The Use of Calmagite in the Differential Pulse Polarographic Determination of Magnesium

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An azo dye calmagite (calm) and its complex with magnesium (Mg–calm) have been studied by differential pulse polarography and absorption spectrophotometry. It has been shown that magnesium can be determined on the basis of the linear increase of the cathodic peak current of the complexed ligand on magnesium concentration within the range from $1 \times 10^{-6}$ to $1 \times 10^{-5}$ mol l$^{-1}$. The effect of accompanying ions on the magnesium determination by the proposed method has been also examined. The proposed method has been employed to determine magnesium in mineral waters. It was possible to demonstrate the mixed adsorptive and diffusional nature of the reduction current of calmagite on the basis of differential pulse polarographic and spectrophotometric studies.

The complex-forming properties of calmagite [1-(1-hydroxy-4-methyl-2-phenylazo)-2-hydroxy-4-naphthalenesulphonic acid], an indicator in titration of calcium and magnesium, are well known [1, 2]. The relatively high stability constant of magnesium–calmagite complex makes possible determination of magnesium bound to calmagite by the spectrophotometric method [3].
Bem and Rubel [4] have reported that this dye is polarographically active and its reduction wave is of diffusional character. The method of electrocapillary curves has been used to detect adsorption of the substrate on the mercury surface, however, no extra adsorption polarographic wave of calmagite was observed.

Since the reduction of the Al–calmagite complex takes place at more negative potential than the reduction of the ligand alone, calmagite has been used in polarographic determination of small quantities of aluminium [5, 6].

Although it is well known that the reduction wave of o,o'-dihydroxyazo-dye is shifted in the presence of a metal ion forming a complex with the dye [7], the cathodic peak current of calmagite bound to magnesium has not been used as yet for the differential pulse polarographic determination of magnesium. The d.c. polarographic methods, which were proposed earlier to determine magnesium after complexating it with 5-sulfo-2-hydroxybenzene-2-naphtol (Mordant Violet 5, Solochrome Violet RS) [8, 9] require either heating or strict time discipline.

The aim of this work was to determine magnesium by differential pulse polarography after transferring it into the calmagite complex (log $\beta_{Mg-cal}$ = 8.1, log $\beta_{Ca-cal}$ = 6.1).

The proposed method is simple, fast and allows to lower the limit of determination of magnesium by the polarographic method to $10^{-6}$ mol l$^{-1}$.

EXPERIMENTAL

Reagents, solutions and apparatus

Water was doubly distilled from glass. Calmagite (Aldrich-Chemie), a commercial product, was purified according to paper [4].

Ammonia, Analar grade (POCh) was purified by microdiffusion.

The following reagents were used as supplied: NaOH, Analar grade (POCh); hydrochloric acid, Analar grade (POCh); hydrochloric acid, ultra-pure (Merck); Eriochrome Black T (Aldrich-Chemie); calcium carbonate, Analar grade (POCh); ethylenediaminetetraacetic acid (EDTA), Analar grade (POCh); ethyleneglycolbis(2-aminoethylether)tetraacetic acid (EGTA), Analar grade (Aldrich-Chemie); potassium cyanide, Analar grade (POCh); ascorbic acid, Analar grade (KZF "Polfa") and argon, pure, in a gas cylinder.

The required concentrations of the solutions used in the study were prepared by dissolving weighed portions in redistilled water in volumetric flasks.

The measuring equipment consisted of a pulse polarograph, type PP-04 (Unitra Telpod, Poland), connected to a XY recorder (Müszner Es Merestechnika, Hungary). The measurements were carried out with the three-electrode system: a dropping mercury electrode as the cathode, a platinum electrode as the anode and a saturated calomel electrode as the reference electrode. Mercury drops at the dropping mercury capillary were dislodged by a magnetic hammer after a required drop time ($t = 3$ s). The following equipment was also used: automatic pipettes, a pH-meter, type N-517 (Mera–Elwro), a Spekol 11 spectrophotometer (Carl Zeiss, Jena), and a UV–VIS spectrophotometer equipped with quartz cells of 1 cm in thickness (Carl Zeiss, Jena).
RESULTS AND DISCUSSION

Preliminary experiments

In order to define whether calmagite is suitable in polarographic determination of magnesium, preliminary experiments were carried out using an ammonium buffer of pH = 10. A series of samples of constant concentration of calmagite \( c(\text{calm}) = 2 \times 10^{-5} \text{ mol l}^{-1} \) and variable concentration of magnesium from \( 5 \times 10^{-6} \text{ mol l}^{-1} \) to \( 8 \times 10^{-5} \text{ mol l}^{-1} \) was prepared. The cathodic peak of calmagite was observed at \(-0.62 \text{ V}\); another peak appeared at \(-0.82 \text{ V}\). Basing on the results obtained, it was found that calmagite with magnesium ion form quickly a complex which is stable enough to be used in the polarographic determination of magnesium.

