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The Precipitation of Traces of Copper, Cadmium, and Lead with 6-Anilino-1,3,5-triazine-2,4-dithiol and Its Application to X-Ray Fluorescence Spectrometry

Hiroto WATANABE* and Takashi UEDA

Department of Applied Chemistry, Muroran Institute of Technology, Mizumoto-cho, Muroran 050

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A selective enrichment procedure for copper, cadmium, and lead is described. This method is based on precipitating the three elements with 6-anilino-1,3,5-triazine-2,4-dithiol (ATD) or with a combination of ATD and benzyldimethyltetradecylammonium chloride (BMTAC), filtering the precipitates to form a suitable X-ray sample, and then analyzing the sample by means of X-ray fluorescence. Microgram amounts of the three elements were precipitated quantitatively with ATD from 50 cm^3 or less of aqueous solutions of pH 7. Several to several tens mg amounts of such other elements as aluminium, iron(III), vanadium(V), zinc, arsenic(III, V), nickel, cobalt, and manganese(II) do not form any precipitates in the presence of citrate. Quantitative recoveries of the three elements from aqueous solutions ranging from 200 to 500 cm^3 were also possible when BMTAC was present as a coagulant aid. ATD was used for the determination of the three elements in reference materials (Orchard Leaves and Pepperbush Leaves). The results agreed with the certified values and with those obtained by isotope-dilution mass-spectrometry, and the precisions were satisfactory. The three elements in hot-spring water at levels from several to several tens ppb were determined by using a combination of ATD and BMTAC.

Various 6-substituted 1,3,5-triazine-2,4-dithiols react with relatively limited numbers of metal ions to give precipitates which are sparingly soluble in water.[1] One of the most remarkable properties of the dithiols is their extraordinary stability. They are not readily oxidized on exposure to air and are stable in either an alkaline or an acid solution.[1] This is quite different from the properties of other sulfur-containing ligands, such as dithiocarbamates, which react rather nonspecifically with a wide variety of metal ions. The dithiols have proved to be very effective in precipitating copper(II), cadmium(II), lead(II), and mercury(II) in industrial waste waters.[2]

Precipitation has long been used for the concentration and separation of trace elements in aqueous samples. Recently emphasis has been placed on the use of polymeric precipitating reagents. Muzzarelli[3] used a naturally occurring chelating polymer, chitosan, and Buono *et al.*[4] employed poly(5-vinyl-8-hydroxyquinoline). However, there has been little mention of utilizing organic ligands which give rise to polynuclear complexes. It is well known that dithiooxamide (DTO) reacts with copper to form a bridged polymer consisting of a series of five-membered rings.[5] Unfortunately, DTO is unstable and readily undergoes hydrolysis to hydrogen sulfide, so that metal ions, such as zinc, cadmium, lead, and mercury, are precipitated as their sulfides.[6] In this respect, the dithiols seem to be potential precipitants. As has been reported by Chudy and Dalziel[7] and by Mori *et al.*,[8] the dithiols are also capable of forming polymeric complexes with metal ions.

Of the commercially available dithiols, 6-anilino-1,3,5-triazine-2,4-dithiol (ATD) was chosen in this study because it gave the most insoluble precipitates. This report will deal with the application of ATD as a precipitant for the determination of copper, cadmium, and lead in conjunction with X-ray fluorescence (XRF) spectrometry.

Experimental

Materials. A 1.0% (w/w) ATD solution was prepared by dissolving 1.0 g of the compound (sodium hydrogen 6-anilino-1,3,5-triazine-2,4-dithiolate tetrahydrate; Sankyo Kasei Co., Ltd., Osaka) in 50 cm^3 of 2 mol dm^{-3} aqueous sodium hydroxide and by then diluting the mixture to 100 g with water.

A 0.001 mol dm^{-3} aqueous solution of benzyldimethyltetradecylammonium chloride (BMTAC) was prepared by using a commercial material (Dojindo Co., Ltd., Kumamoto).

