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Coflotation Separation for the Determination of Heavy Metals in Water Using Colloidal Gas Aphrons Systems

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ABSTRACT

The separation and preconcentration of metal traces using CGA in connection with coflotation processes is described. A 4:1 mixture of anionic surfactants consisting of sodium dodecylsulfate and potassium oleate has been used to generate the CGA system, and $Fe(OH)_3$ has been used as a collector. The separation process has been optimized using the Simplex Method (COFLOT computer program) complemented with a factorial design to investigate the influence of the different parameters in the investigated process. The results obtained evidenced recovery yields over 90% for the elements investigated (Cu, Co, Cd, and Ni), implying flotation times under 5 minutes as applied to samples of varying salinity, concentration, and volume.

Key Words. Coflotation; Colloidal gas aphrons; Preconcentration; Multielemental separation

INTRODUCTION

Colloidal gas aphrons (CGA) are colloidal systems built by small gas bubbles enclosed in a double water–soapy layer which may contain up to 66% air or gas. CGA were first proposed and obtained by Sebba (1, 2) and denominated microgas dispersion (MGD) or microfoams to become finally labeled more suitably as CGA.

Sebba first obtained CGA using a Venturi-type generator (1) which he later modified to obtain a large amount of CGA together with a more uniform bubble size (3).

The structure and properties of CGA have been widely studied and discussed by Sebba et al. (4). From an analytical viewpoint these systems have considerable interest because of their small particle size which provides a large specific surface as well as from the existence of a double layer of surfactant encapsulated around the gas phase. These characteristics make CGA systems very suitable in flotation systems as an alternative to the traditional gas bubble technique (5). As a matter of fact, Sebba et al. (5, 6) investigated more recently the application of CGA in connection with flotation processes of metals, dyestuffs, unicellular algae, etc. Woodburn et al. (7) investigated the flotation of coal particles, and more recently Diaz et al. (8) and Cabezón et al. (9) carried out investigations focused on the application of CGA for the separation of metal traces.

In the present work an account is given of the results obtained in the separation, preconcentration, and simultaneous determination of Co(II), Cu(II), Cd(II), and Ni(II) by coflotation with $Fe(OH)_3$ using CGA generated from a mixture of the anionic surfactants NaLS (sodium dodecylsulfate) and KO (potassium oleate), which offer some advantages comparatively with CGA generated with a unique surfactant as is usually done. The separation process has been optimized by the Simplex Method (COFLOT computer program). Additionally, a factorial design has been carried out in order to investigate the influence of the different parameters on the coflotation process.

The investigation has been carried out in media of varying salinity, ranging from distilled water, 3.5% NaCl solutions (salinity similar to that of seawater) which present special difficulties for most coflotation processes, to synthetic seawater (10). The coflotation process has been applied using different sample volumes and concentrations of metallic elements. As a rule, for operating times of less than 5 minutes, higher than 90% recoveries have been obtained for the investigated elements for concentration levels over 10 ppb.

EXPERIMENTAL

Apparatus and Reagents

All reagents used were of analytical quality with the exception of NaLS (Scharlau, pure) and KO (Aldrich, 40% aqueous slurry). The CGA generating solution was 0.8 g NaLS/L and 0.2 g KO/L. A multistandard Cu, Co, Cd, and Ni 1.000 ppm stock solution was used.

The experiments were carried out using columns similar to those described elsewhere (8, 11, 12) but lacking sintered glass plates which are not necessary since the aphron bubbles are formed before entering the column.

The CGA generator used in these experiments is similar to that described by Sebba (3). The generated CGA is pumped to the flotation column by means of a Eyela MP-3 peristaltic pump.

The determination of the elements in the optimization process as well as in connection with the recovery of sublates was carried out using an atomic absorption spectrophotometer UNICAM PU9200X using an air-acetylene flame. Callibration was accomplished using solutions of composition similar to that of the samples. The instrumental conditions were established by resorting to an optimization process of isolated variables.

Optimization Process for the Simultaneous Coflotation of Cu, Cd, Co, and Ni

One milliliter of multistandard solution (1.000 ppm of each element) was added to 500 mL distilled water followed by the addition of the amount (mL) of Fe(III) solution (about 0.05 M $FeCl_3$) as established by means of the optimization process (Simplex Method). pH adjustment was carried out through addition of NH_3 and NaOH. The solution was stirred during the induction time obtained from the optimization process, and it was transferred into the flotation column.

