Concentration of Trace Metals by Solvent Extraction and Their Determination by Atomic Absorption Spectrophotometry

Sham L. Sachdev and Philip W. West

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803

■ A simple solvent extraction procedure for concentrating trace metals for subsequent determination by atomic absorption spectrophotometry is described for aluminum, beryllium, cadmium, cobalt, copper, iron, lead, nickel, silver, and zinc. Different kinds of organic solvents were examined. A solution of diphenylthiocarbazone, 8-quinolinol, and acetyl acetone in ethyl propionate has been found to be useful. Interference effects of thirty-four diverse ions and compounds were studied and the procedure developed is highly selective. With the exception of aluminum, all of the metals can be determined when present at the low parts per billion level in an aqueous solution. Sensitivity for aluminum is 0.1 μg. per ml. The procedure is well suited for environmental studies and is significant because it includes the majority of the inorganic carcinogens.

Solvent extraction techniques have proved to be very useful for preconcentration of traces of metal ions to the levels where they can be easily and accurately determined by atomic absorption (Mansell and Emmel, 1965; Mulford, 1966; Sachdev, Robinson, *et al.*, 1967; Slavin, 1964; West, West, *et al.*, 1967). Various complexing agents such as diphenylthiocarbazone(dithizone), dithiocarbamate, cupferron, and 8-quinolinol(oxine), can be used for the extraction of a large variety of metal ions. Conditions for extractions into solvents such as chloroform or carbon tetrachloride have already been reported (Morrison, 1957; Sandell, 1959), but chlorinated solvents are undesirable for atomic absorption methods because of the use of flame for atomization. Recently, the extraction of silver into ethyl propionate containing dithizone was reported (West, West, *et al.*, 1967). The silver–dithizone complex was found to be stable in ethyl propionate for several days. These studies have since been extended and conditions for the simultaneous extraction and spectroscopy of seven important metal ions have been reported (Sachdev and West, 1969).

The present paper describes conditions for the extraction of various metal ions into an 8-quinolinol–ethyl propionate solution. By combining dithizonate, oxinate, and acetyl acetonate extractions into ethyl propionate, as many as ten different metal ions (Ag^{+}, Al^{3+}, Be^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}) can be concentrated by a single extraction step. The conditions for such an extraction are described together with pertinent information on the atomic absorption spectroscopy of the metal extract system.

Experimental

Apparatus. Atomic absorption spectrophotometer (Perkin-Elmer Model 303), HETCO burner with triflame burner head (Jarrel Ash Co.), gas flow meter (Hokes Model 993), hollow cathode lamps for the metals to be determined and a pH meter (Leeds and Northrup).

Reagents. Diphenylthiocarbazone (Eastman Kodak), 8-quinolinol, ethyl propionate, acetyl acetone, ammonium tartrate, and tartaric acid. All reagents used were analytical grade. Standard solutions for metal ions were prepared by dissolving appropriate amounts of pure metal into minimum quantity of nitric acid and then diluting to a known volume using double distilled water.

Extraction Solutions. Diphenylthiocarbazone, 0.1 g.; 8-quinolinol, 0.75 g.; and acetyl acetone, 20 ml. were dissolved in ethyl propionate and the volume was made up to 100 ml.

Choice of Solvents. Solvents such as *n*-butyl ether, methyl isobutyl ketone, methyl isopropyl ketone, ethyl propionate, and isoamyl acetate were examined for their suitability for the extraction of metal complexes, for the stability of the extracted species, and for their combustion characteristics for atomic absorption spectroscopy. The extractability of metal complexes was poor in *n*-butyl ether. Ketones such as methyl isopropyl ketone and methyl isobutyl ketone showed good extractability, but the complexes of dithizone are not stable in such solvents. Both of the esters, ethyl propionate and isoamyl acetate were found to be useful because the metal–dithizone and metal–oxine complexes are easily extracted into these solvents and remain stable for many days. Although the solubility of isoamyl acetate in water is much less than ethyl propionate, the latter provides better spectroscopic sensitivity for the various metals involved.

