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ANALYTICAL APPLICATIONS OF SOME FLOTATION TECHNIQUES—A REVIEW

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Summary—A review is given of the principles and more recent applications of foam flotation

Separation techniques based on use of adsorptive bubbles (flotation techniques) have received a great deal of attention in chemical engineering, but have awakened less interest in analytical chemistry Flotation techniques were first used to obtain mineral concentrates or selective separation of them.

In chemical engineering, these techniques began to expand in the 1960s and today have many applications in industry, to separate toxic substances, suspended solids, micro-organisms, *etc* from residual, industrial, sea and drinkable waters. These techniques turned out to be very simple compared with classical separation methods such as liquid–liquid extraction, ion-exchange, co-precipitation *etc*. They allow the handling of large volumes of sample, and present considerable saving in reagents, time and energy. Their analytical applications started to be studied in the middle 1970s, especially in the U.S.A., U S.S.R. and Japan Sometimes, this makes it difficult to achieve a readily accessible bibliography On the other hand, the U S A. papers are basically in chemical engineering

Discussions of these techniques as methods of separation and/or preconcentration are not yet available in analytical chemistry textbooks and they are scarcely found even as monographs and reviews. The monograph edited by Lemlich[1] presents a general treatment of all these techniques, as well as their development up to 1972. There are also some very specialized monographs, such as Sebba's on ionic flotation,[2] and another more recently by Clarke and Wilson[3] that discusses the theory and applications of foam separations. Some books on separation methods contain chapters dealing more or less extensively[4–6] with the general or particular aspects of these techniques.

The most outstanding recent reviews are those by Clarke and Wilson,[7] and by Hiraide and Mizuike [8 9] The first is a very complete review of books, reviews, theories and models of separation by flotation, including a section on metal and organic compound separations The last two reviews consider flotation techniques from an analytical chemistry perspective, especially precipitation and ion flotation of organic and inorganic species; unfortunately, the Russian work is largely ignored.

At the present time flotation studies on most of the elements are known (Fig. 1) as well as on a large number of different species, therefore, in the present review the analytical applications of precipitate flotation are included, as well as ion flotation and solvent sublation, covering the last few years (from about 1980). Furthermore, a description of the techniques, and the theoretical foundations of precipitate flotation and solvent sublation are included, because these are the most interesting in analytical chemistry

DESCRIPTION AND CLASSIFICATION OF THE TECHNIQUES

Lemlich[1] proposed the term "Adsubble Techniques", based on a contraction of "adsorptive bubbles" There are a number of separation methods, based on differences in surface tension, in which dispersed solids, precipitates, colloids and dissolved substances are adsorbed on an ascending gas stream, and thus separated from the liquid mass where they were initially This separation is due to the ability of some species to orient themselves in the air-water interface, and the adsorption on the bubble surfaces is due to the presence of certain functional groups. The substances to be separated

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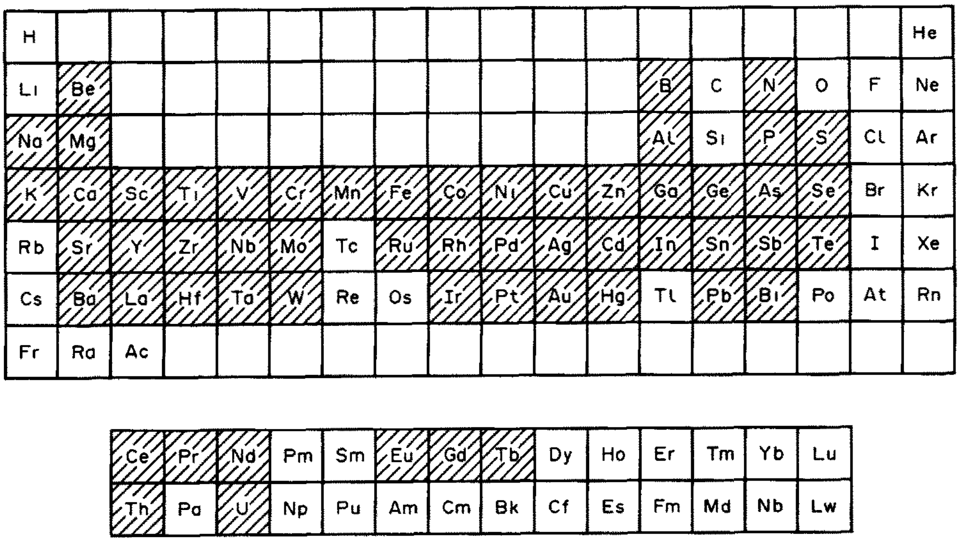


Fig 1 The elements within the shaded area are those with ions amenable to separation by flotation techniques

by means of these techniques must either already possess these groups or be given them by addition of some surfactant agent

Karger *et al*[10] classified these techniques in two large groups based on foam formation (Table 1) Later, Pinfold[11] suggested they should be classified according to the adsorption mechanism, depending on the flotation of particles, ions and molecules

Obviously this second option is more logical, but in practice the classification by Karger *et al* continues to be the more widely accepted. According to it, in the first group (non-foaming techniques) the bubble fractionation technique[12] must be included, which can be used for the separation of the solution components by adsorption on the bubbles of an ascending gas stream, leading to an enrichment of the surface-active substances in the upper zone of the column. This is the simplest "adsubble technique" and also the least used in practice It is mainly applied to the separation and/or preconcentration of surfactants at low concentrations. Obviously, in this case it is not necessary to add a foaming agent. In practice, these phenomena and fractionation processes could occur by accidental bubble formation, as in the liberation of gas during a chemical reaction, and this can give rise to separations of surface-active substances

The technique known as solvent sublation was initially proposed by Sebba[2] as an option for ion flotation, if excessively copious foam formation occurred The main difference from the other techniques is that the substances adsorbed on the ascending bubbles, once they arrive in the column upper zone, find a different layer of solvent, inmiscible with the liquid from which we wish to separate them This immiscible liquid collects the substances (sublates) which arrive at the interface, and this produces the separation of these substances.

The "adsubble techniques" with foam formation are divided into two large groups foam fractionation and flotation

Foam fractionation consists in the separation of dissolved substances which possess a lyophobic group or (in which case they are called colligends) can be made sufficiently surface active by combination with surfactant agents (collectors) by chelate formation, ionic bonding or any other kind of union, the resulting

Table 1 Classification of the flotation techniques according to Karger *et al*[10]

Non-foaming techniques	Solvent sublation	
	Bubble fractionation	
Foam separation	Foam fractionation	
	Flotation	Macroflotation
		Microflotation
		Precipitate flotation
		Ionic flotation

surface-active substances being adsorbed on the surface of the bubbles ascending through the liquid mass

Flotation techniques can be divided, in turn, into four large groups

I—*Macroflotation* An example is mineral flotation, a widespread and intensively studied technique used in the mining industry for obtaining mineral concentrates and eliminating impurities.

II—*Microflotation* Flotation of micro-particles such as colloids, micro-organisms The analyte may be adsorbed on a charged colloidal species generated to act as a carrier, and the colloid may be floated by addition of a surfactant, as in precipitate flotation

III—*Precipitate flotation* Separation of substances by precipitation and gas streaming, in which bubbles are adsorbed on the precipitate, floating it up to the liquid surface It is possible to consider two kinds of precipitate flotation

(a) Precipitate flotation of the first kind The surfactant does not itself form an insoluble compound with the species to be separated, but helps it to reach the surface of the liquid mass when it is precipitated with some other reagent This has been used in two different ways In some cases the ion to be separated is precipitated, and in other cases, is co-precipitated with an excess of some other precipitate or colloid, and then the combined floc is floated This last technique has been the most used, and is probably the one exhibiting greatest analytical interest Sheiham and Pinfold[13] named it co-flotation

(b) Precipitate flotation of the second kind Here the addition of a surfactant is not necessary, because a hydrophobic substance is formed from two hydrophilic ones

IV—*Ion flotation* This was introduced by Sebba,[2,14] and is the separation of ions in solution that are not surface-active, by addition of surfactants (collectors), and the subsequent passage of a gas stream to produce a foam containing a solid compound of the surfactant with the species of interest. Normally the collector is an ion with opposite charge to the colligend, but any suitable type of chemical union can be used.

Some related techniques are "laminae column foaming"[15] and "booster bubble fractionation"[16] The first technique is a flotation process of laminar type, by means of a continuous chain of wall-to-wall bubbles rising up the column. The second uses volatile organic compounds, together with the gas bubbles, in solutions with a low concentration of active substance, causing foam formation and subsequent separation, this may be quicker than the classic flotation technique, and improves the selectivity.

The "adsorptive droplet techniques"[17] are similar to these techniques but, instead of gas bubbles, droplets of inmiscible liquid are added

In "solvent sublation" a water-insoluble organic solvent is floated on top of the column to extract neutral species from the foam.

Finally, it should be mentioned that the term "spectrophotometric-flotation", although apparently related to those above, is different because there is no gas bubbling, and therefore it cannot be considered as an "adsubble technique" It is based on the fact that some ion-pairs are not soluble in polar organic solvents, and when an aqueous phase is shaken with an organic solvent, a precipitate originates in the interface or on the extraction funnel walls Once both phases have been separated the precipitate is dissolved in an appropriate solvent, and the corresponding measurements are made by spectrophotometry This technique was introduced by Marczenko *et al*[18]

INSTRUMENTATION

There are no instruments on the market for these techniques, and because of the simplicity of the necessary devices, these are tailored according to the task in hand. However, all flotation set-ups include several common basic devices.

