

Amperometrically indicated "pseudotitrations"

IV.* Complexometric determination of Cr(III) compounds in low concentrations using deconvolution voltammetry and differential pulse polarography

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The Cr(III) compounds can be determined complexometrically by the direct "pseudotitration" in spite of the fact that the complexation reaction with EDTA is very slow and its range in the bulk phase of titrated solution is negligible. In the vicinity of amperometrical indicating electrode, however, the titration reaction takes place sufficiently rapidly due to the effective redox catalysis. Application of deconvolution voltammetry and differential pulse polarography enables to determine Cr(III) in the minimal concentration 5×10^{-6} mol dm⁻³. Reasons are given which make it impossible to achieve more favourable (lower) limit of determination.

Количество соединений Cr(III) может быть определено комплексометрически посредством прямой «псевдотитрации», не смотря на то, что реакция комплексообразования с этилендиаминтетрауксусной кислотой протекает очень медленно и ее степень в основной массе титруемого раствора пренебрежительно мала. В близости амперометрического индикаторного электрода, однако, реакция протекает достаточно быстро благодаря эффективному окислительно-восстановительному катализу. Использование деконволюционной вольтамперометрии и дифференциальной импульсной полярографии позволяет определять содержание Cr(III) в минимальной концентрации 5×10^{-6} моль дм⁻³. Приводятся причины, не позволяющие улучшить (снизить) предел определения.

In our previous papers [1—3] the principle of the amperometrically indicated pseudotitration is described in which the reaction of titrand and titrant is so slow that its range in the course of titration is negligible. The titration reaction in the bulk phase of the titrated solution practically does not take place. The amperometrical indication system generates, however, small amount of a very effective redox catalyst in the vicinity of the electrode and the electrode records the state of the reaction in the sense of equilibrium of the titration reaction.

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A typical case of the effective redox catalysis used in Cr(III) determination is the redox catalysis of the slow substitution reactions of Cr(III) compounds with ethylenediaminetetraacetic acid and its anions (EDTA) by chromium(II) ion [1]. The redox catalysis of such a substitution for Cr(III) aqua ion can be expressed in the simplified form as follows



Cr(II) and Cr(II)EDTA, respectively, acting as the catalyst of slow substitution reaction (A) is unstable — it reacts with oxygen dissolved in the titration solution or with water. Its preservation in the solution under usual conditions of titration is practically impossible. That is why its generation in the vicinity of the voltammetric indication system is particularly advantageous. The fact that the titration reaction takes place only in the vicinity of the indication electrode, where the reactants are transported from the solution by diffusion, has the consequence that the equivalence point of the pseudotitration is given by stoichiometric ratio of the titration reaction (1/1) multiplied by the correction factor $(D_{\text{EDTA}}/D_{\text{Cr}})^{1/2}$, in which D_{EDTA} and D_{Cr} denote the diffusion coefficients of EDTA and of the hexaquachromium(III) ion, respectively. As the values of diffusion coefficients do not differ very much from each other, this correction factor is close to 1.

This paper is devoted to the indication of complexometric “pseudotitration” of Cr(III) compounds by differential pulse polarography, by convolution and deconvolution voltammetry. It comes of the frequent demand of the practice to determine the Cr(III) compounds in low concentrations.

Experimental

All reagents of anal. grade were used without further purification. The Cr(III) stock solutions were prepared from $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in water acidified with H_2SO_4 ($c = 0.05 \text{ mol dm}^{-3}$) to prevent the formation of polynuclear complexes. Chromium in the solutions was analyzed spectrophotometrically [4] after the oxidation to Cr(VI) by hydrogen peroxide. The Britton—Robinson and acetate buffer solutions were used as base electrolytes. The analyzed solutions were deaerated by bubbling through high purity nitrogen.

The differential pulse polarography was carried out using the polarographic analyzer PA 3 (Laboratorní přístroje, Prague) with the static mercury drop (area 1.52 mm^2) in the

three-electrode arrangement. The pulse amplitude was made -50 mV , the controlled time of drop 2 s , and the polarization rate 2 mV s^{-1} . The voltammetric and chronoamperometric measurements without superposition of the polarization potential by pulses were carried out with the multipurpose polarograph GWP 673 (Academy of Sciences, GDR) on line with the microcomputer Compucorp (USA). The experimental curves sampled by computer were described by 1000 points. Their semiintegration and semidifferentiation, respectively, were carried out using the fast routine based on the Grünwald's definition of the d^n/dt^n operation [5]. When analyzing higher concentration of Cr(III) compounds the semiderivation was carried out also by analogue circuitry [6] which was used as an adapter to the polarograph. At lower values of the semiderivated signal, however, the instability (drift) of the used operational amplifiers complicated the transformation of experimental curves.

