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SEPARATION AND PRECONCENTRATION OF TRACE SUBSTANCES — III. FLOTATION AS A PRECONCENTRATION TECHNIQUE

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SEPARATION AND PRECONCENTRATION OF TRACE SUBSTANCES.
III — FLOTATION AS A PRECONCENTRATION TECHNIQUE

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Abstract - Precipitates and ions in aqueous solutions can be floated to the solution surface by a rising stream of gas bubbles, with (or sometimes without) the aid of surfactants. The application of this simple, relatively new separation technique in trace analysis is reviewed and evaluated.

INTRODUCTION

Flotation is defined as the process by which dispersed solid or liquid particles, precipitates, colloidal particles, and solutes in an aqueous solution are floated to the solution surface with the aid of a rising stream of gas bubbles. In general, the substance to be floated should be hydrophobic and therefore attachable to the bubbles. When the substance itself is hydrophilic, surfactants are used to convert it into a hydrophobic substance before flotation. Therefore the applicability of this technique is very wide. Flotation has been extensively used for the recovery of valuable minerals from ores in the mining industry since this century began and new flotation techniques such as ion flotation have been developed in recent years (Refs. 1-3). This technique was first applied to the preconcentration of trace elements for trace analysis, however in 1966 (Ref. 4).

At present, applications of this technique in this field may be grouped into the following two classes:

1. Precipitate flotation. Inorganic or organic precipitates in an aqueous solution are floated with or without the aid of surfactant ions of opposite charge. Generally, trace ions at the low ppm level or less are quantitatively coprecipitated with small amounts of collector precipitates, which are then floated as described above.

2. Ion flotation. Traces of ions, generally complex ions, at the low ppm level or less in an aqueous solution are floated with the aid of surfactant ions of opposite charge to the ions.

APPARATUS AND GENERAL PROCEDURES

Typical flotation cells made of glass are shown in Fig. 1. A rising stream of nitrogen or air bubbles is produced by passing the gases through the sintered-glass disk in the sample solution, and a scum or foam layer in which the desired substances are concentrated is formed on the solution surface. The scum or foam layer is collected with a spatula, pipet, sampling bottle (Fig. 1C) or sampling tube (Fig. 1D). When the scum adheres strongly to the inner wall of the cell near the solution surface, a detachable polyethylene insert (Fig. 1E) is very helpful to completely collect the scum. Another method for separating the scum or foam layer from the solution is rapid filtration by suction through the sintered-glass disk at the bottom of the cell. The foam can be readily destroyed by addition of small amounts of organic solvents such as ethanol, 1-butanol or diethyl ether, or when kept in contact with vapors of the above solvents.