—Gas generating source This can be a small air compressor or gas cylinder Air is the gas most commonly used, however there are works that report use of nitrogen, helium or argon

—Regulator system for controlling pressure and gas flow (needle valves, *etc.*).

—Gas washing flask Its purpose is to presaturate the gas with water or other suitable solvent, to avoid any change in the volume of the system In some cases it is used to eliminate carbon dioxide from the system to avoid undesirable reactions in the column.

—Flowmeter. This is for measuring the gas flow-rate through the column, normally a soap-bubble flowmeter is used.

—Column. Glass is generally used, but plastic columns are also used. The size and form are based on the system needs, but there is always a sintered-glass plate at the bottom with adequate porosity (usually G3 or G4). The gas passing through this porous plate produces the small ascending bubbles which generate the foam

Auxiliary equipment, varying from case to case, may include peristaltic pumps (generally used for continuous operation), magnetic stirrers, devices for collection of the foam and precipitate (foam suction sets, polyethylene laminae on the walls of the column to keep the precipitate attached; shielding and safety devices for work with radioactive substances, *etc.*), lateral taps (to allow monitoring the kinetics of the process, to discharge the liquid at the end of the process, or as an outlet for effluent in continuous flow operation), and a thermometer.

Figure 2 show some of the devices reported A typical solvent sublation column is illustrated in the paper by Womack *et al.*[28]

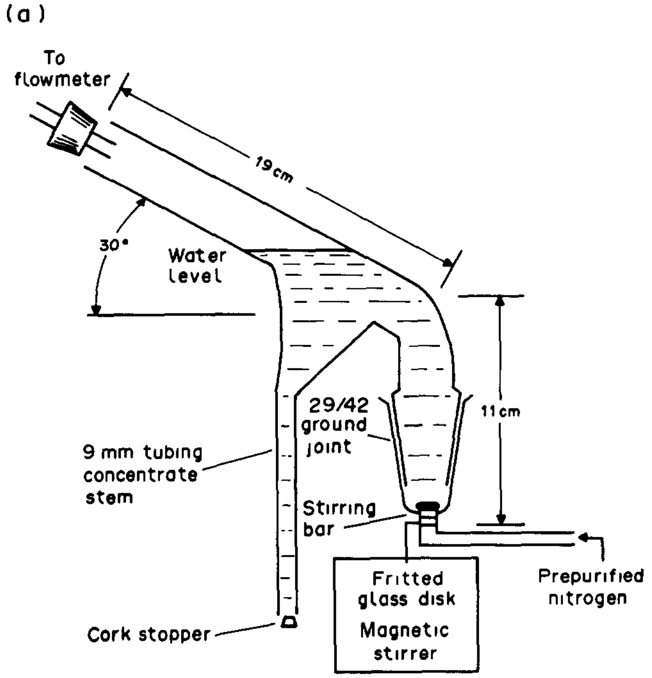


Fig 2(a)

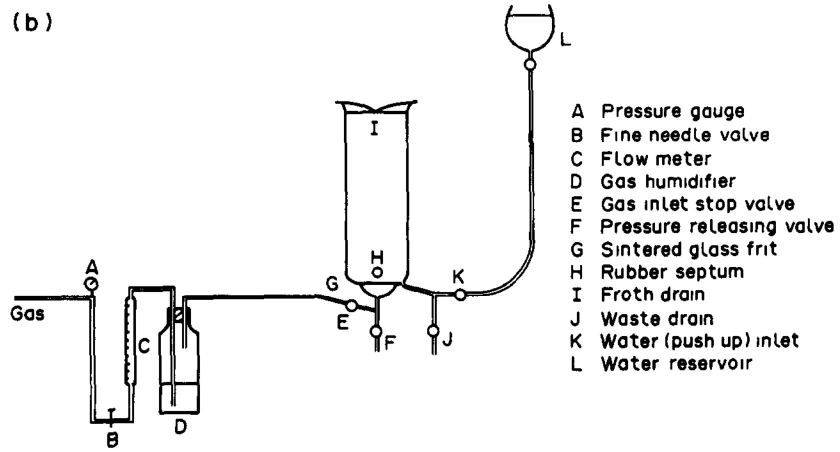
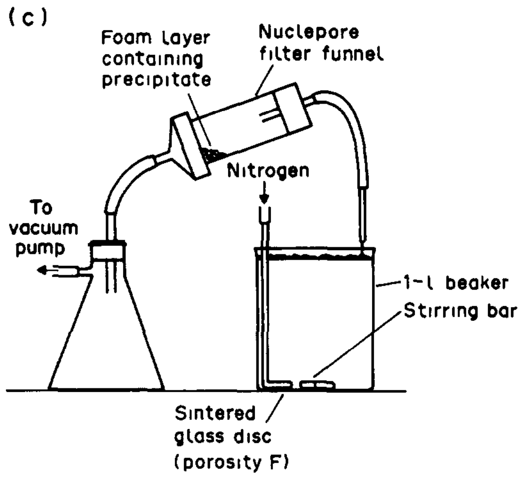


Fig 2(b)



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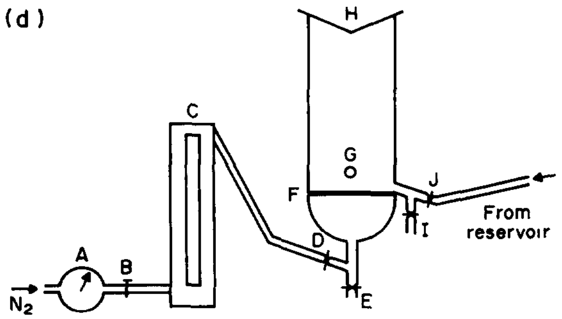
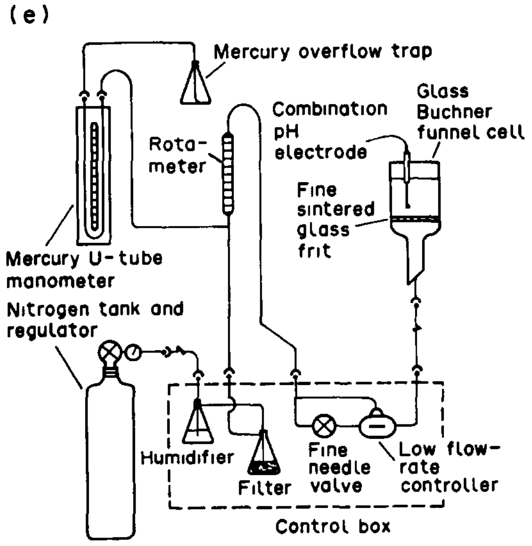


Diagram of flotation cell A, Pressure gauge; B, fine needle valve, C, flow meter, D, gas inlet valve; E, pressure injection point (rubber septum); H, foam drain, I, drain valve; and J, water inlet

Fig 2(d)



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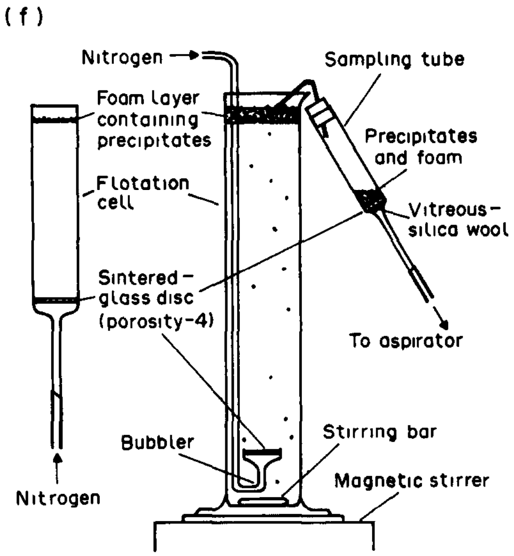

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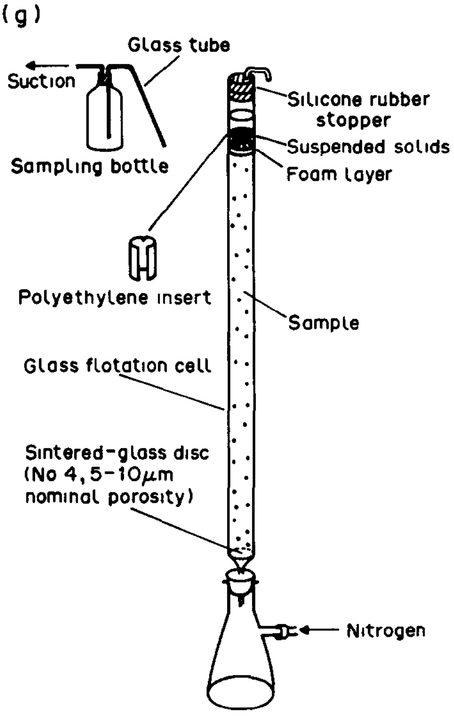