Results and discussion

Pulse amperometric complexometric "pseudotitration" of Cr(III)

Determination limit of the amperometric "pseudotitration" is given similarly like in the amperometric titration by capacity current which represents the balast component of the measured signal. In order to decrease the detection limit we can make use of some of the methods of capacity current elimination with the superposition of rectangular component of the polarization potential. The necessity of presence of the redox catalyst in the diffusion layer in the "pseudotitration" prefers the choice of differential pulse polarography (DPP) or of "square wave" polarography to the normal (integral) pulse polarography where the electrode polarization lasts only several tenths of ms and where the corresponding demands relating to the reaction rate of the redox catalysis (C , D) are great.

The DPP record of the aqua complex Cr(III) in the Britton—Robinson buffer solution ($\text{pH} = 5$) is a peak with the potential of maximum *ca.* -0.9 V *vs.* SCE. This is sufficiently separated from the DPP peak of Cr(III)EDTA the maximum of which has the potential *ca.* -1.2 V *vs.* SCE under the given conditions. In contrast to the polarographic condition [1] the titration course can be pursued either as a decrease of Cr(III) peak of the aqua complex, or as an increase in Cr(III)EDTA peak. In the first case the titration curve has the form \searrow , in the second one the form \swarrow . The results of DPP "pseudotitrations" of Cr(III) with EDTA are summarized in Table 1.

The minimal Cr(III) concentration which can be analyzed by the pulse amperometric "pseudotitration" is $5 \times 10^{-6}\text{ mol dm}^{-3}$. With 10 cm^3 of the titrated solution this corresponds to 50 nmol of Cr(III). At lower concentrations the linear parts of the titration curve are bent and the current readings are reproducible only when the anaerobity is kept extremely carefully.

Table 1

Statistical evaluation of pulse amperometric complexometric "pseudotitration" of Cr(III)

Quantity of Cr(III)		Relative error $\delta_r/\%$	Number of determinations	Limits of confidence for 95 % probability [7]		pH
Taken $m/\mu\text{g}$	Found (arithmetic mean) $\bar{m}/\mu\text{g}$			$\Delta m/\mu\text{g}$	$\left(\frac{\bar{m}}{m} \pm \frac{\Delta m}{m}\right)/\%$	
15.0	14.5 (14.9)	3.3 (0.7)	8 (8)	± 0.48 (± 0.48)	96.7 ± 3.2 (99.3 ± 3.2)	5.6
7.5	7.3 (7.4)	2.7 (1.3)	8 (8)	± 0.24 (± 0.23)	97.3 ± 3.2 (98.7 ± 3.1)	4.7
4.2	3.9 (4.0)	7.1 (4.8)	8 (8)	± 0.20 (± 0.21)	92.9 ± 4.8 (95.2 ± 5.0)	4.7
4.2	4.0 (4.1)	4.8 (2.4)	8 (8)	± 0.18 (± 0.18)	95.2 ± 4.3 (97.6 ± 4.3)	5.6
2.5	2.2 (2.4)	12.0 (4.0)	8 (8)	± 0.20 (± 0.18)	88.0 ± 8.0 (96.0 ± 7.2)	5.6

Values given in brackets were obtained at the potential -1.2 V *vs.* SCE (DPP Cr(III)EDTA peak); other values were obtained at the potential -0.9 V *vs.* SCE (DPP peak of the Cr(III) aqua complex).

In the literature [8] the differential pulse amperometric titration of Cu(II) with EDTA as a titrant is described. The titrated amount makes 6.25 nmol, *i.e.* *ca.* 10 times less than the minimal titrated amount of Cr(III).

The reasons of relatively high minimal analyzable Cr(III) concentration can be following:

- unsatisfactorily high apparent constant of Cr(III)EDTA stability in the used buffer solution;
- very low concentration of the redox catalyst Cr(II).

While the second of the given factors can be influenced only with difficulties, the apparent constant of Cr(III)EDTA stability can be increased increasing pH of the analyzed solution. The substantial pH increase is, however, made impossible by titrand instability, which tends to form oligomers and insoluble polymers in which the central Cr(III) ions are linked by OH bridges. The polarographic reduction of these complexes is shifted towards the more negative potentials in comparison with the Cr(III) aqua complex (-0.9 V vs. SCE).

