we are searching for acceptor systems which are still more favorable than biacetyl, in order to extend the application potential for sensitized RTPL.

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Dibenzylammonium and Sodium Dibenzyldithiocarbamates as Precipitants for Preconcentration of Trace Elements in Water for Analysis by Energy Dispersive X-ray Fluorescence

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Precipitation with combined dibenzylammonium dibenzyldithiocarbamate and sodium dibenzyldithiocarbamate at pH 5.0 can be used to separate 22 trace elements from water. Membrane filtration of the precipitate yielded a thin sample, suitable for analysis by energy dispersive X-ray fluorescence spectrometry. Alkalis, alkaline earths, lanthanides, and halides were not precipitated, permitting a clean separation of trace elements from the macro constituents of drinking water and drinking water supplies. Methods are given for preparation of reagents of higher purity than previously described.

Until the environmental effects of trace elements in water are more fully established, analytical chemists need to perform analyses at the lowest attainable detection limits. The proposed Water Quality Criteria (*1*) for protecting freshwater aquatic life set concentration limits for some elements that are below the capability of conventional analytical techniques without preconcentration of the water sample. Furthermore, energy dispersive X-ray spectrometry (EDXS) is a promising multielement analytical technique that cannot be applied to the trace elements of water without preconcentration and transformation to a solid film. This paper describes the use of salts of dibenzyldithiocarbamate as precipitants, a method first suggested by Linder et al. (*2*) in 1978, for 22 elements found in water and their subsequent determination by EDXS. The role of precipitation techniques in EDXS has been discussed in a recent review article on preconcentration methods by Leyden and Wegscheider (*3*).

EXPERIMENTAL SECTION

Apparatus and Operating Conditions. EDXS analysis was performed with an Ortec, Inc., tube-excited fluorescence analyzer (TEFA). Two X-ray irradiation conditions were used to assure the determination of all precipitated elements. A molydenum target tube equipped with a molybdenum filter operated at 200 μA and 35 kV was used in procedure 1, where a tungsten target tube with a terbium filter operated at 200 μA and 50 kV was used in procedure 2. The counting time range was 800-1000 live-time seconds. The detector was lithium-drifted silicon with a 12.5 mm^2 active area. The resolution was 165 eV at full width half-maximum at 10 μs shaping time and 1000 counts/s on the 5.9 keV manganese Kα peak (^{55}Fe source). The window was 0.088 mm thick beryllium.

Filtrations were made by using water aspiration to provide vacuum. The filters were 25 mm diameter, 0.4 μm porosity Nuclepore polycarbonate membranes. The polycarbonate filter rested on a 0.45 μm porosity Metricel filter. This arrangement produced an even distribution of the precipitate on the polycarbonate filter, eliminated the grid effect of the filter support, but did not increase the time needed for filtration. To minimize background, we mounted the filter with the residue on ultrathin polyester film so that only the film and filter were subject to X-ray irradiation.

Reagents. Dibenzylammonium dibenzyldithiocarbamate (DDDC) and sodium dibenzyldithiocarbamate (NaDDC) are not available commercially but are readily prepared in the laboratory. The preparation procedure for DDDC as described by Linder et al. (*2*) and Haase and R. Wolfenstein (*4*) was modified for this work. The following amended method gives a much better yield and a product of greater purity in a shorter preparation time.

Dissolve 42 mL of dibenzylamine (bp 176 °C, 12 mm) in 50 mL of reagent-grade anhydrous diethyl ether in a 250-mL beaker. Cool below 5 °C. With stirring, add a solution of 6 mL of reagent-grade carbon disulfide in 15 mL of diethyl ether. The solution must be added slowly so that the temperature does not rise above 5 °C. Continue stirring, allowing evaporation to occur, and maintain temperature below 5 °C. In 1-2 h crystallization will start. Keep stirring to keep the crystals small and to prevent caking. When crystallization ceases, filter and wash several times with diethyl ether. Dry under vacuum. The 70% yield of crystals are faintly yellow and have an 83-84 °C melting point.

To prepare NaDDC, dissolve 38 mL of dibenzylamine in 50 mL of reagent-grade acetone in a 250-mL beaker. Cool below 10 °C. Slowly add, with constant stirring, a solution of 12 mL of carbon disulfide in 13 mL of acetone. Do not let the temperature rise above 10 °C. Dissolve 4.4 g of reagent grade sodium hydroxide in 20 mL of water. Cool below 5 °C. Add the sodium hydroxide solution slowly to the acetone solution, keeping the temperature below 10 °C, and stir for 15 min. Evaporate the acetone and water under vacuum. After 30-40 mL have been removed, add 50 mL of anhydrous diethyl ether. Continue evaporation under vacuum until 40-50 mL of liquid has been removed. Repeat the ether evaporation step at least three more times. This will assure the removal of the water and acetone. Crystallization will begin during

