Determination of Citrate as Its Iron(III) Complex by Differential Pulse Polarography

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A method for determining citrate as its complex with iron(III) by differential pulse polarography is described. The method is sensitive to 5 \( \mu g \) ml\(^{-1}\) of citrate, without any interference from equimolar propan-2-onedicarboxylate and propenetricarboxylate ions and 10% of oxalate and tartrate ions. The limits of error in citrate concentrations determined by the proposed method are better than \( \pm 2.5\% \).

The feasibility of determining oxalate, succinate and tartrate by means of differential pulse polarography was also explored and the method was found to be applicable to the determination of oxalate.

**Keywords:** Citrate determination; citrate - iron(III) complex; differential pulse polarography

In recent years differential pulse polarography has become a very popular technique for determining trace amounts of electroactive species in biological, inorganic and organic materials, owing to its high sensitivity and the minimum of interference experienced from excesses of species reduced at more positive potentials and at slightly different half-wave potentials. While Zuman\(^1\) has reviewed theoretical and practical aspects, Heijne and Van der Linden\(^2\) have recently established the current-potential relationship for differential pulse polarography.

The difficulty of obtaining an electrode reduction step for saturated carboxylate ions in aqueous systems is well known, and no polarographic method for the determination of citrate ions has previously been reported.

The proposed method is based on the fact that the half-wave potential of a metal ion is shifted by the formation of a complex and this shift is a function of the stability of the metal complex. The wave produced by the iron(III) - citrate complex is a well defined, reversible wave,\(^3\) which in the present method is used for the indirect determination of the citrate ion.

**Experimental**

**Apparatus**

Polarographic waves were recorded on an X - Y recorder, Model 26000 A3, manufactured by Bryans Southern Instruments. They were obtained by using a Polarographic Analyzer 174A, incorporating a dropping mercury electrode fitted with a mechanical drop timer, a saturated calomel reference electrode and a polarographic cell, which was manufactured by Princeton Applied Research, Princeton, New Jersey, USA.

**Reagents**

All of the solutions were prepared from analytical-grade reagents.

- **Buffer solution, pH 4.5.** Prepared from sodium acetate (1.0 m) and acetic acid.
- **Iron(III) sulphate solution, 1 mm, in 0.01% V/V sulphuric acid.**
- **Trisodium citrate solution, 0.1 mm.**

**Procedure**

An appropriate amount of the sample is transferred into the polarographic cell. About 20 ml of the buffer solution and an amount of iron(III) solution that is about twice the suspected citrate content of the sample are added. The solution is then de-aerated with nitrogen for about 5 min and polarograms are recorded between \(-0.10\) and \(-0.85\) V versus S.C.E.

The peak current is measured and related to the concentration of citrate ion from the appropriate calibration graph, which is obtained by using standard solutions.
Results and Discussion

A detailed polarographic study of the iron(III) - citrate/iron(II) - citrate redox system was made in order to evaluate its reversibility before assessing its use for the determination of citrate.

Polarograms of 1 mg ml⁻¹ of citrate and of iron(III) sulphate, obtained by use of classical d.c. and differential pulse polarography, are presented in Figs. 1 and 2, respectively. Points on the classical d.c. polarogram for the iron(III) - citrate complex (Fig. 1, A) were used to construct a graph of log \( i/(i_d-i) \) versus applied potential in the range from -0.15 to -0.35 V with respect to S.C.E. The graph was found to be linear, with a slope of 58.3 mV, and crossed the line log \( i/(i_d-i) = 0 \) at -0.250 V = \( E_1 \), in close agreement with the theoretical value of 58.1 mV for a reversible, one-electron redox process at 20 °C.

The value of the peak potential from the differential pulse polarogram of iron(III) - citrate (Fig. 1, B) was related to the half-wave potential of a classical d.c. polarogram according to a theoretically derived equation as follows:

\[
E_p = E_1 - \frac{\Delta E}{2}
\]

(1)
where $E_p$ is the peak potential, $E_1$ the half-wave potential and $\Delta E$ the applied pulse amplitude (−50 mV).

A differential pulse polarogram of the iron(III) - citrate complex in the presence of an excess of iron(III) sulphate is shown in Fig. 3. There was no shift in peak potential B at $-0.225$ V versus S.C.E. as a result of the iron(III) - citrate/iron(II) - citrate redox process. Peak A, at $-0.0375$ V versus S.C.E., corresponds to the peak potential due to the reduction step of iron(III) sulphate (Fig. 2).

