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Concentration of Metal Ions by Complexation with Sodium Bis(2-hydroxyethyl)dithiocarbamate and Sorption on XAD-4 Resin

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Sodium bis(2-hydroxyethyl)dithiocarbamate (NaHEDC) is used to form neutral metal complexes with metals of the hydrogen sulfide group. The hydroxy groups present in NaHEDC cause the metal complexes to be water-soluble at low concentrations. The complexed metal ions can be separated into groups or concentrated from very dilute solution by sorption on a small column of XAD-4 resin. Selectivity is achieved by pH adjustment or by masking agents. The sorbed metal complexes are eluted with acidic ethanol for subsequent measurement by AAS or absorption spectrophotometry. Applications to show the utility of the method include concentration of trace metals from seawater and separation of trace metals from uranium.

Multielement trace analysis techniques have found increasing use in the analysis of a number of sample matrices (*1, 2*). The determination of trace metals usually requires that they be separated from the bulk matrix and concentrated prior to the actual analysis step. A number of methods have been proposed for this purpose, including solvent extraction (*3, 4*), chelating ion-exchange resins (*5, 6*), precipitation (*7*), and electrolytic methods (*8*). By far the most widely used procedure is based upon the formation of insoluble metal complexes followed by extraction into an immiscible organic solvent. Solvent extraction techniques suffer from several limitations, however, including relatively low concentration factors (20–30-fold), possible emulsion formation, and increased sample manipulation. In addition, solvent extraction methods are not easily automated.

Concentration methods based upon the reversed-phase adsorption of complexed metals onto a small adsorbent column have shown promise in overcoming the limitations of solvent extraction. The sorbed complexes are eluted from the column with a water-miscible organic solvent. When this method was used, trace metals were concentrated by absorption onto XAD-2 resin after complexation with zinc bis(*n*-butyl-2-naphthylmethyl)dithiocarbamate. The adsorbed complexes were eluted with methanol and determined by HPLC (*9*). Trace metals in seawater were concentrated by complexation with 8-quinolinol followed by adsorption onto a C_{18}-bonded silica gel (*10, 11*) and by complexation with APDC followed by adsorption onto Chromosorb W-DMCS (*12*).

One problem with these adsorption methods is that the metal complexes are insoluble in water, which may cause incomplete adsorption or plugging of the adsorbent column (*2*). The use of chelating reagents which form water-soluble, neutral metal complexes but which are strongly sorbed onto a hydrophobic resin would solve this problem. This approach has been successfully used with *N*-methylfurohydroxamic acid as the complexing reagent and XAD-4 resin as the adsorbent (*13*).

The purpose of the present work was to prepare a dithiocarbamate reagent with these same solubility and sorption properties. A review of the dithiocarbamate literature showed that bis(2-hydroxyethyl)dithiocarbamate (HEDC) has been used as a colorimetric reagent to form a water-soluble, intensely colored complex with copper(II) (*14, 15*). HEDC has also been used as a titrant in the determination of mercury(II) (*16*) and as a colorimetric reagent in the determination of molybdenum(VI), uranium(VI) (*17*), and nickel(II) (*18*). The sodium salt of HEDC (designated NaHEDC) was selected as the most promising reagent for this study. The hydroxy groups present in NaHEDC cause its metal complexes to be soluble in water at low concentrations. A procedure has been developed for concentrating metal ions from solution onto a small column of XAD-4 resin. This method, unlike solvent extraction, can easily be automated to handle large sample loads with a minimum of manipulation.

EXPERIMENTAL SECTION

Apparatus. The XAD resins were sieved with a Model L3P sonic sifter (Allen-Bradley Co., Milwaukee, WI). Resin capacity breakthrough curves were prepared by using a Milton Roy Mini-Pump (Laboratory Data Control, Riviera Beach, FL), a 100 × 2 mm glass column, and a Beckman Model DB-GT grating spectrophotometer (Beckman Instruments, Irvine, CA) equipped with a 10-mm flow-through cell. Metal ion separations and concentrations were performed by using a 175 × 9 mm glass column fitted with a Teflon stopcock and a 24/40 standard taper joint. Solution reservoirs were made from 250- and 2000-mL round-bottom flasks fitted with male 24/40 standard taper joints. Atomic adsorption analyses were performed on a Perkin-Elmer Model 2380 atomic adsorption spectrophotometer equipped with a Model HGA-400 graphite furnace and Model AS-40 autosampler.

