COMPLEXOMETRIC DETERMINATION OF MAGNESIUM IN THE PRESENCE OF LUMINOL (3-amino-phthalic-acidhydrazide) INDICATOR

by

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Application of chemiluminescent indicators is of the greatest importance in determining such solutions where assessing of final limit on the basis of colour change is impossible because of the turbidity of the solution or its own colour. Another possibility for application is in resolving such analytical problems, where determinations are to be accomplished in poor light of varying intensity. Nowadays problems arise mainly in the field where on-the-spot analyses are made. They are faced in carrying out the local investigations of underground streams or filtrating subsurface waters (karst-waters a and β), analyses progressively acquiring greater importance in karstwater research and in the examination of karst-water resources (3, 4, 8 − 10).

The latest observation of SZARVAS, KORONDÁN and RAISZ (11) is that, in the presence of *luminol* indicator — because of its metal-catalyzed oxidation — the Ca^{2+}, Sr^{2+} and Ba^{2+} ions are of great importance in field analyses of karst-waters. Considering that in determining changes in hardness, Mg^{2+} ions could also be of importance in the analyses of karst-waters, it was essential to examine how the method of SZARVAS et al. could be applied in the determination of Mg^{2+} ions. In the following we are accounting for our results.

Experimental part

Materials

1. 0.01 m $MgSO_4.7H_2O$ solution, from p. a. $MgSO_4.7H_2O$.

2. The factor of 0.01 m *Complexon III* solution (p. a. Reanal) was adjusted with *Eriochrome black T.* indicator in 0.01 m $MgSO_4$.

3. 0.1 % solution of *luminol**.

* The luminol indicator was made available by DR. ÉVA BÁNYAI, assistant professor of the General Chemistry Department of the Technical University of Budapest.

4. 3 % of H_2O_2 solution (dissolved from 30 % p. a. H_2O_2).

5. 4 m NH_4OH dissolved from p. a. cc NH_4OH.

6. Karst-water from the *Kistohonya* source of Jósvafö. The Ca + Mg content was determined with the measuring solution *Complexon III* in the presence of *Eriochrome black T.* indicator.

Experimental results

In the course of our experiment, we found that the determinations of Mg^{2+} ions could be done easily with a solution of *Complexon III*, in a quantity of 0.01 m.

The determination was performed by using the method of SZARVAS et al. and the change of the indicator could be readily observed.

For the experiment, we put a solution of 1 to 25 ml of 0.01 m $MgSO_4$ in a titrating retort and we added a quantity of 0.01 m Cu (II) complexonate solution to it. After, we added an equivolume of 4 m of NH_4OH solution to the sample, 1 to 3 ml of 0.1 % *luminol* and at last 5 to 10 ml of a 3 percental H_2O_2 solution. This prepared solution was titrated till the bluish luminescence disappeared. The data concerning the accuracy of the determinations are given in Table I.

Table I.

0.01 m $MgSO_4$ measurement f = 1,000 (ml)	0.01 m Complexon III. decrease f = 1,000 (ml)	v (ml)	$(v)^2$
10.00	9.99	+0.01	0.0001
10.00	9.95	—0.03	0.0009
10.00	9.65	—0.34	0.1156
10.00	10.31	+0.32	0.1024
10.00	10.20	+0.21	0.0441
10.00	10.11	+0.12	0.0144
10.00	9.65	—0.34	0.1165

Mean value: 9.98

Calculated from the quadratic errors, the standard deviation for 95 per cent is +0.46 ml, that is the relative standard deviation for 95 per cent is ≈4.6 %.

The results from Table I. are of experiments carried out at room-temperature (20° C). As the field studies in the caves are made with karst-waters at temperatures between 8 and 12°C, we carried out some experiments to see wether or not the temperature affected the determination. Titrations at a temperature of 15°, 10° and 5°C showed, that determinations at 10°C could be done satisfactorily but at 5°C the change became indistinct and the reaction — the clue of the experiment — was markedly slowed down (Table II.).

