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Voltammetric Determination of Cr(VI) in the Presence of Cr(III) with Application of CDTA as a Masking Agent*

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A selective and sensitive method for determination of traces of Cr(VI) in the presence of a large excess of Cr(III) by differential pulse adsorptive stripping voltammetry is presented. For minimization of Cr(III) interference cyclohexanediaminetetraacetic acid (CDTA) was used as a masking agent. The determinations were performed in a flow system. The calibration graph is linear from 5×10^{-10} to 2×10^{-8} mol l^{-1} for accumulation time 60 s. The relative standard deviation for 1×10^{-8} mol l^{-1} Cr(VI) is 5.8 % (n = 5). The detection limit for an accumulation time of 60 s is 2×10^{-10} mol l^{-1}. The influence of common foreign ions is also presented. The validation of the method was made by comparing the analytical results for water and soil samples with those obtained by reference methods and by a recovery test for river water.

Key words: chromium(VI), determination, stripping voltammetry, CDTA, flow system

In the environmental system chromium occurs mainly as Cr(III) and Cr(VI). Hexavalent chromium is more reactive and more toxic, so the methods for differentiation between two valence states of chromium are of interest. Problems connected with determination of Cr(VI) by different methods are reported in paper [1]. The adsorptive stripping voltammetry is a suitable technique for determination of traces of Cr(VI). Also numerous procedures have been proposed for Cr(VI) determination [2–10]. Some procedures exploited different electrochemical properties of Cr(III) complexes formed from Cr(III) present in the solution and from Cr(III) generated on the electrode as a product of Cr(VI) reduction [2–5].

In other procedures the coprecipitation of Cr(III) on $Al(OH)_3$ was proposed to eliminate the influence of Cr(III) on the Cr(VI) signal [6–8]. Recently a mixture of two complexing agents, N-(2-hydroxyethyl)ethylenediaminetriacetic acid and pyrocatechol violet, was used for simultaneous voltammetric determination of Cr(VI) and Cr(III) by applying multivariate calibration methodology [10]. For calibration the two peaks observed on the voltammogram were exploited. One of whose peaks would be altered with the changing concentration of the two chromium species, while the other responded to the changes of Cr(VI) concentration only.

In this paper to eliminate the influence of Cr(III) on the determination of Cr(VI) by adsorptive stripping voltammetry cyclohexanediaminetetraacetic acid (CDTA)

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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was used as a masking agent. According to the procedure proposed the sample solution was initially mixed with CDTA and heated to complex Cr(III). Then the diethylenetriaminepentaacetic acid (DTPA) was added to the sample and Cr(VI) was determined according to the voltammetric method of total chromium determination in the presence of DTPA and nitrates [11].

EXPERIMENTAL

Reagents: DTPA, acetic acid, KNO_3 and Suprapure NaOH were obtained from Merck. KNO_3 was additionally purified by recrystallization. The standard solutions of Cr(VI) and Cr(III) (1 g l^{-1}) and CDTA were purchased from Fluka. Other reagents were obtained from POCh, Poland, and used as received. All solutions were made using triply distilled water.

Apparatus: All experiments were carried out with an Autolab PGSTAT 10 analyzer (Utrecht, The Netherlands) and a controlled growth static mercury drop electrode in the HMDE mode, made by MTM Cracow, Poland. A three-electrode flow cell consisting of an Hg electrode, a Pt electrode and an Ag/AgCl reference electrode as previously described [7,8] was used. The volume of the cell was about 0.5 ml. The Hg drop area was 1.4 mm^2. The solutions were delivered to the cell using a peristaltic pump IPC 8, Ismatec, Switzerland. The experimental arrangement used for Cr(VI) determination is shown in Fig. 1. Tubes of Tygon and PFA were used for the transport of reagents. A valve was made from PTFE. The soil sample was homogenized in MM-2 vibrational mill (Retsch, Germany).

Sample preparation: An aliquot of the sample was pippeted into a 50 ml volumetric flask. Then 2.5 ml of 0.2 mol l^{-1} CDTA + 0.6 mol l^{-1} acetate buffer (pH = 6.1) solution was introduced and finally the water was added to the mark. The solution was transferred to the test tube and placed in 50°C water bath for 10 min. Before analysis the sample solution was cooled to the room temperature.

