The Spectrophotometric Determination of Cadmium with Xylenol Orange[1]

By Makoto Otomo

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The most sensitive spectrophotometric method for the determination of traces of cadmium has been found to be the extraction procedure employing dithizone.[2-4] In this method, however, different amounts of dithizone must be used, depending on the amount of cadmium to be determined, indicating that the method is unfavorable for the determination of cadmium over a wide concentration range. A rapid, sensitive and accurate method which is applicable over a wide concentration range of cadmium is, therefore, desirable. A spectrophotometric method with xylenol orange was formulated for this purpose by the present author, and a suitable method was developed. This method is based on the formation of the cadmium-xylenol orange complex in a solution buffered with hexamethylenetetramine and nitric acid. The complex has an absorption maximum at 575 mμ and a molar extinction coefficient of 18000. By this method, 20 to 120 μg. of cadmium can be determined rapidly within the range of experimental error. In a study of the complex formation, it has been found that xylenol orange forms a 1 to 1 complex with cadmium and that the complex has an apparent formation constant of 6.1×10^3 at a pH value of 5.5.

Experimental

Reagents.—*Standard Cadmium Solution.*—A stock solution of cadmium (about 0.01 M) was prepared by dissolving a reagent-grade cadmium chloride in distilled water. This solution was standardized against a standard EDTA solution, using xylenol orange as the indicator.[5] A working standard solution was prepared by diluting the stock solution with water.

Buffer Solution.—Except where otherwise indicated, solutions of hexamethylenetetramine in conjunction with potassium nitrate and nitric acid were used for pH adjustments.

Xylenol Orange Solution.—A 1×10^{-3} M solution of xylenol orange was prepared by dissolving a Dotite XO reagent (Dôjindô & Co., Kumamoto) in distilled water.

All the other solutions were prepared from reagent-grade chemicals.

Apparatus.—A Hitachi spectrophotometer, Model EPV-2, was used for all absorbance measurements, using 1-cm. glass cells. A Hitachi glass-electrode pH meter, Model EHP-1, was used for all pH determinations.

All experiments were carried out at 25±0.5°C.

Results and Discussion

Absorption Spectra.—The absorption spectra of xylenol orange and its cadmium complex are shown in Fig. 1. When the absorbance measurements were made against a reagent blank, an absorption maximum was found at 575 mμ. As the considerable absorbance by the blank is evident around the absorption maximum of the complex, all absorbance measurements were made using a reagent blank. The order of the addition of the reagents has no effect on the absorbance values.

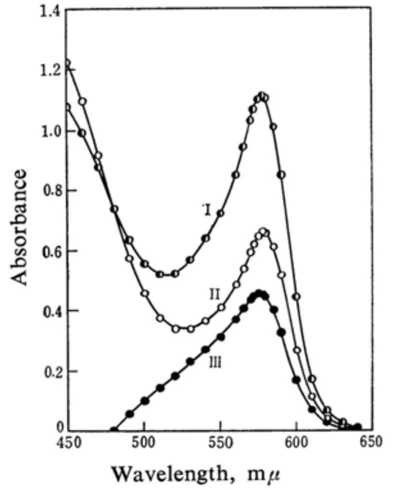

Fig. 1. Absorption spectra of xylenol orange and its cadmium complex at pH 6.3.
Cd : 67.4 μg., XO : 1.114×10^{-4} M, KNO_3 : 0.30 M
I : Cd-XO vs. water
II : XO vs. water
III : Cd-XO vs. a reagent blank

Choice of Buffer and the Effect of pH.—A preliminary test showed that xylenol orange

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[1] A part of this work was presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[2] F. W. Church, *J. Ind. Hygiene Toxicol.*, **29**, 34 (1947).

[3] H. Fischer and G. Leopoldi, *Mikrochim. Acta*, **1**, 30 (1937).

[4] B. E. Saltzman, *Anal. Chem.*, **25**, 493 (1953).

