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The Separation of Zinc and Copper from Seawater by Adsorption Colloid Flotation*

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Summary

Procedures are described whereby zinc and copper present as cations in seawater are brought to the surface in less than 5 min by an adsorption colloid flotation process which utilizes a negatively charged ferric hydroxide collector, a cationic surfactant, dodecylamine, and air. Statistical studies on test series show a mean recovery of 94.0% with a relative standard deviation of 6.1% for zinc and a mean recovery of 95.0% with a relative standard deviation of 6.1% for copper.

INTRODUCTION

In previous papers a rapid method was described for the separation of the trace metallic anionic species, molybdate and uranyl carbonate, from seawater by a colloid flotation process (*1*, *2*). The separation in each case was followed by spectrophotometric determination. The studies showed that the degree of adsorption of ions on a colloidal surface in a seawater matrix was not apparently influenced by ionic strength, but was affected by the charge of the pH dependent collector and the solubility of the compound formed by combination of the ions collected with the lattice counterions of the collector according to the Paneth-Fajans-Hahn rule (*3*). The system used for the separation of

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the two elements consisted of a ferric hydroxide collector, which when present in seawater at a low pH is positively charged and thus able to collect molybdenum as molybdate and uranium as uranyl carbonate, an anionic surfactant sodium dodecylsulfate, and air. The air bubbles coated with the surfactant to which the trace metal enriched collector is electrostatically attracted are floated to the seawater surface as a stable froth which is easily removed. The results obtained from statistical evaluation of recovery data based on spectrophotometric determination showed that the separation was reproducible, virtually quantitative, and was complete in less than 5 min.

The work suggested strongly that colloid flotation should be capable of being extended, under the proper conditions, to the collection of trace cations in seawater by the use of a negatively charged collector, a cationic surfactant, and air. This communication is concerned with the application of the technique to soluble zinc and copper, both of which are known to exist in seawater, primarily as cations. As described below, Zn^{2+} was separated from seawater with ferric hydroxide, dodecylamine, and air and determined by atomic absorption. In a similar fashion, and using the same collector–surfactant–air system, Cu^{2+} was floated to the surface and analyzed spectrophotometrically with Zn-dibenzyldithiocarbamate.

EXPERIMENTAL

Apparatus and Equipment

A Beckman DU spectrophotometer was used for absorbance measurements. The absorbances were read in matched quartz cells of 1.0 cm path length. Atomic absorption measurements were made with a Perkin Elmer 303 atomic absorption spectrophotometer equipped with a zinc hollow cathode lamp. The pH of the solutions was determined with a Beckman Expandomatic pH meter. Millipore filters, HA-47 mm diameter, were used to filter seawater samples. The trace metal separations were carried out with the flotation unit in the manner described previously (*1*).

Reagents

All chemicals used were of analytical reagent grade. Aqueous reagents were prepared in doubly distilled deionized water.

Surfactant: dodecylamine, 0.2% in ethanol (w/v).
Collector: 0.05 *M* ferric chloride.
Sodium citrate, 10%.
Dithizone, 10 mg in 100 ml CCl_4.
0.02 *M* HCl.
4 *M* NH_3.
Concentrated $HClO_4$–HNO_3 (1:1).
Zn-dibenzyldithiocarbamate, 0.1% in CCl_4 (DBDC reagent).

A standard zinc solution was prepared by dissolving 0.2000 g of zinc metal in dilute hydrochloric acid and diluting to a liter with about 0.1 *M* HCl. Ten milliliters of this solution were diluted to 1000 ml. The final solution contains 2 μg of Zn/ml. A standard solution of copper was prepared by dissolving 0.1964 g of $CuSO_4 \cdot 5H_2O$ (99.95%) in 500 ml of 0.1 *N* HCl. Ten milliliters of this solution were diluted to 1000 ml with 0.1 *N* HCl, providing a solution containing 1 μg of Cu/ml.

