

Microquantitative Determination of Calcium as Murexide Complex in the Presence of Magnesium

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Calcium changes the color of a murexide solution¹. This property was utilised in the versenate titration for total hardness in water chemistry²⁻⁴. A thorough investigation of the reactions between metal ions and murexide was performed by Schwartzbach and Gysling⁵. The direct use of the calcium murexide complexes for a spectrophotometric determination of calcium was first mentioned by Ostertag and Rinck in a short communication, where, however, little is said about their technic⁶. In a later paper the same authors give an account of the influence of other metal ions on the sensibility of their method and some details of their technic⁷. The purpose of our investigation is to enable the determination of microquantities of calcium in the presence of magnesium. In order to find the best conditions we investigated the influence of the wave-length of light on the sensibility and studied, moreover, the dependence of the color and stability of the test solutions on pH and the murexide concentration.

ABSORPTION CURVES

The wave-lengths corresponding to absorption maxima in solutions of murexide and solutions containing murexide and calcium and murexide and magnesium were determined. The results are summarized in the principal diagram in Fig. 1.

The point where the lines I and III intersect indicates the wave-length chosen for the determinations of calcium. Magnesium murexide complex and pure murexide absorb light of that wave-length to the same amount. In this way the magnesium complex does not interfere more than the normally established excess of murexide. Fortunately this wave-length (510 $m\mu$) is

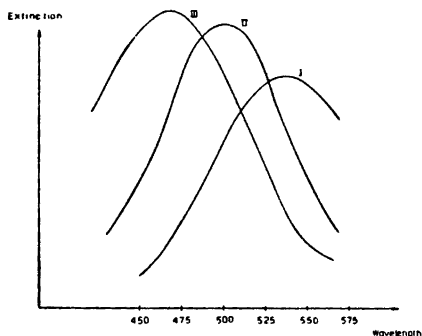


Fig. 1. Extinction as a function of the wave-length for

- I. Murexide solution.
- II. Calcium murexide complex.
- III. Magnesium murexide complex.

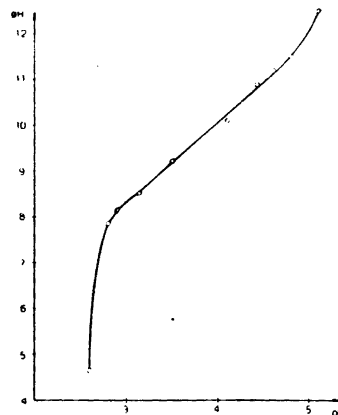


Fig. 2. pK calculated as a function of pH .

not too far from the absorption maximum of the calcium murexide complex. The accurate value of the wave-length giving maximum is, however, determined to be $500\text{ m}\mu$ and in cases where interference from other ions can be neglected this point is preferable. Because of the low concentration of the test solutions and the relatively high equilibrium constant the excess of murexide necessary for complete formation of calcium complex is rather high. At calcium concentrations between $2.5 \cdot 10^{-6}$ and $7.5 \cdot 10^{-5}$ molar the murexide concentration was kept at $2 \cdot 10^{-4}$. This seems to be enough even when magnesium is present in concentrations of the same magnitude as calcium.

INFLUENCE OF pH

The amount of calcium bound to murexide may be calculated from the following formula

$$\frac{\text{Ca} \cdot \text{Mur}}{\text{Ca} \text{ Mur}} = K$$

where Mur is murexide, protolysed or unprotolysed, and CaMur is the concentration of the calcium complexes. K is, however, no real constant but depends on pH according to Fig. 2.

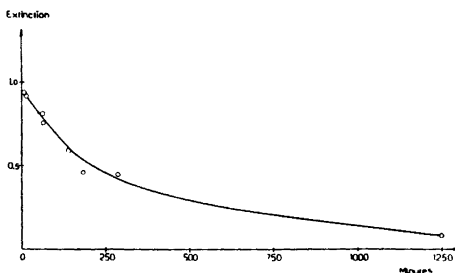


Fig. 3. The extinction as a function of time in a murexide solution at $\text{pH} \approx 11$. The curve shows the decomposition of murexide.

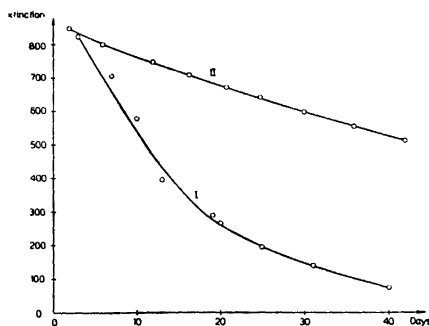


Fig. 4. The extinction of a murexide solution as a function of time at room temperature (I) and 5°C (II).

The diagram shows, that the higher pH the more of the calcium is bound to the murexide and consequently the sensibility of the determination will increase with pH. A counteracting effect is the breakdown of the murexide which increases with increasing pH. At pH about 11 the breakdown was found to be slow enough to permit accurate determinations. A suitable reagent to maintain this pH value is piperidine.

APPARATUS AND SOLUTIONS

The measurements were made by means of a Beckman Quartz spectrophotometer, type Du.

The murexide solution was prepared by saturating water during 24 hours and then filtering off insoluble impurities. This solution has to be stored in the refrigerator to decrease the rate of decomposition. The velocity of the decomposition at room temperature and 5°C is shown in Fig. 4.

The calcium solutions were prepared by dissolving calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in water thus obtaining a stock solution from which the very diluted solutions were made daily. Magnesium solutions were prepared from magnesium sulphate. Immediately before a reading two drops of piperidine (puriss) were added to 10 ml of the test solution.

ANALYSIS

0.5 ml of murexide solution and two drops of piperidine were added to 10 ml of a test solution containing from zero to three mg Ca/l. The results of the extinction readings are summarized in Fig. 5. The curve can be used for calibration of the method and thus enables determinations of unknown

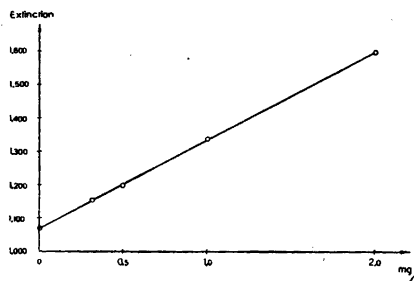


Fig. 5. Extinctions plotted against calcium concentrations. The extinction is determined in solutions containing murexide.

calcium concentrations. Because of the decomposition of the murexide solution a curve of this type has to be determined daily.

DISCUSSION

With the method described it is possible to determine calcium in water solutions, even in the presence of magnesium. In pure calcium solutions the error of the analysis is estimated to be ± 0.15 microgram. In the presence of magnesium the same value is about 0.5 microgram. The upper limit of 3 mg Ca/1. depends on the thickness of the cell (10 mm) and is necessary to avoid loss in accuracy because of too great light absorption. Using cells of different thicknesses it will be possible to extend the range of the analysis. Experiments have been made to test an analogous method for the determination of magnesium, but the equilibrium constant $K_{Mg} = \frac{Mg \cdot Mur}{Mg \cdot Mur}$ is too great to permit accurate values.

SUMMARY

A suitable wavelength for the spectrophotometric determination of the calcium murexide complex is determined. The stability of the reagents is studied and found to be satisfactory for analytical purposes. Influence of pH on the reaction between calcium and murexide and on the sensibility of the spectrophotometric determination is studied. The results show that microquantitative determination of calcium is possible by means of spectrophotometric determination of the calcium murexide complex also in the presence of magnesium.

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