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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To cite this Article Chaine, Frances E. and Zeitlin, Harry(1974) 'The Separation of Phosphate and Arsenate from Seawater by Adsorption Colloid Flotation', Separation Science and Technology, 9: 1, 1 — 12
To link to this Article: DOI: 10.1080/01496397408080038
URL: http://dx.doi.org/10.1080/01496397408080038

SEPARATION SCIENCE, 9(1), pp. 1–12, 1974

The Separation of Phosphate and Arsenate from Seawater by Adsorption Colloid Flotation*

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Abstract

Procedures are described whereby phosphate and arsenate in seawater are brought to the surface in less than 5 min by an adsorption colloid flotation process which uses a positively charged iron(III) hydroxide collector, an anionic surfactant, sodium dodecyl sulfate, and nitrogen. Statistical studies on test series show a mean recovery of 90.7% with a relative standard deviation of 3.1% for phosphate at the 3.0 μg-at./l level, a mean recovery of 91.2% with a relative standard deviation of 1.5% for arsenate at the 3.0 μg-at./l level, and a mean recovery of 94.1% with a relative standard deviation of 0.8% for the combined 0.30 μg-at. AsO_4^{3-}-As/l and 2.25 μg-at. PO_4^{3-}-P/l samples.

INTRODUCTION

In the past 10 years there has been increased interest in a versatile separation technique, known as foam separation, which Sebba (*1*) introduced in 1962 as "...a new technique which makes use of the special properties which characterize interfaces for concentration of ions or other charged entities from aqueous solution." Work by Kim and Zeitlin (*2*, *3*) on the role and behavior of iron(III) hydroxide and thorium hydroxide as collectors of molybdenum present in seawater as molybdate eventually led to the combined use of iron(III) hydroxide with an adsorbing colloid flotation process for the separation of the trace metal molybdenum from

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* Hawaii Institute of Geophysics Contribution No. 582.

seawater. Molybdenum was collected by ferric hydroxide and the colloid formed was floated to the surface by electrostatic attraction between the surfactant anion, dodecyl sulfate, and the positively charged surfaces of the ferric hydroxide colloid enriched with molybdenum (*4*) to form an easily removed foam.

This work prompted investigation that determined that other trace metals which existed as anions in seawater could also be separated. Uranium, present in seawater as the stable tricarbonatouranyl anion, $UO_2(CO_3)_3{}^{4-}$ was collected by the positively charged ferric hydroxide collector at pH 5.7 and floated to the surface in 2 to 3 min by the anionic surfactant, sodium dodecyl sulfate (*5*). Thorium hydroxide was later found to be a more efficient collector of uranium when used in conjunction with another anionic surfactant, sodium dodecanoate (*6*).

Colloid flotation was next extended to the collection of trace cations, zinc(II) and copper(II), in seawater by the use of a negatively charged collector, ferric hydroxide at pH 7.6, and a cationic surfactant, dodecyl amine (*7*). More recent work has applied the flotation technique to such heavy metal pollutants as cadmium (*8*) and mercury (*9*). This communication is concerned with the study of the application of adsorption colloid flotation (ACF) to the separation of the nonmetallic, anionic pollutants, arsenate and phosphate, from seawater using a ferric hydroxide collector, sodium dodecyl sulfate surfactant, and nitrogen.

EXPERIMENTAL

Apparatus and Equipment

A Beckman DU spectrophotometer was used for absorbance measurements. The absorbances were read in matched quartz cells of 10.0 cm path length. The pH values of the solutions were determined with a Corning Digital pH meter. Millipore filters HA-47 mm diameter were used to filter seawater samples. The flotation separations were carried out with the flotation cell described in a previous paper by Kim and Zeitlin (*4*).

Reagents

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

Surfactant: sodium dodecyl sulfate, 0.05 g/100 ml ethanol.

Collector: 0.1 *M* ferric chloride (5.41 g $FeCl_3 \cdot 6H_2O$/200 ml H_2O, made fresh when cloudy).

Concentrated HNO_3.

Concentrated HCl.
1.0 *N* HCl.
0.75 *N* NH_3.
Mixed reagent: as described by Strickland and Parsons (*10*).