To find optimal conditions for determination of magnesium, with maximum concentration equal to \( c(\text{Mg}^{2+}) = 1 \times 10^{-5} \text{ mol l}^{-1} \), the dependence of reduction current of the complex on concentration of calmagite being in excess was studied. It was found that the dye concentration equal to \( 3.2 \times 10^{-4} \text{ mol l}^{-1} \) is high enough to complex magnesium at concentration \( 1 \times 10^{-5} \text{ mol l}^{-1} \).

The optimal pH value of the buffer, 11 to 11.9, was found from polarographic examination of the effect of pH on the peak height of the complex. In examination the Britton-Robinson buffers of pH from 1.5 to 11.9 were used. The obtained results are consistent with both the calculations carried out by the authors and the spectrophotometric data.

According to the aim of this study it was required to use reagents of high purity. Therefore, in further measurements carried out in the ammonium buffer at pH = 11.1, solutions prepared from ultrapure HCl and ammonia purified by microdiffusion were employed.

Character of the calmagite reduction current

In order to characterize the reduction current of calmagite, the current intensity was measured within two ranges of calmagite concentration: \( 1 \times 10^{-6} \text{ to } 10 \times 10^{-6} \text{ mol l}^{-1} \) and \( 1 \times 10^{-5} \text{ to } 6 \times 10^{-4} \text{ mol l}^{-1} \), in ammonium buffer of concentration \((\text{NH}_4\text{Cl} + \text{NH}_3) 0.2 \text{ mol l}^{-1}\) and of pH 11.1 (Fig. 1). A linear relationship between the peak current \( (E = -0.62 \text{ V}) \) and concentration was obtained for concentration level of \( 10^{-6} \text{ mol l}^{-1} \). For higher concentrations the dependence of peak current on concentration is no longer linear (Fig. 2, curve 1), and the peak potential changes with the increase in concentration, reaching \(-0.66 \text{ V}\) for \( 6 \times 10^{-4} \text{ mol l}^{-1} \) calmagite. At the same time, for concentration \( 1.6 \times 10^{-4} \text{ mol l}^{-1} \) polarograms exhibit a new peak at \(-0.59 \text{ V}\), the height of which increases linearly with increasing concentration up to \( 6 \times 10^{-4} \text{ mol l}^{-1} \) (Fig. 2, curve 2). The results obtained point to the adsorptive character of the peak current of calmagite reduction at \(-0.62 \text{ V}\) \[10, 11\], and to diffusional nature of the peak current at \(-0.59 \text{ V}\).

The adsorptive character of the peak current observed at \(-0.62 \text{ V}\) (in the case of higher concentration \(-0.66 \text{ V}\)) is confirmed by the absorption spectra and polarograms obtained for the magnesium–calmagite complex at 300-fold excess of magnesium. Under these conditions the absorption curve of the complex (Fig. 3, curve 2)
Figure 1. A differential pulse-polarographic curve of $4 \times 10^{-4}$ mol l$^{-1}$ calmagite in ammonium buffer, $c(\text{NH}_4\text{Cl} + \text{NH}_3) = 0.2$ mol l$^{-1}$, pH = 11.1, $t = 3$ s, amplitude $\Delta E = 20$ mV

Figure 2. The dependence of the reduction current of calmagite on the concentration of calmagite in ammonium buffer: 1 – the dependence for the peak which appears within the whole range of concentrations of calmagite; 2 – the dependence for the peak which appears from the calmagite concentration $1.6 \times 10^{-4}$ mol l$^{-1}$ (other conditions as in Fig. 1)
Use of calmagite in DPP determination of magnesium

Figure 3. Absorption curves: 1 – free calmagite (1×10^{-5} mol l^{-1}) in ammonium buffer; 2 – calmagite–Mg complex in ammonium buffer, c(calm) = 1×10^{-5} mol l^{-1}, c(Mg^{2+}) = 300×10^{-5} mol l^{-1} (pH and buffer concentration as in Fig. 1).

