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K. R. Solanke[a]; S. M. Khopkar[a]
[a] DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY, BOMBAY, INDIA

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NOTE

Extractive Separation and Direct Colorimetric Determination of Cadmium with Thiothenoyltrifluoroacetone

K. R. SOLANKE and S. M. KHOPKAR

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY
BOMBAY 400,076, INDIA

Abstract

Thiothenoyltrifluoroacetone (STTA) was used for the quantitative extraction of cadmium at tracer level. Cadmium was extracted completely at pH 6.5–7.5 with 0.001 *M* STTA in carbon tetrachloride as the yellow colored complex which could be measured colorimetrically at 450 nm. The system adhered to Beer's law in the concentration range of 0.9 to 19 μg/ml. The complex was stable for at least 96 hr. Ten milliliters 0.001 *M* STTA in carbon tetrachloride was adequate for quantitative extraction of cadmium. The optimum period of equilibration was 10 min. It was possible to effect extractive separation and colorimetric determination of cadmium in the presence of 1 : 200 of alkali, alkaline earths, thallium, germanium, and organic complexing acids. Other ions were tolerated in the ratio > 1 : 20. The method was rendered selective by using sequestering agents, such as citric acid, tartaric acid, or alkali cyanide, or by resorting to selective extraction process with either tributylphosphate or acetylacetone.

Cadmium is extensively used in atomic reactors and in fusible alloys. It is usually associated with lead, aluminum, mercury, and antimony. Very few methods are available for its separation at microgram concentrations. Thiothenoyltrifluoroacetone (STTA), a thiosubstituted derivative of 2-thenoyltrifluoroacetone, is found to be versatile extracting and colorimetric reagent for many transition elements (*1*). Cadmium forms yellow colored complex with this reagent at pH 6.5–7.5 in the presence of 1 *M* ammonium nitrate as the salting-out agent. Such a complex can be measured spectrophotometrically at 450 nm.

Among the various β-diketones, acetylacetone was found to be ineffective (*2*) for the solvent extraction of cadmium. Benzoylacetone (*3*, *4*) could extract cadmium from solution at pH 9.5–11 in chloroform but extraction was not quantitative in carbon tetrachloride. Dibenzoylmethane (*2*) was used for its extraction from alkaline media. 2-Thenoyltrifluoroacetone in chloroform or benzene (*5*) was used for the solvent extraction of cadmium but the method had hardly any practical applications. The several other extractants used for cadmium are best summarized in a recent monograph (*1*). Most of the methods for liquid–liquid extraction of cadmium have some limitations.

The method proposed in this note is simple, rapid, selective, and sensitive. It is possible to accomplish clear-cut separation of cadmium at tracer level.

EXPERIMENTAL

Apparatus and Reagents

Type SP-4 spectrophotometer with quartz cells. Type FEK-57 photoelectric filter photometer with 10 mm corex glass cuvettes. Cambridge pH meter with glass electrodes. Wrist action flask shaker.

Thiothenoyltrifluoroacetone [1,1,1-trifluoro-4(2-thienyl)-4-mercaptobut-3-en-2-one (STTA)] was synthesized from 2-thenoyltrifluoroacetone (Koch Light, England) as per the procedure indicated in an earlier paper (*6*). About 0.001 *M* STTA in carbon tetrachloride was used. The reagent was preferably preserved in a refrigerator. About 1.40 g of cadmium nitrate tetrahydrate (Reanal, Hungary) was dissolved in 100 ml of water containing 0.5% nitric acid and standardized complexometrically (*7*). It contained 4.75 mg of cadmium per ml. The dilute solution containing 95 μg/ml of cadmium was prepared from stock solution by suitable dilution.

General Procedure

An aliquot of the solution containing 95 μg of cadmium was taken. After addition of 10 ml of water the pH of the solution was adjusted to 6.5–7.5 on a pH meter using 0.01 *M* nitric acid or ammonium hydroxide. The volume of the aqueous phase was then made up to 25 ml. The solution was then transferred to a separating funnel after addition of 10 ml of

0.001 *M* STTA in carbon tetrachloride; the solution was shaken on a wrist action flask shaker for about 10 min. The layers were allowed to settle and separate. The aqueous layer was withdrawn and the yellow colored cadmium complex was transferred to a 10-ml volumetric flask. The absorbance of the colored complex was then measured at 450 nm. The amount of cadmium was computed from the calibration curve.