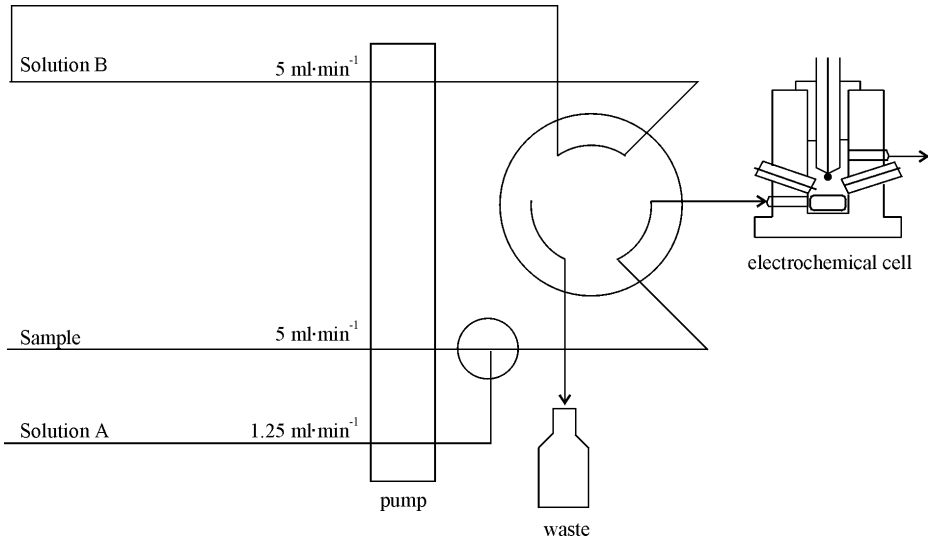

Figure 1. Schematic diagram of the system used for voltammetric determination of Cr(VI).

Procedure: The measurements were performed in a flow system. The standard measuring procedure was as follows: the pump was switched on and the sample solution prepared as described previously was mixed with solution A containing 0.05 mol l^{-1} DTPA + 0.08 mol l^{-1} acetate buffer (pH = 6.1) and the resulting solution was directed to the electrochemical cell. After 30 s of flow of the solution the mercury drop was formed, the potential –1.0 V was applied and the accumulation of the product of reduction of Cr(VI) in the form of Cr(III)–DTPA complex was carried out for 60 s. During the accumulation step the solution was stirred using a magnetic stirring bar. Next solution B containing 0.5 mol l^{-1} KNO_3 + 0.01 mol l^{-1} DTPA + 0.04 mol l^{-1} acetate buffer (pH = 6.1) was directed to the cell for 45 s. The flow of the solution was stopped and after an equilibration period of 10 s the differential pulse voltammogram was recorded while the potential was scanned from –1.0 to –1.375 V. The pulse height was 50 mV. Solution B was deaerated in the reservoir during the entire time of the measurements.

RESULTS AND DISCUSSION

The proposed method of Cr(VI) determination by adsorptive stripping voltammetry consists of several steps:

– complexation of Cr(III) present in the sample by CDTA used as a masking agent;
– accumulation of the product of Cr(VI) reduction in the form of Cr(III)–DTPA complex;
– reduction of the Cr(III)–DTPA complex in the presence of nitrates.

The last step was already described in detail in paper [11] so the optimization of the overall procedure was directed to the first two steps.

Optimization of complexation of Cr(III) by CDTA. Complexation of Cr(III) by CDTA was performed before the voltammetric measurement. According to literature data [12–14] this reaction proceeds slowly and the reaction time depends on the temperature of the solution and on the concentration of CDTA. In this study we chose the temperature of 50°C. The temperatures of Cr(III) complexation by CDTA as high as 80°C were also recommended in the literature [13]. However, it must be noted that at such high temperatures the reduction of Cr(VI) by the organic matter present in the natural water samples is more probable. The complexation time was changed from 10 to 30 min. It was found that the prolongation of the reaction time from 10 to 30 min. does not influence the Cr(VI) signal, however, it causes a small decrease of the Cr(III) signal. As a compromise between the influence of Cr(III) on the analytical signal and the total analysis time the complexation time of 10 min. was chosen for further measurements.

