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Analysis of Metals by Solid-Liquid Separation. Spectrophotometric Determination of Cadmium by Extraction of Cadmium Salt of Oxine with Melted Naphthalene

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A method is described for the spectrophotometric determination of a minute quantity of cadmium. A cadmium complex stable at 90 °C is easily extracted with melted naphthalene. The resulting mixture of cadmium complex and naphthalene is dissolved in dimethylformamide and absorbance of the solution is measured at 400 nm. Effects of pH, amounts of oxine, naphthalene and diverse salts are given.

Oxine (8-hydroxyquinoline) reacts with various metal ions to form stable complexes which have been widely used for spectrophotometric determination of metal ions by extraction from aqueous solution into organic solvents such as chloroform or benzene. However, this method cannot be applied to metals such as zinc, magnesium and cadmium, since their salts of oxine are insoluble in organic solvents; zinc and magnesium salts extracted are not very soluble, those of cadmium and beryllium are hardly soluble.

We found that most metal salts of oxine in aqueous solution can be easily extracted with melted organic compounds such as naphthalene and diphenyl as in the case of liquid-liquid extraction. The method was named "analysis by solid-liquid separation", and applied to the spectrophotometric determination of copper,[1] zinc,[2] and magnesium.[3] It is particularly convenient for the determination of metals whose salts of oxine are strongly hydrated. The method is also applicable to the determination of nickel[4] and palla-

1) T. Fujinaga, T. Kuwamoto, T. Yonekubo, and M. Satake, *Bunseki Kagaku*, **18**, 1113 (1969).

2) T. Fujinaga, M. Satake, and T. Yonekubo, *ibid.*, **19**, 216 (1970).

3) M. Satake, *Memoirs of the Faculty of Engineering, Fukui University*, **18**, 225 (1970).

4) T. Fujinaga, M. Satake, and T. Yonekubo, *Bunseki Kagaku*, **20**, 1255 (1971).

dium[5] using dimethylglyoxime as the chelating reagent.

Cadmium was chosen in the present work, and its salt of oxine was extracted completely with melted naphthalene from aqueous solution at pH above 5.5. The solidified naphthalene crystals containing the metal salt of oxine were separated and dissolved in dimethylformamide, the absorbance of the solution being measured at 400 nm against the reagent blank. Effects of diverse ions were studied. The method seems to be promising since the extract with naphthalene has adequate solubility, colour intensity and stability in dimethylformamide. Cadmium salt of oxine is insoluble in organic solvents except dimethylformamide.

Experimental

Reagents. Reagents of analytical grade were used without purification. Water used was redistilled after deionization.

Standard cadmium solution, 1.997×10^{-3} g per ml: Prepared by dissolving 0.99855 g of cadmium metal (purity 99.999%) in 3 ml of concentrated nitric acid, diluted to 500 ml with water. More dilute cadmium solution (19.97 μg per ml) was prepared as required.

Oxine solution, 1%: Prepared by dissolving 1.0 g of oxine in glacial acetic acid (2 ml) on a water bath, diluted to 100 ml with water.

Alkali metal salt solutions, 10 mg of the corresponding salt per ml: Prepared by dissolving 1.000 g of the salt in water, diluted to 100 ml.

Other metal salt solutions, 1 mg of the individual salt per ml: Prepared by dissolving 0.100 g of each salt in water. In some cases, a small amount of acid was added to prevent hydrolysis.

Apparatus. A Hitachi Model 124 spectrophotometer was employed for the absorbance measurements with matched 10 mm glass cells. A Toa-Denpa HM-6A pH meter equipped with combined glass and calomel electrodes was used for all pH measurements.

Procedure. Pipet a sample solution containing 10—160 μg of cadmium into an 80 ml tightly stoppered Erlenmeyer flask, and dilute with water to *ca.* 30 ml. Add 1.5 ml of 1% oxine and adjust the pH of the solution to 6—10 with 0.5—1.0 N ammonia. Heat the flask on a water bath to precipitate cadmium salt of oxine completely. Add 2.0 g of naphthalene and warm the flask at 90 °C until naphthalene melts completely. Remove the flask from the bath and shake vigorously. Naphthalene will be solidified forming fine crystals suspended in the solution. Warm the flask again and melt slowly the fine crystals. Cool the mixture to room temperature. Larger crystalline deposits will grow up in the solution. Filter the mixture and wash the solidified deposits on the filter paper with water. Remove the water from the filter paper with a separate piece of paper. Spread the yellow deposits on a dry filter paper for air-drying. Transfer them to a volumetric flask and add dimethylformamide so that the final volume becomes 10 ml. Shake well and measure the absorbance of the solution in a 10 mm cell against the reagent blank. The amount of cadmium can be determined using a calibration curve.

