Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Young S. Kim[a]; Harry Zeitlin[a]
[a] DEPAETMENT OF CHEMISTRY, HAWAII INSTITUTE OF GEOPHYSICS UNIVERSITY OF HAWAII, HAWAII

To cite this Article Kim, Young S. and Zeitlin, Harry(1971) 'A Rapid Adsorbing Colloid Flotation Method for the Separation of Molybdenum from Sea water', Separation Science and Technology, 6: 4, 505 — 513
To link to this Article: DOI: 10.1080/00372367108056035
URL: http://dx.doi.org/10.1080/00372367108056035

SEPARATION SCIENCE, 6(4), pp. 505–513, August, 1971

A Rapid Adsorbing Colloid Flotation Method for the Separation of Molybdenum from Seawater*

YOUNG S. KIM and HARRY ZEITLIN

DEPARTMENT OF CHEMISTRY AND HAWAII INSTITUTE OF GEOPHYSICS
UNIVERSITY OF HAWAII
HONOLULU, HAWAII 96822

Summary

A procedure is described whereby the molybdenum in a 500-ml seawater sample is brought to the surface in 5 min by an adsorbing colloid flotation process which utilizes iron(III) hydroxide, sodium dodecyl sulfate, and air. Statistical studies on a test series for recovery of molybdenum by means of spectrophotometric analysis show a mean recovery of 95.3% and a relative standard deviation of 2.6%.

INTRODUCTION

The separation and removal of trace constituents present in large volumes of liquid ordinarily requires pretreatment. This is most commonly accomplished when applied to natural waters by ion exchange, solvent extraction, cocrystallization, and coprecipitation. More recently there has been increasing interest in a novel separation technique known as foam separation because of its versatility and its potential for purposes ranging from chemical analysis to plant scale operations. The various systems separable by foam separation and related techniques together with a discussion of the principles upon which they are founded have been the subject of a book by Sebba (*1*) and reviews by Karger and DeVivo (*2*) and Lemlich (*3*).

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* Hawaii Institute of Geophysics Contribution No. 393.

The generic name for all related flotation techniques according to a joint set of recommendations for nomenclature (*2*) is "adsorptive bubble separation methods" of which "adsorbing colloid flotation," the removal of dissolved material first adsorbed on colloidal particles, is a subdivision. According to Karger and DeVivo, almost all of the work to-date has involved flotation of ions using an oppositely charged surfactant. The technique referred to as adsorbing colloid flotation represents a relatively unexplored field that appears particularly suitable for the removal of trace nonsurface active ionic species present in natural waters. Grieves and coworkers (*4*, *5*) have studied the foam separation of an aqueous ferric oxide–sodium dodecyl sulfate sol system and Voznesenskii and coworkers (*6*) have separated by foam flotation some radio isotopes in waste waters through adsorption on a ferric hydroxide precipitate. In a comparison of adsorbing colloid flotation with ion flotation, Karger and DeVivo conclude that the former is inherently more efficient for the removal of dissolved ions. They state that the development of the newer adsorptive bubble methods should in the future lead to the mining of the oceans although as far as can be ascertained such a development has not yet appeared in the literature. Sebba (*1*) has also raised the possibility of the concentration of metallic elements in seawater by the ion flotation technique.

Recent work by Kim and Zeitlin (*7*, *8*) on the role and behavior of iron(III) hydroxide and thorium(IV) hydroxide as collectors of molybdenum from seawater demonstrated that at optimum conditions virtually all the molybdenum present in a sample of seawater was adsorbed on the two collectors and could be removed as coprecipitates by filtration and determined spectrophotometrically. The work in turn suggested the feasibility of an approach which combines the use of iron(III) hydroxide with that of an adsorbing colloid flotation process for the separation of a trace metal from seawater. This communication is concerned with a study of the separation of a model trace metal molybdenum from seawater using colloidal iron(III) hydroxide, dodecyl sodium sulfate, and air, which appears to offer considerable promise when applied to natural waters.

EXPERIMENTAL

Reagents

All chemicals employed were of analytical reagent grade. Aqueous reagents were prepared in doubly distilled deionized water. Standard molybdenum solution was prepared by dissolving 0.3015 g dried MoO_3 (99.5%) in 5 ml 1 *N* NaOH and neutralizing with 1 *N* HCl. The resulting solution was diluted to 500 ml of which 5 ml was further diluted to 1 liter, producing a final solution containing 2 µg molybdenum/ml. For analytical determination appropriate aliquots when added to filtered seawater furnished concentrations of molybdenum ranging from 0 to 6.0 µg/500 ml not including that originally present in the seawater. Surfactant solution was prepared by dissolving 0.05 g sodium dodecyl sulfate in 100 ml 50% ethanol–water (v/v). All other solutions were prepared as described previously (*7*).