A standard phosphate solution was prepared by diluting 0.816 g of anhydrous potassium dihydrogen phosphate, KH_2PO_4, to a liter with water and storing it in a dark bottle with 1 ml of chloroform to prevent evaporation. A secondary standard was prepared from 50.0 ml of the concentrated standard diluted to 1 liter, and it was stored up to 10 days in a dark glass bottle with 1 ml of chloroform. Final standards were prepared fresh for use by standard additions of the secondary standard to filtered seawater, with an added concentration of 3.0 μg-at. PO_4^{3-}-P/l.

A standard arsenate solution was prepared by diluting 0.624 g $Na_2HAsO_4 \cdot 7H_2O$ to a liter with water and storing it in a dark bottle with 1 ml of chloroform. A secondary standard arsenate solution was prepared from 50.0 ml of the concentrated standard diluted to 1 liter with water, and it was stored up to 10 days in a dark glass bottle with 1 ml of chloroform. Fresh standards were prepared for use by standard additions of the secondary standard solution to filtered seawater with a concentration of 3.0 μg-at. AsO_4^{3-}-As/l.

Phosphate and Arsenate

The principal parameters which were directly related to the efficiency of collection and stability of foam formed were (a) the type and amount of collector, (b) the type and amount of surfactant, and (c) the pH of the system. Optimum conditions were found to be similar for phosphate and arsenate (see Discussion).

Analytical Procedure

Sample. Clear, uncontaminated, nearshore seawater, filtered prior to analysis with 0.45 μ millipore filters, was used to prepare the "sample/standard" (usually about 4 liters were prepared) by standard addition of 3.0 μg-at./l with the secondary standard solutions of either phosphate or arsenate. Low level arsenate samples which contained 0.30 μg-at. AsO_4^{3-}-As/l were prepared. To 500 ml samples were added 2 ml of the ferric chloride solution, and the pH was adjusted to 4.0 ± 0.1. The sample was transferred to the flotation cell, nitrogen was passed through at a rate of 15 ± 2 ml/min, and 4 ml of surfactant solution were injected. The foam was scraped into a beaker after 4 to 5 min with a Teflon-coated spatula. Two drops of concentrated HCl and water were used to rinse adhering ferric hydroxide from the spatula into the beaker. Then, one eyedropper full (2 ml) of concentrated HNO_3 and more water were added to the beaker to dissolve the foam samples. The solution was transferred to 500 ml volumetric flasks with four or five portions of water, and the samples were diluted to 500 ml with water. The low level arsenate samples of 0.30 μg-at. AsO_4^{3-}-As/l were subsequently diluted to 250 ml. Two 100-ml portions of this solution measured into 125 ml polyethylene bottles were then used in the Strickland and Parsons spectrophotometric method for phosphate determination (*10*), as modified by Johnson (*11*) for arsenate determination. (See Discussion.) Both phosphate and arsenate were determined by this method; however, the absorbance of the phosphate samples was read after 15 min and the absorbance of the arsenate samples after 2 hr.

Treatment of Blanks. The same mixed sample of nearshore seawater that was used for standard additions was treated as above and foam blanks handled similarly.

Treatment of Standards. Four 100-ml portions of the unfloated "sample/standard" solution were measured into 125 ml polyethylene bottles and 10 drops of concentrated HNO_3 were added to retard deterioration of the sample and to adjust the pH to the approximate range of the dissolved foam samples. These samples were then analyzed by the modified Strickland and Parsons (*10*) method for dissolved phosphate. Blanks for the standards were the same mixed sample of nearshore seawater used to prepare the samples and standards. Four 100-ml portions with 10 drops of concentrated HNO_3 in 125 ml polyethylene bottles were analyzed.

Recovery of Phosphate and Arsenate

In order to evaluate the reproducibility of recovery of phosphate and arsenate, five replicate samples of seawater to which had been added 3.0 μg-at./l of AsO_4^{3-} or PO_4^{3-} were analyzed according to the above flotation scheme. Five replicate samples to which were added both 0.30 μg-at.AsO_4^{3-}-As/l and 2.25 μg-at. PO_4^{3-}-P/l or a combined concentration of 2.55 μg-at./l of AsO_4^{3-} and PO_4^{3-} were also analyzed for percent recovery. Comparison was made with the absorbances obtained from direct analysis of the "sample/standard" solution. These absorbances, corrected for blanks, were considered to represent 100% recovery of arsenate or phosphate (Tables 1–4).