Reagents. The Amberlite XAD resins were obtained from the Rohm and Haas Co. (Philadelphia, PA). Each resin was washed with water, Soxhlet-extracted overnight with methanol, dried, ground, and sieved. Resin fines were removed by washing with methanol, allowing the resin to settle, and decanting the fines.

The 74–105-μm fractions were used in the adsorption studies.

All solutions were prepared with deionized water further purified by a Milli-Q water purification system (Millipore, Bedford, MS). Hydrochloric and nitric acids were Ultrex grade (J. T. Baker, Phillipsburg, NJ). Stock 1000 mg/L metal ion solutions were obtained from Fisher Scientific Co. (Fair Lawn, NJ). Standard mercury(II) titrant was prepared from primary standard grade mercuric chloride. Trace metal ion solutions of known concentration were prepared by dilution of metal ion quality control standards supplied by the U.S. Environmental Protection Agency (Quality Assurance Branch, E.M.S.L., Cincinnati, OH).

Buffer solutions were prepared from trichloroacetic acid (pH 1–2), monochloroacetic acid (pH 3), acetic acid (pH 4–5), pyridine (pH 6), ammonium acetate (pH 7), THAM (pH 8–9), and ammonium hydroxide (pH 10). Each buffer solution was adjusted to the desired pH with either sodium hydroxide or hydrochloric acid. All other reagents were reagent grade and were used as received.

Synthesis of NaHEDC. In a 1-L round-bottom flask fitted with an overhead stirrer, inert gas inlet, and addition funnel dissolve 40.0 g (1 mol) of sodium hydroxide and 105.1 g (1 mol) of diethanolamine (Fisher Scientific) in 400 ml of methanol. Purge with inert gas (N_2 or Ar) and cool to below 10 °C. Add 114 g (1.5 mol) of carbon disulfide dropwise while keeping the temperature below 10 °C. After 2 h, remove the methanol with a rotary evaporator at a bath temperature of 35 °C. To crystallize the viscous liquid, add 400 mL of 2-propanol and mix vigorously. Filter and dry under vacuum at ambient temperature. Yield of sodium bis(2-hydroxyethyl)dithiocarbamate is 154 g 76% of theoretical: mp 156 °C [lit. mp 155 °C (*19*)]. Anal. Calcd for $C_5H_{10}NO_2S_2Na$: C, 29.55; H, 4.96; N, 6.89; S 31.55; Na, 11.31. Found: C, 31.04; H, 5.32; N, 7.00; S, 32.30; Na, 11.21. Concentration of the filtrate and washings gives an additional 28 g of product. Total yield is 182 g, 89% of theoretical. The NMR and infrared spectra were consistent with the assigned structure of NaHEDC.

Analytical Methods. Solutions of NaHEDC were assayed by titration with standard mercury(II) solution at pH 7 by using Thiomichler's ketone as visual indicator (*16*, *20*). Trace concentrations of mercury(II) were determined by the cold-vapor method (*21*). Adsorption spectrophotometry was used for the determination of bismuth(III) with thiourea (*22*), molybdenum(VI) with thiolactic acid (*23*), and uranium(VI) with Arsenazo (*24*). All other metal ions were determined by either flame or graphite furnace atomic absorption spectrophotometry (*25*). All graphite furnace analyses were quantified by using the peak height mode and the method of standard additions.

Resin Capacity Breakthrough Curves. Resin capacity breakthrough curves were prepared by pumping a solution containing 5×10^{-5} M copper(II), 5×10^{-3} M NaHEDC, and 1.6×10^{-2} M sodium sulfite through a 100 × 2 mm column packed with 100 mg of 74–105-μm XAD resin. A flow rate of 1.00 mL/min was used. The sodium sulfite was added to stabilize the copper/HEDC complex during the time required to generate the breakthrough curves.