We carried out experiments with a cold karst spring (the *Kistohonya* spring of Jósvafö) to determine its Ca + Mg content. The results were in agreement with those reached in the presence of a *Eriochrome black T.* indicator (Table III.).

Table II.

Temperature (°C)	0.01 m MgSO₄ measurement. f = 1.000 (ml)	0.01 m Complexon III. decrease. f = 1.000 (ml)
15	10.00	9.75
15	10.00	10.11
15	10.00	10.02
10	10.00	9.56
10	10.00	9.91
10	10.00	9.98
5	10.00	8.70
5	10.00	8.20
5	10.00	11.02

Table III.

Measurement of spring water *	0.01 m Complexon III. decrease f = 1.000, in the presence of luminol (ml)
25.00	9.35
25.00	9.44
25.00	9.34
25.00	9.14
25.00	9.48

Mean value: 9.35

We determined the indicator-error, this was found to correspond to 0.20 ml 0.01 m of *Complexon III* solution. This value was adjusted in connection with the above results.

Finally, we can conclude that the oxidizing decomposition of *luminol* in the presence of Cu^{2+} ions, followed by the phenomena of chemiluminescence (1, 2, 11) is catalyzed, along with Ca^{2+}, Sr^{2+} and Ba^{2+} ions, by the Mg^{2+} ions, too. The presence of copper ions — as was proved with a solution devoid of Cu^{2+} — is indispensable even for Mg^{2+} ions.

* Titrating with a 0.01 m factor—1.000 Complexon III solution in the presence of Eriochrome-black T. indicator, the mean value of five measurements is 9.39 ml decrease.

Summary

A complexometric process for the determination of Mg^{2+} ions in the presence of the *luminol* indicator was developed. Combined with taht proposal by SZARVAS et al. for the Ca^{2+} ions, this method makes it possible to determinate the changing hardness of karst waters $(Ca^{2+} + Mg^{2+})$ and is applicable in geochemical field observation of subsurface water systems.

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KOMPLEXOMETRISCHE BESTIMMUNG DES MAGNESIUMS IN ANWESENHEIT EINES LUMINOL
(3-Amino-Phtalsäure-Hydrazid) INDIKATORS

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Zusammenfassung

Wir haben ein komplexometrisches Verfahren zur Bestimmung von Mg^{2+}-Ionen in Anwesenheit eines Luminol-Indikators entwickelt. Diese Methode — mit der für die Ca^{2+}-Ione ausgearbeiteten Methode von SZARVAS und seinen Mitarbeitern kombiniert -ermöglicht die Bestimmung der veränderlichen Härte ($Ca^{2+} + Mg^{2+}$) der Karstwässer und kann — bei der chemischen Untersuchung an der unterirdischen Wassersysteme an Ort und Stelle — vorteilhaft angewendet werden.

КОМПЛЕКСОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАГНИЯ В ПРИСУТСТВИИ ЛУМИНОЛЬНОГО ИНДИКАТОРА (3-АМИНО-ФТАЛЕВАЯ КИСЛОТА-ГИДРАЗИД)

Дь. ПАЛЬИ

Резюме

Автор разработал комплексометрический метод для определения ионов Mg^{2-} в присутствии луминольного индикатора. Данный метод — в сочетании с разработанным для инов Ca^{2+} методом Сарваша и его со-авторов — делает возможным определение изменчивой жесткости карстовых вод ($Ca^{2+} + Mg^{2+}$) и может выгодно применяться для химического исследования системы подземных вод в полевых условиях.

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Resumo

La aŭtoro faris kompleksometrian procezon por determini Mg^{2+} jonojn en ĉeesto de la indikilo (indikatoro) "luminol". Kombinita kun la propono de Szarvas kaj de la ceteraj koncerne Ca^{2+} jonoj, tiu ĉi netodo donas eblon por determini la ŝanĝigantan malmolecon de la karstakvo ($Ca^{2+} + Mg^{2+}$) kaj estas aplikebla ĉe geohemia esploro de subteraj akvosistemoj.