TABLE 1

Statistics for Recovery of Phosphate from Seawater by ACF

Sample No.	PO_4^{3-} (μg-at./l)[a]	Absorbance[b]	% Recovery	x	x^2
I 1	3.0	0.469	86.5	−4.2	17.64
2	3.0	0.468	86.3	−4.4	19.36
3	3.0	0.461	85.1	−5.6	31.36
4	3.0	0.473	87.3	−3.4	11.56
5	3.0	0.460	84.9	−5.8	33.64
Standard[c] I	3.0	0.542	100.0		
II 1	3.0	0.523	94.0	+3.3	10.89
2	3.0	0.523	94.0	+3.3	10.89
3	3.0	0.502	90.3	−0.4	0.16
4	3.0	0.512	92.1	+1.4	1.96
5	3.0	0.510	91.7	+1.0	1.00
Standard[c] II	3.0	0.556	100.0		
III 1	3.0	0.504	93.0	+2.3	5.29
2	3.0	0.509	93.9	+3.2	10.24
3	3.0	0.511	94.3	+3.6	12.96
4	3.0	0.513	94.6	+3.9	15.21
5	3.0	0.497	91.7	+1.0	1.00
Standard[c] III	3.0	0.542	100.0		
IV 1	3.0	0.485	89.6	−1.1	1.21
2	3.0	0.494	91.3	+0.6	0.36
3	3.0	0.487	90.0	−0.7	0.49
4	3.0	0.495	91.5	+0.8	0.64
5	3.0	0.499	92.2	+1.5	2.25
Standard[c] IV	3.0	0.541	100.0		
Mean	3.0		($\bar{X}$) 90.7		$\Sigma x^2 = 188.11$
Relative standard deviation $C = \sqrt{\bar{s}}/\bar{X} = 3.4\%$					$s = \Sigma x^2/(n - 1)$ $s = 188.11/19$ $s = 9.9$

[a] Added to 500 ml seawater.

[b] Appropriate blank subtracted.

[c] Unfloated.

TABLE 2

Statistics for Recovery of Arsenate from Seawater by ACF

Sample No.	AsO_4^{3-} (μg-at./l)[a]	Absorbance[b]	% Recovery
1	3.0	0.487	90.7
2	3.0	0.479	89.2
3	3.0	0.479	92.6
4	3.0	0.496	92.4
5	3.0	0.490	91.2
Mean	3.0	0.490 ($\bar{X}$)	91.2
Standard[c]	3.0	0.537	100.0

Standard deviation $\sqrt{s} = (\Sigma x^2/(n-1))^{1/2} = \pm 0.0073$

Relative standard deviation $C = \sqrt{s}/\bar{X} = 1.5\%$

[a] Added to 500 ml of seawater.

[b] Appropriate blank subtracted.

[c] Unfloated.

TABLE 3

Statistics for Recovery of Low Level Arsenate from Seawater by ACF

Sample No.	AsO_4^{3-} (μg-at./l)[a]	Absorbance[b]	AsO_4^{3-} (μg-at./l) recovered	% Recovery
I 1	0.30	0.092	0.26	87
2	0.30	0.081	0.23	77
3	0.30	0.094	0.26	87
4	0.30	0.081	0.23	77
5	0.30	0.088	0.25	83
Mean	0.30	0.087 ($\bar{X}$)		82
Standard[c]	2.0	0.356		

Recovered arsenate in μg-at./l equals the absorbance divided by 2 (due to concentration factor of the ACF method) and multiplied by F. F equals the concentration of the standard divided by the absorbance of the standard:[b] $F = 2.0/0.356 = 5.618$

Standard deviation $= \sqrt{s} = (\Sigma x^2/(n-1))^{1/2} = \pm 0.0061$

Relative standard deviation $C = \sqrt{s}/\bar{X} = 7.0\%$

[a] Added to 500 ml seawater.

[b] Appropriate blank subtracted.

[c] Unfloated.

TABLE 4

Statistics for Recovery of Arsenate and Phosphate from Seawater by ACF

Sample No.	AsO_4^{3-} (μg-at./l)[a]	PO_4^{3-} (μg-at./l)[a]	Absorbance[b]	% Recovery
1	0.30	2.25	0.429	92.9
2	0.30	2.25	0.432	93.5
3	0.30	2.25	0.439	95.0
4	0.30	2.25	0.437	94.6
5	0.30	2.25	0.437	94.6
Mean	0.30	2.25		94.1 ($\bar{X}$)
Standard	0.30	2.25	0.462	100.0

Standard deviation $\sqrt{s} = (\Sigma x^2/(n - 1))^{1/2} = 0.73\%$

Relative standard deviation $C = \sqrt{s}/\bar{X} = 0.8\%$

[a] Added to 500 ml of seawater.