Standard solutions containing 1 g dm^{-3} portions of a number of elements were prepared by dissolving weighed quantities of the high-purity metal, oxide or salt in a minimum amount of acid and then diluting the mixtures to known volumes. Working solutions containing the cations at concentrations of from 1 to 100 μg cm^{-3} were prepared by dilution.

A buffer solution of pH 7.0 was made by mixing 0.5 mol dm^{-3} of sodium dihydrogenphosphate and 0.5 mol dm^{-3} of disodium hydrogenphosphate.

A 0.5 mol dm^{-3} portion of sodium citrate was prepared by dissolving the compound in water.

The citrate and the buffer solutions were cleansed of metal contaminants by precipitation with ATD, as in Method A described below.

The other reagents, such as nitric, hydrochloric, hydrofluoric, and perchloric acids, were purified by sub-boiling distillation.[9]

Apparatus. A Rigaku model SX X-ray fluorescence spectrometer with a tungsten target tube, a LiF(200) crystal, and a NaI(Tl) scintillation counter was used. However, in the determination of cadmium, it was necessary to use a chromium target tube, an EDDT crystal, and a flow proportional counter. The X-ray tubes were operated at 40 kV and 35 mA. Both sample and spectrometer chambers were evacuated to a pressure of less than 13.3 Pa.

Procedure. *Precipitation of Copper, Cadmium, and Lead with ATD (Method A)*: To a test solution (usually 25 cm^3) containing 10 μg or less of the respective element, 1 cm^3 of a 1.0% ATD solution and 1 cm^3 of 0.5 mol dm^{-3} sodium citrate were added. Then the pH was adjusted to 7.0 with 2 cm^3 of the phosphate buffer and, if necessary, with an appropriate amount of ammonium hydroxide or hydrochloric acid. The resulting mixture was allowed to stand for 20 min at room temperature and then filtered under suction through a Millipore filter disk (25 mm diameter, 0.45 μm pore size). The precipitate on the filter disk was washed with a small amount of water and subsequently allowed to dry at 60 °C for 10 min. The XRF specimens thus prepared were placed between 6 μm Mylar films in an XRF sample holder. A titanium disk was inserted into the holder to keep the filter flat. The XRF intensities were then measured at the $K\alpha$ line of copper (45.02°) and the $L\alpha$ lines of cadmium (53.38°) and lead (33.92°). The counting times were 40 s except in the case of cadmium, for which the counting time was 100 s. The background counts were measured at the following 2θ values: copper (44.52°, 45.52°), cadmium (52.38°, 54.38°), lead (33.72°, 34.12°).

Precipitation of the Three Elements with a Combination of ATD and BMTAC (Method B): To a test solution (usually 200 cm^3) containing 10 μg or less of the respective element, 1 cm^3 of a 1.0% ATD solution, 1 cm^3 of 0.5 mol dm^{-3} sodium citrate, 1 cm^3 of 0.001 mol dm^{-3} BMTAC, and 2 cm^3 of the phosphate buffer were added successively. Precipitation and XRF sample preparation were then performed as in Method A, but the time of precipitation was extended to 25 min. These methods were selected in view of the results of the optimization study to be described in the next section.

Throughout the present study, the recovery yields of the three elements (5.0 μg each) were expressed as ratios of the net counts of samples prepared under various conditions to that of a reference sample. The reference sample was prepared by applying Method A to a 25 cm^3 aqueous solution containing 5.0 μg of the respective element. For the reference sample, the recoveries of the three elements were confirmed to be quantitative by determining the three elements remaining in the filtrates. Atomic absorption spectrometry was used for this purpose.

Results and Discussion

Effect of the pH *on the Precipitation of Various Elements.* The recovery yields of various elements from 25 cm^3 of aqueous solutions were examined as a function of the pH in the absence of BMTAC. This procedure was practically the same as Method A except that no buffer was used and filtration was done 60 min after precipitation. Copper was precipitated over the pH range of 4—9, while the range for cadmium and lead was 6 to 9, as is shown in Fig. 1. Thus, a pH value of 7 was chosen in Method A. The precipitates thus formed were easily filtered and did not adhere to glass.