[5] K. Ueno, "Kireto Tekitei (Chelatometric Titration)" (in Japanese), Nankodo, Tokyo (1960), p. 241.

reacts with cadmium only in a slightly acidic or a neutral solution, giving a red color. Therefore, two buffers are found to be useful: sodium acetate - acetic acid and hexamethylenetetramine - mineral acid. The former has a great buffering capacity in the pH range from 3.5 to 5.6 and has widely been used for many purposes. However, acetate ions form certain acetato-complexes with cadmium[6-8] to inhibit the color formation between cadmium and xylenol orange. The latter, with a great buffering capacity in the pH range from 4.5 to 6.5, has occasionally been used in complexometric titrations. It has no complexing action for cadmium ions. At the same pH values, the cadmium - xylenol orange complex always gave higher absorbances in solutions buffered with the latter than with the former. A hexamethylenetetramine - nitric acid - potassium nitrate buffer was, therefore, adopted throughout the investigation. Potassium nitrate was always used to reduce the error caused by the indicator salt effect.

The variation in the absorbances of the reagent blank and of the cadmium complex with a change in pH value was then studied; the results are shown in Fig. 2. The optimum pH range is fairly narrow, the maximum color development for the complex being found to occur in the pH range from 6.2 to 6.4.

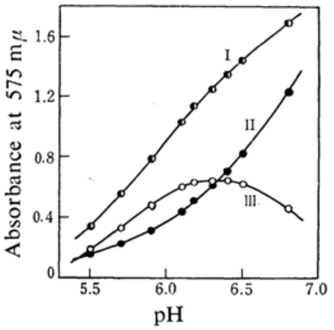

Fig. 2. Effect of pH on color development.
Cd: 112 μg., XO: 1.114×10^{-4} M
KNO_3: 0.20 M, Hexamethylenetetramine: 20% soln. 4 ml.
I: Cd-XO vs. water
II: XO vs. water
III: Cd-XO vs. a reagent blank

The Effect of the Amount of Buffer.—In order to investigate the effect of the amount of the buffer on the absorbances of the reagent and complex, experiments were made with solutions containing 90 μg. of cadmium, 2.8 ml. of a 1×10^{-3} M solution of xylenol orange, and varying amounts of a 20% hexamethylenetetramine solution which had been titrated with nitric acid to give a pH value of 6.3. The results showed that, both for the solution containing no potassium nitrate and for the solution containing potassium nitrate (0.35 M at a final concentration), the intensity of the absorbances of xylenol orange and of the complex is greatly affected by the amount of the buffer; larger amounts of the buffer must be added to obtain higher absorbances. However, 10 ml. of a 20% hexamethylenetetramine - nitric acid solution was used for further investigation. The addition of 10 ml. of the buffer to the system gave a reproducible absorbance.

The Effect of the Potassium Nitrate Concentration.—The absorbance of a solution containing a fixed amount of cadmium was found to be dependent also upon the concentration of potassium nitrate. This effect was studied by varying the concentration of potassium nitrate. The pH value of the solution was held constant at 6.3 by the addition of the buffer. The results are shown in Fig. 3. Both xylenol orange and the complex give the maximum absorbance at the potassium nitrate concentration of 0.30 to 0.35 M in a final volume. In further experiments, therefore, 5 ml. of a 1.5 M solution of potassium nitrate was used. This gives 0.30 M at a final concentration.

The Effect of the Amount of Xylenol Orange.—In measuring the effect of the amount of xylenol orange on color development, the amount of a 1×10^{-3} M solution of xylenol orange was varied from 0.7 to 4.5 ml., keeping

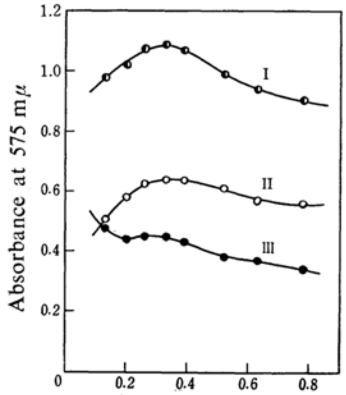

Fig. 3. Effect of KNO_3 concentration.
Cd: 67.4 μg., XO: 1.114×10^{-4} M, pH: 6.3
Hexamethylenetetramine: 20% soln. 10 ml.
I: Cd-XO vs. water
II: XO vs. water
III: Cd-XO vs. a reagent blank

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[6] A. Jacques, *Trans. Faraday Soc.*, **5**, 225 (1910).