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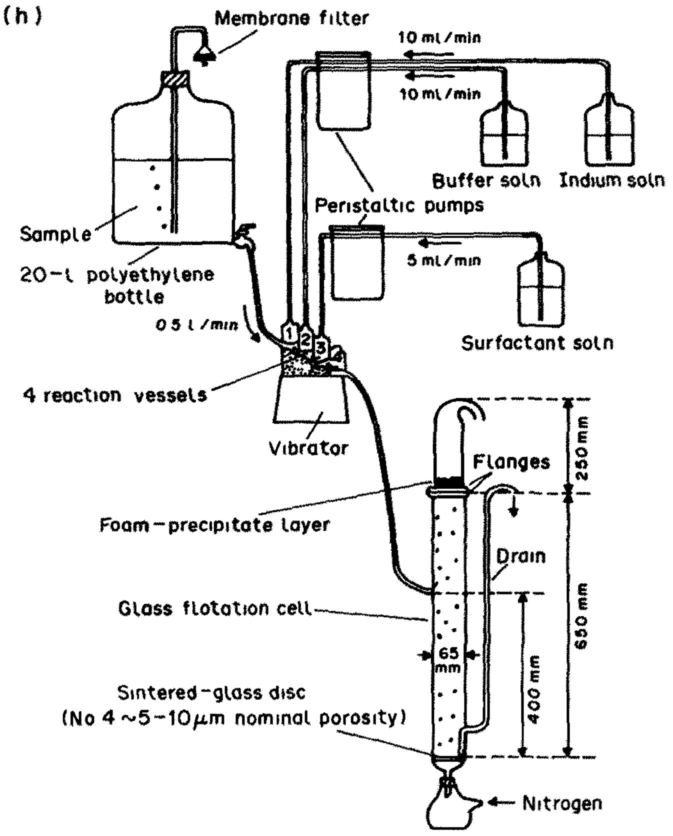

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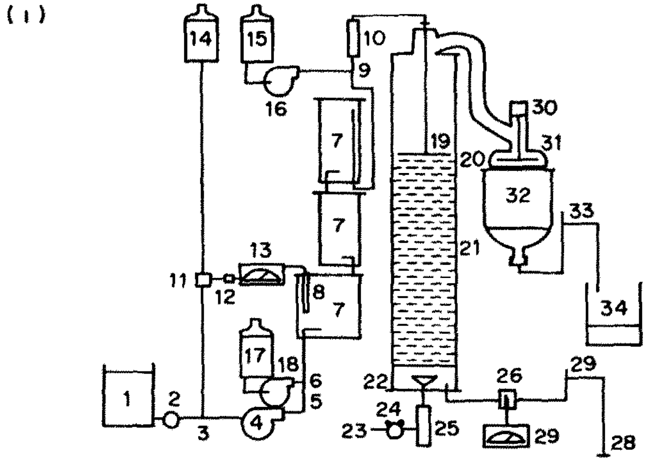
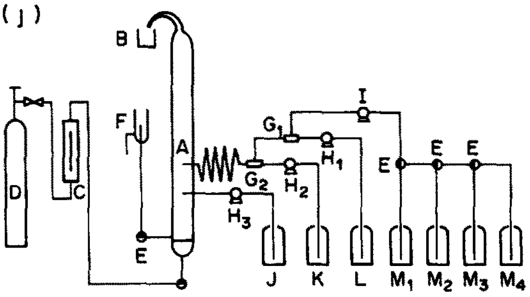


Schematic diagram of 30 cm pilot plant

1 Waste tank
2 Waste tank valve
3 NaOH injection tee
4 Main pump
5 Flow control valve
6 $FeCl_3$ injection tee
7 Mixing chamber
8. Control pH electrode
9. NLS injection tee
10 Waste flow rotameter
11 NaOH solenoid valve
12 Electrical junction box
13 Control pH meter
14 NaOH tank
15 NLS tank
16 NLS feed pump
17 $FeCl_3$ tank
18 $FeCl_3$ feed pump
19 Flow dispersion head
20. Column
21. Baffles
22 Air diffuser
23. Air supply line
24 Air pressure regulator
25 Air flow rotameter
26 Monitoring pH electrode
27 Column liquid level control
28 Effluent line
29 Monitoring pH meter
30 Foam breaker motor
31 Foam breaker
32 Clarifier
33 Clarifier liquid level control
34 Broken foam container

Fig 2(i)

(j)



(A) Separation tube; (B) foam collector (containing 5 ml of 1-propanol); (C) flow meter; (D) nitrogen cylinder, (E) three-way cock; (F) effluent drain, (G_1, G_2) mixing chambers, (H_1, H_2, H_3) plunger pumps; (I) diaphragm pump, (J) surfactant solution (1% SLS) reservoir; (K) 1% NEDA solution reservoir, (L) 2% ABSA solution reservoir, (M_1, M_2, M_3, M_4) sample reservoirs The coil between G_2 and A is 8 m long

Fig 2(j)

(k)

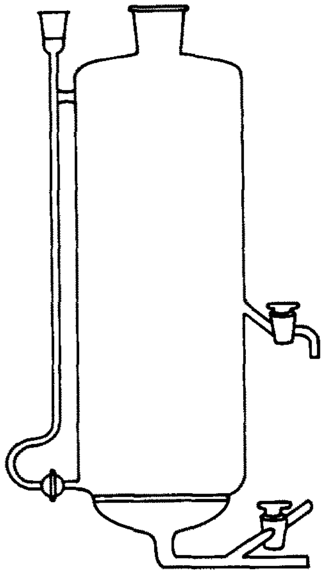


Fig 2(k)

Fig 2 Some examples of flotation apparatus Reproduced, with permission, from (a) reference 19, p 158, by courtesy of Marcel Dekker, Inc, (b) reference 20, p 507, by courtesy of Marcel Dekker, Inc, (c) R S S Murthy and D E Ryan, *Anal Chem*, 1983, **55**, 682, copyright 1983, American Chemical Society, (d) W J Williams and A H Gillam, *Analyst*, 1978, **103**, 1239, copyright 1978, Royal Society of Chemistry, (e) reference 23, p 358, by courtesy of Marcel Dekker, Inc, (f), (g) reference 6, by courtesy of Springer-Verlag, Heidelberg, (h) reference 24, copyright 1983, Elsevier Science Publishers, (i) reference 25, p 606, courtesy of Marcel Dekker, Inc, (j) reference 26, copyright 1982, Elsevier Science Publishers, (k) reference 27, p 621, by courtesy of Marcel Dekker, Inc

PARAMETERS AFFECTING THE FLOTATION PROCESSES

Several factors influence the processes: some affect the solution and others are operational factors. Some of the first group are of basic importance for all the flotation techniques (*e g*, colligend and collector concentrations and their relationship, pH and ionic strength); others are important for particular techniques (for example, the induction time). The operational variables include gas flow-rate, porosity of the sintered-glass plate, average bubble size, and the column geometry

Collector and colligend concentration

If the collector concentration is too low, there will not be enough colligend–collector product (ion-pair, complex, adsorption compound, *etc.*) formed, so not all of the colligend will be separated by adsorption on the gas bubbles

On the other hand, if too high a concentration of collector is present, although ion separation is favoured, the excess of collector will compete for sites in the bubble surface, and may even form micelles if its CMC (critical micelle concentration) is reached In all cases undesirable effects on the flotation process are observed As a rule, to achieve a complete separation in ion flotation and solvent sublation, it is necessary to have a collector concentration in excess over the stoichiometric amount In precipitate flotation the collector concentration has to be large enough to form a foam that is stable and persistent enough to keep the precipitate suspended; this is not related to the sublate stoichiometry

The colligend concentration is related to the collector, and it may be necessary to use different concentrations with different techniques For example, in precipitate flotation, the relationship between the amounts of colligend and precipitate has to be considered, as well as the precipitate solubility, to avoid redispersion of the precipitate into the bulk solution

pH of the solution

The most critical variable for all the techniques is the pH of the solution, since it will determine the sign and magnitude of the charges on the surface and some of the ionic species involved in the process Variation of pH can produce colligend charge variations by hydrolysis or by formation of other complexes that can produce colligends, precipitates and changes in the collector behaviour. In ion and precipitate flotation, the pH has an influence on foam stability

Ionic strength

The influence of the ionic strength of the medium varies from technique to technique, probably because of the different effects that take place in the adsorption process on the interface responsible for the separation Usually, an increase in the ionic strength will decrease the effectiveness of separation, probably because of competition between the colligend and the other ions for the collector Since surfactant adsorption in the gas–liquid interface is increased with increasing ionic strength, foam-type separations are improved when the ionic strength is increased, unless the surfactant concentration reaches the CMC In precipitate flotation of the first kind and in ion flotation the effectiveness of separation usually decreases when the ionic strength of the medium is increased, owing to competition by the foreign ions for the collector, on the other hand, the surfactant will float more quickly Finally, in precipitate flotation, increasing the ionic strength will increase the solubility of the precipitate However, the addition of foreign ions could produce changes in the nature of the colligend, thus enabling separations which would not be possible otherwise For instance, the addition of certain ions may give rise to formation of complexes with opposite charge to that expected, changing the behaviour of the surfactant, and consequently give rise to an effective separation

Induction time

The duration of agitation of the sample before it is transferred to the flotation cell could have a positive influence on the separation This is the case for precipitate flotation, because the longer the time, the bigger the particles formed in the precipitation or co-precipitation reaction Nevertheless some workers[1,29] advise not to use an induction period, but to add the surfactant at the beginning of the flotation or even stepwise during the flotation process This factor is important in connection with optimization of the process, though less so than the flow-rate, pH, and ionic strength of the medium

Temperature

The effect of temperature varies according to the particular system Thus in some cases an increase of temperature has no effect on ion flotation, whereas in others it may have positive or negative effects. In precipitate flotation a temperature increase has a positive effect due to its influence on the size of the particles formed On the other hand it will also increase the solubility of the precipitate and the instability of the foam, giving rise to partial dissolution of the precipitate and insufficient foam consistency to hold up the precipitate. Increase or decrease in the separation yield as the temperature increases can be explained as due to collector adsorption being a temperature-dependent physical or chemisorption process Since this parameter has an important and variable influence on the flotation process, it is very interesting to study each particular case, especially for large temperature variations.