Ten micrograms of other elements, such as cobalt, nickel, arsenic(III, V), manganese(II), vanadium(V), zinc, aluminium, iron(II, III), bismuth, calcium, and magnesium, gave no precipitates over the entire pH range studied. In the absence of citrate aluminium, iron(III) and bismuth were precipitated, but their precipitates seemed to be hydroxides because the precipitation of these elements was also observed for solutions from which ATD was omitted. When the pH was adjusted to 7 by using the phosphate buffer in the presence of citrate, the other elements did not form any precipitates.

Although it has been pointed out that mercury(II) forms a highly insoluble precipitate with ATD,[1,2] the sensitivity of XRF for mercury is low, thus precluding its determination in the present study. ATD itself did not precipitate at pH 7, but it was precipitated below pH 4. This is due to the insolubility of the protonated form of ATD.

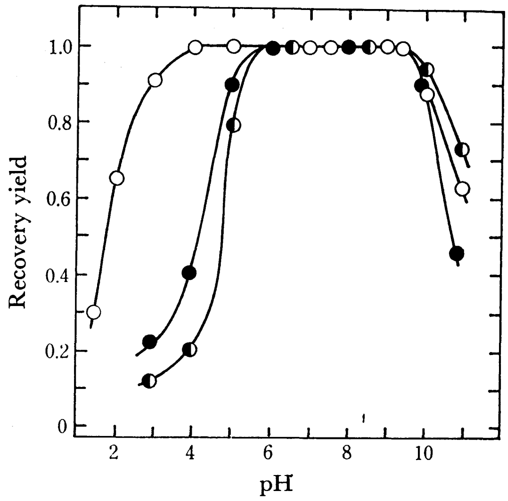

Fig. 1. Effect of pH on the precipitation of copper(II), cadmium(II), and lead(II) with ATD.
○: Cu, ●: Cd, ◐: Pb.
Counting time: 10 s. Total volume of aqueous solutions: 25 cm^3. Amount of each of the three elements: 5.0 μg.

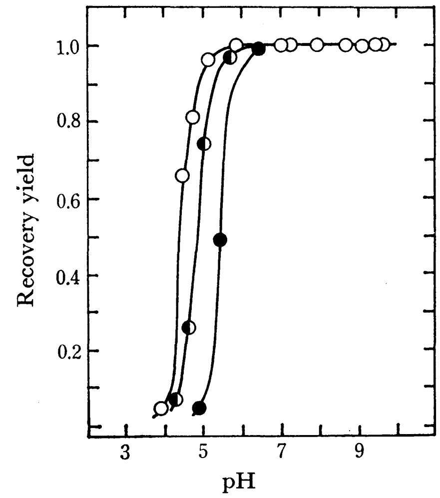

Fig. 2. Effect of pH on the precipitation of copper(II), cadmium(II), and lead(II) with the ATD–BMTAC combination.
○: Cu, ●: Cd, ◐: Pb.
Counting time: 40 s for Cu and Pb, 100 s for Cd. Total volume of aqueous solutions: 200 cm^3. Amount of each of the three elements: 5.0 μg.

Figure 2 shows the effect of the pH on the collection of the three elements from 200 cm^3 portions of aqueous solutions containing BMTAC. For this purpose, Method B, from which the phosphate buffer had been omitted, was used. The recoveries of the three elements were quantitative over the pH range of 6—9. Working at pH values greater than 9 appeared to be time-consuming for filtration (>30 min): thus, no further studies were carried out. For the filtration of 200 cm^3 portions of the aqueous solutions prepared over the pH range of 6—9, a period of 5 min was required. For experimental convenience, a pH value of 7 was also chosen in Method B.

ATD itself did not form any precipitates with BMTAC. This was verified by the fact that no intensities due to sulfur $K\alpha$ line were observed for samples from which the three elements had been omitted.

Effect of ATD. Ten-μg amounts of the three elements were precipitated from 25 cm^3 (Method A) or 200 cm^3 (Method B) of test solutions containing various amounts of ATD. The recoveries were independent of the amounts of the ATD solution in the range >0.8 cm^3. Thus, 1 cm^3 of the ATD solution was used for both methods.