Results and Discussion

Absorption Spectra. Cadmium in the test solution containing 99.86 μg of cadmium was extracted with melted naphthalene as complex salt of oxine at pH *ca.* 7.5. The mixture of cadmium-oxine complex and naphthalene was dissolved in dimethylformamide, and the absorbance of the solution was measured at various wavelengths between 360 and 470 nm. The result is shown in Fig. 1. Curves 1 and 2 show the absorption spectra of the reagent blank and the complex, respectively. Curve 3 shows the absorption spectra of the complex against the reagent blank. The curve has a maximum at 400 nm, beyond which the absorbance decreases gradually and becomes insignificant beyond 470 nm. Wavelength 400 nm was chosen for the measurement.

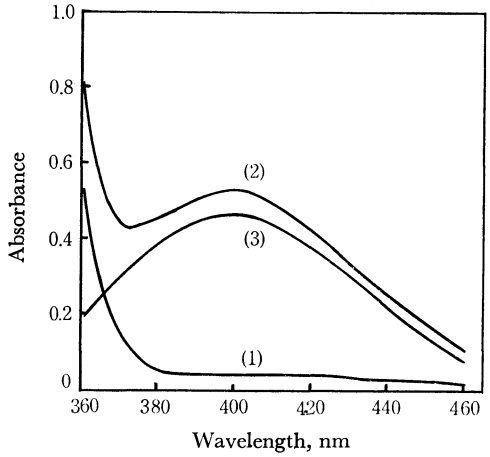

Fig. 1. Absorption spectra of oxine and cadmium oxinate in naphthalene-dimethylformamide.
Cadmium: 99.86 μg, 1% oxine: 1.5 ml, pH: 7.5, naphthalene: 2.0 g, (1) Reagent blank *vs.* water, (2) Cadmium oxinate *vs.* water, (3) Cadmium oxinate *vs.* reagent blank.

Effect of pH. The pH of a solution containing 99.86 μg of cadmium and 1.5 ml of 1% oxine solution was carefully controlled to 4—10 with dilute ammonia. The solution was heated on a water bath till the precipitate of complex salt between cadmium and oxine appeared, and the complex salt was extracted with melted naphthalene. The absorbance of the mixture of the salt and naphthalene in dimethylformamide was

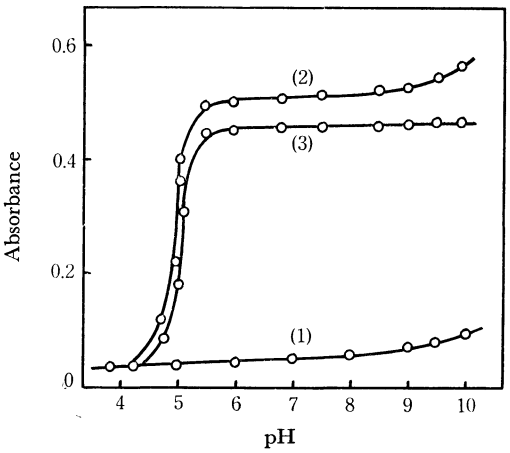

Fig. 2. Effect of pH on absorbance.
Cadmium: 99.86 μg, 1% oxine: 1.5 ml, naphthalene: 2.0 g, wavelength: 400 nm, (1) Reagent blank *vs.* water, (2) Cadmium oxinate *vs.* water, (3) Cadmium oxinate *vs.* reagent blank.

5) T. Fujinaga, M. Satake, and T. Yonekubo, *Talanta*, **19**, 689 (1972).

measured. Curves 1 and 2 show respectively the effect of pH on the absorbance of the reagent blank and on that of the salt in the solution against water. Curve 3 shows the difference in the absorbances between the reagent blank and the salt at each pH value. We see that extraction starts from pH 4.0, increases sharply with increasing pH and reaches the maximum, then becomes constant beyond pH 6.0. Thus the pH range 6—10 is suitable.

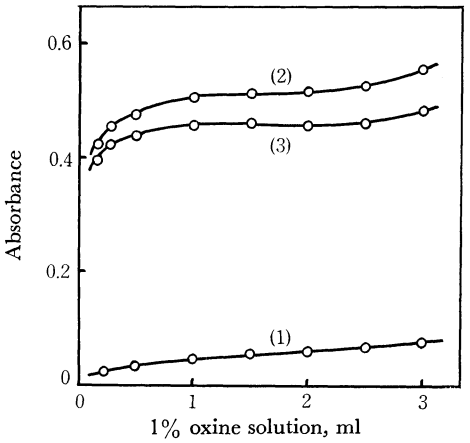

Fig. 3. Effect of oxine concentration on absorbance
Cadmium: 99.86 μg, pH: 7.5, naphthalene: 2.0 g, wavelength: 400 nm, (1) Reagent blank *vs.* water, (2) Cadmium oxinate *vs.* water, (3) Cadmium oxinate *vs.* reagent blank.