[b] Appropriate blank subtracted.

[c] Unfloated.

DISCUSSION

Past investigation of marine arsenic has been hampered by poor analytical techniques and by reagents contaminated by the element. Routine shipboard measurements have proved impossible, so data are of limited oceanographic scope, mostly surface and nearshore measurements (*12*). Goldberg reports an average concentration in seawater of 0.003 mg As/l or 0.04 μg-at. As/l (*13*). This value is accepted by Portmann and Riley (*14*) who suggest that thermodynamic considerations and observations by Armstrong and Harvey (*15*), that arsenite is oxidized to arsenate in seawater, favor arsenate (AsO_4^{3-}) as the most abundant species. Gorgy et al. (*16*) stated that only 8 to 16% is present as arsenate, 53 to 60% occurring as arsenite, and the remainder being organic complexes or particulate compounds of arsenic. Recent studies by Johnson and Pilson (*12*) are in agreement with the Goldberg value. Johnson's method has proved only marginal for natural levels of arsenate in seawater (*17*).

Phosphate, an important biological nutrient, has been more throughly studied. Average abundance in seawater is given by Goldberg (*13*) as 0.07 mg/l or 2 μg-at. P/l as orthophosphate (50 times more than arsenate). The concentration, closer to 0 at the surface due to biological productivity, increases to a maximum of about 3 μg-at. PO_4^{3-}-P/l at the sea floor. However, it is variable with temperature, productivity, and the current characteristics of the oceans.

The accepted oceanographic method for the determination of (dissolved) reactive phosphate in seawater is that of Strickland and Parsons (*10*). This

TABLE 5

Effect of Surfactant on Phosphomolybdate Color Development

Without[a]		With[b]	
Sample	Absorbance	Sample	Absorbance
1	0.885	1	0.870
2	0.915	2	0.895
3	0.905	3	0.915
4	0.910	4	0.932
Mean	0.904	Mean	0.903
$C = 1\%$		$C = 3\%$	

[a] Sample without surfactant: 5 ml secondary standard phosphate solution diluted to 500 ml (3.0 μg-at.PO_4^{3-}-P/l added).

[b] Sample with surfactant added: 5 ml secondary standard phosphate solution and 4 ml sodium lauryl sulfate solution diluted to 500 ml (3.0 μg-at.PO_4^{3-}-P/l added).

method has strong interference from arsenate if it is present in appreciable amount. Johnson (*11*) found that the same method could be used for arsenate determination though sensitivity was gained by reading the molybdenum blue absorbance at 865 nm instead of at 885 nm. It was also found that the time for the arsenomolybdate color formation was considerably longer than the 15 min for the same phosphate reaction (*11*). All tests were read at 865 nm and the arsenic absorbance was read after 2 hr. Samples of 100 ml, to which 10 ml of mixed reagent were added in 125 ml polyethylene bottles, were used. Arsenate and phosphate tests were done separately.

Tests showed that the ferric hydroxide collector, while increasing the absorbance of the blank, did not interfere with color formation at the concentrations used. This was supported by Murphy and Riley (*18*) who found no interference with twice the concentration of Fe^{3+} ion. Surfactant also caused no apparent interference in the color formation (Table 5).

Collector

Studies were made to find a suitable quantitative collector for arsenic and phosphate. It was suspected that ferric hydroxide would be suitable since phosphate is found in nature adsorbed on ferric and aluminum hydroxides (*19*), and arsenate has been removed from water by coprecipitation with ferric hydroxide at pH 7.0 (*14*).

Cadmium sulfide was tested first. There was little or no apparent collection as the visual measurement of blue color developed by the Strickland

and Parsons method was as marked in the filtrate of the precipitated samples as in the standard.

Preliminary tests with ferric hydroxide (2 ml of 0.1 M $FeCl_3$ in 500 ml of sample) showed that there was appreciable coprecipitation of phosphate. There was no pH adjustment of the samples at first, but upon hydrolysis of the ferric chloride the pH of the solutions dropped to between 5.7 and 6.0 pH. Rough tests run on the filtrate and on the dissolved precipitate confirmed the effectiveness of ferric hydroxide as a collector of phosphate and arsenate.