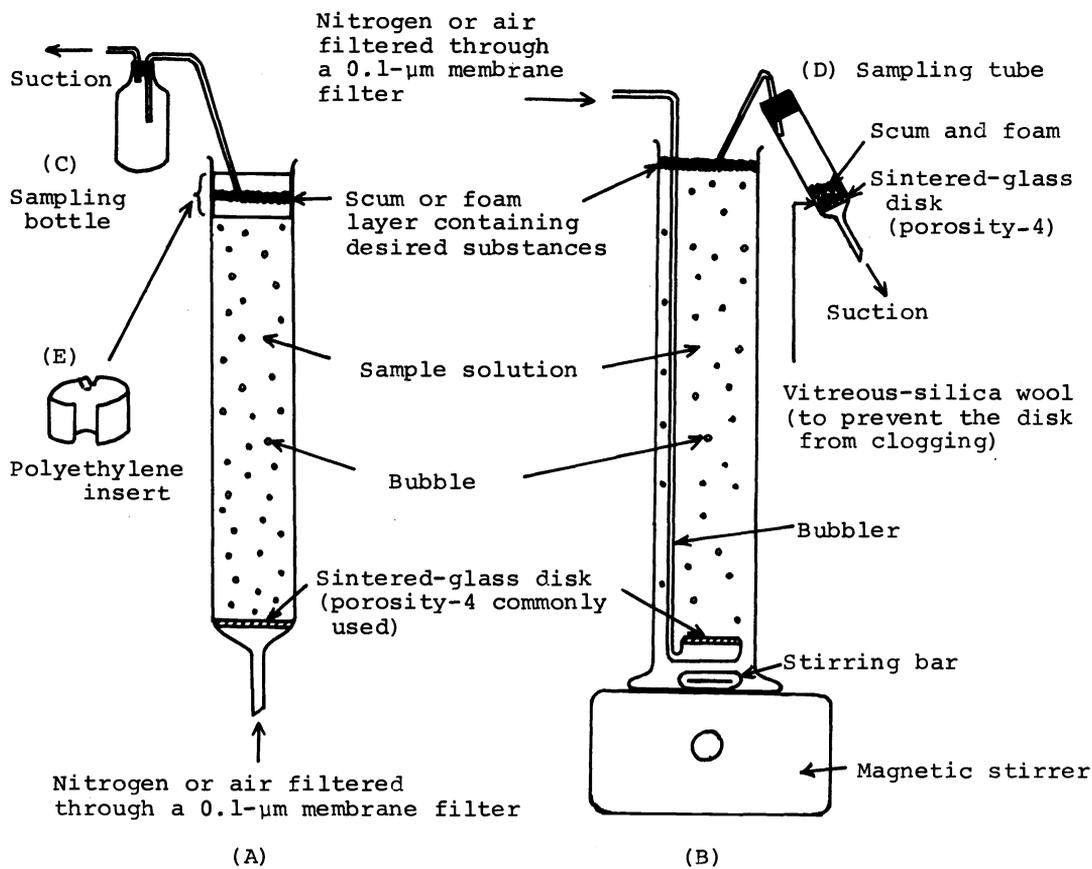


Fig. 1. Flotation cells.

PRECIPITATE FLOTATION

Coprecipitation with colloidal or flocculent inorganic precipitates followed by flotation

Desired trace ions in an aqueous solution are coprecipitated with colloidal or flocculent metal hydroxide or sulfide precipitates, which are then floated with the aid of numerous tiny gas bubbles. Two typical examples are described.

Example 1: Multielement preconcentration of trace heavy metals in water (Ref. 5). A 1200-ml water or seawater sample is placed in a flotation cell (Fig. 1B), 1 ml of indium nitrate solution ($100 \text{ mg In ml}^{-1}$) is added, and the pH is adjusted to 9.5 with 0.3 M sodium hydroxide while stirring with a magnetic stirrer to form a flocculent hydrated indium oxide precipitate. A bubbler is immersed in the solution, and 2 ml of sodium oleate solution (1 mg ml^{-1} in 70 % ethanol) and 1 ml of sodium dodecyl sulfate solution (4 mg ml^{-1} in 70 % ethanol) are added. While gently stirring, nitrogen is passed for ca. 3 min to attain complete mixing and flotation of the precipitate with the aid of numerous bubbles having diameters below ca. 0.5 mm. The resulting foam layer containing the precipitate is sucked into a sampling tube (Fig. 1D). Another 1-ml portion of the sodium dodecyl sulfate solution is added and the above procedure is repeated. The foam in the sampling tube is destroyed with two 1-ml portions of ethanol, and the solution is removed by filtration under suction. The precipitate is washed with three 2-ml portions of water, and dissolved in 2 ml of conc. nitric acid and ca. 3 ml of water. The resulting 5-ml solution is analyzed by inductively-coupled plasma atomic emission spectrometry for Cr(III), Mn(II), Co, Ni, Cu(II), Cd, and Pb down to 0.5 μg . The recoveries of the metals are better than 90 %.

The concentrations of the heavy metals are increased 240-fold, while those of the alkali and alkaline earth metals in seawater are reduced to 1/50-1/20 for Na and K, and ca. 1/2 for Mg, Ca, and Sr. The time required for the preconcentration is ca. 40 min.