Zinc

The two principal parameters, pH and volume of surfactant, which bear directly on the stability of the froth formed and efficiency of collection of zinc, were studied. The results of the pH study are given in Fig. 1. Tests with varying amounts of surfactant are summarized in Fig. 2.

Analytical Procedure

The basic working procedure utilized clear and uncontaminated near-shore seawater which was filtered prior to analysis with the Millipore

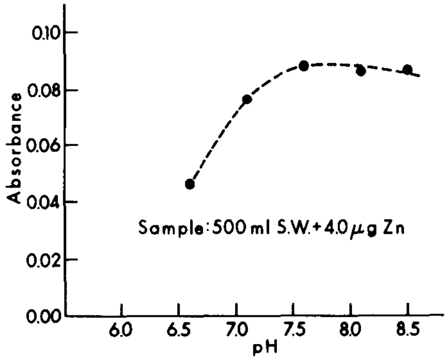

FIG. 1. Optimum pH for separation of zinc.

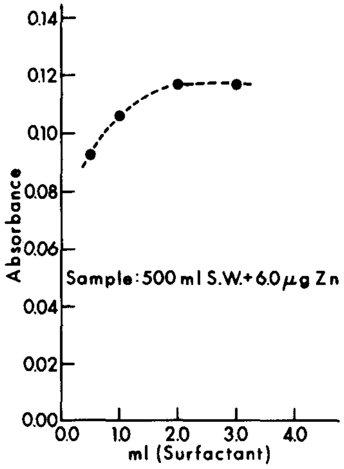

FIG. 2. Optimum volume of surfactant solution for separation of zinc.

filter. To 500 ml samples were added 0.0, 2.0, 4.0, and 6.0 μg of zinc together with 3 ml of the ferric chloride solution and the pH adjusted to 7.6 ± 0.1 (see Discussion). The sample was transferred to the flotation cell, air passed through at a rate of 10 ± 2 ml/min, and 2 ml of surfactant were injected. The froth was collected into a beaker after completing the flotation. Two and one-half milliliters of $HClO_4$–HNO_3 acid mixture were added to the separated froth and the mixture boiled until white fumes appeared. After cooling, 10–20 ml of water were added and the mixture heated until the solution became clear. Upon cooling, 5 ml of sodium citrate reagent were added and the pH of the solution adjusted to 8–9 by addition of dilute ammonia with the aid of universal indicator paper. The solution was transferred into a separatory funnel of 150 ml capacity and water added to a total volume of ca. 40 ml. Five milliliters of the dithizone reagent were added and the mixture shaken for 1 min. The bottom organic layer was removed to a vial (40 ml capacity). A second extraction with 2.5 ml of dithizone was carried out and the organic extract drained and collected into the vial. The zinc in the organic solvent was extracted into an aqueous phase by adding 25.0 ml of 0.02 *N* HCl and shaking the vial for 2 min (*4*). The vial was centrifuged in order to separate the two layers and the zinc in the aqueous phase determined by atomic absorption. It was not necessary to separate the two phases for the analysis. A working curve was constructed by measuring the absorbances of analyzed stand-

TABLE 1

Calibration and Working Curve Data for Zinc

Zn (μg)	Absorbance			Recovery (%)
	A[a]	B[b]	C[c]	
0.0	0.0000	0.0263	0.0000	
2.0	0.0320	0.0550	0.0287	90.0
4.0	0.0626	0.0870	0.0607	97.0
6.0	0.0973	0.1183	0.0920	94.5
			Mean	94.0

[a] Standard solution (analyzed without flotation).

[b] 500 ml of seawater + zinc.

[c] B − 0.0263.

ards and plotting them against concentration. The data are given in Table 1.

Recovery of Zinc

In order to evaluate the reproducibility of recovery of zinc by flotation, five replicate samples of seawater to which 6.0 μg of zinc were added were analyzed according to the above procedure. Comparison was made with the absorbances obtained from the direct analysis of replicate distilled water standard samples containing 6.0 μg of added zinc in which the coprecipitation and flotation steps were omitted. The latter absorbances were considered to represent 100% recovery of zinc present. Results are compiled in Table 2.