Presence of ethanol

Addition of small quantities of ethanol (or any other substance for the same purpose) to the solution has several functions, such as avoiding micelle formation and decreasing bubble size, which will improve the separation. However, large quantities of ethanol could give rise to foam breakage (too quick coalescence) or cause no foam at all to form. Most of the collectors are added in ethanolic solution, because of their low solubility in aqueous solutions Usually it is not necessary to add more ethanol than that added with the collector, but this has to be decided from the results obtained for each case

Gas flow-rate

One of the most important parameters is the gas flow-rate, which depends on the technique to be used, the quantity of sample, and the porosity of the sintered-glass plate fitted in the column. When fine-porosity plates are used the flow-rates are lower and the separation yield increases with the flow-rate, a mild turbulence being produced, causing precipitate redispersion. Thus fine-porosity plates are used in ion flotation and solvent sublation, with low flow-rate to avoid fluctuation of the organic layer or turbulence near the foam layer In precipitate flotation sintered-glass plates of higher porosity are used together with higher gas flows, in order to maintain a consistent foam that supports the precipitate, thus avoiding its re-entry into solution in cases characterized by slow kinetics.

Sintered-glass plate porosity and bubble size

The sintered-glass plate porosity and the bubble size are usually very closely related to the gas flow-rate. Normally, it is better to use small and uniform bubbles, because the gas–liquid interface surface is increased.

Column form and size

The column form, size and arrangement influence the efficiency of the process. There are some works in the literature proving that the cross-section, capacity,[30] and inclination from the vertical[31] have an influence on the sublate recovery.

PRECIPITATE FLOTATION AND SOLVENT SUBLATION MECHANISMS

Precipitate flotation

There are currently several physical models available to explain precipitate separation by flotation; those most often used are based on coulombic attraction (the Gouy–Chapman double-layer) and on the contact angle (for mineral flotation).

Both models are complementary and valid, as shown in the theoretical developments published by Wilson and co-workers[32–50] since 1974, in which they have been trying to predict and justify the influence that some variables have on the flotation process, introducing successive modifications and considerations in both models, and reporting experimental results to support their arguments.

Coulombic attraction model. Jaycock and Ottewill[51] observed that in a colloidal dispersion of silver iodides initially exhibiting a negative electrophoretic mobility, the charge was first neutralized and eventually became positive when HEDABr (see surfactants abbreviation key on p 292) was added. They explained that in this phenomenon the polar groups of the surfactant are linked to the charged particle surface by electrostatic forces, forming a single layer, but if all the surface charges are neutralized the zeta potential becomes zero, and if a second layer of surfactant molecules is adsorbed, held by van der Waals forces, this would give rise to an increase of the zeta potential, even up to positive values.

DeVivo and Karger[52] started from this model and took into account that the zeta potential will be related to the surface charge, and will depend not only on the type and concentration of the surfactant but also on the presence of electrolytes and the quantity of particles present. They studied the correlation between potential, ionic strength and particle size with the purpose of evaluating the influence of these variables on the flotation process From experimental results on flotation of kaolin and montmorillonite with HEDABr, they proved that addition of electrolytes produced a decrease in the initial zeta potential and a loss of efficiency in the flotation process, therefore, in principle, an inverse relation is expected to exist between the aggregate sizes and the degree of flotation. However, this result disagreed with that published by Rubin and Lackey[53] to the effect that flotation of *Bacillus cereus* is considerably better when it is coagulated with alum. Taking into account the work of Spargo and Pinfold[27] on the influence of bubble size, DeVivo and Karger[52] found that this difference arose from the use of smaller bubble sizes and smaller flow-rate by Rubin and Lackey To prove this they examined the clay separation with sintered-glass plates of lower porosity, and obtained much better results with coagulated species.

Thus the bubble size can affect the capacity of the particle–surfactant species to become attached to the bubbles, and consequently the effectiveness of flotation When plates of higher porosity are used, bubbles of the same size as the particles, or even bigger, are formed; therefore, the attachment of more than one bubble to a particle will be less likely, and the particles' capacity to float will be consequently reduced Using smaller bubbles will increase the probability of union of more than one bubble with an aggregate, and therefore increase flotation separation The bubble size also has an influence on the stability of the foam,[54] foam obtained with big bubbles is usually less stable.

Just before the work of DeVivo and Karger[52] was published, a paper by Jorné and Rubin[55] appeared in which they applied the Gouy–Chapman theory of the double electric layer to predict the distribution of species by foam fractionation, taking into account the sizes and charges of the species They found that the experimental results agreed with the theoretical model

Wilson and Wilson, in the first work of their series tried to apply the Gouy–Chapman theory to justify the fact, already very well known, that increasing the ionic strength causes a decrease in flotation efficiency By means of a series of calculations, they determined the free energy responsible for the attraction forces between the precipitate particles and the surfactant film Using a computer simulation program, they calculated the variation of the free energy with ionic strength, concluding that these values were in good agreement with those expected from the influence of ionic strength

Later, Huang and Wilson[33] studied the equilibrium of separation of the precipitate from the liquid mass. Starting from the Gouy–Chapman model they studied the effect of several factors on the kinetics and equilibrium of precipitate flotation. Starting from a 1-cm^2 film surface area and thickness L, they calculated the variation of the colloid concentration with time and distance from the film, as a function of the solution potential, which itself is influenced by the distance, ionic strength, dielectric constant and temperature The results of this model indicated that the migration of the colloids must be extraordinarily fast, so the equilibrium between the precipitate particles in the boundary layer and the inner part of the foam should be the process-controlling factor.

Wilson and Wilson also studied the influence of ionic strength, charge and floc size on the flotation process, taking into account the floc volume [34] A first study on the attachment of surfactant film to colloids, in agreement with a simple model, allowed them to obtain expressions in accordance with the experimental results, that increasing precipitate floc size decreases the process efficiency With a model based on the Gouy–Chapman theory, they studied the electrostatic attraction between the charged surfactant surface and the flocs, in terms of electrolyte concentration and dielectric constant of the medium This last model was found to furnish results similar to those obtained with the simple one, but was more precise.

Wilson[36] calculated the adsorption isotherms by using three different approximations, taking into account the finite volume of the flocs and the ions responsible for the ionic atmosphere With any of these models there is a decrease in the adsorption isotherms when the ionic strength and temperature increase (in the last model to only a slight degree), but there is only very small influence of the ion size

Wilson, using methods from statistical mechanical studies of non-ideal gases, calculated the adsorption isotherm, taking into account the attractions and repulsions produced between the flocs.[37] He developed four models to calculate the isotherms, and studied the influence of ionic strength, temperature, *etc* on them, obtaining slightly different isotherms according to the approximations used, especially when the floc size is large. All these models predict a more or less marked decrease in the adsorption when the ionic strength increases, whereas the temperature has a much less marked effect.

According to the data published by Riddick,[56] some colloids with negative zeta potential produced an even smaller zeta potential when small quantities of electrolytes were added, and this might cause some colloids to float more efficiently On this basis, Clarke *et al* [39] studied the effect produced by different variables on the zeta potential, and on ion adsorption by flocs They applied it to the adsorption of different anions, and the effect of glycerine (by means of the possibility of iron-complex formation) on the flotation of $Fe(OH)_3$ with NaLS. According to the Gouy–Chapman model and taking as a basis the effect of electric potential, they calculated the influence of the adsorbed ion and the temperature at different electrolyte concentrations, observing that larger differences appeared when low electrolyte concentrations were considered.

The contact angle model. For mineral flotation Fuerstenau and Healy[57] proposed a model in which the surfactant polar tail is directly adsorbed on the solid surface. At sufficiently high concentrations, the surfactant hydrocarbon tail presents a rather hydrophobic surface to be attached to the bubble, this allowing the flotation In this model, hemimicelle formation on the solid surface has a special interest; it occurs when there is a high enough concentration of the surfactant, and is caused by the van der Waals forces between the surfactant hydrocarbon chains. Therefore, the larger the surfactant chain the smaller the surfactant concentration required to produce the flotation. The same phenomenon explains the rapid increase observed in flotation when the surfactant concentration is increased

Fowler and Guggenheim[58] described a method for the approximate calculation of adsorption isotherms, with models similar to those later proposed by Fuerstenau and Healy. Wilson used these approximations for the isotherm calculation, taking into account the electric potential in the vicinity of the solid surface.[38] From the results obtained it was concluded that a temperature increase will increase the surfactant concentration necessary to form the hemimicelle, and an increase of the ionic strength will decrease the quantity of surfactant agent needed.