The column effluent was continuously monitored for breakthrough of the copper/HEDC complex by recording the effluent absorbance at 433 nm. The breakthrough curves were constructed by plotting the percent extraction ($C/C_0 \times 100$, C = absorbance of the column effluent, C_0 = absorbance of the column influent) against the total volume of effluent. The breakthrough capacity, in millimoles of copper/gram of resin, was obtained by calculating the number of millimoles of copper adsorbed by the resin at 50% extraction. Upon the completion of each breakthrough curve, the resin was regenerated by pumping a solution of 1.0 M nitric acid in ethanol through the column.

Sorption of Metal Ions on XAD-4 Resin. The effect of pH and masking agents on the absorption of metal dithiocarbamates on XAD-4 resin was studied by using a 175 × 9 mm gravity column packed with 500 mg of 74–105-μm XAD-4 resin. The following procedure was used.

(1) To a solution containing from 0.1 to 1.0 mg of the metal ion under study add 10.0 mL of 0.1 M masking agent, 10 mL of 1.0 M buffer, and 5 mL of 0.25 M NaHEDC solution.

(2) Adjust the solution pH to the desired value with hydrochloric acid or sodium hydroxide and dilute to 100 mL.

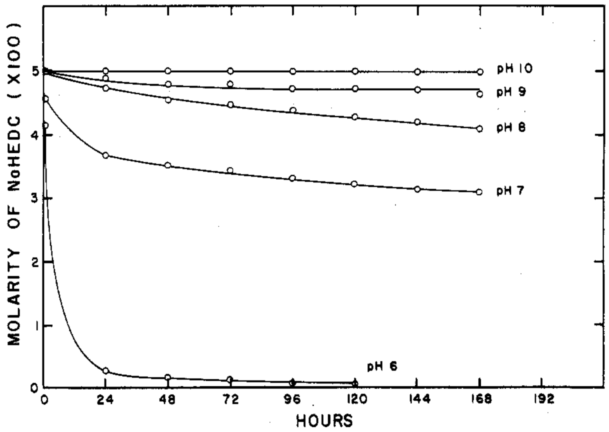

Figure 1. Stability of NaHEDC as a function of solution pH.

(3) Condition the column by passing 50 mL of 0.1 M buffer through the column.

(4) Pass the metal/HEDC solution through the column at a flow rate of 25 mL/min.

(5) Rinse the column with two 10-mL portions of water.

(6) Elute the adsorbed metal complex with 10 mL of 1.0 M nitric acid in ethanol and analyze the eluate for the metal concentration by colorimetric or atomic adsorption methods.

The percentage of metal adsorbed on the column was calculated from the milligrams of metal in the original sample and the milligrams of metal eluted from the column. Blanks were determined by applying the above procedure to 100 mL of demineralized water with no metal ions or buffer added.

Reagent Concentration Dependence. A series of 5×10^{-5} M copper(II) solutions, buffered to pH 8.0, were prepared which contained increasing molar ratios of HEDC to copper(II). The percentage of copper(II) retained on the resin for each solution was determined by the procedure described in the previous section.

Concentration of Metal Ions from Seawater. Artificial seawater, prepared from Turk's Island salt (*26*), was spiked with U.S. EPA quality control standard. To 1 L of this solution, 10 mL of 0.25 M NaHEDC was added. The solution was passed through the XAD-4 column at a flow of 50 mL/min and washed twice with deionized water, and the adsorbed metals were eluted with 5 mL of 1.0 M nitric acid in ethanol into a 10-mL volumetric flask. The concentrations of the eluted metals were determined by atomic absorption.

Separation of Trace Metal Ions from Uranium(VI). A 100-mL solution of 0.1 M uranium(VI), prepared from uranyl nitrate hexahydrate, was spiked with the U.S. EPA quality control standard. Sodium bicarbonate was added to mask the uranium(VI) and 5 mL of 0.25 M NaHEDC was added to complex the trace metals. The solution was passed through the XAD-4 column and washed with 10-mL portions of 0.1 M sodium bicarbonate and deionized water, and the adsorbed metals were eluted with 5 mL of 1.0 M nitric acid in ethanol into a 10-mL volumetric flask. The concentrations of the eluted metals were determined by atomic absorption.