[7] E. Ferrell, J. M. Ridgion and H. L. Riley, *J. Chem. Soc.*, **1934**, 1440.

[8] N. Tanaka, M. Kamada, H. Osawa and G. Sato, This Bulletin, **33**, 1412 (1960).

other variables constant. As can be seen from Fig. 4, the maximum color formation is obtained when 2.2 to 3.8 ml. of the reagent solution is used. Therefore, 2.8 ml. was chosen as the working volume of the reagent.

The Stability of the Color.—The absorbances of a solution, prepared under the optimum condition, were measured as a function of time following the preparation of the solution. There was no change of absorbance over a period of 3 hr.

Adherence to Beer's Law.—To ascertain the adherence of the system to Beer's law, a calibration curve was prepared in the following manner: To a series of 25 ml. volumetric flasks were added varying quantities of cadmium, 10 ml. of the buffer and 2.8 ml. of a 1×10^{-3} M solution of xylenol orange; the solutions were then diluted to the mark with water. After about 15 min., the absorbance of each solution was measured at 575 mμ against a reagent blank which had been treated in a similar manner. The data showed a linear relationship between concentration and absorbance over the 20 to 120 μg. range of cadmium.

Sensitivity.—According to the notation of Sandell,[9] the sensitivity of the reaction is 0.006 μg. of cadmium per cm^2. The molar extinction coefficient was calculated from the calibration curve to be 18000 at 575 mμ.

Effect of Diverse Ions.—The data concerning the effect of diverse ions were obtained on solutions containing 67.4 μg. of cadmium and the diverse ions added individually. Alkali metal salts of the anions were used. Diverse cations were added as the chloride, nitrate or sulfate salts.

Of the anions tested, the following did not interfere under the described conditions: chloride and sulfate up to 500 μmol., thiocyanate up to 100 μmol., and fluoride and phosphate up to 50μmol. NTA and EDTA, especially the latter, bleach the color of the complex, even when only trace amounts are present.

Because all of the metal cations tested, with the exception of alkaline earth metals, interfere seriously, attempts were made to eliminate the interfering cations with some masking agents; the addition of 60 μmol. of fluoride was effective for rare earths up to 0.5 μmol. and for thorium and zirconium up to 0.05 μmol., while the addition of 50 μmol. of thiocyanate was effective for mercury(II) up to 0.5 μmol.

A Comparison with Other Methods.—Except for dithizone, of the previously-proposed reagents for the spectrophotometric determination of cadmium, di-β-naphthylthiocarbazone[10] and 1-(2-pyridylazo)-2-naphthol (PAN)[11] are perhaps the most sensitive. These reagents can be used even for the determination of a few micrograms of cadmium. Diethyldithiocarbamate[12] has also been reported to be sensitive for cadmium and has been widely utilized for the determination of 50 to 300 μg. of cadmium. All the above reagents, however, form water-insoluble complexes with cadmium. Therefore, these cadmium complexes must be extracted into a suitable organic solvent; this complicates the process of the determination.

Other reagents which have been utilized successfully for the determination of cadmium are 4-hydroxy-3-nitrophenylarsonic acid,[13] chrome dark blue[14] and cadion IREA.[15] These reagents can form water-soluble complexes with cadmium but are far less sensitive than xylenol orange. The colloidal cadmium sulfide formed with cadmium and thiosinamine is unstable,[16] indicating that the absorbance measurements must be made in the presence of a stabilizing agent. An indirect method, based on the interaction of cadmium and the zinc-complex of α-β-γ-δ-tetraphenylporphine,[17] has been proposed for the determination of cadmium, but it is not capable of determining traces of cadmium.

Therefore, it may be concluded that, of the reagents which can form water-soluble cadmium complexes, xylenol orange is the most pre-eminent colorimetric reagent for cadmium. The proposed method, which is rapid, sensitive and accurate, seems to be applicable for the determination of traces of cadmium in many samples, when cadmium is preliminarily separated from the interfering ions by an ion-exchange or a precipitation method.