Wilson and Kennedy, using the same model, studied the effect of an increase in the surfactant concentration on hemimicelle formation.[40] In this case, there will be a situation in which the formation of a second layer over the first will change the character of the particle, making it hydrophilic, and consequently no separation will take place From a theoretical analysis of this adsorption phenomenon on the first layer, the effects of the ionic strength, length of the hydrocarbon chain, temperature *etc.* were inferred. The results obtained are as expected; an ionic strength increase will bring about a decrease in the flotation effectiveness. An increment in the carbon chain length generates an increment of the van der Waals forces and, facilitates the formation of a second layer, which blocks the flotation. Therefore, it is necessary to take special care when the concentration of long-chain surfactants is increased.

With the same model Kiefer and Wilson studied the effects (on the adsorption isotherms) of the coulombic repulsions of the surfactant ionic heads, and the van der Waals attractions in the hydrocarbon chains.[42]

In the last works of the series Wilson and co-workers undertook the calculation of isotherms for surfactant mixtures.[46,48,50] The results obtained[46] show that the isotherms can vary widely, depending on the factors to be considered; it was therefore suggested that for industrial use these isotherms should be calculated to economise in use of expensive surfactants.[40]

Solvent sublation

According to Sebba[2] the separation mechanism in the solvent sublation technique is very simple. As the gas bubbles pass through the liquid mass they collect the colligend–collector species, which is then transferred to the organic phase on the upper surface of the liquid mass

Later, Karger's group and associates made a series of studies and deduced a much more complex mechanism.[27,59–63] The bubbles are enriched in the material when they are passing through the aqueous medium. When they arrive at the liquid–liquid interface they are not able to overcome the interfacial tension immediately. Also, some bubbles coalesce before passing through the interface. It is expected that repulsions between the bubbles, deriving from the zeta potentials, would result in a slow bubble coalescence process. Consequently, a relatively stationary bubble layer is formed under the liquid–liquid interface; the liquid trapped in this layer is protected from the turbulence of the ascending bubbles in the aqueous phase

When the coalescing bubbles are moving through the liquid–liquid interface, they carry away a small quantity of the liquid contained in the aforementioned interfacial region, although its amount is much less than the quantity of liquid trapped in some other bubble flotation techniques. The collector and colligend (sublate) that go to the organic phase dissolve in it quickly, while the accompanying water returns to the aqueous phase as small drops once the bubbles are broken down. All these are experimental phenomena readily observed in the laboratory.

In Karger's hypothesis it is accepted that probably an equilibrium is established between the drops of aqueous phase and the organic phase, although for volume-ratio reasons it is logical to accept that the quantity of sublate dissolved in the small water drops returning to the aqueous mass must be very small. Moreover, this sublate does not itself return to the aqueous mass but to the intermediate stationary interface

On the basis of this model it is obvious that an equilibrium between the aqueous mass and organic phase is not established, and therefore it is easy to deduce that there are fundamental differences between solvent sublation and liquid–liquid extraction This distinction was pointed out by Pinfold and co-workers[61,63]

The studies of Karger's group, whose fundamental conclusions have just been summarized, gave a better qualitative approximation to the separation mechanism that controls solvent sublation In fact, they allow rational justification of most of the experimental phenomena associated with this technique. Nevertheless they were not translated into a mathematical model suitable for a theoretical and predictive treatment of these phenomena This has been remedied, however, by Wilson's group, since 1981[28,30,64–68] In this series of papers, the equations that constitute the theoretical model are deduced in full detail and have been submitted to continuous refinement by the authors. For that reason, here only the most outstanding results from the conceptual point of view and the final formulae will be summarized as a basis for the discussion.

In practice, Wilson's model did not accept Karger's hypothesis, because it was considered that the experimental results contradict it

Two contributions by Karger and co-workers point to the fact that the separation velocity decreases considerably as the process deviates further from first-order kinetics.[59,62] These authors interpret this phenomenon as derived from progressive dissolution and saturation of the organic solvent in the aqueous mass, giving rise to a second equilibrium competitive with the fundamental one of the separation at the interface. Wilson and co-workers showed the error of this working hypothesis by using presaturated aqueous phases in the organic solvent, observing that a sharp change in the sublation during the process is also produced under these conditions Obviously there were some other limiting factors involved in the rate of mass transfer. These time-dependent factors must be taken into account when a mathematical model with predictive capacity is to be developed.

The Wilson group has developed different models which are initially based on the adsorption of volatile compounds on a stream of bubbles. In these models the rate-limiting step is the mass transfer of solute from the solution to the air–water interface. The next approximation was the consideration of non-volatile compounds, taking into account the Langmuir isotherm of adsorption in the air–water interface, as well as the mass transfer throughout the bubble limiting layer. Finally models were developed for single or multiple stage columns controlled by an equilibrium or a mass transfer process

The first work of the series dealt with the solvent sublation of 1,1,1-trichloroethane and developed a mathematical model for processes of this kind involving surface-active and volatile compounds.[64] Later the effects of some variables, such as the air flow-rate and the addition of a salt, on the solvent sublation of two ion-pairs (Methylene Blue–tetradecylsulphate and Methyl Orange–hexadecyltrimethylammonium) were studied[28]

In the case of separation by solvent sublation of molecular, surfactant and volatile substances the rate of transfer is given by

$$\frac{\mathrm{d}m_\mathrm{b}}{\mathrm{d}t} = 4\pi r^2 k \left[\tfrac{4}{3}\pi r^3 K_\mathrm{w} c_\mathrm{w} + \frac{4\pi r^2 \Gamma_\mathrm{m}}{(1 + c_{1/2}/c_\mathrm{w})} - m_\mathrm{b} \right] \Big/ \tfrac{4}{3}\pi r^3 \qquad (1)$$

where

t = time elapsed after bubble formation
m_b = moles of solute associated with a bubble
r = bubble radius
k = mass transfer rate coefficient (cm/sec)
K_w = Henry's law constant for the solute in water, ($= c_\mathrm{vap}/c_\mathrm{water}$ at equilibrium)
c_w = solute concentration in the aqueous phase
Γ_m = Langmuir's isotherm parameter (saturation concentration of the solute in the air–water interface)
$c_{1/2}$ = Langmuir isotherm parameter (concentration in the aqueous phase at which the surface concentration is $\frac{1}{2}\Gamma_\mathrm{m}$)

In equation (1) it is assumed that the axial diffusion in the column is large enough to warrant considering the column liquid phase as a single well-mixed pool. The bubble radius is kept constant all along its ascending path in the column. Furthermore, mass transfer to the bubble is proportional to the difference between the solute mass associated with the bubble, and that which could be associated with it assuming that the bubble was in equilibrium with the surrounding liquid mass.

The solute mass separated from the aqueous phase by a bubble, if we accept that c_w does not change during the time necessary to allow a bubble to pass through the liquid mass, is obtained by integrating equation (1)

$$m_{b(out)} = \frac{4\pi r^3}{3}\left[K_w c_w + \frac{3\Gamma_m}{r(1 + c_{1/2}/c_w)}\right] \times \left[1 - \exp\left(-\frac{3kh_w}{ru_w}\right)\right] \quad (2)$$

where

h_w = aqueous column height

u_w = bubble ascension velocity (which is a function of the density and viscosity of the aqueous phase)

Taking into account the volume of air introduced into the column as bubbles, the following equation is obtained

$$V_w \frac{dc_w}{dt} = -N_b \frac{4\pi r^3}{3}\left[1 - \exp\left(-\frac{3kh_w}{ru_w}\right)\right] \times \left[K_w c_w + \frac{3\Gamma_m}{r(1 + c_{1/2}/c_w)}\right] \quad (3)$$

where

V_w = aqueous phase volume

N_b = number of bubbles introduced into the aqueous phase per second

t = time elapsed from the beginning of the process (sec)

If the solute is a non-volatile species, equation (3) is simplified to

$$\frac{dc}{dt} = -A(1 + c_{1/2}/c_w) \quad (4)$$

where A incorporates a group of constant factors. By integration the following equation is obtained

$$c_w(t) - c_w(0) + c_{1/2}[\ln c_w(t)/c_w(0)] = -At \quad (5)$$

When $\ln c_w(t)/c_w(0)$ was plotted *vs.* t, Womack *et al.*[28] obtained plots that were in disagreement with the experimental results for the Methylene Blue–tetradecylsulphate pair, and it was necessary to consider the value of the mass transfer coefficient (k). To do this, the diffusion of solute through the boundary layer around the air bubbles had to be taken into account.

Starting from this conclusion and from the calculations of the solute chemical potential, they obtained the expression

$$K = r\lambda_1/3 \quad (6)$$

where λ_1 is a time constant associated with the diffusion process and r is the bubble radius This is thus a limiting factor of the separation rate, that causes the formation of curves similar to those obtained experimentally.

Let us assume that formation of ion-pairs between the solute (ionizable) and the surfactant gives rise to the sublate that has to be separated, assuming that the surface concentrations of the surface-active species are given by linear isotherms.

We can assume the establishment of the following equilibrium in solution

$$AC + BD \rightleftharpoons AD + BC$$

$$K_e = \frac{[AD][BC]}{[AC][BD]} \quad (7)$$

where

A = surfactant anionic agent

B = solute anion

C = solute cation

D = surfactant cationic agent

AC = sublate (ion-pair)

AD = non-dissociated surfactant

The species AC and AD are surfactants and will compete for the gas bubbles. The anion B cannot be separated by means of solvent sublation, so

$$[BC] + [BD] = [B] = \text{constant} \quad (8)$$

Furthermore, there is only one possible way for the solute cation to be separated from the solution, so

$$\frac{d}{dt}([AC] + [BC]) = -K_{AC}[AC] \quad (9)$$

where K_{AC} is the mass transfer rate parameter for AC.