Copper

The optimum pH and volume of surfactant used for the separation of copper were similar to those for zinc. Studies were carried out in order to determine the optimum acidity for the extraction of copper from the acidic solution obtained following dissolution of the froth. This was done through a series of tests in which 2 μg of standard copper solution plus 3 ml of ferric chloride solution were mixed with varying volumes of 9 *M* sulfuric acid and the copper extracted with the DBDC reagent and determined by the Sandell procedure (*5*). The results are given in Table 3.

TABLE 2

Statistics for Recovery of Zinc

Sample No.	Zn[a] (μg)	Absorbance	Deviation
1	6.0	0.1161	−0.0025
2	6.0	0.1249	+0.0063
3	6.0	0.1243	+0.0057
4	6.0	0.1231	−0.0045
5	6.0	0.1085	−0.0101
	Mean	0.1186	

[a] Added to 500 ml of seawater. Standard deviation = $[d^2/(n-1)]^{1/2}$ = 0.0073. Relative standard deviation = 6.1%.

TABLE 3

The Optimum Acidity for Extraction of Copper

Sample No.	Cu (μg)	Acidity (*N*)	Absorbance[a]
1	2.0	0.50 (1.7 ml of 9 *N* H_2SO_4 in 30 ml)	0.424
2	2.0	0.75 (2.5 ml of 9 *N* H_2SO_4 in 30 ml)	0.425
3	2.0	1.00 (3.3 ml of 9 *N* H_2SO_4 in 30 ml)	0.374
4	2.0	1.25 (4.1 ml of 9 *N* H_2SO_4 in 30 ml)	0.380
5	2.0	1.50 (5.0 ml of 9 *N* H_2SO_4 in 30 ml)	0.352

[a] The reagent blank was not subtracted.

Analytical Procedure

The working procedure used in the construction of a working curve and analysis of samples were essentially similar to that for zinc. To 500 ml samples were added 0.0, 1.0, 2.0, and 3.0 μg of copper. After addition of 3 ml of ferric chloride solution the pH was adjusted to 7.6 ± 0.1 with ammonia. The sample was transferred to the flotation unit and 2 ml of surfactant injected while gas was passed through. After approximately 2–3 minutes of gas flow the froth formed was skimmed off and treated with 4 ml of the $HClO_4$–HNO_3 mixture. The solution was heated and evaporated until white fumes were given off without baking. About 20 ml of water were added and the mixture heated to dissolve all salts. The cooled solution was transferred into a separatory funnel and water added to give a total volume of 30 ml, thus providing optimum acidity for extraction. The copper was extracted with 3.0 ml of DBDC reagent, the bottom organic layer transferred to an absorption cell, and the absorbance measured at 435 nm against a reagent blank. The data for the working curve are given in Table 4.

TABLE 4

Calibration and Working Curve for Copper

Cu	Absorbance[a]			Absorbance[b]		Recovery
(μg)	H_2SO_4	HCl	$HClO_4$–HNO_3	A	B	(%)
0.0	0.000	0.000	0.000	0.000	0.034	
1.0	0.092	0.091	0.098	0.092	0.126	93.0
2.0	0.170	0.189	0.187	0.178	0.212	95.2
3.0	0.264	0.270	0.269	0.261	0.295	96.6
					Mean	95.0

[a] Standard solution (analyzed without flotation).

[b] 500 ml of seawater + copper ($HClO_4$–HNO_3 was used). A = B − 0.034.

Recovery of Copper

The reproducibility of recovery of copper by flotation was carried out by the complete analysis of five replicate seawater samples to which 3.0 μg of Cu were added and comparison with distilled water standards similar to that accorded zinc. The results are given in Table 5.