RESULTS AND DISCUSSION

The procedure used for the synthesis of NaHEDC outlined in the Experimental Section gave a product of high purity and excellent yield. The total yield of 89% NaHEDC compares favorably with a reported yield of 12.5% by using a procedure by Klopping (*19*). The advantages of preparing sodium dialkyldithiocarbamates below 10 °C have been discussed by Moore (*27*). It was also found in this work that purging the reaction mixture with inert gas results in a much less colored product. The NaHEDC crystals are white when freshly prepared but tend to yellow after several months of storage. This yellowing did not appear to affect the reagent's metal complexing ability, even after 1 year of storage.

The stability of NaHEDC in aqueous solution as a function of pH is shown in Figure 1. The NaHEDC decomposition was found to be directly proportional to the solution hydrogen

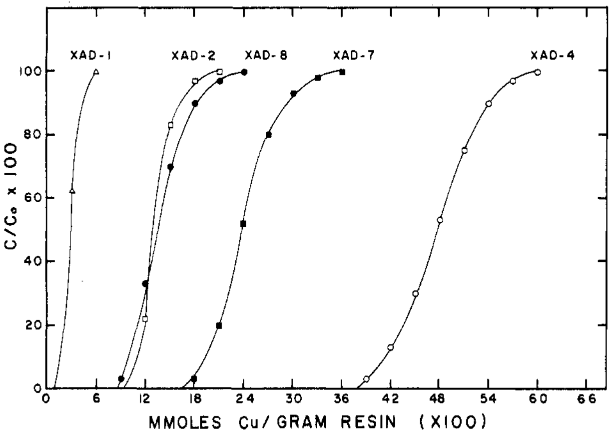

Figure 2. Resin capacity breakthrough curves for the copper/HEDC complex on various XAD resins.

Table I. Physical Characteristics[a] and Breakthrough Capacities of XAD Resins

adsorbent	type	surface area, m²/g	pore size, Å	capacity, mm of Cu/g
XAD-1	polystyrene/ DVB	100	100	0.027
XAD-2	polystyrene/ DVB	300	90	0.132
XAD-4	polystyrene/ DVB	725	40	0.474
XAD-7	polyacrylate	450	90	0.239
XAD-8	polyacrylate	160	225	0.132

[a] Physical characteristics are from ref 31.

ion concentration. This confirms work by Bode on the solution decomposition of sodium diethyldithiocarbamate (NaDDC) (*28*). He determined the NaDDC half-life to be 51 min at pH 6.0 and 35 days at pH 9.0. In the present work, the NaHEDC concentration was virtually unchanged after 7 days at pH 10.0.

The copper(II) complex of HEDC was chosen as a model compound for the determination of the adsorption capacities of the XAD resins. The copper/HEDC complex is strongly colored, which permitted continuous spectrophotometric monitoring of the column effluent for breakthrough. The first attempts at generating breakthrough curves were unsuccessful because of slow decomposition of the copper/HEDC complex during the curve generation time. This was evident from a decrease in the color intensity of the solution along with a corresponding increase in solution turbidity. This turbidity was evidently from the oxidation of the dithiocarbamate by dissolved oxygen (*29*). It was found that the addition of 2.0 g/L of sodium sulfite to the test solution eliminated the dissolved oxygen and stabilized the copper/HEDC complex.

The capacity breakthrough curves of XAD-1, XAD-2, XAD-4, XAD-7, and XAD-8 are shown in Figure 2. The symmetrical S-shape of the curves, rather than a sharp perpendicular rise, is due to the nonequilibrium condition which develops when the eluent flow through the column is faster than the diffusion rate of the adsorbate to the adsorbent surface (*30*). A flow rate of 1.00 mL/min was chosen as a compromise between unreasonably long curve generation times and excessive curve broadening.