The concentration of CDTA not only controls the Cr(III) complexation time but it also influences the efficiency of accumulation of the Cr(VI) reduction product in the next step of the measurement. With the increase of the CDTA concentration the Cr(III) ions arising from the electrochemical reduction of Cr(VI) form complexes with CDTA instead of DTPA and as a consequence the signal corresponding to Cr(VI) decreases. As a compromise between the effectiveness of complexation of Cr(III) present in the solution and the value of the analytical signal the 0.01 mol l^{-1} concentration of CDTA was chosen for further measurements.

To confirm the stability of Cr(VI) in the conditions used for the complexation of Cr(III) we carried out the measurement for samples of Bystrzyca river water spiked with 1×10^{-8} mol l^{-1} of Cr(VI). It was found that the prolongation of the sample heating from 10 to 30 min. does not alter the analytical signal corresponding to Cr(VI).

Optimization of the voltammetric procedure. Effect of accumulation potential and time: The accumulation potential equal to –1.0 V was chosen on the basis of the literature data [3,11]. The effect of accumulation time was studied under the standard measuring conditions. The time of accumulation was changed from 15 to 300 s. Fig. 2 presents the obtained results. The dependence obtained in this study differs from those presented in the original paper [11] which reported that the peak current increases with accumulation time to 240 s. The observed dependence may be attributed to the equilibrium attained between the speed of accumulation of the Cr(III)–DTPA complex and the conversion of this complex to Cr(III)–CDTA. The effect of electrode surface saturation by the Cr(III)–DTPA complex after 90 s accumulation time can be excluded because the prolongation of the accumulation for further 90 s from the CDTA free solution causes a substantial increase of the analytical signal.

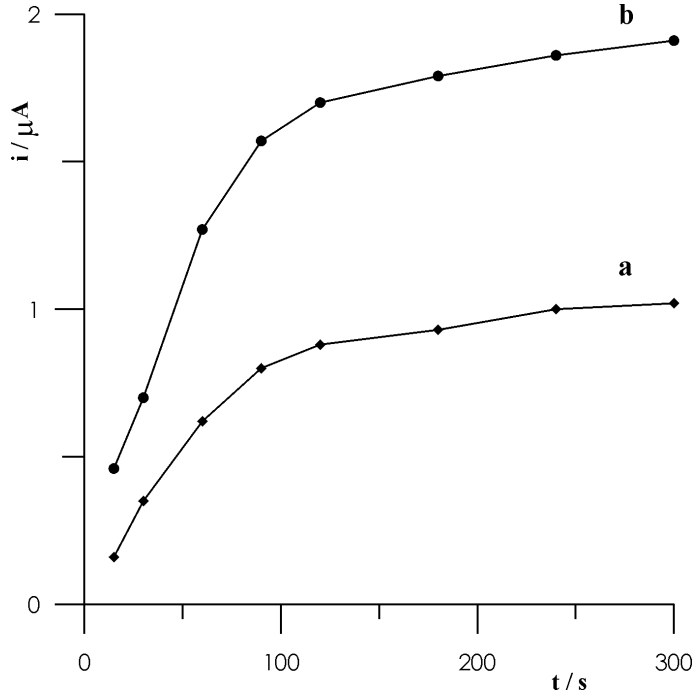

Figure 2. Effect of accumulation time on the Cr(VI) peak current. Concentration of Cr(VI): a) 5×10^{-9}; b) 1×10^{-8} mol l^{-1}.

Calibration graph: The calibration graph for Cr(VI) for an accumulation time of 60 s was linear in the range from 5×10^{-10} to 2×10^{-8} mol l^{-1} and obeyed the equation y = 124x – 7, where y and x are the peak current (nA) and Cr(VI) concentration (nmol l^{-1}), respectively. The linear correlation coefficient was r = 0.9992. The relative standard deviations for a Cr(VI) concentrations of 5×10^{-10} and 1×10^{-8} mol l^{-1} were 12 and 5.8% (n = 5), respectively. The detection limit estimated from the tripled standard deviation of the lowest determined Cr(VI) concentration was about 2×10^{-10} mol l^{-1}.