Table I. X-ray Intensities of Precipitated Elements as a Function of pH of Precipitation

element	concn, μg/500 mL	counts/s at pH 2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
As	100	597	634	639	650	660	656	625	611		322	204	91
Ga	100	502	546	531	581	537	534	510	502	515		514	414
Mn	98	23	123	158	161	163	179	172	170	183	168	174	175
Mo	100	240	243	244	239	251	283	264	214	20	1	0	0
Sn	101.9	284	281	269	303	287	291	288	294	293	301	187	34
Th	92.46	18	78	175	153	83	64	14	19	21	29	20	13
Tl	135.1	240	333	386	365	405	397	400	397	407	401	413	405
W	80.44	514	491	460	447	327	26	8	23	7	0	0	0
Zn	101	397	446	500	507	521	519	492	499		508	519	514

one of the evaporation steps. Repeat the ether evaporation step at least twice after crystallization has started. Filter and wash several times with diethyl ether. If the filtrate and wash liquid are further evaporated, a second crop of crystals will form. A 50% yield of snow white crystals with a melting point of 238–239 °C will be obtained.

Both DDDC and NaDDC are soluble in methanol, forming colorless solutions. Reagent concentrations used were as follows: DDDC, 1.0 g/100 mL; NaDDC, 0.62 g/100 mL of methanol; DDDC–NaDDC mixture, 1.0 g and 0.62 g/100 mL of methanol, respectively; ascorbic acid, 5 g/100 mL of water; sodium thiosulfate, 0.7 g/100 mL of water; potassium iodide, 4 g/100 mL of water. Bulk chemicals used were all ACS, reagent grade. Hydrochloric acid was reagent grade redistilled at the constant boiling point. Elemental standard solutions were commercially obtained and diluted for subsequent use. The solutions of DDDC, NaDDC, ascorbic acid, and sodium thiosulfate were prepared just before use. Only glass-distilled water was used.

Procedures. The procedures given herein are based on 500 mL of sample. For more concentrated samples the volume may be reduced as needed to avoid excessive X-ray absorption by the filtered specimen.

Reduction and Precipitation. Add 25 mL of the redistilled hydrochloric acid (to reduce the pH below 1) and 5 mL of potassium iodide to the sample in a 1-L beaker and heat to boiling. Add 2.0 mL of ascorbic acid solution and 1.0 mL of sodium thiosulfate solution and continue boiling for 15 min. Add 2.0 mL of ascorbic acid, boil for 15 min, and remove from heat. Add 1.0 mL each of ascorbic acid and sodium thiosulfate. Cool below 40 °C. Neutralize with ammonium hydroxide to just below the desired pH. Cool to room temperature. Slowly add, with constant stirring, 10 mL of precipitant. Adjust the pH to the desired level. Allow the precipitate to age for 40 min before filtering.

Experiments involving pH were conducted from pH 2.5 to 8.0 at 0.5 pH intervals. Each experiment included up to three elements, at approximately 100 μg/L, chosen so that the fluorescence X-rays would not overlap. Concentration data were obtained over the concentration range of approximately 10–600 μg/L. Again, up to three noninterfering elements were used in each experiment at different concentrations such that the total filter loading did not exceed 550 μg of test elements. All precipitations in the calibration series were made at pH 5.0.

RESULTS AND DISCUSSION

Reagents. The reagent DDDC, prepared according to the Linder et al. (*2*) and Haase and Wolfenstein (*4*), crystallized with difficulty and varied in color and melting point. The original procedure specified a 70 °C temperature for the reaction between dibenzylamine and carbon disulfide. Reducing this temperature to 5 °C results in a high quality product, easily produced, with a melting point about 2 °C above the published value.

The reagent NaDDC was prepared by using equal molar amounts of dibenzylamine and carbon disulfide, followed by an equal molar amount of sodium hydroxide (*5*). If the reaction was carried out at ambient temperature, the product had a yellow color. If the temperature was maintained below 10 °C, a snow white product was made with a melting point 2 °C higher than published.

DDDC must be protected from air oxidation. After standing in an open vessel in a desiccator, the product changed color with time, an indication of decomposition.

Precipitation reagents prepared by the previously published procedures (*2*, *4*) gave unpredictable precipitation results. Manganese was not precipitated significantly, and the precipitation of bismuth and mercury was markedly dependent on pH. The superiority of the reagents prepared as described here was indicated by the higher, more reproducible X-ray intensities observed for the same elements, by the quantitative precipitation of manganese, and by the pH independence of the determination of bismuth and mercury.

Elements Studied. Particular attention was given to evaluating the procedure with respect to the toxic elements included in the Environmental Protection Agency's priority pollutant list (*1*). Elements below argon in the periodic table have low-energy fluorescence X-rays and were not included in the study. Elements in groups 1A, 2A, 3B, and 7A were not precipitated and were removed by washing from any precipitate formed. Of the 13 elements of the priority list, only beryllium and chromium could not be determined (beryllium could not be detected and chromium was not precipitated). The precipitation of arsenic, thallium, and zinc was pH dependent, whereas the precipitation of the remaining eight elements (antimony, cadmium, copper, lead, mercury, nickel, selenium, and silver) was independent of pH in the range studied. Because arsenic was precipitated only in the +3 valence state by either DDDC or by NaDDC, a chemical reduction process was employed in the analytical procedure. Reagents were added at intervals to maintain the reducing medium and to compensate for the decomposition and oxidation of the ascorbic acid enhanced by the catalytic action of some metallic ions such as copper (*6*).