Equipment

Spectrophotometer, Beckman DU, matched quartz cells of 1-cm path length. pH meter, Beckman Zeromatic. Filters, millipore, HA-47 mm diameter. Separatory funnels used for extraction were equipped with Teflon stopcocks.

Flotation Cell

The schematics of the cell constructed and used in the study are given in Fig. 1. Flotation was carried out in a glass cylinder with a 6-cm di-

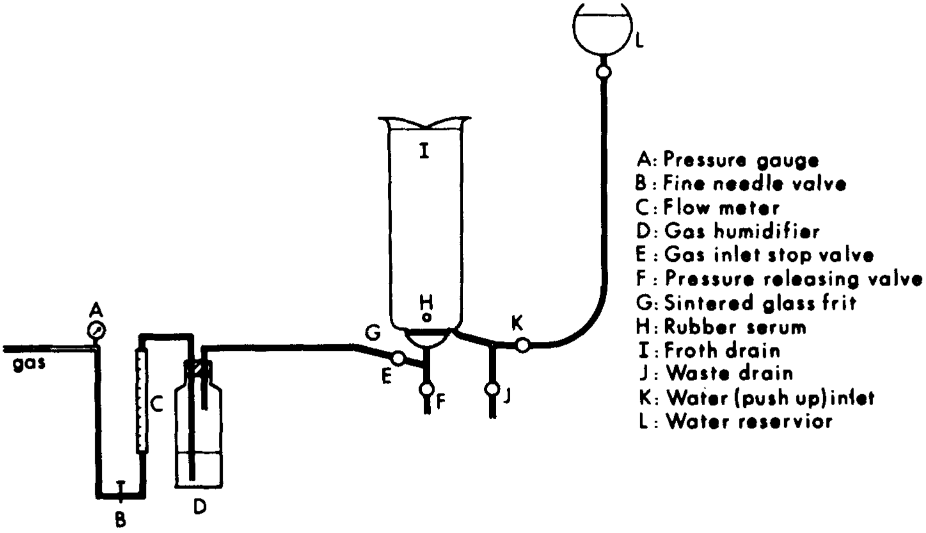

FIG. 1. Flotation unit.

ameter and a height of 23 cm which was fitted with a medium fine porous glass frit to generate multiple small bubbles. In operation, the compressed air or nitrogen was measured in a flow meter, adjusted by a fine needle valve to a pressure of 6.5 psi, and passed through a gas humidifier and the flotation cell. The meter was calibrated at 6.5 psi from the data supplied by the manufacturer. The gas flow rate was converted to atmospheric pressure and room temperature and measured as ml/min. All experiments were batch type using an experimental volume of 500 ml.

General Procedure

Five hundred milliliter samples of filtered seawater to which 6.0 μg of molybdenum were added were transferred to the flotation cell and analyzed by the flotation method under various conditions for purposes of evaluation and to obtain optimum conditions for recovery of molybdenum. The variables investigated included porosity of glass frit, gas used, rate and period of gas flow, comparison of ionic strength of aqueous medium, recovery from distilled water and seawater, volume of ferric chloride solution, and volume of surfactant solution.

Assessment was made by comparison of the absorbances obtained from the analysis utilizing the flotation technique with those obtained from the direct analysis of replicate distilled water standards containing 6.0, 9.0, and 12.0 μg molybdenum/500 ml solution in which the coprecipitation and flotation steps were omitted. The latter absorbances were considered to represent 100% recovery of molybdenum present.

An analytical procedure for the determination of molybdenum in seawater incorporating optimal conditions for use of the flotation method was worked out and its precision and accuracy measured at one concentration.

