elevated 0.5 m above the cell. The flow rates of each solution were about 18 ml min^{-1} .

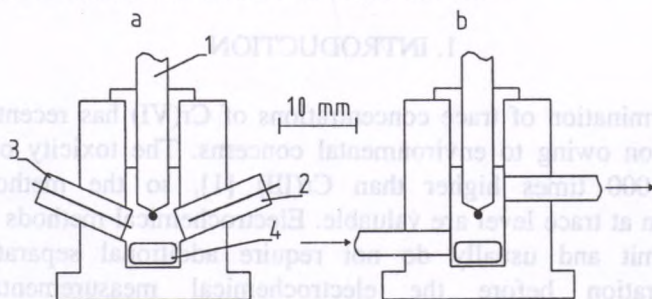


Fig. 1. A schematic diagram of the flow cell used for Cr(VI) determination. (a) and (b) front and side view, respectively. 1 - SMDE, 2 - Ag/AgCl electrode, 3 - Pt electrode, 4 - magnetic stirring bar

Sample preparation. To 100 ml volumetric flask add 100 ml of water sample and 0.2 ml $0.125 \text{ mol}\cdot\text{l}^{-1} \text{ NH}_4\text{Al}(\text{SO}_4)_2$. Then swirl the sample and add 2 ml of ammonia buffer at $\text{pH} = 8.5$. The final pH of the sample solution should be equal 8.5 ± 0.1 ; if necessary, adjust pH to 8.5 using HCl or NH_4OH .

Procedure. The flow of the prepared sample solution into the electrochemical cell was started and a new drop of mercury was formed. A potential of -1.7 V was applied and the deposition of chromium was carried out within 60 s. Then, the flow of $0.01 \text{ mol}\cdot\text{l}^{-1}$ ammonium buffer at $\text{pH} 8.5$ used as a washing solution was started and after 60 s the potential was changed to -1.35 V . The flow of the washing solution was further continued at this potential within 60 s. The flow of the buffer was stopped, the potential was changed to -0.8 V , and after 5 s the flow of the complexing solution containing $1 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1} \text{ PIPES} + 1 \times 10^4 \text{ mol}\cdot\text{l}^{-1}$ cupferron ($\text{pH} = 7.0$) was directed into the cell for 35 s. After an equilibration time of 5 s, the differential pulse voltammogram was recorded, while the potential was scanned from -0.8 to -1.15 V at a scan rate $20 \text{ mV}\cdot\text{s}^{-1}$. The pulse amplitude was -50 mV . From the beginning of the measurement up to the change of the potential to -0.8 V the solutions were stirred using a magnetic stirring bar. The complexing and washing solutions were deaerated in the reservoir during the entire time of the measurements. After the measurement the flow of $0.01 \text{ mol}\cdot\text{l}^{-1}$ ammonium buffer ($\text{pH} = 8.5$) was started for at least 60 s before the next measurement.

3. RESULTS AND DISCUSSION

The proposed voltammetric method of Cr(VI) determination in the flow system consists of several main steps:

- deposition of Cr(VI) to the metallic state onto HMDE in the presence of Cr(III) coprecipitated on $\text{Al}(\text{OH})_3$
- oxidation of Cr^0 to Cr(III) with the formation of $\text{Cr}(\text{OH})_3$ adsorbed onto the electrode
- complexation of chromium hydroxide by cupferron
- catalytic reduction of the Cr(III)-cupferron complex

The last step was already described in detail in paper [16], so the optimisation of the overall procedure was directed to the first three steps.