Example 2: Preconcentration of traces of molybdenum(VI) in seawater (Ref. 6). To a 500-ml seawater sample is added 2 ml of iron(III) chloride solution (5.6 mg Fe ml⁻¹), and the pH is adjusted to 4.0±0.1 with dilute aqueous ammonia to form colloidal hydrated iron(III) oxide. The solution is transferred to a flotation cell, air is passed, and 4 ml of sodium dodecyl sulfate solution (0.5 mg ml⁻¹ in 50 % ethanol) is slowly injected into the cell. The precipitate is floated and a scum followed by a foam layer is produced on the solution surface. The air flow is terminated after 5 min, and the scum and foam are collected with the aid of a spatula and dissolved in 2 ml of conc. nitric acid-hydrochloric acid (1:4). The solution is evaporated to dryness, and the resulting residue is dissolved in 5 ml of 6 M hydrochloric acid. The final solution is analyzed for molybdenum by the spectrophotometric thiocyanate method. The concentration of molybdenum at the µg l⁻¹ level is increased 100-fold with recoveries of greater than 90 %.

Important experimental factors to be considered for successful flotation are discussed briefly below.

1. Precipitates. Bulky flocculent precipitates are desirable, because numerous tiny gas bubbles are easily trapped in the interstitial spaces and on the surfaces of the precipitates to give sufficient buoyancy. The following elements form flocculent hydrated oxide precipitates suitable for quantitative separations by flotation (Ref. 7): Mg, Al, Ti, Cr(III), Fe(II, III), Co, Ni, Cu(II), Zn, Zr, In, Sn(IV), Sb(III), Bi, and Th.

2. Gas bubbles. Bubbles having diameters below ca. 0.5 mm are desirable, because they are easily trapped by flocculent precipitates and form a stable foam layer on the solution surface (see (4) below). Organic solvents such as methanol, ethanol, acetone and methyl cellosolve (ca. 1 %) added to an aqueous sample solution are essential to obtain a stream of numerous tiny bubbles, because these solvents disturb coalescence of the gas bubbles which appear from adjacent pores of a sintered-glass disk (Ref. 8).

3. pH of the solution. The optimum pH range should be selected from the standpoints of quantitative coprecipitation of the desired trace ions and flotation of the gathering precipitates.

4. Surfactants. Surfactant ions of opposite charge to the precipitate surfaces are used to make the surfaces hydrophobic. Another important role of the surfactants is to form a stable foam layer to support the precipitates on the solution surfaces, which is often important for complete collection of the precipitates. Combined use of two kinds of surfactants, e.g., sodium oleate and sodium dodecyl sulfate, is sometimes recommended, as described in Example 1. Surfactants are generally dissolved in ethanol, which is effective for producing tiny gas bubbles, as described previously. Flotation without surfactants is possible in some cases. For example, bulky flocculent hydrated iron(III) oxide precipitate is floated with small amounts (1 %) of methyl cellosolve (Ref. 9), or with solid paraffin (m.p. 56-58°C) particles having diameters below 1 mm produced by adding a hot (ca. 65°C) ethanol solution of paraffin to an aqueous sample solution (Ref. 10).

The advantages of coprecipitation and flotation with colloidal or flocculent inorganic precipitates are: (i) This method is more rapid and convenient than conventional coprecipitation methods using time-consuming and troublesome filtration and centrifugation for the separation of collector precipitates from mother liquor. (ii) Flotation of bulky flocculent precipitates needs less experimental skill and is more reliable and rapid than ion flotation described later. (iii) Much higher preconcentration coefficients (the ratios of the recovery of the desired trace element to the recovery of the matrix) are obtained compared with those obtainable by ion flotation. (iv) Simultaneous multielement preconcentration can be achieved.

Table 1 summarizes the applications of this method reported to date.

TABLE 1. Applications of coprecipitation with colloidal or flocculent inorganic precipitates followed by flotation