Procedure for Extraction. An appropriate volume of aqueous solution was conditioned using 10 ml. of 1 *M* ammonium tartrate per 100 ml. of the sample and the pH adjusted to 6 ± 0.5 using ammonium hydroxide or tartaric acid solution. The solution was then transferred to a separatory funnel, shaken briskly for a minute with an extractant solution, and the two layers were then allowed to separate. The organic extract was then isolated and transferred into a small glass stoppered bottle for subsequent spectroscopic examination.

Effect of pH. The effect of pH on the extraction of metal ions by ethyl propionate containing 8-quinolinol was studied and the results are shown in Table I. The results indicate that Al^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, and Ni^{2+} can be easily and effectively extracted. By adding diphenylthiocarbazone and acetyl acetone to the above systems, more than ten species of metal ions can be extracted. The presence of more than one kind of

Table I. Effect of pH on the Extraction of Metal Ions by 8-Quinolinol in Ethyl Propionate

pH	Al^{3+} 25 μg./ml.[a]	Be^{2+} 0.5 μg./ml.[a]	Cd^{2+} 0.5 μg./ml.[a]	Co^{2+} 5.0 μg./ml.[a]	Cu^{2+} 5.0 μg./ml.[a]	Fe^{3+} 5.0 μg./ml.[a]	Ni^{2+} 5.0 μg./ml.[a]	Zn^{2+} 0.5 μg./ml.[a]
1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3.0	0.0	0.0	0.0	0.0	17.5	3.0	0.0	0.0
4.0	7.0	0.0	0.0	20.0	36.0	42.0	30.0	5.0
5.0	17.5	0.5	0.0	30.0	40.0	42.6	33.0	12.4
6.0	17.4	1.0	3.0	30.0	25.0	42.6	33.5	16.0
7.0	15.6	7.0	7.0	30.0	22.5	42.0	33.0	2.6
8.0	13.5	7.0	3.0	28.0	6.5	40.5	22.2	5.0
9.0	...	15.0	0.0	18.0	5.0	41.5	5.0	6.5

[a] Percentage absorption for metals at their respective absorption wavelengths.

Table II. Effect of pH on the Extraction of Metal Ions by Extractant Solution[a]

(Concentrations of metal ions are in terms of their aqueous solutions before extraction)

pH	Ag^{+} 0.05 μg./ml.[b]	Al^{3+} 2.0 μg./ml.[b]	Be^{2+} 0.05 μg./ml.[b]	Cd^{2+} 0.05 μg./ml.[b]	Co^{2+} 0.05 μg./ml.[b]	Cu^{2+} 0.05 μg./ml.[b]	Fe^{3+} 0.1 μg./ml.[b]	Ni^{2+} 0.05 μg./ml.[b]	Pb^{2+} 0.1 μg./ml.[b]	Zn^{2+} 0.05 μg./ml.[b]
1.0	5.9	0.0	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0
2.0	6.0	0.0	3.2	8.6	0.0	9.0	2.2	0.0	0.0	3.0
3.0	6.6	2.0	15.4	11.2	0.0	9.0	5.0	2.2	3.5	21.0
4.0	6.6	8.0	18.0	11.5	5.6	9.0	6.0	6.2	6.9	32.4
5.0	6.6	15.9	25.0	11.6	6.2	9.0	14.2	6.5	9.3	32.8
6.0	6.6	15.9	25.0	11.6	6.2	9.0	14.2	6.5	9.6	33.0
7.0	6.5	14.8	22.7	11.6	6.2	9.0	14.2	6.5	9.7	33.0
8.0	5.6	13.8	19.8	11.6	6.2	8.9	14.2	6.5	9.6	31.5

[a] Composition of extractant solution is described along with the reagents on page 749.
[b] Percentage absorption for metals at their respective absorption wavelengths.

ligand has been reported to enhance the extraction (Freiser, 1968) and may provide a broader range of pH for optimum extraction efficiency in many cases. Thus, pH conditions were studied using a mixture of diphenylthiocarbazone, 8-quinolinol, and acetyl acetone in ethyl propionate. The results, as given in Table II, show that all metals ions studied can be extracted between pH 5 to 7. Any change of pH within this range has no significant effect on the extraction.