Analysis

To 500 ml samples of filtered seawater in duplicate were added 2.0, 4.0, and 6.0 μg of molybdenum with one pair of samples to which no molybdenum was added serving as seawater blanks. Each sample was treated with 1 ml 18 N sulfuric acid and 2 ml 0.1 M ferric chloride solution. The samples were adjusted with dilute ammonia to pH 4.0 (±0.1). The solution containing colloidal ferric hydroxide was transferred to the

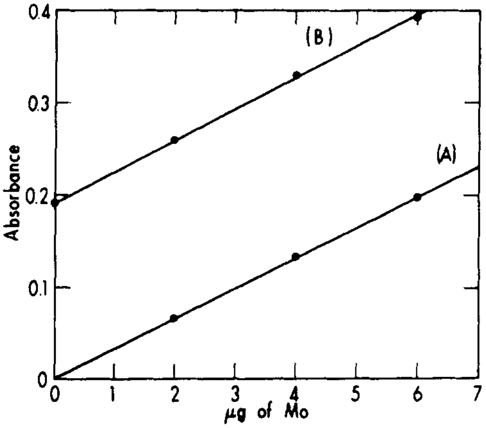

FIG. 2. Calibration plot for molybdenum separation by flotation. Sample: 500 ml seawater + 6.0 µg Mo. $A = B - 0.192$.

flotation cell and compressed air passed through the unit. Four milliliters of surfactant solution was slowly injected in the cell at point G (Fig. 1) with a glass syringe. The flow rate of air was adjusted to 10 ± 2 ml/min and allowed to pass for 5 min. About 10 sec after injection of the surfactant a yellow froth was formed on the surface of the solution which was followed within 2-3 min by the formation of a thick white foam below the yellow froth layer. The gas flow was terminated after 5 min by manipulation of stopcock E. After all gas bubbles floated to the surface, the solution became clear. The froth and foam layers were pushed up to the drain outlet I by opening stopcock K and introducing distilled water from reservoir L. The layers were skimmed off the surface into a small beaker with aid of a spatula. Repeated studies showed that quantitative separation of the surface layers was achieved by these means. The froth and foam were dissolved in 1–2 ml concentrated HNO_3–HCl (1:4) and heated for a few minutes. The solution was evaporated to dryness on a hot plate, the residue dissolved in 5 ml 6 *N* HCl, and molybdenum determined by the Sandell thiocyanate method described previously (*7*). A straight line, obtained when absorbance was plotted vs. concentration, passed through the origin when the seawater blank absorbance was subtracted (Fig. 2).

RESULTS

Results obtained from a study of the experimental parameters affecting the recovery of molybdenum by the adsorbing colloid flotation method follow.

Porosity of Frit. A frit of very fine porosity will produce very small bubbles and should be more effective than larger bubbles in the surface adsorption process. However, it requires higher gas pressures, which may pose a hazard to glass equipment. Good results were obtained with a medium fine frit which produced an easily handled flow of relatively uniform small gas bubbles.

Gas. Initial experiments on the gas used were conducted with nitrogen but similar results were obtained with compressed air.

Gas Flow Rate. The gas flow rate did not appear to affect significantly the removal of molybdenum by the flotation technique. If the bubbling rate is too high, considerable turbulence is created at the surface of the solution and there is difficulty in the formation of a stable froth and foam layer. A flow rate of 10 ± 2 ml/min for the equipment used was finally adopted since reproducible recoveries were obtained under this condition.

Period of Gas Flow. Tests on the effect of time of gas flow on recovery showed conclusively that removable surface layers containing prac-

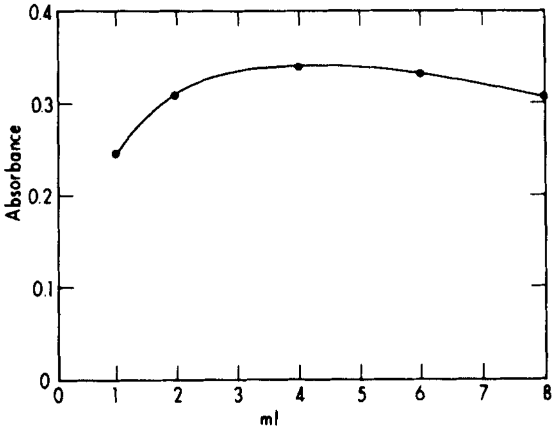

FIG. 3. Optimum volume of surfactant solution (0.05%) for maximum recovery of molybdenum. Sample: 500 ml seawater + 6.0 μg Mo. Solvent used as a blank in absorbance measurement.

