NOTES

# Studies of Calcichrome as a Spectrophotometric Reagent. VI. A New Spectrophotometric Method for the Determination of Magnesium with Calcichrome

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The present authors have investigated the complex formation of Calcichrome with various metals and its analytical application to the determination of the latter; they have already reported new spectrophotometric methods for the determination of copper,[1,2] iron,[3,4] aluminum,[5] and titanium[6] on the basis of the formation of a complex with each. Furthermore, the present authors have recently found that this reagent also forms a complex with magnesium. The present paper will describe a new spectrophotometric method for the determination of magnesium using the magnesium-Calcichrome complex formation.

## Experimental

**Reagents.** *Calcichrome Solution.* A Calcichrome solution ($3\times10^{-4}$ M) was prepared in a manner similar to that described in an earlier paper.[2]

*Standard Magnesium Solution.* A standard magnesium solution corresponding to $1.0\times10^{-2}$ mol/*l* of magnesium was prepared by dissolving 0.243 g of metallic magnesium in a small amount of water and a minimum amount of hydrochloric acid (1 : 1). After dissolution, the solution was evaporated to dryness. The residue was dissolved in water, and the resulting solution was then diluted to 1 *l*. The amount of magnesium in this solution was checked complexometrically. Working solutions of magnesium were then prepared from this solution by dilution.

*Buffer Solutions.* Buffer solutions were prepared by mixing, in the ratios required, a 0.1N sodium hydroxide solution and a 0.1M glycine solution containing 0.1 mol of sodium chloride per liter.

**Apparatus.** The apparatus used in this study was the same as that used in an earlier work.[2]

**Procedure.** To a suitable aliquot of a neutral or a slightly acidic sample solution containing magnesium in a 25 m*l* volumetric flask, 5 m*l* of the Calcichrome solution and then 5 m*l* of a buffer solution are added in order to adjust the pH value of the solution 11.4. The solution is diluted to the mark with water. The difference between the absorbances of this solution and a reagent blank solution treated in a similar manner is then measured at 630 m$\mu$.

## Results and Discussion

**Absorption Curves.** The absorption curves of Calcichrome and its magnesium complex at pH 11.3 are shown in Fig. 1, from which it will be found that the complex has two absorption maxima, in the ultraviolet ($\lambda_{max}$ 307 m$\mu$) and visible ($\lambda_{max}$ 560 m$\mu$*1) regions. On the other hand, in the curve obtained as the difference between Calcichrome and its magnesium complex, two absorption maxima and two absorption minima are found at approximately 308 and 535 m$\mu$, and at approximately 344 and 630 m$\mu$, respectively. Furthermore, it will be found that the difference between the absorbances of Calcichrome and its magnesium complex is largest at about 308 m$\mu$. Therefore, if the absorbance measurement is carried out at this wavelength, we may effect to obtain the highest sensitivity. At this wavelength, however, Calcichrome

1) H. Ishii and H. Einaga, This Bulletin, **38**, 1416 (1965).
2) H. Ishii and H. Einaga, *ibid.*, **39**, 1154 (1966).
3) H. Ishii and H. Einaga, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 440 (1966).
4) H. Ishii and H. Einaga, *Bunseki Kagaku* (*Japan Analyst*), **15**, 577 (1966).
5) H. Ishii and H. Einaga, This Bulletin, **39**, 1721 (1966).
6) H. Ishii and H. Einaga, *Bunseki Kagaku* (*Japan Analyst*), **15**, 821 (1966).

*1 This maximum absorption wavelength is thought to be affected by the reagent present in excess; according to further experiments, its true value may be thought to occur at 555 m$\mu$.

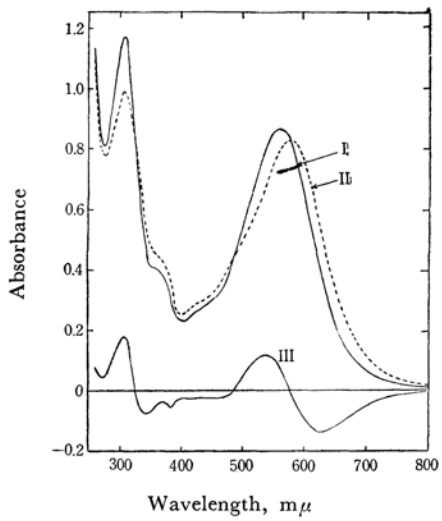


Fig. 1. Absorption spectra of Calcichrome and its magnesium complex.
Calcichrome: $4.0\times10^{-5}$ mol/l
Mg: $3.2\times10^{-5}$ mol/l
pH: 11.3, Reference: Water
I: Magnesium-Calcichrome complex
II: Calcichrome alone
III: Difference between I and II

itself gave such an intense absorption, and the precision of the absorbance measurement was so poor that the absorbance measurements in this study were carried out mainly at 630 mμ, at which wavelength a higher sensitivity was obtained than at 535 mμ.