Several other elements were tested at the 1000 μg/L level by including either manganese, iron, nickel, or zinc as a carrier and chosen to have noninterfering spectra. A few elements (In, Nd, La, Ta, and Yb) may be candidates for inclusion in the procedure. Even at a concentration of 1000 μg/L the following elements gave very low response, such response probably due to occlusion with the carrier precipitate: Ce, Cr, Dy, Eu, Ge, Hf, Nb, Re, Rh, Sc, Sm, Tb, Ti, and Zr. Other elements, not mentioned or referred to, were not tested.

Effect of pH. Linder et al. (*2*) indicated that from pH 2 to 5, there was no effect on six elements, Cu, Fe, Ni, Pb, Se, and Zn. This study was extended to the 24 elements found to respond to the precipitants. The pH range studied was 2.5–8.0. The precipitant was an equimolar solution including both DDDC and NaDDC. Nine elements responded variously to pH changes (see Table I). The other 15 elements were not affected. Data are presented only for the dominant fluorescence energy peak for each element.

From these data a recommended procedure could be derived. Similar data were obtained for the same elements using each precipitant, DDDC or NaDDC, alone. The dual precipitants broadened the plateau somewhat for the elements

Table II. X-ray Intensities of Precipitated Elements pH Independent

element	concn, μg/L	mean I,[a] counts/s	std dev
Ag	196	278.1	13.0
Au	199.2	266.9	10.9
Bi	200	309.1	2.3
Cd	200	313.3	7.2
Co	197.8	283.1	6.6
Cu	198.2	332.0	11.5
Fe	200	224.9	10.3
Hg	200	264.5	14.2
Ni	198.8	361.2	14.9
Pb	200	305.6	9.7
Sb	200	216.8	7.4
Se	200	494.8	54.1
Te	159.9	142.2	4.4
U	160.06	269.6	10.6
V	201	108.2	7.6

[a] $n = 12$.

affected by pH and gave a smaller standard deviation from the mean for those elements unaffected by pH.

At pH 3.5 and 4.0 an undesirable side effect was encountered frequently which was due to the development of a flocculent precipitate. The residue on the filter paper was not homogeneous, and, frequently, a thick rim formed around the edge of the filter. This caused anomalies in the precipitation curves.

The elements Th and W had no pH precipitation plateau. When these elements were precipitated with other elements, the quantity of precipitate changed, but the shape of the curves did not. This indicated coprecipitation with the other elements acting as carriers.

A pH of 5.0 was chosen as a general procedure. This choice eliminated W and Th from the analysis but gave a greater confidence in the determinations of the other 22 elements. A semiquantitative procedure for Th and W could be made at pH 3.5.

Statistics. Table II gives statistical values for those elements that show no pH effect. These data were taken from the results of the pH evaluation, and included in the statistics are the values obtained at pH 3.5 and 4.0. In each case 500 mL of solution was used.

The range of counting error was determined by counting single samples with multiple elements 10 times each using both counting procedures. Individual peak energies ranged from 2.3 to 26.1 keV. Peak intensities (counted fluorescent events per second) ranged from 0.5 to 127 counts/s. Standard deviations from mean intensities never exceeded 4%.

Reagent contribution to error was limited to iron, nickel, copper, zinc, and lead. Mean intensities of these sources ranged from 0.6 to 7.3 counts/s ($n = 6$), with iron and zinc being the main impurities. Lead made the lowest contribution. Standard deviations from the mean ranged from 0.9 for lead to 2.1 for nickel.

The filter contribution to error was very small, less than 2% of the reagent contribution, except for bromine. The mean bromine error was 11.8 counts/s ($n = 9$) with a standard deviation of 0.3. This error varies with manufacturers lot number of the filters.

Table II shows relative standard deviation from mean intensities ($n = 12$) ranging from 0.7% to 5.8% except for selenium, 11%. The filter bromine seriously affected the Kα peak of selenium because of peak overlap.

The linear regression coefficients of intensity on micrograms of element ranged from a low for vanadium of 0.866 to a high for 6.666 for arsenic, with the majority being between 2 and 4. The deviation from regression range was 7.1 for antimony to 36.1 for selenium. The concentration range varied from about 10 μg/L to 600 μg/L, with 500 mL of solution being used. The limit of detection, determined as three times the standard deviation from the regression (7), varied from 10 to 50 μg/L.

CONCLUSION

A preconcentration and analysis procedure has been described for determining commonly occurring trace elements in water while completely separating them from the macro elements also present. The amended methods of preparation of the two precipitants give better quality products than the methods previously published.

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