Solid-liquid Separation after Liquid-liquid Extraction. Spectrophotometric Determination of Magnesium after Extraction of Its Oxinate with Melted Naphthalene

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A new method by "solid-liquid separation after liquid-liquid extraction" was proposed for the spectrophotometric determination of trace amount of magnesium. This method is based on the formation of a yellow chelate (oxinate) which is quantitatively extractable by melted naphthalene in the pH range of 10—12. The extract of oxinate in naphthalene is not soluble in ethyl alcohol, benzene or chloroform, but is soluble in methyl alcohol. The optical absorbancy at 375 nm was measured against the reagent blank and the Beer's law was obeyed with 5—120 μg of magnesium in 25 ml of methyl alcohol. The chelate in methyl alcohol solution is very stable for a long time.

1 Introduction

Oxine has been used for the spectrophotometric determination of aluminum, iron, copper and various other metals by extracting their oxinates from the aqueous solution into organic solvents such as chloroform or benzene.

The auther has already mentioned in the previous paper[1] that the method cannot be applied for the determination of some metals such as zinc, magnesium, cadmium or beryllium. On the contrary, a new method called "solid-liquid separation after liquid-liquid extraction" can be applied for these cases. The characteristic of the method is to extract metal oxinate into melted organic compound with appropriate degree of melting point such as naphthalene, diphenyl, paraffins, etc.. In the present study, magnesium was chosen as a metal to be determined and its oxinate was extracted into melted naphthalene. After cooling the mixture of oxinate and naphthalene, the solidified crystals were dissolved in methyl alcohol (transparent yellow solution). Spectrophotometric determination of magnesium by this method has been discussed in details.

2 Experiemntal method

2・1 Reagents

Standard magnesium solution (10^{-2}M) was prepared by dissolving 2.0333 g of magnesium chloride in water and diluting to 1 liter. This solution was standardized against EDTA solution. More dilute magnesium solutions were prepared as required by diluting the standard solution. The other reagents and apparatus are the same as that reported in the previous paper.[2]

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2・2 Procedure

In a 50-ml tightly glass-stoppered Erlenmeyer flask was added 0.5—4 ml of 10^{-3} M standard magnesium solution, approximately 20 ml of distilled water, 2 ml of 1% oxine solution, 2 ml of 1 M ammonium chloride-ammonia buffer solution and several drops of concentrated ammonia water to give a solution (pH about 10) and the total volume of approximately 30 ml. The solution was mixed thoroughly, allowed to stand for 30 minutes, and warmed 15 minutes on a water bath at 60°C. Add 1.6 g of naphthalene and warm the mixture at 90° C resulting the naphthalene layer to melt completely. Shake it vigorously till naphthalene layer solidifies forming many fine crystals, and stand to cool them to room temperature. Again heat and melt slowly the suspended naphthalene in a water bath, and the fine crystals grow up to larger crystalline deposit. After cooling at room temperature, the solidified deposit was washed with distilled water by decantation, spread them on a dry filter paper for air-drying. Dissolve the naphthalene crystals with methyl alcohol, and dilute the solution to 25 ml. Transfer a portion of this solution into a cell and measure the absorbance at 375 nm against the reagent blank to determine the amount of magnesium.

3 Results and discussion

3・1 Absorption spectra

The absorption spectra of magnesium oxinate in naphthalene-methyl alcohol solution, which contains 49 μg of magnesium, had an absorption maximum at 375 nm as is seen in Fig. 1. Beyond this wavelength, there

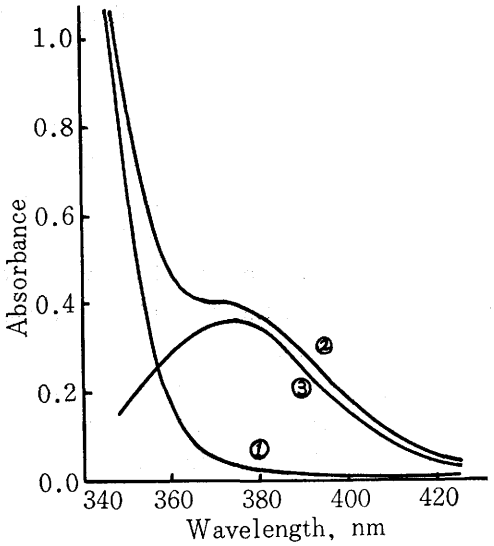

Fig. 1 Absorption spectra of oxine and magnesium oxinate in naphthalene-methyl alcohol
Mg : 49μg ; 1% oxine : 2ml; Naphthalene : 1.6 g ;
pH : 10 ; Buffer solution : 2ml ;
① Reagent blank against water
② Mg+reagent blank against water
③ Mg+reagent blank against reagent blank

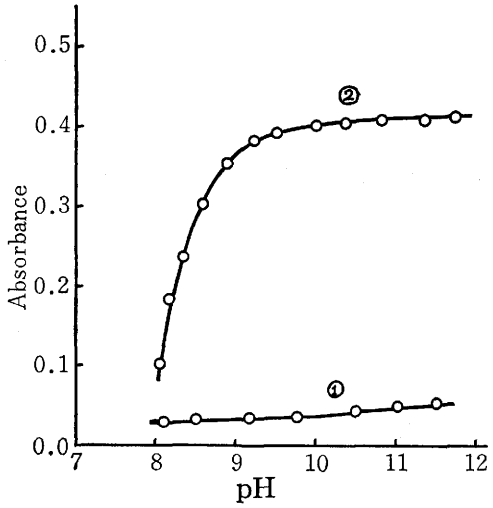

Fig. 2 Effect of pH on absorbance
Mg : 49 μg ; 1% oxine: 2ml ;
Naphthalene : 1.6g ; pH : 10 ;
Buffer solution : 2ml ; Reference : Water ;
① Reagent blank ② Mg-oxinate

was a slight absorption due to the reagent blank (curve 1). Therefore, 375 nm was chosen as the optimum wavelength throughout this experiment.