Effect of foreign ions: The influence of foreign ions on the determination of Cr(VI) was studied at a fixed concentration of Cr(VI) of 1×10^{-8} mol l^{-1} and an accumulation time of 60 s. It was found that at least 10^6 – fold amounts of Ca^{2+}, Mg^{2+}; 10^3 – fold amounts of Fe^{3+}, Zn^{2+}, Pb^{2+}, Cu^{2+}; 2×10^2 – fold amounts MoO_4^{2-}, VO_3^-, Mn^{2+} do not interfere. 10^4 – fold amounts of Fe^{3+} caused a decrease of Cr(VI) peak to 66% of its original value. Special attention was paid to the influence of Cr(III), because the unmasked Cr(III) gives the analytical signal at the same potential as Cr(VI), although the sensitivities observed for both forms are different [15]. It should be taken into account that those of the Cr(III)–CDTA complexes formed during the sample preparation for analysis, which are not adsorbed on the mercury electrode can be partially converted to Cr(III)–DTPA complexes when the sample solution is mixed with the solution containing DTPA. To minimise the time of potential conversion of Cr(III)–CDTA to Cr(III)–DTPA the DTPA was added to the sample solution just before directing the sample to the electrochemical cell. The possible interference of Cr(III) on the Cr(VI) signal was initially studied for the Cr(VI) free samples with Cr(III) concentration changed from 1×10^{-6} to 2×10^{-5} mol l^{-1}. It was found that below 2×10^{-6} mol l^{-1} concentration the Cr(III) ions do not give analytical signal in the range of Cr(VI) peak potentials, while at Cr(III) concentrations equal to 5×10^{-6} and 2×10^{-5} mol l^{-1} the peak current of 0.14 and 1.35 μA was observed, respectively. The latter indicated that CDTA is an effective masking agent for Cr(III), as the interference is observed for high concentrations of Cr(III) only. When, under the same conditions of complex formation, the oxalate was used as the masking agent the interference from 2×10^{-6} mol l^{-1} Cr(III) correspond to Cr(VI) concentration of 1.3×10^{-9} mol l^{-1}. In paper [3] it was reported that Cr(III) complexes of oxalate do not give an analytical signal, however, for study in this case the concentration of Cr(III) equal to 2×10^{-8} mol l^{-1} was chosen. The influence of Cr(III) on the signal corresponding to 2×10^{-9} mol l^{-1} of Cr(VI) was also studied. We have found that Cr(III) does not influence the Cr(VI) signal up to the concentration of 1×10^{-6} mol l^{-1}, while at the concentration of 2×10^{-6} mol l^{-1} it causes a 9.5% increase of the Cr(VI) peak. The above results demonstrate high sensitivity and selectivity of the method proposed.

Analytical applications: The discussed method was applied to determine Cr(VI) in the Bystrzyca river water sample (filtered using 0.45 μm Milipore membrane filter) and in a unfiltered tap water sample. The results of Cr(VI) determinations were compared with these obtained by other commonly used electrochemical method [2]. The latter was based on the adsorption of the Cr(III)–DTPA complex and the

conversion of the complex formed with Cr(III) present in the solution to its inactive form. The determinations were performed using the method of standard additions. Additionally, a recovery test for the river water spiked with Cr(VI) was carried out. The voltammograms obtained during the recovery test from river water are presented in Fig. 3. The results of determinations and of the recovery test are presented in Table 1. The results obtained for tap and river waters by the proposed method are in good agreement with those obtained by the reference method. In the case of the river sample spiked with Cr(III) the results obtained by the proposed method were also acceptable, while the results obtained by the reference method were too high.

