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

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Received 23 April 1985

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 concentra­
tion $5 \times 10^{-6}$ mol dm$^{-3}$ Reasons are given which make it impossible to
achieve more favourable (lower) limit of determination.

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 am­
perometrical 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.

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

\[
\begin{align*}
\text{Cr(III)} + \text{EDTA} & \iff \text{Cr(III)EDTA} \quad \text{(slow)} \quad (A) \\
\text{Cr(III)} + e^- & \Rightarrow \text{Cr(II)} \quad \text{(B)} \\
\text{Cr(II)} + \text{EDTA} & \iff \text{Cr(II)EDTA} \quad \text{(fast)} \quad (C) \\
\text{Cr(III)} + \text{Cr(II)EDTA} & \iff \text{Cr(III)EDTA} + \text{Cr(II)} \quad \text{(fast)} \quad (D)
\end{align*}
\]

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 \(D_{\text{EDTA}}\) and \(D_{\text{Cr}}\) 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 KCr(SO₄)₂·12H₂O in water acidified with H₂SO₄ \((c = 0.05 \text{ mol dm}^{-3})\) 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 mm²) in the
three-electrode arrangement. The pulse amplitude was made $- 50 \text{ mV}$, the controlled
time of drop 2 s, and the polarization rate $2 \text{ mV s}^{-1}$. The voltammetric and chronoam-
permetric 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 semidif-
ferentiation, respectively, were carried out using the fast routine based on the Grünwald’s
definition of the $d^n / d^n$ 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 trans­
formation 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 “pseu­
dotitration” 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 corre­
sponding 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 (pH = 5) is a peak with the potential of maximum $ca. - 0.9 \text{ V vs. SCE}$. This is sufficiently separated from the DPP peak of Cr(III)EDTA the
maximum of which has the potential $ca. - 1.2 \text{ V vs. SCE}$ 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 $\int$, in the second one the form $\int$ 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 $10 \text{ cm}^3$ of the ti-
trated solution this corresponds to $50 \text{ nmol of Cr(III)}$. 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)

<table>
<thead>
<tr>
<th>Quantity of Cr(III)</th>
<th>Found (arithmetic mean)</th>
<th>Relative error δ,/%</th>
<th>Number of determinations</th>
<th>Limits of confidence for 95 % probability [7]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taken m/µg</td>
<td>m/µg</td>
<td></td>
<td></td>
<td>Δm/µg</td>
<td>(m ± Δm/m) / %</td>
</tr>
<tr>
<td>15.0</td>
<td>14.5 (14.9)</td>
<td>3.3 (0.7)</td>
<td>8 (8)</td>
<td>±0.48 (±0.48)</td>
<td>96.7 ± 3.2</td>
</tr>
<tr>
<td>7.5</td>
<td>7.3 (7.4)</td>
<td>2.7 (1.3)</td>
<td>8 (8)</td>
<td>±0.24 (±0.23)</td>
<td>97.3 ± 3.2</td>
</tr>
<tr>
<td>4.2</td>
<td>3.9 (4.0)</td>
<td>7.1 (4.8)</td>
<td>8 (8)</td>
<td>±0.20 (±0.21)</td>
<td>92.9 ± 4.8</td>
</tr>
<tr>
<td>4.2</td>
<td>4.0 (4.1)</td>
<td>4.8 (2.4)</td>
<td>8 (8)</td>
<td>±0.18 (±0.18)</td>
<td>95.2 ± 4.3</td>
</tr>
<tr>
<td>2.5</td>
<td>2.2 (2.4)</td>
<td>12.0 (4.0)</td>
<td>8 (8)</td>
<td>±0.20 (±0.18)</td>
<td>88.0 ± 8.0</td>
</tr>
</tbody>
</table>

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 $10^{-5}$ mol dm$^{-3}$ EDTA, the titration curve had the shape \[. 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 \[, in the second one the form \[. 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
Statistical evaluation of convolution and deconvolution voltammetric "pseudotitration" of Cr(III) with EDTA

(a, b — different ways of evaluation described in the text)

<table>
<thead>
<tr>
<th>Taken m/µg</th>
<th>Found m/µg (arithmetic mean)</th>
<th>Relative error δ_i /%</th>
<th>Number of determinations</th>
<th>Limits of confidence for 95 % probability</th>
<th>pH of Britton—Robinson buffer solution</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a b</td>
<td>(m ± Δm) /%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>14.8</td>
<td>14.8</td>
<td>± 0.53 ± 0.51</td>
<td>98.7 ± 3.5 98.7 ± 3.4 4.7</td>
</tr>
<tr>
<td>7.5</td>
<td>7.4</td>
<td>7.4</td>
<td>8 8</td>
<td>± 0.24 ± 0.24</td>
<td>98.7 ± 3.2 98.3 ± 3.2 4.7</td>
</tr>
<tr>
<td>4.2</td>
<td>4.0</td>
<td>3.9</td>
<td>4.8 7.1</td>
<td>± 0.13 ± 0.16</td>
<td>95.2 ± 3.1 92.9 ± 3.8 5.6</td>
</tr>
<tr>
<td>4.2</td>
<td>4.1</td>
<td>4.1</td>
<td>2.4 2.4</td>
<td>± 0.16 ± 0.18</td>
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</tr>
</tbody>
</table>
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 \( ... \) 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].

References


Translated by D. Bustin