RESULTS AND DISCUSSION

Zinc

Selection of Surfactant. The surfactant should be cationic in nature in order to collect a negatively charged colloidal collector. Cationic surfactants tend to be adsorbed strongly on negatively charged solid surfaces (*6*). Cationic surfactants such as hexadecylammonium chloride and dodecyl pyridinium chloride were tested but unsatisfactory results were obtained from basic solution. This is ascribed to the fact that a

TABLE 5

Statistics for Recovery of Copper

Sample No.	Cu[a] (μg)	Absorbance[b]	Deviation
1	3.0	0.472	−0.047
2	3.0	0.519	—
3	3.0	0.569	+0.050
4	3.0	0.502	−0.017
5	3.0	0.532	+0.013
	Mean	0.519	

[a] Added to 500 ml of seawater.

[b] H_2SO_4 was used, the blank was not subtracted. Standard deviation = $[d^2/(n-1)]^{1/2}$ = 0.032. Relative standard deviation = 6.1%.

cationic amine will lose its proton in alkaline solution and hence its cationic properties as a result of the reversion to the uncharged form. The dissociation of an organic base such as an alkyl amine in water depends upon the pH:

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

$$K_A = \frac{[B]\,[H_3O^+]}{[BH^+]}$$

At low pH there should be a relatively high concentration of protonated species with the reverse situation as the pH increases. If the pK_A of the alkylamine is larger than the pH of the solution, the concentration of the protonated form should be greater than that of the basic form at that pH. According to the literature (*7*), the pK_A of dodecyl amine is 10.63 and the ratio of protonated to unprotonated species is >100:1 at pH ca. 8. Consequently, this compound should be an effective cationic surfactant in a solution of pH ca. 8. However, although the pK_A of hexadecylamine (10.61) is about the same as that of dodecylamine, experimental results showed that it is an ineffective surfactant since the foam is not stable at the basic pH employed. Since the stability of the foam or froth is very much dependent on the pH of the solution (*8*), it was necessary to select a suitable surfactant which was carried out by trial and error.

Effect of pH. The effect of pH on the recovery of zinc in seawater by flotation is shown in Fig. 1. Maximum recovery is attained at pH 7.6, and this pH was chosen for the procedure. The pH of 7.1 is reported in the literature to be the isoelectric point of ferric hydroxide in water (*9*). The isoelectric point of ferric hydroxide in an aqueous solution depends largely on the over-all composition and history of the solution (*10*). For this reason a wide range of values (6.0–8.5) has been reported (*11*). Very little is known concerning the zero point of charge of this collector in a solution of high ionic strength such as seawater. It is believed that at pH 7.6 the ferric hydroxide should possess a negative surface charge in order to account for its ability to collect cations such as zinc and copper (*12*). Below this pH the stability of the froth and recovery of the trace metal enriched ferric hydroxide diminish. At higher pH the ratio of cationic to nonionic species becomes smaller. For this reason tests were limited to the 7–9 pH range, as shown in Fig. 1.

Amount of Surfactant. Since the degree of protonation of the dodecylamine is relatively low at a high pH, a large amount of the surfactant should be employed in order to have sufficient protonated species present to adsorb the ferric hydroxide quantitatively. The results of tests with varying amounts of a 0.2% solution of dodecylamine in ethanol (w/v) on 500 ml seawater samples containing added zinc show (Fig. 2) that 2 ml of surfactant give maximum and reproducible recovery of zinc.

Recovery of Zinc. The recovery of zinc from seawater was evaluated by comparing the working curve obtained by the complete analysis of

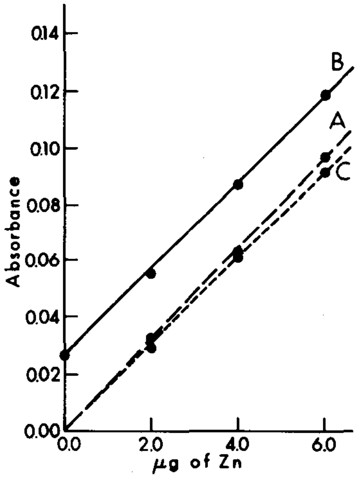

FIG. 3. Calibration and working curve for zinc.