Figure 4. A polarogram of Mg(II)–calmagite complex in the presence of free cation in ammonium buffer: 1 – a peak of the adsorbed dye; 2 – a peak of the complexed dye (conditions as in Fig. 3, curve 2).

shows no maximum characteristic for a free dye at λ = 600 nm (Fig. 3, curve 1). On the other hand, the polarograms (Fig. 4) show both the peak of a pure dye (peak 1) and that of calmagite in the complex (peak 2).
Determination of magnesium by the method of standard line

A possibility of differential pulse polarographic determination of magnesium, that was confirmed in preliminary experiments, was extended for the determination of magnesium by the method of the standard line. In order to obtain such a calibration line several samples were prepared in volumetric flasks (25 ml) containing ammonium buffer of pH 11.1 and of concentration \((\text{NH}_4\text{Cl} + \text{NH}_3) \times 10^{-4} \text{ mol l}^{-1}\). The components were added in the following order: magnesium, calmagite, ammonium buffer. After stirring the samples were transferred to polarographic cells. Oxygen was removed by passing argon for 5 min. The curves were recorded from -0.66 V to about -1 V. The solutions contained no other depolarizers. The results, processed statistically, are given in Table 1.

Table 1. Differential pulse polarographic determination of magnesium based on measuring the reduction peak current of the magnesium–calmagite complex, and statistical evaluation of the results \((E = -0.82 \text{ V}, n = 6, \text{ confidence coefficient } \alpha = 0.99)\)

<table>
<thead>
<tr>
<th>Concentration of Mg</th>
<th>Relative standard deviation %</th>
<th>Error (\frac{(x - c)c}{100} %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>taken, (\mu\text{mol l}^{-1})</td>
<td>found, (\mu\text{mol l}^{-1})</td>
<td>(c)</td>
</tr>
<tr>
<td>10.00</td>
<td>9.92 ± 0.25</td>
<td>1.5</td>
</tr>
<tr>
<td>8.00</td>
<td>8.04 ± 0.51</td>
<td>3</td>
</tr>
<tr>
<td>6.00</td>
<td>6.06 ± 0.61</td>
<td>6</td>
</tr>
<tr>
<td>4.00</td>
<td>3.99 ± 0.45</td>
<td>7</td>
</tr>
<tr>
<td>2.00</td>
<td>1.98 ± 0.14</td>
<td>6</td>
</tr>
<tr>
<td>1.00</td>
<td>1.16 ± 0.14</td>
<td>8</td>
</tr>
</tbody>
</table>

The effect of accompanying ions on the determination of magnesium

Effects of barium, cobalt, calcium, chromium, iron, lead, manganese, nickel, strontium and zinc on the determination of magnesium present at concentration of \(1 \times 10^{-5} \text{ mol l}^{-1}\), by the above proposed method, were examined. The solutions were prepared in 25 ml volumetric flasks, and the reagents were added in the following order: metal ions, calmagite, ammonium buffer. The results are presented in Table 2.

Table 2. The effect of accompanying ions on the determination of magnesium \(c(\text{Mg}^{2+}) = 1 \times 10^{-5} \text{ mol l}^{-1}\), in ammonium buffer of pH 11.1, \(c(\text{NH}_4\text{Cl} + \text{NH}_3) = 0.2 \text{ mol l}^{-1}\), \(c(\text{calm}) = 3.2 \times 10^{-4} \text{ mol l}^{-1}\)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (\text{mol l}^{-1})</th>
<th>Effect</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba}^{2+})</td>
<td>(1 \times 10^{-5})</td>
<td>does not interfere</td>
<td>No peak is observed at (E = -0.82 \text{ V}).</td>
</tr>
<tr>
<td>(\text{Cr}^{3+})</td>
<td>(1 \times 10^{-5})</td>
<td>interferes</td>
<td>The peak of Co–calm complex is close to the peak of Mg–calm complex ([E(\text{Co–calm}) = 0.91 \text{ V}]). Their close positions and considerable width at half-height bring about an interference of the peaks. Since cobalt is absent in mineral waters, elimination of its interfering effect was not carried out.</td>
</tr>
</tbody>
</table>
### Table 2 continued