Supporting electrolyte for chromium deposition. For deposition of Cr(VI) to the metallic state, $0.015 \text{ mol}\cdot\text{l}^{-1}$ ammonium buffer ($\text{pH} = 8.5$) and the deposition potential -1.7 V were chosen. The change of the buffer concentration from 0.01 to $0.03 \text{ mol}\cdot\text{l}^{-1}$ does not influence the peak current. To avoid the simultaneous

reduction of Cr(III) to the metal, the sample solution was first spiked with $\text{NH}_4\text{Al}(\text{SO}_4)_2$ and then the pH was raised to pH 8.5 using ammonium buffer. As shown in paper [17], at this pH the coprecipitation of Cr(III) on $\text{Al}(\text{OH})_3$ was quantitative. However, Cr(III) complexes with an organic ligands are not quantitatively coprecipitated on hydroxides [18] and can be present in the solution. The interference of these complexes in proposed voltammetric procedure is lower than in other methods because a part of these complexes is not reduced to the metal at the potential used in the accumulation step. The $\text{AlNH}_4(\text{SO}_4)_2$ was added to concentration of $2.5 \times 10^{-4} \text{ mol}\cdot\text{l}^{-1}$. Although the addition of Al(III) at this concentration causes decrease of the peak corresponding to Cr(VI) to about 75% of its original value, the peak corresponding to Cr(III) in such conditions is not observed up to the concentration $1 \times 10^{-6} \text{ mol}\cdot\text{l}^{-1}$. The decrease of the chromium peak current in the presence of added Al(III) ions is probably connected with incomplete removal of these ions from the cell during the subsequent washing step and their influence on the voltammetric signal. After the deposition step the flow of the ammonia buffer was directed into the cell. The solution removes from the cell the substances which potentially can interfere in the determination.

Deposition time. The effect of the deposition time was studied using Cr(VI) at concentrations of 1×10^{-9} and $5 \times 10^{-9} \text{ mol}\cdot\text{l}^{-1}$. It was observed that the peak current increases linearly with the deposition time up to 120 and 60 s, respectively.

Equilibration (complexation) time. As shown in the experimental part the flow duration of the complexing solution was fixed at 35 s and the equilibration time at 5 s. A further prolongation of the flow of the complexing solution or the equilibration time does not influence the chromium peak current.

Calibration graphs, precision and detection limit. The differential pulse voltammograms for Cr(VI) obtained under optimised conditions are presented in Figure 2. The calibration graph for Cr(VI) for a deposition time of 60 s was linear in the range from 1×10^{-9} to $5 \times 10^{-9} \text{ mol}\cdot\text{l}^{-1}$ and obeyed the equation $y = 12.5 x + 1.7$ ($r = 0.998$), where y and x are the peak current (nA) and Cr(VI) concentration ($\text{nmol}\cdot\text{l}^{-1}$), respectively. The relative standard deviation for a Cr(VI) concentration of $3 \times 10^{-9} \text{ mol}\cdot\text{l}^{-1}$ was 5.7% ($n = 5$). The calibration graph for a deposition time of 120 s was linear in the range from 5×10^{-10} to $2.5 \times 10^{-9} \text{ mol}\cdot\text{l}^{-1}$ and obeyed the equation $y = 28.2 x + 1.5$ ($r = 0.997$). The relative standard deviation for a Cr(VI) concentration of $5 \times 10^{-10} \text{ mol}\cdot\text{l}^{-1}$ at these conditions was 12 % ($n = 5$) and the detection limit was $2 \times 10^{-10} \text{ mol}\cdot\text{l}^{-1}$.

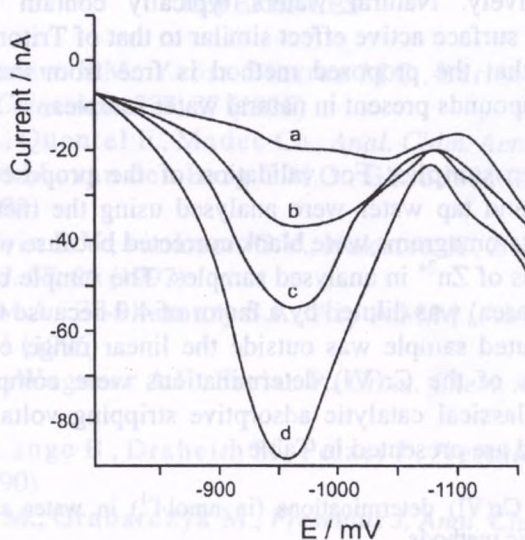


Fig. 2. Differential pulse voltammograms for the different Cr(VI) concentrations: (a) 0; (b) 5×10^{-10} ; (c) 1×10^{-9} ; (d) 2×10^{-9} mol·l⁻¹. Deposition time 120 s

