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**SEPARATION OF TRI- AND HEXAVALENT
CHROMIUM PRIOR
TO VOLTAMMETRIC DETERMINATION¹**

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A pre-treatment procedure for determination of traces of Cr(VI) in samples with large excess of Cr(III) by catalytic adsorptive stripping voltammetry is described. Selective determination of Cr(VI) was possible due to quantitative sorption of Cr(III) on chelating resin-Chelex 100. The chelating medium was added directly to the voltammetric cell containing a sample with fixed pH (pH = 6.2). After the sorption step, the CAdSV procedure was applied. This procedure was compared to other methods of elimination of the voltammetric signal from Cr(III) excess.

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Introduction

Chromium and its compounds are widely used by modern industries resulting in large quantities of this element being discharged into the environment. Chromium can occur in a number of oxidation states, but in natural samples it exists as Cr(III) and Cr(VI). These two species have different toxicity, bio-availability and mobility. The relatively inert Cr(III) is an important microelement for plant and animal nutrition. Contrary to this, Cr(VI) compounds, mobile in soil/water systems, are known to be toxic and have been classified as carcinogenic to humans and other mammals. Therefore the determination of total chromium concentration in the sample is not sufficient information about its biomedical consequences. Application of valence-non-specific techniques, such as: Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP MS) or x-ray Fluorescence Spectroscopy (XFS) requires the preliminary separation of both chromium forms. This step comprises mainly extraction, ion-exchange chromatography, co-precipitation procedures and sorption on membranes or in micro columns. Direct measurement of Cr(VI) is feasible when utilizing electrochemical methods due to its natural tendency to act as a speciation probe [1]. Among a great deal of electrochemical procedures, mainly Catalytic Adsorptive Stripping Voltammetry (CA_dSV) is used [2]. Depletion of Cr(III) signal is based on the time dependant decay of the catalytic activity of the Cr(III)-DTPA complex [3]. In samples with a large excess of Cr(III), the above described procedure is insufficient to obtain a selective signal of Cr(VI). As a pre-treatment procedure to voltammetric determination, Cr(III) can be bound in stable complexes with NTA [4] or co-precipitated as Cr(OH)₃ with Al₂O₃ [5].

In the present study, a selective retention of Cr(III) on a chelating resin – Chelex 100 has been examined. This batch procedure was previously proposed in AAS determination of tap and ground water samples [6].

Experimental

Reagents

All the reagents were of analytical grade purity. Chelex-100[®] (iminodiacetic acid-sodium form) was purchased from Sigma-Aldrich, Germany. Stock solutions of Cr(III) and Cr(VI) were prepared by dissolving metallic chromium and K₂Cr₂O₇ in HCl and water, respectively. KNO₃ (POCh, Poland) was additionally purified by recrystallization. Acetate buffer (2M, pH 6,2) was prepared by mixing the corresponding amounts of 96 % acetic acid and 25 % ammonia solution (both Suprapur[®], Merck). Diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid (DTPA) solution (0.2M) was prepared by dissolving an appropriate amount of the reagent

(Carl Roth, Germany) and addition of 25 % ammonia (Suprapur[®]) to obtain pH 6.2. All the solutions were prepared using deionised water produced in an ion-exchange purification system (Cobrabid-Aqua, Warsaw, Poland). Argon (99.99 %) was used to removed dissolved oxygen from solutions before analysis.

Apparatus

All the voltammetric measurements were carried out with multipurpose electrochemical analyzer (model "EA9", MTM, Krakow, Poland) connected to a personal computer and controlled by EAGRAPH software, version 5.0. A three-electrode cell comprising: Controlled Growth Mercury Drop Electrode (CGMDE, MTM, Krakow, Poland) as a working electrode, Pt-wire and a self made Ag/AgCl electrode with 3M KCl as the auxiliary and reference electrode, respectively, was used.

Sample Preparation

An 8 ml aliquot of the sample was pipetted into the voltammetric cell. Then, 0.5 ml 2M acetic buffer (pH 6.2) was added to ensure conditions for the most effective sorption in the batch technique [3]. After the addition of Chelex-100, the mixture was stirred for 60 min. Then the sample was analyzed.

Analytical Procedure

Catalytic adsorptive stripping voltammetry [6]. To the previously prepared sample, as described above, a portion of 2.5 M KNO₃ (1 ml) was added. After 5 min. of deaeration step with pure argon, an addition of 0.5 ml DTPA (0.2M) was pipetted into solution to a total volume of 10 ml. Potential scan in differential pulse (DP) mode was preceded by new drop generation, adsorptive preconcentration and 5 s equilibration. All voltammograms were recorded in the cathodic direction from -0.95V to -1.42 V. Accumulation was performed by applying a potential of $E_{acc} = -0.95V$ for $t_{acc} = 20$ s with stirring. The other experimental parameters were: step potential $E_s = 2$ mV, pulse potential $\Delta E = 50$ mV, scan rate = 25 mV s⁻¹. Quantitative measurements were performed using standard addition procedure.