Complexometric "pseudotitration" of Cr(III) indicated by convolution chronoamperometry and by deconvolution voltammetry

Convolution and deconvolution were accomplished *via* time semiintegration and semiderivation, respectively, of the signal numerically or by analogue circuitry. The possibility to apply the method to indication of the titration was tested on the 8 nmol Cd^{2+} titration by disodium salt of ethylenediaminetetraacetic acid. The titration was carried out in *ca.* 10 cm^3 KCl solution of the concentration 0.1 mol dm^{-3} . If the Cd^{2+} current maximum was plotted against the volume of the titrant added, the titrant being $10^{-5}\text{ mol dm}^{-3}$ EDTA, the titration curve had the shape $\sqrt{\quad}$. Its arms showed linearity in the range which is sufficient to satisfactory determination of the equivalence point of titration.

Pursuing the "pseudotitration" by both convolution and deconvolution voltammetry we proceeded as follows:

a) Registration of the cyclic voltammogram with the linear potential sweep in the potential range -0.4 to -1.5 V vs. SCE , with the subsequent semiderivation and evaluation of reduction peak of Cr^{3+} or Cr(III)EDTA. In the first case the titration curve had the form $\sqrt{\quad}$, in the second one the form $\sqrt{\quad}$. Plotting the sum of Cr(III)EDTA cathodic peak and of the opposite anodic peak of Cr(II)EDTA of the deconvolution cyclic voltammogram was found to be advantageous.

b) Semiintegration of chronoamperograms sampled always after titrant addition with the potential jump from -0.4 to -0.9 V vs. SCE (the Cr^{3+} reduction). The convolutional chronoamperograms obtained in this way are

Table 2

Statistical evaluation of convolution and deconvolution voltammetric "pseudotitration" of Cr(III) with EDTA
(*a*, *b* — different ways of evaluation described in the text)

Quantity of Cr(III)			Limits of confidence for 95 % probability								pH of Britton—Robinson buffer solution
Taken <i>m</i> /μg	Found (arithmetic mean) <i>m</i> /μg		Relative error δ_r /%		Number of determi- nations		[7]				
							$\Delta m/\mu g$		$\left(\frac{\bar{m}}{m} + \frac{\Delta m}{m}\right)/\%$		
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	
15.0	14.8	14.8	1.3	1.3	8	8	± 0.53	± 0.51	98.7 ± 3.5	98.7 ± 3.4	4.7
7.5	7.4	7.4	1.3	1.3	8	8	± 0.24	± 0.24	98.7 ± 3.2	98.3 ± 3.2	4.7
4.2	4.0	3.9	4.8	7.1	8	8	± 0.13	± 0.16	95.2 ± 3.1	92.9 ± 3.8	5.6
4.2	4.1	4.1	2.4	2.4	8	8	± 0.16	± 0.18	97.6 ± 3.8	97.6 ± 4.3	5.6
2.5	2.4	2.3	4.0	4.0	8	8	± 0.18	± 0.20	96.0 ± 7.2	92.0 ± 8.0	5.6

time-independent in the time interval 0.5 to 5 s. This constant value decreases after each titrant addition. Reaching the equivalence point it does not change with the titrant addition any more. This means that the titration curve has the form \backslash in this case. The results of the voltammetric "pseudotitrations" with semiderivation and semiintegration, respectively, are summarized in Table 2.

Regardless of the chosen way of evaluation (*a* or *b*), the minimal titrand concentration was *ca.* $5 \times 10^{-6} \text{ mol dm}^{-3}$. This concentration is sixfold higher than the cadmium concentration used for testing the method. At lower concentrations of Cr^{3+} the arms of the titration curve stop being linear, this being probably connected with the unsufficiently high equilibrium constant of the titration reaction or with the unsufficient concentration of the redox catalyst in the diffusion layer similarly as it has been mentioned with differential pulse polarographic indication.

The comparison of Table 2 with Table 1 for pulse amperometric Cr(III) "pseudotitration" carried out at the same concentration levels shows that both precision and accuracy are approximately equal for both methods.

It appears that indication of Cr(III) pseudotitration with EDTA both by pulse polarography and convolution or deconvolution methods shows that it is possible to carry out this also in the case when the titrated solution contains other ions which react with EDTA. The analysis of such titration curve comes out of the similar analysis given in Ref. [2].

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