Samples	Trace elements	Precipitates (amount of cation, mg)	pH	Surfactants (ethanol soln)	Tech- niques	Refs.
Water, seawater (1000 ml)	Cr(III), Mn(II), Fe(III), Co, Ni, Cu(II), Zn, Cd, Pb (>0.001 ppm)*	Al(OH) ₃ (50)	9.5	SO	AAS	11
Water, seawater (1200 ml)	Cr(III), Mn(II), Co, Ni, Cu(II), Cd, Pb (>0.0001 ppm)	In(OH) ₃ (100)	9.5	SO+SDS	ICP-AES	5
Water, seawater (250-500 ml)	As(III), As(V) (>0.001 ppm)	Fe(OH) ₃ (10)	8-9	SO	AAS	12, 13
Water, seawater (1000 ml)	Sn(II), Sn(IV) (>0.0001 ppm)	Fe(OH) ₃ (10)	4	SDS	AAS	14
Water, seawater (1000 ml)	Se(IV) (>0.0001 ppm)	Fe(OH) ₃ (10)	4	SDS	AAS	15
Water, seawater (1000 ml)	Bi (>0.0001 ppm)	Fe(OH) ₃ (10)	4	SO+SDS	AAS	16
Water (1000 ml)	Sb(III), Sb(V) (>0.0001 ppm)	Fe(OH) ₃ (10)	4	SO+SDS	AAS	17
Seawater (500 ml)	Mo(VI) (>0.01 ppm)	Fe(OH) ₃ (11)	4.0 ± 0.1	SDS	SP	6
Seawater (500 ml)	Cu(II), Zn (>0.01 ppm)	Fe(OH) ₃ (8.4)	7.6 ± 0.1	DA	SP, AAS	18
Seawater (500 ml)	P(V), As(V) (>0.001 ppm)	Fe(OH) ₃ (11)	4.0 ± 0.1	SDS	SP	19
Seawater (500 ml)	V(V) (>0.1 ppm)	Fe(OH) ₃ (8.4)	5.00 ± 0.02	SDS	AAS	20
Seawater (500 ml)	Se(IV) (>0.001 ppm)	Fe(OH) ₃ (17)	3.5 -5.3	SDS	SP	21
Seawater (500 ml)	U(VI) (>0.001 ppm)	Fe(OH) ₃ (8.4)	5.7 ± 0.1	SDS	SP	22
Seawater (500 ml)	U(VI) (>0.001 ppm)	Th(OH) ₄ (46)	5.7 ± 0.1	SD	F	23
Seawater (500 ml)	Hg(II) (>0.0001 ppm)	CdS (93)	1	OTAC	Flame- less AAS	24
Seawater (500 ml)	Ag (>0.01 ppm)	PbS (5)	2	Stearyl- amine	AAS	25
Seawater (500 ml)	U(VI) (>0.001 ppm)	Preformed hydrated TiO ₂ (ca. 30)	6.6 ± 0.2	SDS	SP	26
Zinc metal (3 g Zn, 100 ml)	Fe(III), Pb (≥ 0.1 ppm)	Bi(OH) ₃ (10)	**	SO	AAS	27
Zinc metal (5-10 g Zn, 200 ml)	Sn(IV) (>0.01 ppm)	Fe(OH) ₃ (30)	6	(Paraffin in hot ethanol)	SP	10

* Concentrations in original samples, ** Excess aqueous ammonia is added to mask zinc against precipitation. **Surfactants:** SO: Sodium oleate, SDS: Sodium dodecyl sulfate, DA: Dodecylamine, SD: Sodium dodecanoate, OTAC: Octadecyltrimethylammonium chloride. **Techniques:** AAS: Atomic absorption spectrometry, ICP-AES: Inductively coupled plasma-atomic emission spectrometry, SP: Spectrophotometry, F: Fluorometry.

Coprecipitation with organic precipitates followed by flotation

A water-insoluble organic precipitant (e.g., dithizone, 1-nitroso-2-naphthol) in a water-miscible organic solvent (e.g., methyl cellosolve, ethanol) is added to an aqueous sample solution to precipitate the precipitant. The resulting flocculent precipitates containing desired trace ions are floated with the aid of numerous tiny bubbles having diameters below ca. 0.5 mm. Two examples are as follows.