A summary of the resins' physical characteristics and measured breakthrough capacities are shown in Table I. Several factors contribute to a resin's capacity for a given solute, including surface area, pore diameter distribution, surface polarity, and solvent polarity (*31*). XAD-1, -2 and -4 have the lowest surface polarity of the XAD resins. Within this resin series, there is a marked increase in resin capacity with increasing surface area. This same trend is evident in the more polar XAD-7 and -8 resin series. Since XAD-4 exhibited the highest breakthrough capacity of the resins tested, it was used during the remainder of this study.

Table II. Percent Recovery[a] of Metal Dithiocarbamates as a Function of pH

	solution pH							
element	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Ag(I)	95	100	100	100	100	100	100	100
Cd(II)	19	100	100	100	100	100	100	100
Fe(III)	0	52	100	100	100	100	84	31
Mo(VI)	100	100	73	37	0	0	0	0
Ni(II)	74	100	100	100	100	100	100	100
U(VI)	0	0	33	100	100	33	16	13
V(V)	100	100	100	100	100	82	53	14
Zn(II)	0	1	100	100	100	100	100	100

[a] Single determination, rounded to the nearest integer.

Table III. Percent Recovery[a] of Metal Dithiocarbamates with 0.01 M EDTA as Masking Agent

	solution pH		
element	5.0	7.0	9.0
Ag(I)	100	100	100
Bi(III)	100	100	100
Cd(II)	46	27	0
Co(II)	100	31	0
Cu(II)	100	100	100
Fe(III)	0	0	0
Hg(III)	100	100	100
Ni(II)	0	0	0
Pb(II)	64	16	0
Zn(II)	0	0	0

[a] Single determination, rounded to the nearest integer.

Table IV. Percent Recovery[a] of Metal Dithiocarbamates with 0.01 M Cyanide as Masking Agent at pH 9.0

element	% recovery	element	% recovery
Bi(III)	100	Fe(III)	31
Cd(II)	100	Ni(II)	0
Co(II)	0	Pb(II)	100
Cu(II)	5	Zn(II)	3

[a] Single determination, rounded to the nearest integer.

The retention of small amounts of metal ions on a small column containing XAD-4 resin was studied as a function of pH. In addition to an excess of NaHEDC and an appropriate buffer, tartrate was added to the sample solution to complex the metal ion weakly and avoid any precipitation. The results show that the following seven metal ions studied are completely retained on the resin at all pH values between 1.0 and 10.0: bismuth(III), cobalt(II), copper(II), lead(II), mercury(II), thallium(I), and tin(II). The other eight metal ions studied are completely retained at some (but not all) pH values between 3.0 and 10.0, as shown by Table II. .

Selectivity can be achieved through the use of auxiliary complexing agents (masking agents) as well as through pH adjustment. The retentions of metal dithiocarbamates on XAD-4 with EDTA and cyanide as masking agents are shown in Tables III and IV, respectively. The results obtained with NaHEDC are similar to those obtained by Bode for the solvent extraction into carbon tetrachloride of metals complexed with NaDDC (*32*). For multielement analyses a solution pH between 6.0 and 7.0 should be chosen, as this will result in the largest number of metals being complexed by NaHEDC and sorbing onto the XAD-4 resin. Greater selectivity can be achieved by choosing a lower or higher pH or by adding one of the masking agents studied.

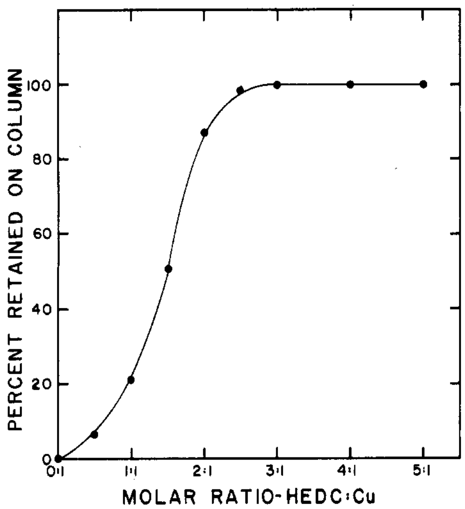

Figure 3. Retention of copper(II) on XAD-4 resin with increasing molar ratios of HEDC.