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration</th>
<th>Interference</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ca}^{2+})</td>
<td>(1 \times 10^{-4})</td>
<td>does not interfere</td>
<td>Calcium at this concentration does not affect the height of the Mg-calm peak. The peak of Ca-calm, which appears the same potential as that of Mg-calm, introduces an error.</td>
</tr>
<tr>
<td>(\text{Ca}^{2+})</td>
<td>(1 \times 10^{-3})</td>
<td>interferes</td>
<td>Iron(II) at this concentration does not affect the height of the Mg-calm peak. A peak height of Fe(II)-calm complex, appearing at (-0.83) V, precludes the recording of pure peak of the Mg-calm complex. Using potassium cyanide ((c = 0.8) mg ml(^{-1})) as a masking agent in the medium of ascorbic acid (0.8 mg ml(^{-1})) it is possible to eliminate the influence of Fe(II).</td>
</tr>
<tr>
<td>(\text{Fe}^{2+})</td>
<td>(1 \times 10^{-6})</td>
<td>does not interfere</td>
<td>Iron(II) at this concentration does not affect the height of the Mg-calm peak. A peak height of Fe(II)-calm complex, appearing at (-0.83) V, precludes the recording of Mg-calm complex. Using potassium cyanide in ascorbic acid as masking agent ([c = 2.4) mg ml(^{-1}]; (c(C_6H_8O_6) = 0.8) mg ml(^{-1})] it was possible to obtain a pure peak of the Mg-calm reduction current.</td>
</tr>
<tr>
<td>(\text{Fe}^{3+})</td>
<td>(5 \times 10^{-7})</td>
<td>does not interfere</td>
<td>Iron(II) at this concentration does not affect the height of the Mg-calm peak. A peak height of Fe(III)-calm complex, appearing at (-0.83) V, precludes the recording of Mg-calm complex. Using potassium cyanide in ascorbic acid as masking agent ([c = 2.4) mg ml(^{-1}]; (c(C_6H_8O_6) = 0.8) mg ml(^{-1})] it was possible to obtain a pure peak of the Mg-calm reduction current.</td>
</tr>
<tr>
<td>(\text{Mn}^{2+})</td>
<td>(2 \times 10^{-6})</td>
<td>does not interfere</td>
<td>A narrow peak of Mn-calm complex does not interfere in determination of Mg-calm complex. A high peak of Mn-calm complex ((i = 4.1) μA), with a small width at half height ((0.049) V), precedes the peak of Mg-calm complex ([E(Mn-calm) = -0.78) V]. Using the masking agent EGTA ([c(EGTA) = 1 \times 10^{-5}) mol l(^{-1})] the height of the Mn-calm peak was lowered and the peaks were separated. However, too high concentration of the masking agent affects also the Mg-calm peak.</td>
</tr>
<tr>
<td>(\text{Ni}^{2+})</td>
<td>(1 \times 10^{-5})</td>
<td>interferes</td>
<td>The peak of Ni-calm complex appears at a potential very close to that of Mg-calm complex ([E(Ni-calm) = -0.83) V]. Since nickel is absent in mineral waters, elimination of its interfering effect was not carried out.</td>
</tr>
<tr>
<td>(\text{Zn}^{2+})</td>
<td>(1 \times 10^{-5})</td>
<td>interferes</td>
<td>The peak of Zn-calm complex precedes the peak of Mg-calm complex ([E(Zn-calm) = -0.78) V]. Close positions of the peaks and their large width at half height bring about a peak interference. Since zinc is absent in mineral waters, elimination of its interfering effect was not carried out.</td>
</tr>
</tbody>
</table>

### Application of the method for the determination of magnesium in mineral waters

The presented method was used to determine magnesium in mineral waters such as "Wielka Pieniawa", "Zuber" and "Jan" (trade names of Polish mineral waters). It was found that iron, calcium and manganese due to their low contents in the above waters do not affect the results of magnesium determination.

The magnesium content in the mentioned waters was determined by the method of standard addition.

Independently, the magnesium content was also determined by photometric titration, using EDTA solution of concentration \(2.5 \times 10^{-4}\) mol l\(^{-1}\) in the presence of Eriochrome Black T as indicator. The results are compared in Table 3.
Table 3. The results of determination of magnesium in mineral waters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg taken (producer's certificate) mmol l⁻¹</th>
<th>Mg found, mmol l⁻¹</th>
<th>polarographic method</th>
<th>photometric method</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Wielka Pieniawa&quot;</td>
<td>1.25</td>
<td>1.29</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>&quot;In&quot;</td>
<td>1.08</td>
<td>1.11</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>&quot;Zuber&quot;</td>
<td>19.00</td>
<td>18.70</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Calcium content in the above waters was 6.50, 4.24, 2.70 mmol l⁻¹, respectively.

Conclusion

Basing on differential pulse polarographic measurements of calmagite and its complex with magnesium, it has been found that the current of calmagite reduction is of mixed adsorptive and diffusional character. A new peak, appearing for increased calmagite concentration at −0.59 V, 30 mV off the primary peak, cannot be observed when d.c. polarography is used. Lalikov and Sister [12] in their study on another azo dye, Eriochrome Black T, have also suggested the mixed adsorptive and diffusional character of the cathodic current.

An examination of the effect of calcium on the determination of magnesium by the proposed method has shown that calcium even in a 10-fold excess does not interfere in determination of magnesium at an ammonium buffer of pH in the range from 11 to 11.9.

The determination of magnesium in commercial mineral waters has been carried out without previous masking of interfering ions, since their content in these products is very low. The obtained results are in good agreement with the producer’s data.

REFERENCES


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