seawater containing added zinc, including separation by flotation, with a calibration plot obtained by the analysis of zinc containing standards in which the coprecipitation and flotation steps were omitted. In both cases the plots were linear in confirmity with Beer's law. Comparison of the two slopes (Fig. 3) shows that the average recovery of zinc from the seawater for each concentration examined was 94.0%. According to the working curve the concentration of zinc in filtered seawater present as soluble Zn^{2+} was 3.2 μg/1. The concentration range of this element reported in the literature by other workers is 0.59–20 μg/1 (*13*) and consequently comparisons are not useful. It seems that the results are very much dependent on the analytical technique and source of samples. Analysis of filtered and unfiltered seawater obtained from the east coast of Oahu showed no significant difference in zinc content. The results of the reproducibility tests from the analysis of five replicate samples of seawater are compiled in Tables 1 and 2 and show a mean recovery of 94.0% and a relative standard deviation of 6.1% which includes the analytical deviation by atomic absorption spectrophotometry.

Copper

The principal experimental parameters affecting the recovery of zinc by flotation which were studied included surfactant, volume of surfactant, and optimum pH. Similar studies carried out on copper present as soluble Cu^{2+} showed that identical conditions applied equally well. As a result, 2 ml of 0.2% (w/v) dodecylamine in conjunction with 3 ml of 0.05 *M* ferric chloride at pH 7.6 ± 0.1 were adopted. In order to determine the copper in the separated and dissolved froth it was necessary to adjust the acidity and decompose completely the organic matter prior to extraction with the DBDC reagent. In the discussion of the proper acidity for extraction of copper with this reagent, Sandell recommended an acidity of about 1 *N* (*5*). The present study suggests that the optimum concentration of the H_2SO_4 required for the extraction of copper is in the 0.5–0.75 *N* range (Table 3). Three acid mixtures including H_2SO_4 tested with standards for adjustment of acidity gave essentially comparable results (Table 3). In the decomposition studies carried out on the separated froths obtained from seawater samples following flotation, unexpected difficulty arose in the extraction of the copper following decomposition with concentrated HNO_3–HCl (1:4). Only a small portion of the copper present was extracted by the use of

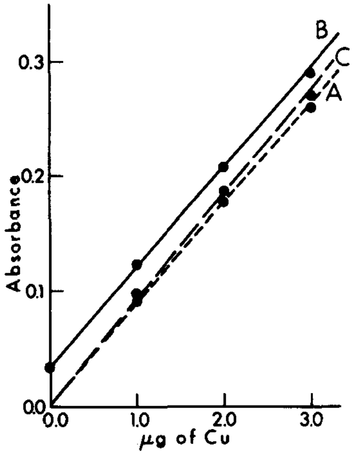

FIG. 4. Calibration and working curve for copper.

this mixture. The failure may be due to the formation of an unextractable metal–surfactant complex, the nature of which has not been established. Other decomposition experiments were carried out by treating the froth with concentrated H_2SO_4 and heating the mixture until white fumes appeared. This treatment was successful since extraction within the DBDC reagent appeared to be complete. However, an insoluble and fine precipitate was formed which was undesirable because of its carry-over into the organic solvent. The difficulty was avoided by use of the decomposition mixture of concentrated $HClO_4$–HNO_3 (1:1) which gave satisfactory and reproducible results. Consequently this mixture was selected and incorporated in the procedure. In this study the concentration of copper in seawater was found to be 0.8 μg/l and represents the soluble cationic Cu^{2+}. The value is somewhat lower than those reported by other authors. This may be explained on the basis that copper is believed to be present in seawater, in part, as organic complexes which cannot be collected by the flotation method without pretreatment of the seawater. This is supported by the observation that direct solvent extraction usually gives lower values for copper than other pretreatment methods (*14*), indicating that copper tends to form stable complexes with various organic compounds (*15*). An analysis of the linear Beer's law plots (Fig. 4) of the distilled water and seawater standards and recovery tests showed an average recovery of 95.0% with a 6.1% relative standard deviation (Tables 4 and 5).

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