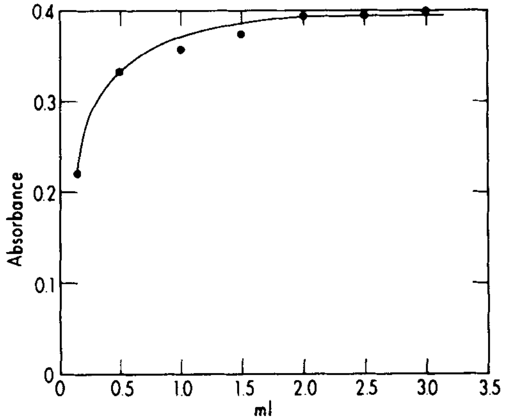

FIG. 4. Optimum volume of 0.1 *M* ferric chloride for maximum recovery of molybdenum. Sample: 500 ml seawater + 6.0 μg Mo. Solvent used as a blank in absorbance measurement.

tically all the molybdenum present in the 500-ml seawater sample were formed within 5 min at a flow rate of 10 ± 2 ml/min.

Surfactant. Tests were carried out with varying amounts of a 0.05% soldium dodecyl sulfate surfactant solution in 50% water–ethanol (v/v) using 0.5 ml 0.1 *M* ferric chloride solution. The results given in Fig. 3 led to the adoption of 4.0 ml surfactant solution.

Volume of Ferric Chloride. Previous work by Kim and Zeitlin (*7*) had shown that an excellent recovery of molybdenum from seawater was obtained by use of 0.1 *M* ferric chloride solution. The optimum volume of this solution for use in the flotation procedure was determined by varying the volume and examining the effect on recovery. The results are shown in Fig. 4. Two milliliters of 0.1 *M* ferric chloride solution was chosen for use in the final procedure.

Ionic Strength. The effect of ionic strength of the aqueous matrix was examined by comparing the recovery of molybdenum from a solution of zero ionic strength (distilled water) to that of 0.7 (seawater). Relatively little measurable effect on recovery resulted by varying the ionic strength within these limits under the above conditions.

Statistical Results. The flotation procedure may be used as an analytical method for the separation and determination of molybdenum in seawater and other natural waters since reproducible straight lines and virtually identical calibration plots in conformity with Beer's law were

TABLE 1

Statistical Data on Recovery of Molybdenum from Seawater[a] by the Colloid Flotation Method

Sample	Absorbance	Deviation	Recovery (%)	Deviation (%)
1	0.390	−0.001	95.1	−0.2
2	0.381	−0.010	93.0	−2.3
3	0.406	+0.015	99.0	+3.7
4	0.387	−0.004	94.4	−0.9
Mean	0.391	0.0075	95.3	1.8

[a] 500 ml sample seawater plus 6.0 μg Mo added.

obtained from molybdenum enriched distilled water and seawater. The results of the evaluation for precision and accuracy of four replicate filtered seawater samples containing 5.7 μg of molybdenum originally to which 6.0 μg of molybdenum was added to furnish a total of 11.7 μg are given in Table 1. The relative standard deviation of the series of test results is 2.6%. The accuracy was assessed by comparing the absorbance obtained by the flotation analysis with that of distilled water standard of the same concentration which was analyzed directly by the Sandell method with the omission of the coprecipitation and the flotation steps and assumed to represent 100% accuracy. For illustration, the mean absorbance from a 500-ml seawater samples containing 11.7 μg of molybdenum with the flotation technique is 0.391. The absorbance from a distilled water sample containing the same amount of molybdenum analyzed directly is 0.410. Comparison of the two absorbances gives a recovery of 95.3% since the slopes of the seawater and distilled water calibration curves are identical.

DISCUSSION

As reported by Kim and Zeitlin, optimum collection of molybdenum from seawater by ferric hydroxide takes place at pH 4.0 when the colloid has an apparent maximum positive charge density and is able to adsorb molybdenum quantitatively as molybdate anion in accord with the Paneth-Fajans-Hahn rule. This requires that the collector contain an ion which forms a compound of low solubility with the counter ion adsorbed, in this case, iron(III) molybdate. The attraction between the iron colloid and the molybdenum species is most likely electrostatic and chemical in nature. The adsorption phenomenon is expressed by the well-known Freundlich isotherm. Ishibashi (*9*) has shown that this empirical equation applies approximately in the adsorption of molybdenum on solid ferric hydroxide.

The second step occurs upon addition of the surfactant and the bubbling of gas through the solution. The surfactant anions are oriented with the hydrophilic part of the molecule pointing toward the water phase of a gas bubble and the hydrophobic hydrocarbon chain pointing toward the gas phase at the bubble surface. There is an electrostatic attraction between the surfactant anions and the Stern layers of the positively charged surfaces of the ferric hydroxide particulates enriched with molybdenum. The gas bubbles on which the ferric hydroxide is attached are floated to the surface of the solution from which they are easily removed.

Acknowledgment

This investigation was supported in part by NSF Grant GU-3855.

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Received by editor August 17, 1970