![Fig. 3. Differential pulse polarogram of iron(III) - citrate in excess of iron(III) ions. A, Peak due to free iron(III) ions; B, peak due to the complexed iron(III) ions.](image)

The peak potential $-0.225$ V versus S.C.E. was independent of the citrate concentration (Fig. 4). The peak current was found to increase linearly with increasing citrate concentration (Fig. 5), giving a further check on the reversibility of the iron(III) - citrate reduction wave.

The effects of other functional groups on the determination of citrate by the proposed
method were studied by adding various dibasic and polybasic carboxylate ions. Standard solutions containing different amounts of foreign carboxylate ions were added to 100-ml flasks containing 1.0 and 5.0 ml of the proposed iron(III) and citrate reagent solutions, respectively, and diluted to 100.0 ml with the acetate buffer. The solutions were de-aerated and polarograms were recorded in the suggested potential range. The dominant polarographic wave due to the reduction step of iron(III) - citrate ion was examined in each instance and it was found that oxalate and tartrate complexes of iron(III), with peak potentials at -0.175 and 0.030 V versus S.C.E., respectively, did not interfere at a concentration of 10% m/V of the iron(III) - citrate complex. Propan-2-onedcarboxylate and propenetricarboxylate ions, degradation products of the citrate ion, also did not appear to interfere with the proposed method, even at concentrations equal to that of the iron(III) - citrate complex. Excellent recovery values were obtained when small amounts of citrate (0-1.00 mg) were added to an iron(III) solution containing 20 mg of citrate; these results are given in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>Citrate added/*mg</th>
<th>Citrate found/*mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>20.00</td>
</tr>
<tr>
<td>0.20</td>
<td>20.09</td>
</tr>
<tr>
<td>0.50</td>
<td>20.20</td>
</tr>
<tr>
<td>0.80</td>
<td>20.50</td>
</tr>
<tr>
<td>1.00</td>
<td>21.00</td>
</tr>
</tbody>
</table>

In order to overcome an interference on the lower range of the calibration graph (Fig. 5) caused by the small separation between peak potentials for iron(III) - citrate and iron(III) sulphate reduction processes the peak potential shift for the copper(II) - citrate system was examined. The polarograms in Fig. 6 were obtained by using copper(II) sulphate and copper(II) - citrate in 2 M sodium acetate. A peak potential shift from 0.075 V [copper(II) sulphate] to -0.310 V [copper(II) - citrate] versus S.C.E. was observed, which was about 20% greater than the shift for the iron(III) - citrate system.

However, when the polarograms for copper(II) - citrate were examined it was found that the electrode reduction step for copper(II) - citrate was irreversible, firstly because the graph of log i/(i_d - i) versus applied potential was not linear and the slope was 79 mV, which is higher than expected (58.1 mV) for a one-electron reversible redox process, secondly because the peak
potential was not related to the half-wave potential according to equation (1), the calculated value of $E_p$ being $-0.265$ V compared with an observed value of $-0.310$ V, and thirdly because the peak potential shifted towards a more negative value as the concentration increased (Fig. 7) and the peak current was not directly proportional to the concentration of citrate.

The possibility of determining oxalate, succinate and tartrate as their iron(II1) complexes was also explored. Attempts to determine succinate failed completely because of the low stability of the iron(III)-succinate complex. The results of classical d.c. and differential pulse polarographic studies on the iron(III)-tartrate system (Fig. 8) revealed that the redox couple was not reversible. The non-linear graph of log $i/(i_d-i)$ versus applied potential had a slope of 86 mV and the observed peak potential (0.0375 V versus S.C.E.) did not agree with the calculated value (0.048 V versus S.C.E.).
Oxalate ions gave results similar to those of the successful iron(III) - citrate system. Polarograms of iron(III) - oxalate obtained by classical d.c. polarography and differential pulse polarography are shown in Fig. 9; the graph of log i/(i_d - i) versus applied potential for the classical d.c. polarogram is linear with a slope of 58.4 mV, in agreement with the theoretical value of 58.1 mV for a one-electron reversible redox system at 20 °C. The peak potential of the differential pulse polarogram (0.175 V versus S.C.E.) is also in good agreement with the value of 0.200 V versus S.C.E. required by the relationship indicated in equation (1), reported by Heijne and Van der Linden. 2

The author is indebted to Inco Europe Limited for permission to publish this paper and to EDT Research, London, for the loan of the instrument.

References

Received December 29th, 1976
Accepted April 7th, 1977