Example 3: Preconcentration of traces of silver in seawater (Ref. 28). To a 3-l sample (acidified to pH 1) is added 50 ml of 2-mercaptobenzothiazole solution (40 mg ml⁻¹ in acetone), and after 30-min vigorous stirring, the solution is transferred to a flotation cell (Fig. 1A). Nitrogen is passed for 1 min to effect complete mixing and flotation of the flocculent precipitate. The mother liquor is sucked off through a sintered-glass disk. The precipitate is washed with two 100-ml portions of 1 M nitric acid followed by two 100-ml portions of water, and then dissolved in 70 ml of acetone. The solution is evaporated and the organic precipitate is destroyed with 35 ml of conc. nitric acid and 7 ml of 30 % hydrogen peroxide. The resulting residue is dissolved in 3 ml of conc. nitric acid and ca. 2 ml of water. The 5-ml solution is analyzed by atomic absorption spectrometry for silver. The concentration of silver is increased 600-fold with recoveries of greater than 95 %. The time required for an analysis is ca. 4 h. Silver in seawater was found to be 0.09 µg l⁻¹.

Example 4: Preconcentration of copper and silver in high-purity zinc and lead metals (Ref. 29). A 2-5-g sample is dissolved in 10-50 ml of 5 M nitric acid, the solution is diluted to 90 ml with water, and the pH is adjusted to between 1 and 1.5 with conc. aqueous ammonia. A 5-ml dithizone solution (4 mg ml⁻¹ in methyl cellosolve) is added and the sample solution is vigorously stirred for 30 min. In a flotation cell (Fig. 1A), the flocculent precipitate is floated by passing nitrogen for ca. 15 s. The mother liquor is sucked off through the sintered-glass disk. The precipitate is washed with 10 ml of 0.1 M nitric acid, and dissolved in 1 ml of conc. nitric acid, 3 ml of acetone, and ca. 1 ml of water. The resulting 5-ml solution is analyzed by atomic absorption spectrometry for copper and silver. The limit of determination is as low as 0.04 ppm for both metals. The desired trace metals are recovered in greater than 95 % yields. Preconcentration coefficients are 1000 to 2400 for 2 to 5 g of zinc and 450 to 1200 for 2 to 5 g of lead. The time required for an analysis is ca. 1.5 h.

Important experimental factors for successful flotation are as follows (Ref. 30):

1. Precipitates. By mechanical stirring, suspended organic reagents coagulate to form bulky flocculent precipitates larger than bubble diameters, which easily trap numerous tiny bubbles in the interstitial spaces and on the surfaces of the precipitates. Precipitates separated quantitatively by flotation include p-dimethylaminobenzylidenerhodanine, dithizone, thionalide, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, α-benzoin oxime, and 1-nitroso-2-naphthol.

2. Gas bubbles. See above discussion for flotation of colloidal or flocculent inorganic precipitates.

3. pH of the solution. See above discussion for flotation of colloidal or flocculent inorganic precipitates.

4. Surfactants. Both with and without surfactants, bulky flocculent organic precipitates are easily floated with the aid of tiny bubbles, and a stable precipitate layer containing bubbles is formed on the solution surface. With surfactants, however, an excess of stable foam is produced, which cannot be destroyed with organic solvents because of the redissolution of the precipitates.

The advantages of coprecipitation and flotation with organic precipitates are: (i) It is a rapid and convenient technique for separating organic precipitates from the mother liquor. Filtration or centrifugation is often impossible because of clogging of the pores of a filter or incomplete sedimentation due to the low density of the precipitates. (ii) Compared with ion flotation, this method needs less experimental skill and is more reliable and rapid. (iii) Compared with inorganic collector precipitates, organic collectors are generally much more selective in the separations of metal ions.

Table 2 summarizes the applications of this method reported to date.

TABLE 2. Application of coprecipitation with organic precipitates followed by flotation

Samples	Trace elements	Precipitants	pH or acidity	Tech-niques*	Refs.
Seawater (3000 ml)	Ag (>0.00001 ppm)	2-Mercaptobenzothiazole (2000 mg in acetone)	0.1 M HNO ₃	AAS	28
Copper metal (0.5 g Cu, 100 ml)	Ag (>1 ppm)	p-Dimethylaminoben- zylidenerhodanine** (0.5 mg in ethanol -nitric acid)	0.1-0.5 M HNO ₃	SP	4
Zinc and lead metals (2-5 g Zn and Pb, 100 ml)	Ag, Cu(II) (>0.1 ppm)	Dithizone (20 mg in methyl cellosolve)	pH 1-1.5	AAS	29
Zinc metal (3 g Zn, 100 ml)	Co (>0.1 ppm)	1-Nitroso-2-naphthol (70 mg in ethanol)	pH 3	AAS	31

* For explanation of abbreviations used in this column confer Table 1.