Table I The effect of Chelex-100 addition upon the chromium signal for Cr(III) at concentration of 8×10^{-6} mol l⁻¹ (sorption time 30 min)

Chelex-100, g	0.04	0.06	0.08	0.10	0.12	0.14
CadSV response, nA	235	214	176	145	131	128

Optimization

The sorption of Cr(III) on Chelex-100 was performed before voltammetric measurement. In the first step the time of sorption was fixed at 30 min., while concentration of Chelex-100 was changed from 0.04 g to 0.14 g. The effect of sorbent addition on the chromium signal for Cr(III) at the concentration of 8×10^{-6} mol l⁻¹ is presented in Table I. For further measurements, an amount of 0.1 g of Chelex-100 was chosen. The effect of sorption time was studied using a 0.1g Chelex-100 addition to the water sample containing 8×10^{-6} mol l⁻¹ Cr(III). The time of sorption was changed from 30 to 120 min. The results presented in Table II. show the gradual fading of the measured current. The process of sorption is quite slow, thus in the case of a high concentration of Cr(III), the time required for quantitative retention of Cr(III) exceeds 120 min.

Table II The effect of sorption time on the chromium signal for Cr(III) at concentration of 8×10^{-6} mol l⁻¹; addition of 0.1 g of Chelex-100

Time, min	30	40	60	80	120
CadSV response, nA	145	102	77	43	28

Analytical Applications

The method was applied to determination of Cr(VI) in tap water spiked with a known amount of Cr(VI) and Cr(III). The results were compared with those obtained for other methods employed for masking or deactivating Cr(III) during voltammetric measurements. These comparative procedures utilized: nitrilotriacetic acid (NTA) used as masking agent [3] and the time-dependent effect of the conversion of DTPA-Cr(III) complex into electrode-nonactive one [2]. The determination was performed using the method of standard additions. The voltammograms obtained for tap water sample spiked with ca. 100-fold excess of Cr(III) over Cr(VI) are presented in Fig. 1. The results calculated from determination preceded with selective retention on Chelex-100 are in good agreement both with those acquired for the sample without Cr(III) addition and when NTA as masking agent for Cr(III) was used.

Table III Results of determination and recoveries of Cr(VI) in tap water

Procedure	Chromium added nM		Chromium Cr(VI) found nM	Recovery %
	Cr(III)	Cr(VI)		
Stabilization of DTPA-Cr(III) complex (30 min ¹⁾) [6]	0.0	44.0	44.37	101
Retention on Chelex-100	4000	44.0	47.01	107
Masking with NTA [3]	4000	44.0	45.71	104
Stabilization of DTPA-Cr(VI) complex (60 min ¹⁾) [6]	4000	44.0	58.12	132

¹⁾ time of stabilization (stirring) before determination

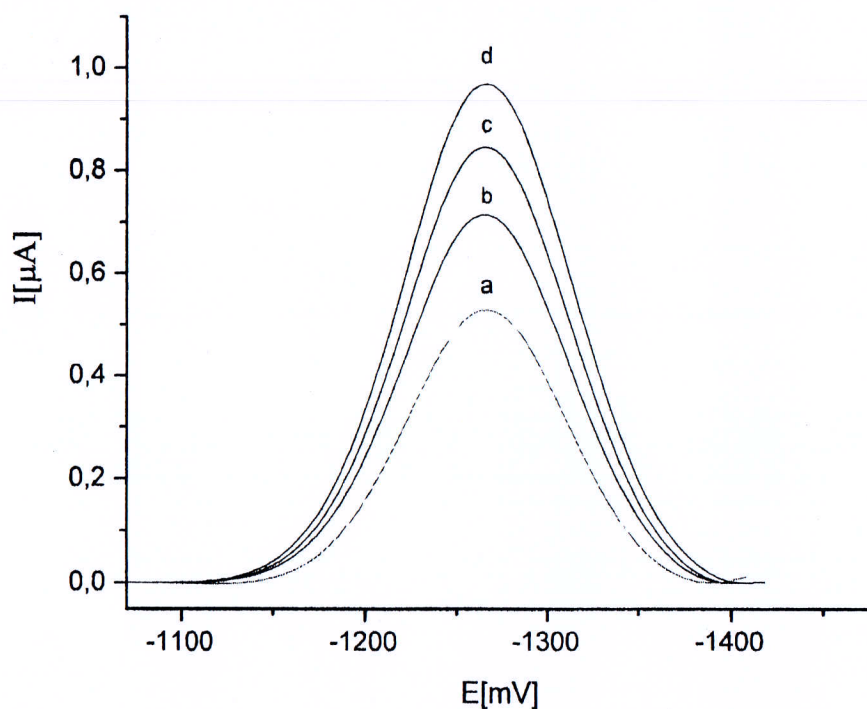


Fig. 1 DP voltammograms of Cr(VI) determination in spiked [$4.4 \times 10^{-8} \text{ mol l}^{-1} \text{ Cr(VI)}$ and $4 \times 10^{-6} \text{ mol l}^{-1} \text{ Cr(III)}$] tap water sample (a), triple ($1 \times 10^{-8} \text{ mol l}^{-1} \text{ Cr(VI)}$) standard addition procedure (b-d). Preconcentration of Cr(III) on Chelex-100 (0.01 g ml^{-1}) was carried out for 60 min before analysis

Conclusion

As we can see from the presented study, the phenomenon of Cr(III) sorption allows us to utilize Chelex-100® in the preconcentration step in order to eliminate the voltammetric signal from Cr(III) during Cr(VI) determination. This procedure ensures quantitative sorption even with a large excess of Cr(III) and therefore

appears as an alternative to the use of NTA as a masking agent [3]. The simplicity of Chelex-100[®] use is achieved either by direct introduction of the sorbent into the voltammetric cell prior to determination, or by the fact that a pH of 6.2 is optimal for sorption and the determination step as well.

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