**The Effect of pH on the Color Development.** The effect of pH on the color development of the magnesium-Calcichrome complex was examined at 630 mμ. The results are shown in Fig. 2, from which it may be seen that the maximum absorbance can be obtained at about pH 11.8 and that the pH range in which nearly the same absorbance can be obtained is rather narrow. Therefore, it seems to be better for the color development of the complex to be carried out at approximately pH 11.8; in this case, however, the complex is rather unstable, and magnesium tends to precipitate as magnesium hydroxide. Therefore, it is suitable to select a pH value slightly lower than 11.8, approximately 11.4 was chosen for the procedure. In any case, it is important that the pH be carefully controlled in the determination of magnesium.

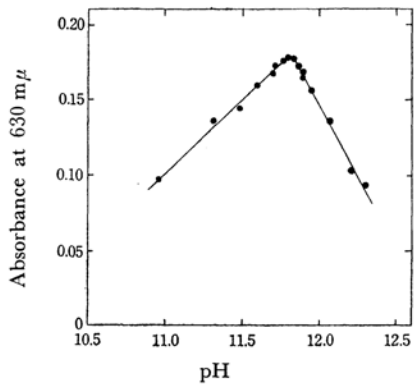


Fig. 2. Effect of pH.
Calcichrome: $4.0\times10^{-5}$ mol/l
Mg: $3.2\times10^{-5}$ mol/l

**The Stability of the Color.** The color development between magnesium and Calcichrome occurs instantaneously at room temperature. The color intensity of the solution remains almost constant for at least 4 hr after preparation, either at pH 11.4 or 10.8. Above pH 11.8, however, the color intensity of the solution decreases gradually with time upon standing, although the color development occurs instantaneously. This tendency is probably attributed to be to the formation of magnesium hydroxide.

**The Effect of the Amount of Calcichrome.** The effect of the amount of the reagent on the absorbance was then examined. The results are shown in Fig. 3, in which it may be noticed that the absorbance is increased by an increase in the Calcichrome concentration. Therefore, it is desirable to keep the Calcichrome concentration constant in the determination of magnesium.

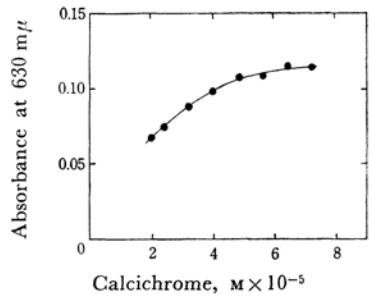


Fig. 3. Effect of Calcichrome concentration.
Mg: $2.0\times10^{-5}$ mol/l, pH: 11.4

**The Relationship between the Concentration of Magnesium and the Absorbance.** A linear relationship was maintained between the concentration of magnesium and the absorbance. The range of the magnesium concentration in which the linearity was noticed was, however, dependent on the Calcichrome concentration; the linearity was noticed up to the molar ratio of magnesium to Calcichrome of about 0.7. Figure 4 shows the calibration curves for magnesium at 630 mμ. The molar extinction coefficient and the sensitivity for $\log(I_0/I)=0.001$ under the recommended conditions were about 4700 and $5.2\times10^{-3}$ μg Mg/

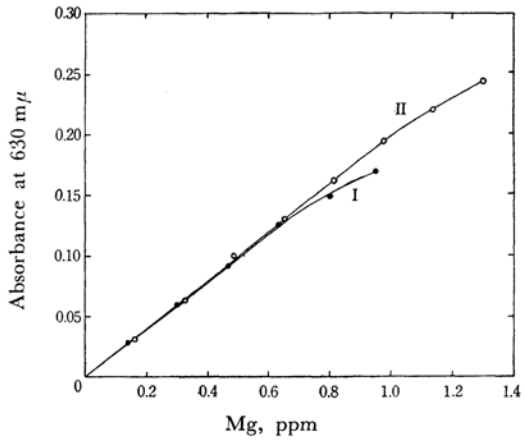


Fig. 4. Calibration curves for magnesium.
pH: 11.4
Calcichrome I: $4.0\times10^{-5}$ mol/$l$
II: $6.0\times10^{-5}$ mol/$l$

$cm^2$ respectively. If the color development is made at pH 11.8, a higher sensitivity can be obtained, as may be seen from Fig. 2. However, this can not be recommended, because the color intensity of the solution is rather unstable, as has been described already.

**The Effect of Diverse Ions.** The effect of diverse ions on the determination of magnesium was examined at pH 11.4. From the results it was found that many other ions, especially calcium (II), cobalt (II), chromium-(III), copper (II), manganese (II), nickel (II), titanium (IV), and zirconium (IV). interfere remarkably with the determination, because of the formation of their complexes with Calcichrome as well as with magnesium under the experimental conditions. For this reason, it is desirable that the sample solution to be analyzed be free from these interfering ions.

## Conclusion

It has been found that Calcichrome forms a stable complex with magnesium in an alkaline medium, and that magnesium can be determined using the complex formation if the pH value of the solution to be analyzed is adjusted to a fixed value between 11.0 and 12.0.