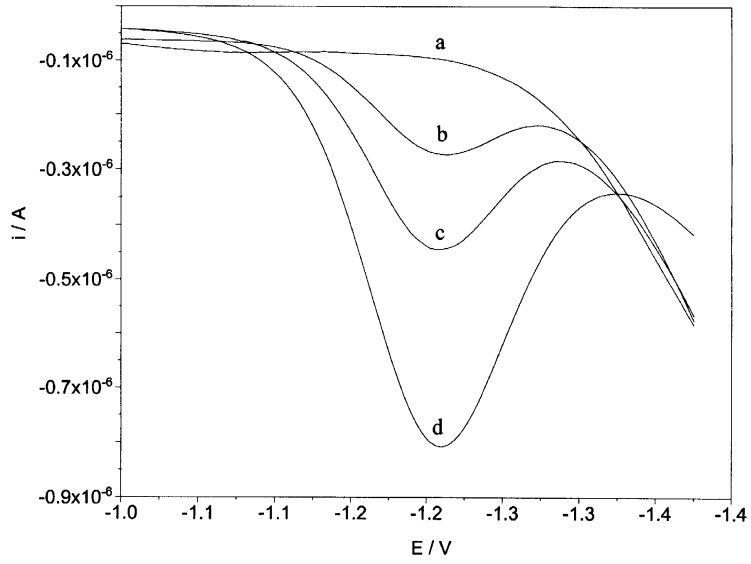

Figure 3. Differential pulse voltammograms obtained during the recovery test of Cr(VI) from river water samples. Concentration of Cr(VI): a) 0; b) 5×10^{-9}; c) 1×10^{-8}; d) 2×10^{-8} mol l^{-1}. Accumulation time 30 s.

Table 1. Results of Cr(VI) determinations in water samples. Number of measurements: n = 5.

Sample	Cr(VI) added (nmol l^{-1})	Cr(III) added (nmol l^{-1})	Cr(VI) found (nmol l^{-1})		Recovery in % this method
			this method	reference method [2]	
Tap water I	–	–	2.49 (6.2)	2.42 (4.7)	–
Tap water II	–	–	5.1 (5.8)	5.25 (4.2)	–
Bystrzyca	–	–	< DL	–	–
river water	5	–	5.2 (4.8)	–	104
(Sample I)	10	–	10.3 (5.4)	–	103
Bystrzyca	–	–	1.05 (6.6)	1.11 (5.9)	–
river water	2.5	–	3.57 (4.4)	3.42 (4.9)	101
(Sample II)	–	250	1.07 (6.0)	2.28 (6.1)	–

In brackets the relative standard deviations in % are given. DL – detection limit.

Such results for the reference method are in accordance with the results of the previous studies [16], where it was shown that the reference method can be applied successfully only in the presence of 50 – fold excess of Cr(III). The results presented above reveal high selectivity of the proposed method. The recoveries for river water are acceptable. The method was also applied to determine Cr(VI) in soil sample collected from the area close to a cement plant. Cr(VI) was extracted from five portions of the sample according to the 3060A method proposed by EPA [17]. Than it was analysed by the proposed method and by spectrophotometry according to the procedure described in [18]. Analysis results showed that the Cr(VI) content obtained by the proposed method was 12.2 ± 0.8 mg kg^{-1}, while that obtained by spectrophotometry equalled 11.7 ± 0.4 mg kg^{-1}. In the spectrophotometric determination the error is associated mainly with the extraction procedure, because of the high precision of the method. When the proposed method is used the error is a sum of errors of two steps of the analytical process. The above data show that the proposed method can be successfully used for Cr(VI) determination in water and soil samples.

CONCLUSIONS

The work shows that the complexation of Cr(III) by CDTA is a good way of elimination the Cr(III) influence on the voltammetric determination of Cr(VI) with the standard voltammetric method of chromium determination in the presence of DTPA and nitrates [11]. With CDTA as a masking agent it was possible to determine subnanomolar concentrations of Cr(VI) in the presence of 2×10^{-6} mol l^{-1} of Cr(III). The method offers a wide range of linearity of the calibration graph and a low detection limit. In the proposed procedure the analysed solutions do not require acidification to low pH. The latter can be credited as an additional advantage of the presented procedure because according to the literature data [19–21] Cr(VI) is not reduced by the organics present in the samples at the pH used.

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