In contrast, the surfactant can be separated in two ways:

$$\frac{d}{dt}([AC] + [AD]) = -K_{AC}[AC] - K_{AD}[AD] \quad (10)$$

The K parameters depend on the bubble radii, the gas flow-rate, the volume and height of the aqueous phase, and the rising velocity of the bubbles.

Therefore we have four equations for the four unknowns. This system is conveniently solved,[28] yielding the expression:

$$K_e = \frac{([AD]_0 - [AC])([BC_0] - [AC])}{[AC]([BD]_0 + [AC])} \qquad (11)$$

where the subscript zero indicates the initial nominal concentration

Equation (11) is arrived at from equation (10) by choosing the root of this equation that conforms to all the following conditions $[AC] \geqslant 0$; $[AD] = ([AD]_0 - [AC]) \geqslant 0$, $[BC] = ([BC]_0 - [AC]) \geqslant 0$ and $[BD] = [BD]_0 + [AC]$

From these initial values the differential equations (8) and (9) can be solved, yielding expressions to calculate the curves of the separation kinetics during the process

On studying the effect of the equilibrium constant shown in equation (7) on dissociation of the ion-pair, it was observed that when this increases, the sublate separation velocity decreases In this case, the theoretical curves are similar to the experimental ones

At the same time it was observed that decreasing the surfactant concentration would be expected to give a lower yield and separation velocity, in accordance with the experimental results. Finally, the effect was examined of adding salts, which would obviously displace the formation equilibrium of the ion-pair and, therefore, cause a serious loss of efficiency when the technique is applied to brines or sea-waters

This theoretical treatment accounts very well for the experimental behaviour of the technique, with the exception that in practice the rates of removal early in a run are much higher than those predicted by the model Womack *et al.* accounted for these differences by considering the occurrence of secondary ionic equilibria [28]

Because one of the most useful characteristics of the technique is the possibility of working with large volumes of sample, there is an obvious interest in obtaining theoretical treatment of systems working in the continuous flow mode. This technique should be useful in chemical analysis (avoiding the use of large experimental devices, increasing the sensitivity of determinations by means of greater preconcentration factors, *etc*) as well as in chemical engineering (treatment of large quantities of water). Wilson and Valsaraj have suggested a quick and efficient algorithm for the treatment of this situation, taking into account that the axial dispersion is not great enough, in a continuous feed regimen of the column, to guarantee homogeneity.[30]

This model allows design and adjustment of the device in the continuous operation mode, which is of obvious interest industrially, and this mode of operation could also be used in some analytical work.

In a later work,[65] these authors developed another theoretical model that allows the calculation of the adsorption isotherm, at the air–water interface, of the compounds of interest when they are intrinsically hydrophobic In this way it is possible to predict the applicability of this method for the removal of as yet unstudied compounds

ANALYTICAL APPLICATIONS

Bearing in mind all the techniques discussed, the most interesting ones, from the analytical point of view, are precipitate flotation, ion flotation and solvent sublation, therefore the bibliographic review will be restricted to these.

Precipitate flotation

Precipitate flotation is the most interesting technique, analytically Co-flotation has a very special interest within precipitate flotation, voluminous metal hydroxides and organic reagents have been used as co-precipitating agents in this kind of process, however, during the period that we are considering, metal hydroxides are practically the only ones used, especially ferric hydroxide, as shown in Tables 2 and 3 On the other hand, multi-elemental separations have also been developed during this period (Table 3), these had not received much attention previously Co-flotation, compared with centrifugation and co-precipitation, presents several advantages

(1) It allows for the use of very large volumes of sample, thus increasing the preconcentration factor

(2) It is quicker and more convenient, because the other techniques require more time, also separation of voluminous precipitates is difficult

(3) It eliminates the difficulties associated with separation of colloidal precipitates.

Table 2 Precipitate flotation single-element separations

Species	Sample medium	Co-precipitant or precipitated compound	Surfactants	Observations	Reference
Ag	Sea-water	PbS (colloid)	SA	AAS	69
As	Sea-water, pH 8–9	$Fe(OH)_3$	NaO	AAS, hydride generation	70
	Natural waters		NaO	Idem	71
	Geothermal fluids, pH 6.5		NaLS + LACl	Idem	72
Bi	Water, pH 4	$Fe(OH)_3$	NaLS + NaO	AAS, hydride generation (detn limit 0.6 ng/ml)	73
Cd	Waste waters	$Fe(OH)_3$ or $Al(OH)_3$	NaLS or NaE + HTABr	AAS	74
	River and tap water, pH 9.1	$Zr(OH)_4$	NaO	AAS, electrothermal atomization	75
	Water	$Ti(OH)_4$, $Zr(OH)_4$	BACl, NaO NaDBS	Detn limit 20 ng/ml, recoveries >97%	76
		$In(OH)_3$			
Co	Waste waters	$Fe(OH)_3 + Al(OH)_3$	NaLS	pH 9	77
	Sea-water, pH 8.5–9	$In(OH)_3$	NaLS + NaO	Liquid scintillation	78
Cr	Natural and waste waters $Fe(OH)_3$, pH 4.5–6 $Al(OH)_3$, pH 5.5–7.5	$Fe(OH)_3$ or $Al(OH)_3$	NaLS	Spectrophotometric detn	79
	Prior reduction with Fe(II)	$Fe(OH)_3$	NaLS	pH 5–8	79
	Waste waters Prior reduction with Fe(II), pH 4.5–7	$Fe(OH)_3$	NaLS	Continuous spectrophotometric detn	25
Cs	Waste waters from radiochemical processes	$CuFe(CN)_6$	NaLS or HTMABr		80
Cu	Aqueous solutions of high and low salinity	$Fe(OH)_3$, $Al(OH)_3$ $La(OH)_3$, $Sn(OH)_2$ $Th(OH)_4$	NaDBS, NaO HDBl	AAS Experimental parameter study and influence of the nature of co-precipitant and surfactant	81
Cu	Aqueous solutions	$Fe(OH)_3$	NaO	AAS Development of simplex optimization procedure	82
	pH >7	$Fe(OH)_3$	NaLP + TX100 or HTMABr	AAS Study of the influence of different species (anionic)	83
	pH 7.5–11	$Fe(OH)_3$	LDC	AAS Study of the influence of several ions	77
Hg		$Fe(OH)_3$ or $Al(OH)_3$	NaLS, NaE, HTMABr	Study of the influence of several factors in the separation	84
Mn	pH >9	$Fe(OH)_3$	NaLP + TX100	AAS Study of the influence of several anionic species	83
Mo	Sea-water, natural waters	$Fe(OH)_3$	HTMABr + ODA	ODA not necessary for natural waters	85

continued overleaf

Table 2—*continued*

Species	Sample medium	Co-precipitant or precipitated compound	Surfactants	Observations	Reference
Pb	Waste waters	$Fe(OH)_3$	NaLS		86
	Pilot plant, pH 6–7	$Fe(OH)_3$	NaLS	Separation and recovery of Pb	87
	Aqueous solutions	$Fe(OH)_3$ or $Al(OH)_3$	HTMABr, NaE NaLS	Study of the variables affecting lead separation	88
Sb	Natural waters, pH 4 0	$Fe(OH)_3$	NaLS + NaO	AAS, hydride generation	89
	Sea-water, pH 4 0	$Fe(OH)_3$	NaLS + NaO	AAS, hydride generation	90
Sc	Aqueous solutions pH 6–9 (NaO), pH > 10 (HTMABr)	$Fe(OH)_3$	NaO or HTMABr	Spectrophotometric detn with Arsenazo III, or GFAAS NaO shows better results	91
Se	Sea-water, pH 4 0	$Fe(OH)_3$	NaLS	AAS, hydride generation	92
Sn	Natural and marine waters, pH 4 0	$Fe(OH)_3$	NaLS	AAS, hydride generation	93
	Water	$Fe(OH)_3$ or $Al(OH)_3$	NaLS	Recoveries >99 8%	94
Te	Water and sea-water, pH 8–9	$Fe(OH)_3$	NaLS	AAS, hydride generation	95
Zn	Water pH ≫7	$Fe(OH)_3$	NaLP + TX100	AAS Study of the influence of several anionic species	83
Phosphate	Waste waters	$Al(OH)_3$	NaN	Phosphate separation	96