Effect of Time. The minimum time required to obtain quantitative precipitation was determined by varying the time of precipitation. Method A was used for several 25 cm^3 solutions, filtration being done for a specified period of time ranging from 5 min to 24 h. It was found that filtration should be performed after 20 min in Method A.

Method B was applied to several 200 cm^3 portions of test solutions. After the addition of the ATD solution and the phosphate buffer to the test solutions, the mixtures were allowed to stand for from 5 to 60 min. Twenty-five min was found to be adequate for the completion of the precipitation of the three elements.

Table 1. Effect of sample volume on the recovery yields of the three elements[a)] at pH 7

Method A				Method B			
Volume	Recovery yield			Volume	Recovery yield		
cm^3	Cu	Pb	Cd	cm^3	Cu	Pb	Cd
10	1.00	1.00	1.00	200	1.00	1.00	1.00
25	1.00	1.00	1.00	300	0.99	0.98	0.99
50	1.00	1.00	1.00	400	1.01	0.99	1.00
100	1.00	0.98	0.81	500	1.00	1.00	0.99
150	0.74	0.66	0.51				

a) A 5-μg portion of the respective element was used.

Effect of Sample Volume. Method A was applied to various volumes (10—150 cm^3) of test solutions. The results, shown in Table 1, indicate that the influence of the sample volume is significant. It is thus recommended that the sample volume should be made up to 50 cm^3 or less for the simultaneous determination of the three elements.

On the other hand, when BMTAC was present, the recovery yields were essentially independent of the sample volume, as is shown in Table 1. A 5 μg portion of the respective element was precipitated quantitatively even from 500 cm^3 of aqueous solutions. This fact makes it possible to determine the three elements present in water at levels of from several to several tens ppb. This marked effect of BMTAC is probably due to the formation of a large anionic polynuclear complex of ATD. This interpretation seems to be consistent with the failure of a usual organic solvent such as *N*,*N*-dimethylformamide to dissolve the precipitates prepared by Method A. Working with sample volumes larger than 500 cm^3 was not done, but it appeared to be too time-consuming to be practical.

Effect of BMTAC. The three elements were collected from 200 cm^3 portions of aqueous solutions containing various amounts of BMTAC. When the amount of the BMTAC solution added was 1 cm^3 or larger, the recoveries were quantitative. However, a longer period (>30 min) was required for filtration because of the dispersing action when 3 cm^3 or more of the BMTAC solution was added. When 1 cm^3 of the BMTAC solution was added to test solutions ranging from 200 to 500 cm^3, a period of 5 to 10 min was required for filtering off the precipitates. Thus, in Method B a 1 cm^3 portion of the solution was employed.

Table 2. Effect of foreign ions on the determination of the three elements[a)]

Foreign ion	Added mg	Method A			Method B		
		Cu	Pb	Cd	Cu	Pb	Cd
Fe(III)	1.0				0.97	0.98	0.96
	10	1.01	1.03	0.97			
Mn(II)	2.0				1.01	1.00	1.00
	40	1.00	1.01	0.99			
Zn(II)	2.0				1.00	1.01	1.01
	10	1.00	0.98	1.02			
Co(II)	2.0				0.99	0.99	0.98
	10	0.98	0.97	0.96			
Ni(II)	2.0				1.01	1.02	1.00
	10	1.00	0.99	0.98			
V(V)	5	0.98	0.97	0.96			
Bi(III)	0.3	1.03	1.02	1.01			
Al(III)	1.0				0.96	0.97	0.98
	20	0.99	0.98	0.99			
Ca(II)	20				1.00	1.01	1.00
	30	0.97	0.97	0.98			
Mg(II)	20				1.00	1.00	1.01
	50	0.97	0.98	0.98			

a) A 5-μg portion of the respective element was used.