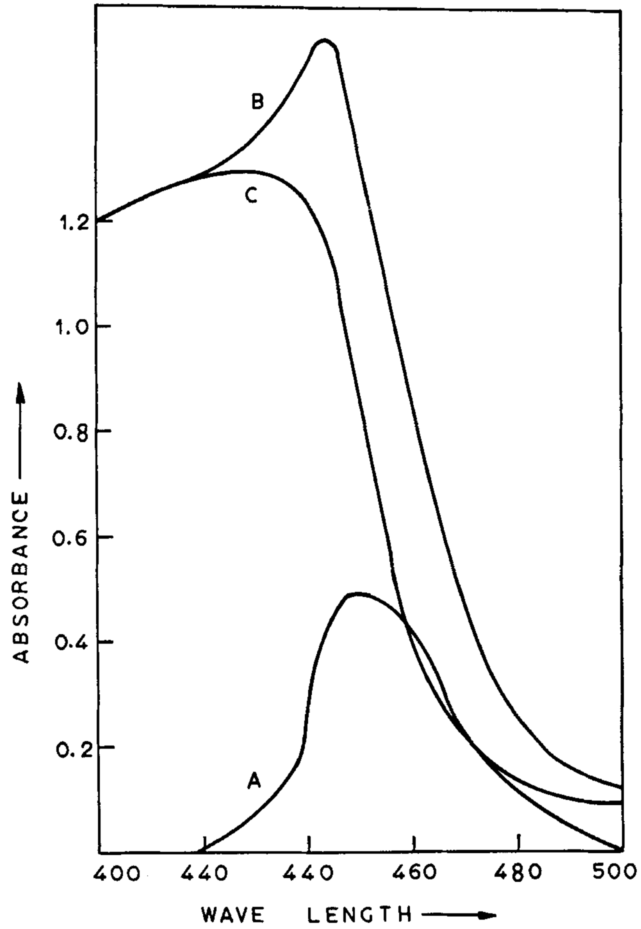

FIG. 1. Absorption spectra of Cd–STTA complex. Cd = 8.052×10^{-4} *M*, pH = 7.0, 2×10^{-3} *M* STTA in CCl_4. (A) Cd–STTA complex against reagent blank. (B) Cd–STTA complex against CCl_4. (C) Reagent blank against CCl_4.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of cadmium–STTA complex (Cd = 8.05 × 10^{-4} *M*) against the reagent blank (A) is shown in Fig. 1. The spectrum of the reagent blank against carbon tetrachloride (C) and also the spectrum of the cadmium complex against carbon tetrachloride are also given (B). It is seen that the complex showed a maximum absorbance at 450 nm. Hence all absorption measurements were taken at 450 nm. The molar absorptivity at 450 nm is 5.97 × 10^3. The sensitivity (Sandell's definition) is 0.0018 μg/cm^2 per ml at 450 nm.

Extraction as a Function of pH

The extraction of cadmium was carried out from pH 2–10 with 0.001 *M* STTA–carbon tetrachloride (Fig. 2). The results show that the extraction commenced at about pH 4 and was quantitative in the pH region of 6.5 to 7.5. The extraction was incomplete below and above this pH. Thus the optimum pH for extraction is 6.5–7.5.

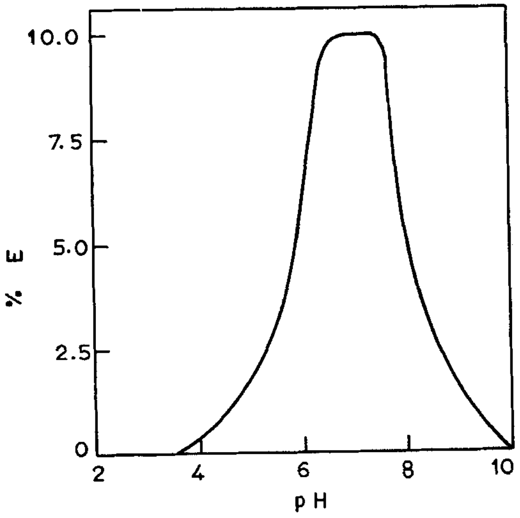

FIG. 2. Extraction of cadmium as a function of pH. Cd = 8.052 × 10^{-4} *M*, 1 × 10^{-3} *M* STTA in CCl_4.

Effect of Salting-out Agents

The nitrates of ammonium, lithium, sodium, potassium, magnesium, and calcium were used as the salting-out agents, when 95 μg of cadmium was extracted at pH 7.0 with 0.001 *M* STTA in carbon tetrachloride. The results (Table 1) show that there was slight improvement in the extraction when nitrates of lithium, sodium, or potassium were used. The use of calcium and magnesium nitrates indicated the enhancement in the extraction. The extraction significantly improved when ammonium nitrate was used as the salting-out agent. Therefore, throughout this work 1 *M* ammonium nitrate was used as the salting-out agent.

TABLE 1

Effect of Salting-out Agents[a]

Salting-out agents	*M*	Absorbance at 450 nm	Extraction (%)	Distribution ratio (*D*)
None		0.210	52.5	2.8
NH_4NO_3	0.25	0.310	75.25	7.6
	0.50	0.390	97.5	97.5
	1.0–2.0	0.400	100	∞
$LiNO_3$	2–6	0.220	55.0	3.0
	8.0	0.280	70.0	4.41
$NaNO_3$	1–3	0.300	75.0	7.5
KNO_3	1.0	0.230	57.5	3.25
	1.5–2.0	0.290	72.5	6.6
$Mg(NO_3)_2$	1–2	0.300	75.0	7.5
$Ca(NO_3)_2$	0.5–2.0	0.310	75.25	7.6

[a] Cd = 95 μg; pH = 7.0; 0.001 *M* STTA–CCl_4.