Table 3 Precipitate flotation multi-elemental separations

Species	Sample medium	Co-precipitant or precipitated compound	Surfactants	Observations	Reference
Ag, Au	Aqueous solutions	$Sn(OH)_2$	Succipon, octandiol	AAS	97
As, Cd, Co, Cu, Hg, Mo, Sb, Sn, Te, Ti, U, V, W	Synthetic sea-water, pH = *f*(species)	$Fe(OH)_3 + Fe(APDC)$	NaLS + NaO	Activation	98
As, Ge, Sb, Sn	High salinity solutions, pH 5 5	$Fe(OH)_3$	NaLS	AAS, hydride generation	99
As, Mo, Se, U, V, W	Sea-water, pH 5 7	$Fe(OH)_3$	NaLS	Activation	21
Bi, Sb, Sn	Water, pH 9 1	$Zr(OH)_4$	NaO	AAS, hydride generation	100
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Sea-water, pH 9 5	$Al(OH)_3$	NaO	AAS	101
Cd, Co, Cr, Cu, Mn, Ni, Pb	Water water and sea-water, pH 9 5	$In(OH)_3$	NaO + NaLS	ICP	102
	Idem			Idem but continuous technique for separation	24
Cd, Co, Cu	Sea-water, pH 9 5–9 9	$Fe(OH)_3$	SA + NaLS	AAS	103
Cd, Co, Cu, Ni	High salinity solutions, sea-water	Phenolphthalein or 2-naphthol	ODA	Flame AAS Cd, Co, Ni >90% yield, Cu lower	104
Cd, Co, Cu, Zn	High and low salinity aqueous solutions	$Fe(OH)_3$, $Al(OH)_3$, $Th(OH)_4$	HTMABr	AAS Study of influence of sample salinity on separation and recoveries	105
Cd, Cr, Cu, Hg, Pb, Zn	High ionic strength (μ) solutions	$Fe(OH)_3$ or $Al(OH)_3$ (colloids)	NaLS	Efficiency decreases with increasing μ, can compensate with Al, Mg, Zn as activators	106
Cd, Pb	Water, pH 8–10	$Fe(OH)_3$ or $Al(OH)_3$	NaDBS	AAS	107
	Water	$Fe(OH)_3$ or $Al(OH)_3$	Fatty acid, sodium salts	AAS	108
Co, Cu, Mn, Ni	Mn nodules	$Fe(OH)_3$ (colloid)	HClLA	AAS Quantitative recovery Cu at pH >6, Co, Mn, Ni at pH 9	109
Co, Cu, Mn, Ni, Zn	Lixiviates from ferromanganese nodules, pH 8–10	$Fe(OH)_3 + Mn(OH)_2$	HClLA or HTMACl + TX100	AAS The lixiviates and the residual liquors are analysed	110
Co, Cu, Ni	Water, pH 9 1	$Zr(OH)_4$	NaO	AAS, electrothermal atomization	111
Cr, Cu, Zn	Waste waters, pH 7–7 6	$Fe(OH)_3$	NaLS	AAS Pilot plant studies on the separation of these elements from waste waters	112
PAHs	Water	CH_2Cl_2	TX100	Maximum recovery at pH 3–4	113

Precipitate flotation of the first kind has received much less attention, nevertheless it has been used with organic and inorganic species in development of single and multi-element separations (Table 4) and presents, in contrast to precipitate separation, the same advantages as does co-flotation with respect to co-precipitation.

Ion flotation

This technique and precipitate flotation are the most used, and have particularly been developed in the U S.S.R., as shown in Tables 5 and 6. Usually, the ions to be separated are in complex form and bound to a surfactant of appropriate charge. Ion flotation has been used in connection with both single and multielemental separation schemes (Tables 5 and 6)

On comparing ion flotation with precipitate flotation techniques, it can be said that the former have several disadvantages They are slower, and give lower preconcentration factors Also it requires destruction of the surfactant in the foam, so more care is needed than in precipitate flotation

Solvent sublation

Solvent sublation, in comparison with ion flotation, has an advantage in that it allows analysis of the organic phase directly, and it is not necessary to destroy the foam (which is not always a very easy task).

Solvent sublation has practical and theoretical advantages over liquid–liquid extraction, although most of the reasoning and practical knowledge and experience in solvent extraction could be applied to develop efficient solvent sublation procedures. In liquid–liquid extraction the quantity of substance transferred from one phase to another is determined and limited by an equilibrium constant. In contrast, equilibrium in solvent sublation is only established in the aqueous–organic interface This interface can be kept motionless when the flow-rates are low enough. Except when saturation of the organic phase occurs, the quantity of sublate collected by the organic layer is independent of its volume because no equilibrium is established in the overall system, and the passage of a sublate into the organic phase through the interface is a process forced by the gas stream, not a spontaneous distribution process related to the relative solubility of the sublate in the two phases Further advantages over solvent extraction arise from the absence of formation of emulsions, because the interface remains practically immobile, and the possibility of handling large volumes of samples On the other hand, in solvent extraction the equilibrium is reached quickly Moreover, in solvent sublation it is necessary to have a close control of the gas flow-rate and bubble size to obtain good separation and reproducibility in the results

In spite of the advantages mentioned above, together with the possibility of its use as an alternative to ion flotation and extraction, solvent sublation has so far not been used for the separation and determination of trace metals (see Table 7). Nevertheless, theoretical studies on the separation process mechanism for organic species[28,64–68] confirm the advantages that the technique presents for the determination of a number of important organic pollutants. It is therefore very likely that in the next few years this technique will attract much closer attention from analytical chemists

SURFACTANTS ABBREVIATION KEY

Cationic Surfactants

Quaternary ammonium salts

ABDACl	Alkylbenzyldimethylammonium chloride
ATACl	Alkyltrimethylammonium chloride
BACl	Benzalkonium chloride
BDDABr	Benzyldimethyldodecylammonium bromide
CTAB	Cetyltrimethylammonium bromide
DPCl	Laurylpyridinium chloride
HDMABr	Hexadecylethyldimethylammonium bromide
HPBr	Hexadecylpyridinium bromide
HPCl	Hexadecylpyridinium chloride
HTBABr	Hexadecyltributylammonium bromide
HTEABr	Hexadecyltriethylammonium bromide
HTMABr	Hexadecyltrimethylammonium bromide
HTMACl	Hexadecyltrimethylammonium chloride
HTPABr	Hexadecyltripropylammonium bromide
LACl	Laurylammonium chloride
LDC	Ammonium lauryldithiocarbamate
STACl	Stearyltrimethylammonium chloride
TACl	Trimethylammonium chloride
TCMACl	Tricaprylmethylammonium chloride
TDBACl	Tetradecyldimethylbenzylammonium chloride (zephiramine)

Amines

ANP-2	Aliphatic amine hydrochlorides
HA	Hexadecylamine
HClLA	Laurylamine hydrochloride
HClLDT	Lauroyldiethylenetriamine hydrochloride
LA	Laurylamine
ODA	Octadecylamine
SA	Stearylamine
TDEDAHCl	Tridecylethylenediamine hydrochloride
TEA	Triethanolamine
TOA	Trioctylamine

Table 4 Precipitate flotation of the first kind

Species	Sample medium	Precipitate nature	Surfactants	Observations	Reference
Al	Waste water	Hydroxide			114
Cd	Water, pH 10	Hydroxide	NaLS	Polarography	115
Cd, Cu	Cyanide solutions	Ferrocyanide	NaO	Separation of copper from cadmium	116
Co	Waste waters, pH 11	Hydroxide	NaLS	Recovery of Co in the waste water effluent	77
		Hydroxide	HTMABr	Study of the influence of addition of several salts	117
Co, Cu, Mn, Ni	Cu, pH >7 5 Ni, Co, Mn, pH 9	LIX 65, LIX 63 compounds	HTMABr + TX100	AAS Study of the effect of addition of different salts and comparison with the use of NaLS	118
Co, Cu, Zn	Aqueous solutions Zn and Cu, pH 10 Co and Cu, pH 12 3	Hydroxide	NaDBS BDDABr		119
Cu	pH 7 5–9 5	Hydroxide	NaLP + TX100	AAS Study of the influence of several ions	83
Fe, In, Ni, Sb, Sn, Ti, Zr		Hydroxide	BACl, NaO NaDBS		76
Hg	Waste water	Colloidal Hg	KM	Bentonite addition	120
	Waste water	Colloidal Hg	aliphatic amines		121
	Waste water	Colloidal Hg	KP, KS		122
	Waste water	Colloidal Hg and Hg oxide	KA		123
Mg	Aqueous solutions, pH 11 5	Hydroxide	NaLS		124
	High salinity media	Hydroxide	KO	Study of the influence of several salts	125
Mn	pH 8 5–10	Hydroxide	NaLP + TX100	AAS Study of the influence of several ions	83
U	Sulphuric acid pH 2 2–2 3	Oxinate	TOA + ANP-2		126
	pH variable	Oxinate	HTMABr, NaLS	Spectrophotometry with Tiron or Arsenazo	127
Zn	pH 9 5–10	Hydroxide	NaDBS		128
	pH 9	Hydroxide	NaLP + TX100	AAS Study of the influence of several ions	83