Effect of Foreign Ions. Test solutions containing 5.0 μg of the respective element and various amounts of a foreign ion were analysed. The results are summarized in Table 2. Lower results were obtained when foreign ions other than calcium, magnesium, and arsenic(III, V) were present in amounts higher than those indicated in Table 2. In Method A, several to several tens mg of foreign ions do not interfere with the determination of the three elements. It is well known that arsenic interferes seriously with the determination of lead because of mutual line interference. However, ATD does not react with arsenic(III, V), so the interference for lead is thus eliminated. At least 1 mg of arsenic was tolerable for the determination of 5 μg of lead.

In Method B the tolerance limits of foreign ions are lower than those in Method A. This is due to the precipitation of foreign ions to such an extent that the

XRF intensities of the three elements are lowered significantly. For example, when 1 mg of iron(III) was added about 10 μg portions of iron were found on the filter disk by measuring the XRF intensity of the iron *Kα* line. The precipitation of iron(III) becomes more significant as the quantities of iron(III) exceed 1 mg. This precipitation of iron(III) may be caused by the reaction between a citrate complex of iron(III) and BMTAC, for a similar tendency was observed on samples prepared by Method B from which the ATD solution and the buffer had been omitted. The precipitate of iron(III) has a very small grain size; hence, filtration is made more time-consuming (>30 min). Though it was not shown in Table 2, the recoveries of the three elements were quantitative from test solutions (200—500 cm^3) of any salinity up to that of seawater.

Mutual interferences among the three elements must also be taken into account. When one of the three elements was present in an amount higher than 100 μg, the XRF intensities for the other two elements were reduced. The total amounts of the three elements in an aliquot should be below 100 μg for both methods.

TABLE 3. SENSITIVITY AND PRECISION

	Cu	Pb	Cd
Sensitivity (counts/s)/μg	253	42.1	38.7
Background counts/s	1100	1113	19.9
95% confidence limit[a)] μg	5.05±0.10[b)] 5.03±0.20[c)]	5.05±0.11[b)] 5.02±0.24[c)]	5.02±0.05[b)] 5.03±0.13[c)]
Limit of detection μg	0.04	0.24	0.03

a) Confidence limit (95%) for the median of the eleven samples used for the preparation of the calibration curves. The median sample contains 5.00 μg of the respective element. b) Method A. c) Method B.

Calibration Curve. Linear calibration functions were obtained for the three elements in the concentration range of up to 10 μg. Table 3 lists the sensitivity of the XRF measurements; the background counts; the confidence limits (95%), *C*, for the median of the eleven samples used for the preparation of the calibration curves, and the limit of detection, *D*. The limit of detection at the 95% confidence level was calculated from the D-$3C\sqrt{B}\,M^{-1}$ relationship, where *M* is the slope of the calibration curves, and *B*, the background counts, based on a 40 s counting period for copper and lead or a 100 s counting period for cadmium. From this table it may be seen that the precision of the two methods is satisfactory.

Application of the Present Methods. Method A was applied to the determination of the three elements in NBS Orchard Leaves (National Bureau of Standards, U.S.A., Standard No. 1571). A weighed sample (3.0896 g) was placed in a Teflon beaker, together with 30 cm^3 of 14 mol dm^{-3} nitric acid, 5 cm^3 of 26 mol dm^{-3} hydrofluoric acid, and 4 cm^3 of 8 mol dm^{-3} perchloric acid. This mixture was warmed until a clear solution was obtained. The solution was then gently evaporated to dryness. The residue was dissolved in 5 cm^3 of 1 mol dm^{-3} hydrochloric acid and finally diluted to 100 cm^3 with water. A 15 cm^3 aliquot of this solution was used for the determination of the three elements. The confidence limits (95%) for the average of five determinations are shown in Table 4. In the table the present results are also compared with the values obtained by Murozumi[10)] by isotope-dilution mass-spectrometry and those given by the NBS.[11)] The data indicate a very satisfactory agreement between the present results and the others.

Method A was also used for the determination of the three elements in a reference sample, NIES Pepperbush Leaves (*Clethra barbinervis Sieb. et Zucc.*), distributed by the National Institute for Environmental Study, Japan. The sample (0.9788 g) was decomposed in the same manner as the Orchard Leaves. The results are presented in Table 4, in which the values given by Murozumi[10)] are also included. They are in acceptable agreement.