Complex Formation.—*Continuous Variations.*—A very rapid and excellent method for determining the composition of the main complex formed in a given concentration range of the reactants is Job's method[18] of continuous variations as extended by Vosburgh and Cooper.[19]

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[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd Ed., Interscience Publishers Co. Inc., New York (1950), p. 49.

[10] J. Cholach and D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **16**, 333 (1944).

[11] M. Ishibashi, T. Shigematsu, M. Tabushi, Y. Nishikawa and J. Goda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 295 (1962).

[12] E. Sudo, ibid., **73**, 693 (1952).

[13] W. Nielsch and G. Böltz, *Chem. Ztg.*, **79**, 364 (1955).

[14] G. G. Lomakina and V. N. Tolmacheva, *Zavodskaya Lab.*, **26**, 62 (1960).

[15] A. M. Lukin, G. G. Karanovich and G. S. Petvova, *Trudy Vsesoyuz. Nauch. -Issledovatel. Inst. Khim. Reaktivov*, **1959**, No. 23, 55; *Chem. Abstr.*, **54**, 24117 (1960).

[16] F. Sabon and H. Grigon, *Bull. soc. pharm. Bordeaux*, **94**, 47 (1955).

[17] C. V. Banks and R. E. Bisque, *Anal. Chem.*, **29**, 522 (1957).

[18] P. Job, *Ann. Chim.*, **9**, 113 (1928); **6**, 97 (1936).

[19] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

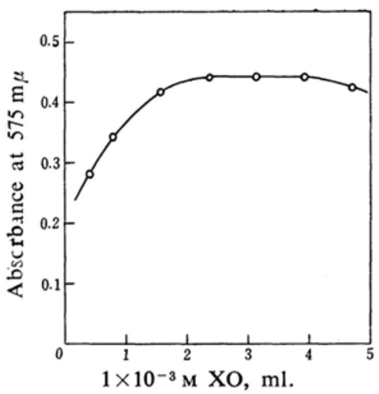

Fig. 4. Effect of amount of xylenol orange.
Cd : 67.4 μg., pH : 6.3
Hexamethylenetetramine : 20% soln. 10 ml.
KNO_3 : 0.30 M

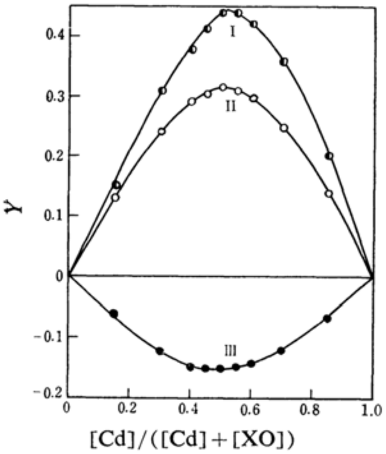

Fig. 5. Method of continuous variations.
[Cd]+[XO]=3.2×10^{-5} M
pH : 6.3, KNO_3 : 0.30 M
Hexamethylenetetramine : 20% soln., 10ml.
I : 580 mμ
II : 560 mμ
III : 440 mμ
Reference : water

Figure 5 shows, for three wavelengths, the absorbances, Y, that exceed the absorbances expected for no reaction in various mixtures of equimolar solutions of cadmium and xylenol orange. The pH value was held constant at 6.3 and the potassium nitrate concentration, at 0.3 M. The total concentration of cadmium and xylenol orange was 3.2×10^{-5} M throughout. The curves in Fig. 5 clearly indicate that only one complex, 1 to 1, is formed in solutions containing cadmium and xylenol orange.

The Absorption Spectra of the Complex at Various Concentrations of Cadmium.—Prior to the calculation of the apparent formation constant, the absorption spectra of solutions with a constant concentration of xylenol orange, 2.4×10^{-5} M, and potassium nitrate, 0.30 M, but with various concentrations of cadmium, were studied. The location of the absorption maximum was constant at 578±2 mμ for the range of cadmium concentration investigated. The results are shown in Fig. 6, indicating the existence of only one form of the complex.