3・2 Effect of pH

The relation between the absorbance of the extract and the pH of the aqueous solution was investigated in the pH range of 8—12, and the result obtained is shown in Fig. 2. A curve at 375 nm shows that magnesium oxinate begins to be extracted from pH 8 and increases with the increase of pH, finally reaching to almost constant beyond pH 9.5. The pH of the solution was adjusted to 10 throughout the experiment ; 2 ml of the buffer solution were added.

3・3 Effect of oxine concentration

The effect of the oxine concentration on extraction was investigated, and the result obtained is shown in Fig. 3, which indicates that 2 ml of 1% oxine solution are enough for the quantitative work.

3・4 Effect of amount of naphthalene

The effect of the amount of naphthalene on extraction was investigated. The result obtained is shown in Fig. 4. It indicates that the absorbance increases with the increase of the amount of added naphthalene, and becomes almost constant by the addition of more than 1.5 g of naphthalene.

The volume of methyl alcohol required to dissolve 1 g of naphthalene was 13 ml.

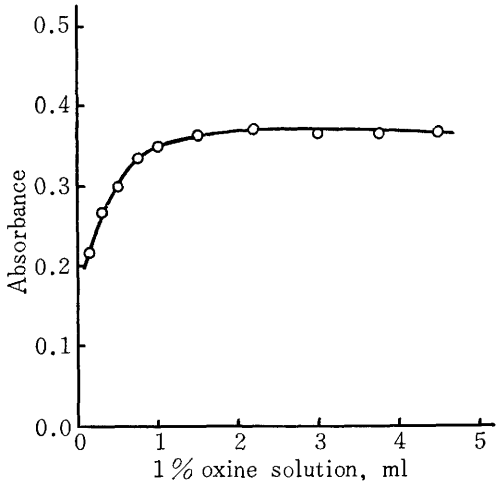

Fig. 3 Effect of reagent concentration on absorbance
Mg : 49μg ; pH : 10 ; Naphthalene : 1.6g ; Buffer solution : 2ml ; Refere nce : Reagent blank

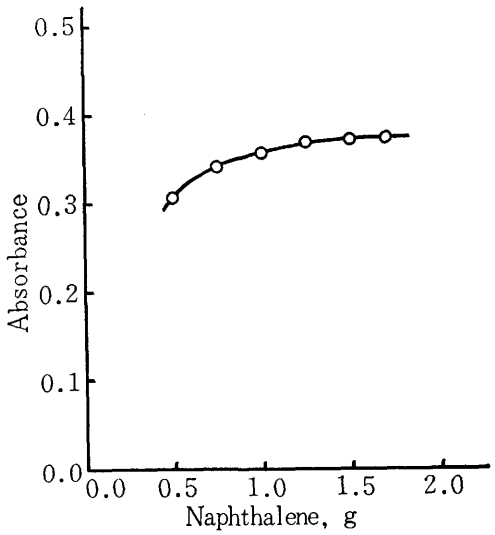

Fig. 4 Effect of addition of naphthalene on absorbance
Mg : 49μg ; 1% oxine : 2ml ; Naphthalene : 1.6g ; pH : 10 ; Buffer solution : 2ml ; Reference: Reagnt blank

3・5 Effect of shaking time

The effect of the shaking time on extraction of magnesium oxinate by melted naphthalene was investigated. It shows that the absorbance reaches to a constant value by shaking of more than 1 minute.

3・6 Calibration curve

Based on the optimum conditions obtained from the experiments described above, the absorbances of the standard magnesium solutions of various concentrations were measured against the reagent blank. The absorbance of the extracts shows a linear relationship to the concentrations of magnesium over the range of 5—120 μg in 25 ml of methyl alcohol. The calculated molar absorbancy under these conditions is 4.5×10^3 at the wavelength of 375 nm.

3・7 Effect of diverse ions

The effect of diverse ions on magnesium determination was investigated, and the result is shown in Table I. The absorbance measurements were made with magnesium in the presence of various amount of diverse ions. The following ions gave considerable interferences : F^-, CO_3^{2-}, $H_2PO_4^-$, tartrate, Mo^{6+}, Ni^{2+}, Co^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Ca^{2+}, Hg^{2+}, etc.. Especially large amount of citrate and even small amount of EDTA gave serious interference. The interference of Co^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} could be masked with the addition of 2 ml of 5% potassium cyanide.

Table I Effect of diverse metal ions on the determination of magnesium

Ion	Ion added (μg)	Absorbance
None	—	0.360
Pb^{2+}	104	0.509
Mo^{6+}	54	0.377
〃	136	0.406
Ni^{2+}	51	0.453
Co^{2+}	51	0.531
Al^{3+}	15	0.490
Fe^{3+}	25	0.404
Mn^{2+}	69	0.802
Fe^{2+}	35	0.493
Cu^{2+}	26	0.550
Zn^{2+}	120	0.530
Ca^{2+}	70	0.507
Hg^{2+}	106	0.409
〃	176	0.482

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References

1) M. Satake : This memoirs, to be submitted.
2) M. Satake : This memoirs, to be submitted.