** Sodium dodecylbenzenesulfonate is used for flotation.

Other applications of precipitate flotation

Example 5: Preconcentration of trace heavy metals existing in various chemical states in natural waters (Ref. 32). To a 500-ml sample is added 0.5 ml of indium nitrate solution (100 mg In ml⁻¹), and the pH is adjusted to between 9 and 9.5 with 5 ml of buffer solution (8.5 g of Na₂CO₃ and 10.0 g of NaHCO₃ in 200 ml) to form flocculent hydrated indium oxide precipitate. Three ml of mixed anionic surfactant solution (100 mg of sodium oleate and 200 mg of sodium dodecyl sulfate in 300 ml of 70 % ethanol) is added, and the sample solution is transferred to a flotation cell (Fig. 1A) with a polyethylene insert (Fig. 1E). Nitrogen is passed for 30 s to attain complete mixing and flotation of the precipitate with the aid of numerous tiny bubbles (below 0.5 mm in diameter). The resulting foam layer containing the precipitate is collected in a sampling bottle (Fig. 1C). Trace heavy metals, associated with suspended matter, complexed with humic acid, and existing as inorganic colloidal particles and ions, are simultaneously recovered in yields greater than 95 %. The time required for the preconcentration is ca. 15 min.

ION FLOTATION

In this technique, desired trace ions in an aqueous solution are converted into hydrophobic substances by adding complexing agents and surfactants, floated with the aid of numerous bubbles, and concentrated in a scum or copious foam layer on the solution surface. Ion flotation, in which the floated desired constituents are collected in a water-immiscible organic solvent placed over the sample solution is also useful (solvent sublation). Some examples are described below.

Example 6: Preconcentration of traces of heavy metals from large amounts of matrix elements (Ref. 33). To a 200-ml sample solution containing 0.1 to 1 µg of a trace element [Fe(III), Co, Cu(II), Ag, Au(III)] and 0.5 to 3 g of a matrix element (Na, Mg, Zn) is added 2 ml of 0.01 M complexing agent solution (C₂H₂O₄, KCN, Na₂S₂O₃), and the pH of the solution is adjusted to between 3 and 13 with dil. nitric acid or sodium hydroxide to form anionic complexes of the trace elements. After addition of 4 ml of ethanol and 4 ml of benzalkonium chloride solution (0.5 mg ml⁻¹ in ethanol), the sample solution is transferred to a flotation cell (Fig. 1A) and nitrogen is passed for ca. 5 min. The resulting copious foam is collected with the aid of a spatula and destroyed with 8 ml of ethanol. The solution is diluted to 200 ml with water, and the above procedure is repeated in order to improve preconcentration coefficients. Trace elements are recovered in greater than 90 % yields with preconcentration coefficients of ca. 1000. The time required for the two-stage separation is ca. 20 min.

Example 7: Preconcentration of traces of uranium(VI) in seawater (Refs. 34, 35).

To a 500-ml seawater sample, 50 ml of Arsenazo-III solution (1 mg ml⁻¹ in water) and 50 ml of 1 M acetate buffer (pH 3.5) are added to form an anionic uranium(VI)-Arsenazo-III complex. A tetradecyldimethylbenzylammonium chloride (Zephiramine) solution (10 mg ml⁻¹ in water), 4 ml, is added, the sample solution is transferred to a flotation cell (Fig. 1A) and nitrogen is passed for several minutes. After the solution becomes almost colorless, the mother liquor is sucked off through the sintered-glass disk. The scum is washed with 5 ml of water and dissolved in three 5-ml portions of hot conc. nitric acid. The solution is evaporated to dryness. The residue is ignited, and dissolved in 5 ml of 9 M hydrochloric acid. After reducing uranium(VI) to (IV), the latter is determined by the spectrophotometric Arsenazo-III method. The concentration of uranium at the low $\mu\text{g l}^{-1}$ level is increased ca. 100-fold, with quantitative recoveries.

Example 8: Preconcentration of traces of chromium(VI) in water (Ref. 36).