The three elements in a sample of hot-spring water were also determined by Method B. Two 150 g aliquots of the sample, both alone and with 2.0 μg of the respec-

TABLE 5. ANALYSIS OF HOT-SPRING WATER

Sample taken g	Element	Added μg	Element found Total μg	 In water μg/kg[a)]	C.V.[b)] %
150	Cu	—	3.00	20.0	4.6
	Cd	—	0.94	6.3	4.0
	Pb	—	5.80	38.6	4.6
150	Cu	2.00	5.13	20.8	2.7
	Cd	2.00	2.95	6.3	5.6
	Pb	2.00	7.92	39.8	2.9

a) Average of five determinations. b) Coefficient of variation.

TABLE 4. ANALYSIS OF ENVIRONMENTAL SAMPLES[a)]

	NBS orchard leaves μg/g Cu	 Cd	 Pb	NIES pepperbush leaves μg/g Cu	 Cd	 Pb
Present method (Method A)	12.2±0.1	0.12±0.01[b)]	46.3±1.2	11.6±0.2	6.89±0.11	5.4±0.3
Isotope-dilution mass-spectrometry[10)]	12.7±0.2	0.122±0.003	47.4±1.1	11.4±0.2	6.66±0.03	5.35±0.04
NBS[11)]	11±1	0.11±0.01	45±3			

a) The samples were dried at 120 °C for 24 h before the determinations. b) Counting time: 400 s.

tive element added, were analysed. The samples were placed in a polyethylene bottle (1 dm^3) containing 1 g of 6 mol dm^{-3} hydrochloric acid, and the mixture was allowed to stand overnight prior to the determination. It is apparent from Table 5 that from several to several tens ppb level of the three elements in water can be determined with fairly satisfactory precision.

Conclusion

Sodium diethyldithiocarbamate,[12,13] ammonium 1-pyrrolidinecarbodithioate,[14,15] 1-(2-pyridylazo)-2-naphthol,[13,16,17] and sodium dibenzyldithiocarbamate[18] are currently used in the preparation of suitable XRF samples. These organic reagents ordinarily react with a wide range of metal ions. Therefore, as has been reported by Hellman,[19] it is necessary to select certain masking conditions if a limited number of elements are to be precipitated by means of a nonspecific reagent. In this respect, the specificity of ATD toward copper, cadmium, and lead can be useful for separating μg amounts of the three elements from large amounts of other elements. Especially, there are few simple and selective methods for the separation of cadmium and lead, so ATD will be one of the most suitable reagents for their enrichment from multicomponent solutions.

Takemoto *et al.*[20] were the first to introduce a coagulant aid for the precipitation of heavy metal ions as dithiocarbamates. Microgram amounts of heavy metal ions were rapidly and quantitatively precipitated in the presence of dibenzylidene-D-sorbitol. Recently Panayappan *et al.*[21] have reported that a combination of poly(*N*-vinylpyrrolidone) and *N*-(2-naphthyl)mercaptoacetamide was excellent in precipitating heavy metal ions rapidly and forming insoluble compounds. These methods are convenient for the simultaneous precipitation of a variety of metal ions. The combination of ATD and BMTAC proposed in this study is particularly suited for the selective enrichment of the three elements from large volumes of aqueous samples containing considerable amounts of other elements. A number of coagulant aids currently used for water and waste-water purification, in combination with ATD, were tested, but they did not show any promise of being as effective as the ATD-BMTAC combination.

The authors wish to thank Professor Masayo Murozumi of this laboratory for his offer of reference materials (Orchard Leaves and Pepperbush Leaves) and for his kindness in letting us use a part of his analytical results obtained on the samples by means of isotope-dilution mass spectrometry. The XRF measurements were made on the spectrometer in the laboratory of Mr. Katsumasa Yabe, the Goverment Industrial Development Laboratory, Hokkaido, to whom the authors wish to express their gratitude. We also would like to thank Mr. Akira Umehara, Sankyo Kasei Co., Ltd., for kindly supplying a sample of ATD.

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