Stability of Metal Complexes. Although the solvent and the complexing organic molecules are completely destroyed in the flame, their stability is a very important factor controlling the efficiency of production of metal atoms in the flame and enhances the sensitivity and reproducibility of the procedure. The metal ions were extracted into the extractant solution and the absorption of each of the metal ions was measured at its respective wavelength. The extract was stored in a glass-stoppered bottle and after every 4 days, the absorption readings were compared with those of a fresh extract under identical conditions. The absorption readings for each of the metals were found to remain essentially constant over a 20-day period, indicating that the extract remains stable and can be stored for at least 2 to 3 weeks.

Optimum Flame Conditions for the Determination. The rate of aspiration, composition of the flame, and the position of the burner are the three important parameters in the spectroscopy of the respective metals. The rate of aspiration of about 3 ml. per minute provides the optimum sensitivity. This rate can be easily achieved by connecting a polyethylene capillary tube of 0.015-in. i.d. and 2.5 in. length to the capillary of the burner. Slight variation in the length of capillary may be required depending upon the burner used. The position of the burner should be adjusted so that the light beam passes through the flame about a centimeter above its base. The optimum flame conditions, spectral slit width, lamp current, and appropriate wavelengths for the absorption lines are shown in Table III.

Interference Study

Method for Testing Interference. Interference effects of various ions were studied by the following procedure. A stock solution was prepared containing 0.05 μg. per ml. each of beryllium, cadmium, copper, silver, and zinc; 0.1 μg. per ml. of cobalt, iron, and nickel; 0.2 μg. per ml. of lead; and 1 μg. per ml. of aluminum. A 100-ml. portion of this mixture was extracted with 10 ml. of the extractant solution to provide reference values and to confirm the mutual extractability of each ion from the complex mixture. A similar solution containing all of these metal ions together with interfering ions (one at a time), as listed in Table IV, was extracted in the same manner as described above. All of the ions listed in Table IV were added at 100 μg. per ml. level except for VO_3^-, Sn^{4+}, Bi^{3+}, Cr^{3+} Si^{2-}, and TeO_3^{2-} which were added at the 10 μg. per ml. level.

Results of Interference Studies. Most of the ions listed in Table IV had no effect on the determinations. The presence of 100 μg./ml. of HPO_4^{2-}, $HAsO_4^{2-}$, and MoO_4^{2-} lowered absorption readings for lead by 50%. A lower concentration of 10 μg./ml. of these ions, which is still 50 times more than Pb^{2+} concentration, had no significant effects. As would be expected, large concentrations of halides lowered the absorption for Ag^+; but, 100 μg./ml. of Cl^-, 10 μg./ml. Br^-, and 10 μg./ml. I^- can be easily tolerated. Fluoride forms strong complexes with Al^{3+} and Be^{2+}. A fluoride concentration of 1 μg./ml. had a negligible effect on beryllium determination, but only free (uncomplexed) aluminum can be determined by this procedure.