Table V. Absolute Analytical Blanks

element	blank, ng[a] untreated NaHEDC	blank, ng[a] XAD-4 treated NaHEDC
Cd(II)	1.1 ± 0.2	<0.1
Co(II)	<1	<1
Cu(II)	36 ± 7	3 ± 1
Fe(III)	50 ± 8	5 ± 2
Hg(II)	<0.1	<0.1
Ni(II)	5 ± 2	<2
Pb(II)	6 ± 4	<1
Zn(II)	25 ± 6	3 ± 2

[a] Mean and standard deviation for six determinations.

The effect of increasing NaHEDC concentration on the retention of copper(II) on XAD-4 is shown in Figure 3. While the stoichiometric ratio of HEDC to copper in the complex is 2:1, there was no quantitative retention of the copper(II) on the resin until a 3:1 ratio was used. This is apparently due to the dissociation of the complex at low HEDC concentrations. These results indicate that at least a 50% M excess of HEDC should be added to samples to ensure complete complexation and sorption of metals ions on the resin.

Two analytical blanks were determined for the concentration procedure. The first set was determined by using an unpurified 0.25 M NaHEDC solution. The second set was determined by using the same NaHEDC solution after it had been purified by passage through the XAD-4 resin column. The results are shown in Table V. Blank values are significantly lower for the purified NaHEDC solution, indicating that the XAD-4 treatment is effective in removing metal ion impurities from the reagent.

The concentration of trace metal ions from seawater using dithiocarbamates as extractants has been the subject of a number of studies (*33, 34*). The alkali and alkaline-earth elements which are present in seawater are not complexed by NaHEDC and thus are not retained on the XAD-4 resin column. These elements can be washed through the column prior to elution of the adsorbed metals. Recovery data for the concentration of eight trace metals from spiked artificial seawater are summarized in Table VI. A concentration factor of 100 was achieved for this analysis. Higher concentration factors could easily be achieved by increasing the sample size.

Table VI. Concentration of Metal Ions from Seawater

element	μg/L added	μg/L found[a]	recovery, %
Cd(II)	6.5	6.3 ± 0.3	97 ± 5
Co(II)	40	39.6 ± 1.6	99 ± 4
Cu(II)	25	24.9 ± 0.9	100 ± 4
Fe(III)	40	41.0 ± 3.0	103 ± 7
Hg(II)	1.75	1.72 ± 0.11	98 ± 6
Ni(II)	40	39.0 ± 2.1	97 ± 5
Pb(II)	60	63.0 ± 3.0	105 ± 5
Zn(II)	40	41.7 ± 1.5	104 ± 4

[a] Mean and standard deviation for four determinations.

Table VII. Separation of Metal Ions from 0.10 M Uranium(VI)

element	added, μg/L	found,[a] μg/L	recovery, %
Cd(II)	13	13.6 ± 0.8	105 ± 6
Co(II)	80	80.4 ± 4.0	101 ± 6
Cu(II)	50	50.7 ± 1.2	101 ± 2
Hg(II)	3.5	3.48 ± 0.13	99 ± 4
Ni(II)	80	77.3 ± 3.8	97 ± 5
Pg(II)	120	125 ± 6	104 ± 5
Zn(II)	40	38.9 ± 2.7	97 ± 7

[a] Mean and standard deviation for four determinations.

The direct analysis of trace metals in uranium by atomic spectroscopy is often difficult due to interferences from the large number of uranium spectral lines. A separation of the uranium matrix from the trace metals is normally required prior to the analysis step. The uranium(VI)/HEDC complex can be effectively masked at pH 7.0 by the addition of sodium bicarbonate (*24*). The uranium(VI)/carbonate complex is not adsorbed by the resin and can be washed through the column while the trace metals complexed by NaHEDC are adsorbed. Results of the separation and concentration of seven trace metals from a spiked 0.10 M uranium(VI) solution are shown in Table VII. The column eluate was analyzed for uranium(VI) to determine the effectiveness of the bicarbonate masking in separating it from the trace metals. The original sample contained 2.380 mg of uranium(VI) and the eluate contained 0.021 mg of uranium(VI). This is equivalent to a decontamination factor of approximately 113 000.