Table 5 Ion flotation single-element separations

Species	Sample medium	Surfactants	Observations	Reference
Ag	Sea-water, pH 2	SA	AAS	69
Cd	Natural waters, pH 6–8	TEA	AAS, 20–200 ng/ml	129
	Water	NaLS and NaL	Polarography Studies on the effectiveness of several surfactants	130
	Thiocyanate, iodide	HTMABr	Polarography	131
Co	Cyanide media	HPCl and NaDBS	Flotations in media containing different species Radiochemical determination	132
	$CoCl_2$, 4 3 × $10^{-4}M$	Collected with finely dispersed solid solution of saturated aliphatic acids in paraffin	Maximum recovery at pH 10–10 5 Based on electrocoagulation of $Co(OH)_2$	133
Cr	Cr(VI)	HDABr	Spectrophotometry with sensitivities around the ng/ml level	134
	Cr(III)–diphenylcarbazide, 1*M* sulphuric acid	NaLS	Spectrophotometry	135
Cu	Waste waters from mining industry	LA and SA	Studies of the feasibility of copper separation	136
	Butyl xanthate ppte	HTMABr	Concentration factor 100	137
Fe	Waste waters from mining and electroplating industries Cyanide media pH 4–10	TCMACl	Separation of ferrocyanide, ferricyanide and cyanide	138
	1,10-Phenanthroline	NaLS	Spectrophotometry	139
Hf	Waste waters from radiochemical processes	NaLS or HTMABr	Studies of the separation and flotation mechanism	140
Hg	Chloride media, 1 5*M*, pH 6–8	TDEDAHCl	Recoveries 80–92%	141
	Thiocyanate media, pH 3 0 and 9–10 5	Primary aliphatic amines	Studies on the separation and IR spectra	142
	KCl medium, 1 5*M*, pH 5 1	HL		143
	Chloride media, 0 25*M*, pH 6	Aliphatic amines	Studies on the separation mechanism	144
	Nitrate media, pH 5–8 5	KO		145
	KCl media, 0 1*M*	LA + HL	Studies on the influence of different variables affecting the separation process	146
Mo	Sea-water Bromopyrogallol Red	HPCl	Spectrophotometry	147
Nb	pH 5–9	Amines and quaternary ammonium salts	Separation and study of several parameters	148
Ni	KCl 0 05*M*, pH 5	HDMABr	Recoveries around 87%	149
NO_2^-	Natural waters, HCl 0 012*M*, *p*-aminobenzenesulphonamide and *N*-1-naphthylethylenediamine	NaLS	Spectrophotometry	150
	Idem	NaLS	Idem but using a continuous technique for the flotation process	26

continued opposite

Table 5—*continued*

Species	Sample medium	Surfactants	Observations	Reference
NO_3^-	Idem	NaLS	Idem, but prior reduction of nitrate with Zn	151
Pb	Waste waters Waste waters, pH 7.0	KL, KTD, KPD, KP K ethyl xanthate	Optimization studies of the separation conditions in each case	152 153
S	Waters, Methylene Blue formation	NaLS	Spectrophotometry	154
Ta	pH 0.5–1.5 and 5–9	ATACl, ABDACl and ANP-2	Studies on the effect of different variables	155
U	Carbonate media, pH 5–6 Sea-water, pH 5 or lower Sea-water, pH 5–6 Phosphoric acid media Sea-water, pH 3.5	HPBr Amidozimes Stearox-6 + HS Anionic organophosphorus cpds Arsenazo III + TDBACl	Studies on the effect of different variables Studies on the recovery Spectrophotometry with Arsenazo III Studies on the separation mechanism and recoveries Studies on the influence of several parameters Spectrophotometry	156 157 158 159 160, 161
Zn	HCl, 2*M* pH 10	HDMABr KC	 Studies on the separation mechanism and kinetics	162 163
Zr	$UO_2(NO_3)_2$	NaLS, Na decylsulphate, Na tetradecylsulphate	Surface properties of precipitate studied by electrophoresis	164
31 ions	HCl/HNO_3	Cetylpyridinium chloride	Flotation in mixed acids more efficient than in HCl alone	164a

Table 6 Ionic flotation multielemental separations

Species	Sample medium	Surfactants	Observations	Reference
Ag, Au, Cd, Co, Cr, Hg, In, Mn, Pd, Pt, Zn	Cyanide and chloride media	Alkyl + alkylsulphonates	Studies on the mechanism, separation order, kinetics and recoveries of each species	165
Ag, Co, Cu, Fe, Hg, In, Pt, Zn	Thiocyanate media	HPCl, HTMACl, TDBACl	Studies on the feasibility of separations between elements as a function of pH and surfactant nature	166
Al, Bi, Co, Cu, Fe, Ga, In, Pb, Zn	pH 6–6.3 (Al, Ga, Fe, In, Bi) pH 6–9 (Co, Ni, Cu, Zn, Pb)	*N*-Stearoyl-L-glutamic acid	Detn. of the sublate stoichiometry and studies on possible separations between elements	167
Al, Ga, In	Halide and hydroxy complexes, halo-acid and basic media	HPCl + STACl	Structural detn. of the sublates (IR) Optimization of the separation	168
	Idem	HPCl, NaLS and quaternary ammonium salts	Gallium is separated in 7*M* HCl medium	169
Au, Cd, Hg, Zn	Acidic solutions, $1.0 \times 10^{-5}M$	HTMACl	Foam fractionation	170
Au, Hg, Pd, Pt	Medium HBr	HPCl, TDBACl, HTMACl	Separation of the group	171
Au, Ir, Pd, Pt	Chloride media	Quaternary ammonium salts	Radiochemical detn	172
Au, Pd, Pt	Medium HCl, 3*M*	HPCl, TDBACl, HTMACl	Separation from Rh, Ir and Ru	173

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Table 6—*continued*

Species	Sample medium	Surfactants	Observations	Reference
Cd, As	Medium phosphoric acid, 1.7*M*	Diethylphosphate	Study of the influence of several parameters on the separation process	174
Cd, Co	Thiocyanate media	HTMABr	Study of the effect of different alcohols in the process Spectrophotometric detn	175
Cd, Co, Cu, Fe, Ni, Zn	1,10-Phenanthroline	NaLS	AAS	176
Cd, Pb, Sb, Sn	Medium HBr	HPCl, TDBACl, HTMACl	Studies of the feasibility of separations	177
Cd, Zn	APDC	DPCl	Study of separations	178
Cu, Fe, Ga		β-Diketones	Study of the effectiveness of several β-diketones AAS detn Comparative study with solvent extraction methods	179
Cu, Mo, U, Zn	Waste water pH 3–8 (Mo, U) pH 6.5–7 (Cu, Zn)	Amines (Mo, U) ethyl xanthate or butyl xanthate (Cu, Zn)		180
Cu, Pb, Zn	pH 4.5	KL	Studies of the kinetics and possible separation schemes	181
Hg, Pb		KL + KS (Pb) KS, KM, KP (Hg)	Optimization of the flotation process	182
		HC, HTD, HM (Pb) HTD, KP, KS (Hg)	Studies on optimization and feasibility of separation	183
Ir, Pt	Medium HCl, 0.1*M*	Quaternary ammonium salts (best results with HTBABr HTPABr, HTEABr, HTMABr)	Study of the feasibility of the separation as a function of the surfactant nature Hydroxylamine must be added to reduce Ir(III)	184
Ir, Rh	Chloride media, pH 2	Idem	Radiochemical detn Rh detd by spectrophotometry	185
Mo, W		HClHA	Separation from Fe and Cu	186
	pH 6–10 (Mo) (chloride and sulphate media)	LA, HA, SA	Study of the effect of different amines	187
	pH 4 (W) (Waste waters)	LA, HA, SA		187
	Waste waters Mo pH 7 W pH 4	LA, HA, SA	Studies of the influence of pH and other parameters	188
Sc, Gd, Y	(Sc) pH 4.8, (Gd) pH 6.8 (Y) pH 6.9	Fatty acids	Studies on the optimization of pH values and recoveries	189
Th, La	Chloride media (La) pH 5	HPBr + ANP-2	Study of the separation mechanism	190
U, Th	Waste waters, sulphate media pH 0.5–4.0	Primary aliphatic amines	Uranium separation and recovery	191
V, Mo	pH 8–10	HClLDT	Separation of V Mo remains in the solution	192
V, W		Primary amines	Study of the influence of several added salts and other experimental parameters	193
Zr, Nb	Oxalic acid media	NaLS	Niobium is masked with hydrogen peroxide Study of the separation	194

Table 7 Solvent sublation (inorganic compounds)

Species	Medium solvent	Surfactants	Observations	Reference
Cr, Cu, U	LIX 64N (Cu) DEHPA + TOA (U, Cr)	NaDBS	Studies with different organic solvents	195
Co	Chloride and cyanide media	HPCl + NaDBS	Radiochemical detn Study of the influence of several added salts Comparative results with ion flotation are given Solvent sublation results are better	132
Cu	pH 6–6 4, NaDDTC isoamyl alcohol		Spectrophotometry EDTA and tartrate are used as masking agents	196
	Dithizone/MIBK	NaLS	Spectrophotometry	197
Fe	3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine complex	NaLS	Spectrophotometry	198
Ir, Rh	Butyl acetate	Quaternary ammonium salts	Comparison with ion flotation techniques	185

Anionic surfactants

HC	Decanoic acid
HE	Stearic acid
HL	Lauric acid
HM	Myristic acid
HDBI	Heptadecylbenzylimidazole
HTD	Tridecanoic acid
KA	Potassium abietate
KC	Potassium caprate
KL	Potassium laurate
KM	Potassium myristate
KO	Potassium oleate
KP	Potassium palmitate
KPD	Potassium pentadecanoate
KS	Potassium stearate
KTD	Potassium tridecanoate
NaDBS	Sodium dodecylbenzenesulphonate
NaE	Sodium stearate
NaL	Sodium laurate
NaLP	Sodium laurylphosphate
NaLS	Sodium laurylsulphate
NaN	Sodium naphthenate
NaO	Sodium oleate

Non-ionic surfactants

TX100	Triton X-100

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