Effect of foreign ions. The influence of foreign ions on the determination of Cr(VI) was studied using a fixed concentration of Cr(VI) 3×10^{-9} mol·l⁻¹ and a deposition time of 60 s. The addition of either MgSO₄ or CaCl₂ at a concentration of 0.01 mol·l⁻¹ does not influence the peak current, contrary to the method employing the adsorption of the Cr(III)-DTPA complex, where a decrease in sensitivity of nearly one order of magnitude was observed [3]. Further results showed that 10^3 – fold amounts of Fe³⁺; Cu²⁺, Pb²⁺, Ni²⁺, Mn²⁺, MoO₄²⁻, VO₃⁻; 5×10^2 – fold amounts of Cr(III), MnO₄⁻; 10^2 – fold amount of Co²⁺ do not interfere in the Cr(VI) determination. Thousand-fold amounts of Zn²⁺ cause an increase of the Cr(VI) peak current as in the case of the original method [3]. However, in the proposed procedure such an interference can be eliminated by subtracting the blank. The blank was recorded by repeating the measurement from the same sample, but using the potential -1.35 V in the deposition step. At this potential Cr(VI) is not reduced to metal while the reduction of Zn²⁺ proceeds as at potential -1.7 V. After the blank subtraction a signal of interest is obtained. The presence of 10^3 fold amount of Zn²⁺ in the sample deteriorates the precision of Cr(VI) determinations and for determination of 3×10^{-9} mol·l⁻¹ of Cr(VI) the relative standard deviation is equal to 11%. The influence of surface active substances was studied using Triton X-100 and humic acids as model compounds. It was found that the Cr(VI) peak current was not influenced by these compounds up to 6 and

5 mg·l⁻¹, respectively. Natural waters typically contain 0.2-2 mg·l⁻¹ of compounds with a surface active effect similar to that of Triton X-100 [3], so it can be assumed that the proposed method is free from the interference of surface active compounds present in natural water samples.

Analysis of water samples. For validation of the proposed procedure the Czechówka river and tap water were analysed using the method of standard additions. The voltammograms were blank corrected because of the presence of high concentrations of Zn²⁺ in analysed samples. The sample of tap water from Chełm (industrial area) was diluted by a factor of 4.0 because the current of the peak for an undiluted sample was outside the linear range of the calibration graph. The results of the Cr(VI) determinations were compared with these obtained by the classical catalytic adsorptive stripping voltammetric method with DTPA [3] and are presented in Table 1.

Tab. 1. Results of Cr(VI) determinations (in nmol·l⁻¹) in water samples using two different voltammetric methods

Sample	Proposed method	Boussemart et al. [3] method
Tap water from Chełm	9.1 (9.7)	8.7 (4.4)
Czechówka river water	2.3 (6.2)	2.5 (5.8)

In parentheses the relative standard deviation in % are given (n = 5)

The well agreement between the results obtained by both methods for tap and river waters show that the proposed method can be used for determination of traces of Cr(VI) in natural water samples.

4. CONCLUSIONS

The results show that the voltammetric procedure for Cr(VI) determination in the flow system based on the selective preconcentration of Cr(VI) by its deposition to the metallic state followed by its oxidation and complexation by cupferron, and in the final step based on a catalytic reduction of the complex, is very promising. The concentrations of reagents used in the proposed procedure are low as compared to other voltammetric procedures of Cr(VI) determination [3, 11], so purification of reagents is not necessary. The proposed method is characterised by small interference from organic surfactants, contrary to many other voltammetric procedures [2-6], and can be used for direct Cr(VI) determination in natural water samples. The proposed method allows to determine Cr(VI) in the presence of a 500-fold excess of Cr(III).

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