The NaHEDC adsorption method has several advantages over previously proposed multielement concentration methods. High concentration factors (100+), high sample throughput (50 mL/min), formation of soluble metal complexes, and easy elution of adsorbed metals are among the advantages of the method.

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Registry No. NaHEDC, 2801-04-9; XAD-4, 37380-42-0; H_2O, 7732-18-5; Cd, 7440-43-9; Co, 7440-48-4; Cu, 7440-50-8; Hg, 7439-97-6; Ni, 7440-02-0; Pb, 7439-92-1; Zn, 7440-66-6; Fe, 7439-89-6; Ag, 7440-22-4; Bi, 7440-69-9; U, 7440-61-1.

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Influence of the Time of Acidification after Sample Collection on the Preservation of Drinking Water for Lead Determination

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It has been suggested that to obtain accurate data for trace metal analysis of drinking water, immediate acidification at the time of collection is necessary. However, because of problems encountered by EPA in field operations and epidemiology studies, further investigation into this requirement was pursued. Drinking water samples containing known concentrations of lead were acidified at different time intervals after collection. The water samples were then stored at room temperature for varying time intervals before being analyzed for lead. For each time period there were seven samples with three aliquots from each taken for analysis in duplicate by flameless atomic absorption spectrophotometry (AAS). All acidified samples that were spiked with lead gave a higher lead value than the unacidified samples having comparable lead concentrations. Lead recovery varied among the time periods studied: however, the results indicated that acidification of water samples after collection could be delayed up to 14 days without any adverse effect on lead concentration data. This would allow acidification after samples are received in the laboratory and thus facilitate field studies.

Issaq and Zielinski (*1*), by use of flameless atomic absorption, reported on the need for immediate preservation of water samples after collection by comparing the loss of lead from aqueous solutions stored in glass or polyethylene containers. However, no data were reported on the lead concentration variability in those samples preserved immediately or at some other time interval after collection.

During some epidemiological studies investigating the health effects resulting from exposure to certain trace elements in drinking water, problems were encountered in complying with prescribed provisions for collection, preservation, and storage of drinking water samples (*2*). The recommeded U.S. Environmental Protection Agency procedure is that water samples collected for trace metal analysis should be acidified to pH <2 with HNO_3 at the time of collection or refrigerated for immediate shipment to the laboratory followed by acidification immediately upon arrival at the laboratory (*2*). Several factors have rendered these requirements of sample collection and preservation nearly unattainable in most population exposure studies which require a large number of samples; first, these studies require volunteer sample collection in homes by the general populace who are not familiar with the safety precautions necessary in handling the acid used in sample preservation; second, there are difficulties in meeting the U.S. Department of Transportation's regulation on the shipment of acid (corrosive material) because a vial of acid would have to be sent to each participant in the study; finally, it is impractical to arrange for the refrigeration of individual nonacidified samples before being sent to the laboratory for acidification and analyses.

Because of the acid handling problem associated with the sample collection, Guest and Blutstein (*3*) attempted to establish a different approach to adding acid preservative to water samples collected in the field. They inserted a sealed glass ampule containing acid into the sample collection bottle with the ampule being broken by shaking just prior to sample collection. This procedure did not take into consideration either the difficulty of transporting and shipping of the individual containers which are prone to breakage and/or contamination problems.

Sharrett et al. (*4*) reported on the methodology variations of lead analysis in drinking water but did not report on the effects of the sample and container interaction before acidification.

This research aims at improving the reliability of trace metals analysis in water samples which is needed to estimate human exposures to trace elements in toxicological and epidemiological studies and for regulatory purposes. Uncertainties of the time of acidification after collection of water samples have raised questions about the accuracy of their trace metal concentrations. Therefore, this study was designed to determine if preservation of water samples (by acid addition)