Optimum pH was examined. Two milliliters of ferric chloride solution were added to 500 ml samples of filtered seawater to which had been added the equivalent of 3.0 μg-at. PO_4^{3-}-P/l. Results showed that there was 100% collection in all samples tested (the pH ranged from 4 to 7.5). These tests were repeated for arsenate (Table 6). The absorbance of the filtrate was lower than the blanks, which indicated 100.0% pickup at each pH. Addition of phosphate and arsenate seems to enhance coprecipitation of the species present in the seawater. Subsequent tests of percent recovery showed slightly better results for combined phosphate and arsenate samples (Table 4). The optimum volume of ferric chloride to be added for collection was also tested (no pH adjustment). When 3.0 ml were added,

TABLE 6

pH	Absorbance	
	Sample filtrate[a]	Blank filtrate[a]
	Phosphate Collection with Ferric Hydroxide	
4.2	0.140	0.144
5.5	0.141	0.144
6.0	0.137	0.144
6.5	0.137	0.145
7.0	0.138	0.146
7.5	0.138	0.144
	Arsenate Collection with Ferric Hydroxide	
4.0	0.067	0.068
5.5	0.067	0.065
6.0	0.054	0.062
6.5	0.054	0.067
7.0	0.046	0.074
7.5	0.046	0.064

[a] Two milliliters of 0.1 M ferric chloride solution were added to each 500 ml sample and the sample was filtered with 0.45 μ millipore filters.

the solution would not clear during flotation, and consequently a volume of 2 ml was adopted.

Surfactant

Originally, there seemed to be no apparent optimum pH for collection of arsenate and phosphate in seawater, and it was decided to work with as little pH adjustment as possible. When the ferric chloride was added, the pH was lowered to about 6, so this was chosen as the pH for the system. From studies by Matsuzaki and Zeitlin (*20*), three surfactants were chosen which seemed to be acceptable for use with ferric hydroxide at pH 6: (a) sodium dodecanoate, (b) sodium dodecyl sulfate, and (c) dodecyl pridinium chloride. Sodium dodecanoate and dodecyl sulfate were comparable in flotation efficiency with about 85% recovery at pH 7. Dodecyl pridinium chloride recovered only 39%. At pH 4.0 ± 0.1, sodium dodecyl sulfate was favored due to efficiency and ease of recovery. In addition, sodium dodecyl sulfate did not interfere with color development in the spectrophotometric method of analysis. Conveniently, concentrations used were those optimized by Kim and Zeitlin (*4*) for the ferric chloride–sodium

TABLE 7

Arsenate Recovery at pH 6.0

Sample No.	AsO_4^{3-} (μg-at./l) added	Absorbance[a]	% Recovery
1	3.0	0.429	84.0
2	3.0	0.453	90.1
3	3.0	0.321	67.3
4	3.0	0.318	59.1
Standard	3.0	0.557	100.0

[a] Suitable blank subtracted.

TABLE 8

Effect of pH on Recovery of Arsenate and Phosphate

Phosphate			Arsenate		
pH	% Recovery	Number of samples	pH	% Recovery	Number of samples
6.0	62.9	1	7.0	83.8	2
5.6	66.2 ± 12.7	5	6.0	80.4 ± 13.3	12
4.0	90.6 ± 3.1	20	5.6	87.4 ± 6.5	12
			4.0	91.2 ± 1.4	5

dodecyl sulfate–pH 4.0 flotation system. Other combinations were tried but visual results were not good.

Optimum pH of Flotation

At pH 6.0 there was little reproducibility of recovery of arsenate by flotation. Sample data (Table 7) show wide scatter. The effect of pH is shown in Table 8. Efficiency was optimum at pH 4.0 for recovery of arsenate. Results for phosphate recovery (Table 8) also favored pH 4.0.

RESULTS

As compiled in Tables 1–4, results showed a mean recovery of phosphate of 90.7% with a relative standard deviation of 3.1% at the natural seawater level of 3.0 μg-at. $PU_4{}^{3-}$-P/l. The recovery of arsenate at the level of 3.0 μg-at. $AsO_4{}^{3-}$-As/l level was 91.2% with a relative standard deviation of 1.5%. At concentrations 10 times lower, arsenate recovery was also lower. Mean recovery was 82% with $C = 7.0\%$ at the 0.3 μg-at. $AsO_4{}^{3-}$-As/l level. There was a mean recovery of 94.1% with a relative standard deviation of 0.8% for the combined 0.30 μg-at. $AsO_4{}^{3-}$-As/l and 2.25 μg-at. $Po_4{}^{3-}$-P/l samples.

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Received by editor July 6, 1973