A 1-l sample (adjusted to pH 5.5) is placed in a flotation cell, and nitrogen is introduced for 20 min while a cetyledyldimethylammonium bromide solution (10 mg ml⁻¹ in water) is added continuously at a rate of 0.5 ml min⁻¹ from the inlet at the bottom of the cell. The resulting voluminous foam layer is successively collected and destroyed by contact with 1-butanol vapor. After the addition of 5 ml of 0.1 M H₂SO₄ followed by 1 ml of diphenylcarbazine solution (10 mg ml⁻¹ in 50 % acetone), the solution is diluted to 50 ml with water, and analyzed spectrophotometrically for chromium. The recovery of chromium at the $\mu\text{g l}^{-1}$ level is 94 % and the volume ratio of destroyed foam to sample solution is 1/120. This technique is also used for continuous separation of chromium(VI) from water. By feeding sample and cetyledyldimethylammonium bromide solutions at rates of 2-5 l h⁻¹ and 0.5 ml min⁻¹, respectively, chromium is recovered in greater than 90 % yields.

The optimum operating conditions for ion flotation vary widely from system to system. Important experimental factors are:

1. Surfactants. A surfactant which is of opposite charge to the desired ions (or their complex ions), and reacts selectively with the ions, is used for flotation. The quantity of the surfactant should be greater than the stoichiometric amount, but a large excess may decrease trace recoveries.

2. pH of the solution. The optimum pH range should be selected from the standpoints of the reactions of the desired ions with the complexing agent and the surfactant, and the flotation of the product.

TABLE 3. Applications of ion flotation

Samples	Trace constituents	pH	Complexing agents and surfactants*	Techniques*	Refs.
Seawater (500 ml)	U(VI) (>0.001 ppm)	3.5	Arsenazo-III, TDBA	SP	34, 35
Water (1000 ml)	Cr(VI) (>0.001 ppm)	5.5	CEDA	SP	36
Water (1000 ml)	Cu(II) (>0.01 ppm)	9	BX, CTAB	AAS	37
Water (1000 ml)	Methyl mercuric chloride (>0.001 ppm)	9	BX, CTAB	GC	38
Seawater (160-500 ml)	Fe(III)** (>0.001 ppm)	2.5-3.5	PDT, DBS	SP	39
Water (500 ml)	Cu(II)** (>0.01 ppm)	9.0-9.2	PDT, SDS	SP	40

* TDBA: Tetradecyldimethylbenzylammonium chloride, CEDA: Cetyledyldimethylammonium bromide, BX: Potassium *n*-butyl xanthate, CTAB: Cetyltrimethylammonium bromide, PDT: 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine, DBS: Sodium dodecylbenzenesulfonate, GC: Gas chromatography. For other abbreviations confer Table 1. ** Reduction followed by solvent sublation with 3-methyl-1-butanol (isoamyl alcohol) or a mixture of 3-methyl-1-butanol and butyl acetate.

3. Gas bubbles. Numerous bubbles produced by using a sintered-glass disk of porosity-3 or-4 (nominal pore size: 20-30 μm or 5-10 μm) are commonly used. Bubbling time and gas flow rate should be carefully optimized, because in most cases it is difficult to observe when the flotation is complete.

4. Coexisting ions. An increase in the quantity of coexisting ions generally decreases trace recoveries, probably because of competition between the desired ions and other ions for surfactants.

Ion flotation has an advantage in that the desired ions are separated without a collector. Applications of ion flotation are listed in Table 3.

CONCLUSION

The flotation technique enables traces to be rapidly separated from a relatively large volume of sample solution using simple apparatus and procedure and small amounts of reagents. The usefulness of this technique has been proved by a number of examples in analyses of natural waters and high-purity metals for trace elements. It will also be applicable to the separation of surfactants and other organic contaminants in natural and waste waters. Improvements in apparatus and procedure, automation, as well as new applications of this technique are expected in the future.