Beer's Law

Different amounts of cadmium, ranging from 9.0 to 190 μg of cadmium per 10 ml of solution, were taken. They were extracted at pH 7 with 10 ml of 0.001 *M* STTA–carbon tetrachloride. The absorbance of the complex was measured at 440, 450, and 460 nm. It was observed that the system adhered to Beer's law in the concentration limit of 0.9 to 19 μg of cadmium per ml at 450 nm.

Effect of Reagent Concentration

The cadmium was extracted at pH 7.0 with varying volumes and varying concentrations of the reagent (Table 2). The results show that 10 ml of 0.001 *M* STTA was sufficient for quantitative extraction of cadmium.

TABLE 2

Effect of Reagent Concentration[a]

Concentration of the reagent ($M \times 10^{-3}$)	Milliliters added	Absorbance at 450 nm
0.25	10	0.200
0.50	10	0.290
0.75	10	0.400
1.0	10	0.400
1.0	15	0.300
1.0	20	0.200
1.0	2.5[b]	0.200
1.0	5.0[b]	0.310
1.0	7.5[b]	0.360
1.5	10	0.400
2.0	10	0.400

[a] Cd = 95 μg; pH = 7.0; 1 *M* NH_4NO_3.

[b] Diluted to 10 ml.

The extraction was incomplete at lower concentration and the lower volume of the reagent. At higher concentrations of the reagent there was an insignificant increase in the absorption. Thus the optimum reagent concentration is 0.001 *M*.

Stability of the Color of the Complex

The absorption of the color of the complex was measured at elapsed intervals of 0, 4, 8, 16, 24, 48, 72, 98, and 120 hr. It was observed that the complex was stable for at least 96 hr.

Period of Equilibration

Varying the shaking period from 2.5 to 25 min revealed that extraction was incomplete up to a shaking period of 7.5 min. The extraction was quantitative in 10 min of equilibration.

Effect of Diverse Ions

The effect of several ions on the extraction behavior of cadmium was studied (Table 3). The tolerance limit was calculated as described earlier (*6*). The results show that alkali and alkaline earths, germanium, thallium, and the complexing anions of organic acids were tolerated in a ratio of

TABLE 3

Effect of Diverse Ions[a]

Tolerance limits (μg)	Foreign ion present
2.0×10^4	Tl^+, Rb^+, Cs^+, Ba^{2+}, Ca^{2+}, Sr^{2+}, Ge^{4+}, NO_2^- CH_3COO^-, $C_2O_4^{2-}$, Cit^{3-}, $Tart^{3-}$, $Malonate^{2-}$, $Ascorb^-$
1.0×10^4	Th^{4+}, As^{3+}, Mn^{2+}, $Mo_7O_{24}^{6-}$, WO_4^{2-}, SeO_3^{2-} F^-, Br^-, I^-, CN^-, SCN^-, $S_2O_3^{2-}$, PO_4^{3-}
5.0×10^3	TeO_3^{2-}
2.0×10^3	UO_2^{2+}, VO_3^-
1.0×10^3	Sb^{3+}, Au^{3+}, Ce^{4+}, ReO_4^-
5.0×10^2	Ag^+, Hg^{2+}, Cu^{2+}, Os^{6+}, Zr^{4+}
1.0×10^2	In^{3+}, Pt^{6+}, Ti^{4+}, Cr^{3+}, Be^{2+}

[a] Cd = 95 μg; pH = 7.0; 1 *M* NH_4NO_3; 0.001 *M* STTA–CCl_4.

1 : 200. Manganese, arsenic, molybdate, tungstate, selenite, halogens, and pseudohalogens were tolerated in a ratio of 1 : 100. The other ions were tolerated in a smaller ratio. The interferences due to some of the ions were eliminated by using suitable sequestering agents, e.g., silver, iron, cerium, and zirconium were masked with citric acid as unextractable negatively charged complex whereas gold and mercury were masked with alkali cyanide and interferences due to antimony were eliminated with tartaric acid. Similarly, by resorting to the technique of selective extraction, the interferences due to lead (*8*) and chromium (*9*) were eliminated by their extraction with TBP and of copper by extraction with acetylacetone (*1*).

The absorbance of the solution on microcolorimeter from 20 determinations was 0.400 ± 0.010. The relative standard deviation was ±1.0%. The method is applicable at tracer concentrations of cadmium. It was possible to accomplish clean-cut separation of cadmium from various ions such as lead, aluminum, mercury, antimony with which it is usually associated. The method is rapid as the overall time of operation is just 30 min. As little as 0.24 μg/ml of cadmium could be determined by this method.

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