Effect of Oxine Concentration and Amount of Naphthalene. Various amounts of oxine were added to the solution containing 99.86 μg of cadmium at pH about 7.5, and the effect of variation in the oxine concentration on the absorbance of the complex salt has been studied. The absorbance increased with increasing amounts of oxine up to 1 ml of 1% oxine solution, whereas addition of 1—2 ml of it gave difinite absorbance, and the absorbance increased again when more than 2 ml was added. Thus, 1.5 ml of oxine solution was found to be the proper amount. On the other hand, addition of 0.5—3.0 g of naphthalene gave almost no difference.

Effect of Shaking Time and Stability. A mixture containing 99.86 μg of cadmium and 1.5 ml of 1% oxine solution was heated till larger particles of the precipitate of the complex salt were formed. Extraction of the salt was then carried out with melted naphthalene by vigorous shaking, and the absorbance of the extract in the dimethylformamide solution was measured. It was observed that the speed of extraction was very rapid and the salt was easily extracted from aqueous solution merely by contact with melted naphthalene. For the sake of good reproducibility, the precipitate of the salt should be digested sufficiently before extraction with naphthalene. The extracted salt was very stable in naphthalene-dimethylformamide solution as well as in naphthalene, and the absorbance remained unchanged for a long time.

Calibration Curve, Sensitivity and Reproducibility. A linear relationship was obtained between the concentration of cadmium and the absrobance in the range of 10—160 μg of cadmium per 10 ml of dimethylformamide. The molar absorptivity of the extracted complex salt was found to be 5.45×10^4 l·mol^{-1}·mm^{-1} at 400 nm and the sensitivity for the absorbance of 0.001 was 0.00263 μg cadmium per cm^2.

An average of ten determinations on 99.86 μg of cadmium gave a mean absorbance of 0.484 with a standard deviation of 0.0041 (relative standard deviation, 0.85%).

Table 1. Effect of diverse salts

Salts	Added (mg)	Absorbance
—	—	0.484
NaF	50	0.488
	100	0.547
KH_2PO_4	50	0.479
	100	0.484
$Na_2HPO_4 \cdot 12H_2O$	50	0.477
	100	0.484
NaCl	50	0.471
	100	0.475
NH_4Cl	50	0.415
	100	0.332
$CH_3COONa \cdot 3H_2O$	50	0.543
	100	0.623
CH_3COONH_4	50	0.485
	100	0.487
	325	0.489
$CuSO_4 \cdot 5H_2O$	0.25	0.931
$Co(NO_3)_2 \cdot 6H_2O$	0.25	1.009
$MnCl_2 \cdot 4H_2O$	0.25	1.323
$ZnCl_2$	0.25	0.869
$Ni(NO_3)_2 \cdot 6H_2O$	0.25	0.989
Mohr's salt	0.25	0.713
Potassium alum	0.26	0.715
Iron alum	0.10	1.159

Effect of Diverse Ions. Solutions containing 99.86 μg of cadmium were prepared with varying amounts of salt and the determination of cadmium was performed. Some results are given in Table 1. One hundred milligrams of the following salts gave no interference: NaCl, KCl, Na_2SO_4, KH_2PO_4, $Na_2HPO_4 \cdot 12H_2O$, CH_3COONH_4, $Na_2C_2O_4$, sodium tartrate and sodium citrate. Fifty milligrams of sodium fluoride gave no interference, but 100 mg of it did. Sodium acetate and ammonium chloride gave considerable interference, while even a small amount of EDTA gave serious interference. Many metal ions reacting with oxine to form complex salt at pH 4—10 interfered with the determination. Of the metal salts tested, the following gave interference: $CuSO_4 \cdot 5H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $ZnCl_2$, $Ni(NO_3)_2 \cdot 6H_2O$, Mohr's salt, potassium alum, iron alum. Magnesium and calcium gave no interference when pH was adjusted to *ca.* 6.5 with ammonium acetate and dilute ammonia or with phosphate buffer. Copper and iron can be removed by oxine-chloroform extraction at pH 3.5—4.0. The interference should be completely suppressed before extraction by some methods such as ion-exchange separation,[6] addition of masking reagent or pH adjustment.[7]

6) T. Yamabe, "Muki Bunri Kagaku," Gihodo, Tokyo (1971), p. 91.

7) Nippon Bunseki Kagaku Kai, "Bunri Bunseki Ho (the last volume)" Kyoritsu, Tokyo (1963), p. 25.