Table III. Optimum Conditions for the Determinations and the Range for Linear Calibration Curves

Metal	Wavelength (Å)	Spectral slit width (Å)	Lamp current (mA)	Acetylene flow[a]	Sensitivity[b] μg./ml. for 1% absorption	Range for linear calibration curves μg./ml.
Air–acetylene flame air flow[a] = 10 or air pressure = 35 p.s.i.						
Ag^{+}	3281	2.0	12	2.2	0.002	0.0–0.25
Cd^{2+}	2288	6.5	8	2.5	0.001	0.0–0.10
Co^{2+}	2407	2.0	20	2.0	0.004	0.0–0.20
Cu^{2+}	3247.5	2.0	10	2.0	0.002	0.0–0.25
Fe^{3+}	2483.3	2.0	12	2.5	0.004	0.0–0.40
Ni^{2+}	2320	2.0	14	2.5	0.004	0.0–0.30
Pb^{2+}	2170	6.5	30	2.0	0.005	0.0–0.60
Zn^{2+}	2138	2.0	15	2.0	0.001	0.0–0.10
Nitrous oxide–acetylene flame, N_2O flow[a] = 10, N_2O pressure = 35 p.s.i.						
Be^{2+}	2348.6	2.0	20	21	0.002	0.0–0.10
Al^{3+}	3092.7	2.0	15	21	0.100	0.0–10.0

[a] Flow units are arbitrary scale units on Hokes flowmeter model 993. [b] Sensitivity is given for aqueous solution using 10× concentration.

Table IV. Interference Study

Group I	Li^{+}, Na^{+}, K^{+}
Group II	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}
Group III	BO^{2-}, $B_4O_7^{2-}$, Ce^{3+}
Group IV	CO_3^{2-}, Sn^{4+}, SiO_3^{2-}
Group V	NH^{4+}, NO_3^{-}, HPO_4^{2-}, Sb^{5+}, $HAsO_4^{2-}$, VO^{3-}, Bi^{3+}
Group VI	SeO_3^{2-}, $Cr_2O_7^{2-}$, Cr^{3+}, TeO_3^{2-}
Group VII	F^{-}, Cl^{-}, Br^{-}, I^{-}, Mn^{2+}
Miscellaneous:	oxalic acid, citric acid, and detergents (Tide and Dreft)

Analytical Procedure

Calibration Curve. A stock solution containing 0.5 μg./ml. of each of Ag^{+}, Be^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}; 1 μg./ml. of each of Co^{2+}, Fe^{2+}, and Ni^{2+}; 2 μg./ml. of Pb^{2+}; and 20 μg./ml. of Al^{3+} was prepared. Different volumes of this solution from 5 to 50 ml. were diluted to 100 ml. To each of these 100-ml. portions of solutions, 10 ml. of 1 *M* ammonium tartrate solution were added. The pH was adjusted to 6 ± 0.5 by adding a few drops of dilute ammonium hydroxide, and the metal ions were then extracted according to the procedure described for extraction. Atomic absorption measurements were made at the optimum conditions as detailed in Table III. The range for linear calibration curve is also shown in Table III.

Determinations. Take 100 ml. of aqueous solution into a 250-ml. beaker. Add 10 ml. of 1 *M* ammonium tartrate, adjust the pH of solution to 6 ± 0.5 by adding dilute ammonium hydroxide or tartaric acid solution, whichever is necessary. In many samples, the addition of 10 ml. of ammonium tartrate–tartaric acid buffer of pH 6.0 may automatically adjust the pH of sample to about 6.0. Transfer the solution to a 150-ml. separatory funnel, and add 10 ml. of extractant solution. Shake the solution briskly for 1 min. then allow to stand (about 3–5 min.) until the two layers are separate. Drain out the aqueous layer, dry the stem of the funnel from inside with a piece of rolled up filter paper, and pour the organic phase into a glass-stoppered bottle. The organic layer should be free of any aqueous droplets. Measure the atomic absorption for each of the metal ions using the conditions as shown in Table III. The reagents used such as tartrate or 8-quinolinol may contain traces of metal salts; therefore, a blank should be carried out with each set of samples. Either the absorbance for the blank should be subtracted from that obtained for the respective metal ion or the instrument should be adjusted to read zero absorbance when the blank is being aspirated into the flame. By measuring the absorbance for the respective metals, their concentrations can be easily calculated by the use of calibration curve.

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