REFERENCES

1. F. Sebba, Ion Flotation, Elsevier, Amsterdam (1962).
2. R. Lemlich, Ed., Adsorptive Bubble Separation Techniques, Academic Press, New York (1972).
3. R.B. Grieves, Chem. Eng. J. **9**, 93 (1975).
4. K. Fukuda and A. Mizuike, Japan Analyst **17**, 319-322 (1968).
5. M. Hiraide, T. Ito, M. Baba, H. Kawaguchi and A. Mizuike, Anal. Chem. **52**, 804-807 (1980).
6. Y.S. Kim and H. Zeitlin, Separ. Sci. **6**, 505-513 (1971).
7. M. Hiraide and A. Mizuike, Japan Analyst **29**, 84-86 (1980).
8. M. Hiraide and A. Mizuike, Japan Analyst **26**, 47-50 (1977).
9. M. Hiraide and A. Mizuike, Japan Analyst **23**, 522-524 (1974).
10. A. Mizuike and M. Hiraide, Anal. Chim. Acta **69**, 231-234 (1974).
11. M. Hiraide, Y. Yoshida and A. Mizuike, Anal. Chim. Acta **81**, 185-189 (1976).
12. S. Nakashima, Analyst **103**, 1031-1036 (1978).
13. S. Nakashima, Japan Analyst **28**, 561-563 (1979).
14. S. Nakashima, Bull. Chem. Soc. Jpn. **52**, 1844-1848 (1979).
15. S. Nakashima, Anal. Chem. **51**, 654-656 (1979).
16. S. Nakashima, Z. Anal. Chem. **303**, 10-13 (1980).
17. S. Nakashima, Bull. Chem. Soc. Jpn. **54**, 291-292 (1981).
18. Y.S. Kim and H. Zeitlin, Separ. Sci. **7**, 1-12 (1972).
19. F.E. Chaine and H. Zeitlin, Separ. Sci. **9**, 1-12 (1974).
20. M. Hagadone and H. Zeitlin, Anal. Chim. Acta **86**, 289-292 (1976).
21. J.H. Tzeng and H. Zeitlin, Anal. Chim. Acta **101**, 71-77 (1978).
22. Y.S. Kim and H. Zeitlin, Anal. Chem. **43**, 1390 (1971).
23. G. Leung, Y.S. Kim and H. Zeitlin, Anal. Chim. Acta **60**, 229-232 (1972).
24. D. Voyce and H. Zeitlin, Anal. Chim. Acta **69**, 27-34 (1974).
25. N. Rothstein and H. Zeitlin, Anal. Lett. **9**, 461-468 (1976).
26. W.J. Williams and A.H. Gillam, Analyst **103**, 1239-1243 (1978).
27. A. Mizuike, M. Hiraide and T. Kanematsu, Japan Analyst **26**, 137-138 (1977).
28. M. Hiraide and A. Mizuike, Bull. Chem. Soc. Jpn. **48**, 3753-3754 (1975).
29. M. Hiraide and A. Mizuike, Talanta **22**, 539-541 (1975).
30. M. Hiraide and A. Mizuike, Japan Analyst **26**, 655-658 (1977).
31. A. Mizuike, M. Hiraide and T. Suzuki, Japan Analyst **26**, 72-74 (1977).
32. M. Hiraide, J. Mizutani and A. Mizuike, J. Chem. Soc. Jpn. **1981**, 161-165.
33. A. Mizuike, K. Fukuda and J. Suzuki, Japan Analyst **18**, 519-521 (1969).
34. K. Sekine and H. Onishi, Anal. Chim. Acta **62**, 468-471 (1972).
35. K. Sekine, Mikrochim. Acta [Wien] **1975I**, 313-319.
36. M. Aoyama, T. Hobo and S. Suzuki, Japan Analyst **30**, 224-228 (1981).
37. T. Hobo, T. Ogura, S. Suzuki and S. Araki, Japan Analyst **24**, 288-293 (1975).
38. T. Hobo, Y. Sudo, S. Suzuki and S. Araki, Japan Analyst **27**, 104-108 (1978).
39. K. Kotsuji, Y. Kameyama, M. Arikawa and S. Hayashi, Japan Analyst **26**, 475-479 (1977).
40. K. Kotsuji, S. Hatazawa, T. Shikata and S. Hayashi, Japan Analyst **28**, 263-267 (1979).