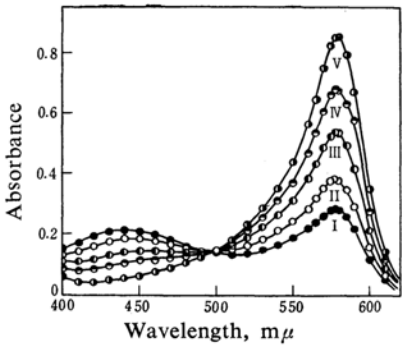

Fig. 6. Absorption spectra of cadmium-xylenol orange complex at pH 6.3.
XO : 2.4×10^{-5} M, KNO_3 : 0.30 M
Cd concn.: I, 0.8×10^{-5} M ; II, 1.6×10^{-5} M ;
III, 3.2×10^{-5} M ; IV, 6.0×10^{-5} M ;
V, 3.3×10^{-4} M
Reference : water

The Apparent Formation Constant.—Using as a guide the results of the experiments reported on the previous sections, the calculation of the apparent formation constant of the cadmium-xylenol orange complex was attempted. A method described by Newman and Hume[20] was employed.

Since only a 1 to 1 complex is formed, the equilibrium constant, K, can be expressed as:

$$K=[\mathrm{Cd(XO)}]\,[\mathrm{H}^+]^x/[\mathrm{Cd}^{2+}]\,[\mathrm{XO}] \qquad (1)$$

where XO and Cd(XO) represent the total unbound xylenol orange and the total cadmium-xylenol orange complex respectively, and x is the number of hydrogen ion liberated from one molecule of xylenol orange by the chelation. Assuming that two species, the complex and xylenol orange, absorb at the wavelengths under investigation, the apparent formation constant, $K'=K/[\mathrm{H}^+]^x$, may be given by:

$$\log\,(D-D_{\mathrm{XO}})/(D_{\mathrm{C}}-D)=\log K'+\log\{[\mathrm{Cd}^{2+}]_t-(D-D_{\mathrm{XO}})/(\varepsilon_{\mathrm{C}}-\varepsilon_{\mathrm{XO}})\} \qquad (2)$$

where ε_{C} and $\varepsilon_{\mathrm{XO}}$ are the molar extinction coefficients of the complex and xylenol orange respectively; D is the absorbance of the solution containing a mixture of cadmium and xylenol orange, and D_{XO} and D_{C} are the absorbances of a solution containing only xylenol orange or a large excess of cadmium ions added to a known amount of xylenol

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[20] L. Newman and D. N. Hume, ibid., **79**, 4571 (1957).

orange respectively. When $\log(D-D_{XO})/(D_C-D)$ is plotted against $\log\{[Cd^{2+}]_t-(D-D_{XO})/(\varepsilon_C-\varepsilon_{XO})\}$, a straight line with a unit slope and intercept $\log K'$ is obtained.

In the work performed in this section, each solution was 2.0×10^{-5} M in xylenol orange, the concentration of cadmium was varied from 1.0×10^{-4} to 4.58×10^{-3} M, the pH value of each solution was adjusted to 5.5 with hexamethylenetetramine - nitric acid, and the concentration of potassium nitrate was maintained constant at 0.3 M. Table I shows the results of the Newman-Hume plots, all of which give good straight lines with a unit slope.

TABLE I. DETERMINATION OF THE APPARENT FORMATION CONSTANT

Wavelength, mμ	Slope	K'
570	1.05	5.1×10^3
575	1.04	5.4×10^3
578	1.06	5.9×10^3
580	1.09	7.1×10^3
585	1.09	7.1×10^3

Av.: Slope = 1.07 ; $K'=6.1\times10^3$

Summary

The red cadmium - xylenol orange complex has been studied spectrophotometrically to establish the optimum conditions for determining traces of cadmium. The absorption spectrum of the colored complex showed a maximum absorption at 575 mμ when measured against a reagent blank. The reaction was carried out in a buffered solution at a pH value of 6.3. Beer's law is obeyed over the 20 to 120 μg. range of cadmium. The sensitivity of the reaction was 0.006 μg. cadmium per cm². Job's method of continuous variations and the method of Newman and Hume have been applied to determine the composition of the complex. Both methods showed the existence of only one form of the complex, 1 to 1. The apparent formation constant was calculated to be 6.1×10^3 at a pH value of 5.5.

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Department of Chemistry
Faculty of Literature and Science
Hirosaki University
Hirosaki, Aomori