The CGA flow (prepared just before the transference of the solution to the column) was introduced through the lower part of the column by means of a peristaltic pump, the flow rate of which was regulated according to the optimization process. Two samples (about 10 mL) were taken from the lateral tap of the column and introduced into tubes containing 0.15 mL of 12 M HCl, the first one before initiating the CGA flow and the second one 3 minutes afterwards.

The sum of the flotation percentages of the four elements investigated was taken as the response function.

Procedure for the Recovery of the Sublates

7.8 mL of the Fe(III) solution is required for sample volumes amounting up to 500 and 1000 mL, while the addition of 15.6 mL is necessary for 2–1 samples. pH adjustment to 10.0 ± 0.1 was carried out through the addition of NH_3 and NaOH. The solution was then stirred for 6–7 minutes and transferred to the flotation column, which allowed the CGA solution to flow for about 5 minutes by means of the peristaltic pump regulated in position 7.2 (about 25 mL/min flow).

After the CGA flow is stopped, most of the liquid is discharged through the lower tap of the column. The precipitate and the foam are treated with 5 mL of 12 M HCl and 15–20 mL distilled water, and they are all collected in a measuring flask which is then filled to 50 mL with distilled water.

RESULTS AND DISCUSSION

Optimization of the Process

The optimization process was carried out by means of the Simplex Method and a factorial design. By taking into account our previous experience with flotation processes using aphrons (13), we concluded that the parameters needed to optimize control should essentially be: pH, amount of the coprecipitant species, CGA flow at the inlet of the column, induction time.

Optimization by Means of the Simplex Method

Optimization by the Simplex Method was carried out by means of a computerized COFLOT (14) program. Two Simplex procedures were tried, one beginning in the zone where a good response was expected (according to our previous knowledge as applied to similar systems) (Simplex 1) while the second one was initiated in a less favorable zone (Simplex 2). In both cases the parameters accounted for were those presented above. Other possible parameters, such as surfactant's concentration and the mixing ratios, were not considered since that would imply the need to vary the concentrations and proportions of the mixture in each experiment, which would result in excessive prolongation of the process. On the other hand, our previous knowledge (8, 9, 13) of this type of systems allowed us to conclude that the generating concentration of CGA does not appreciably influence the process once the CGA is formed. As regards the mixture (NaLS:KO), a 4:1 ratio was selected since it allows for good solubility in distilled water in connection with the recovery of the sublates. The flotation time was not evaluated since all the experiments carried out previously had indicated that 3–5 minutes is quite suitable to achieve good separation. As a matter of fact, in most experiments good results were obtained after 2–3 minutes of flotation.

The evolution of the Simplex in the two cases considered, together with the flotation percentage achieved, are reproduced in Figs. 1 and 2. In both cases the search for the optimum values of the variables ended when the sum of the flotation percentages of the four elements exceeded a value of 390 in all the retained vertexes. Optimum values were obtained in both Simplex Methods after a relatively low number of experiments (8 for Sim-

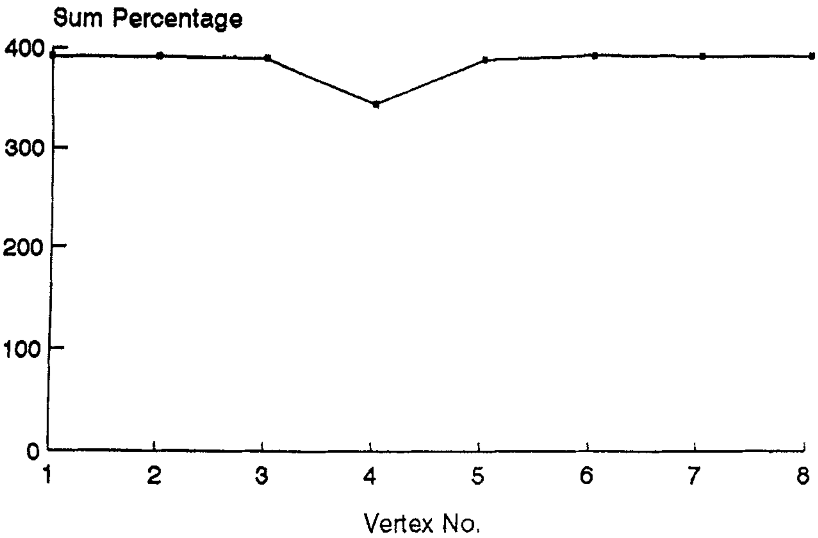

FIG. 1 Response evolution in Simplex optimization 1.

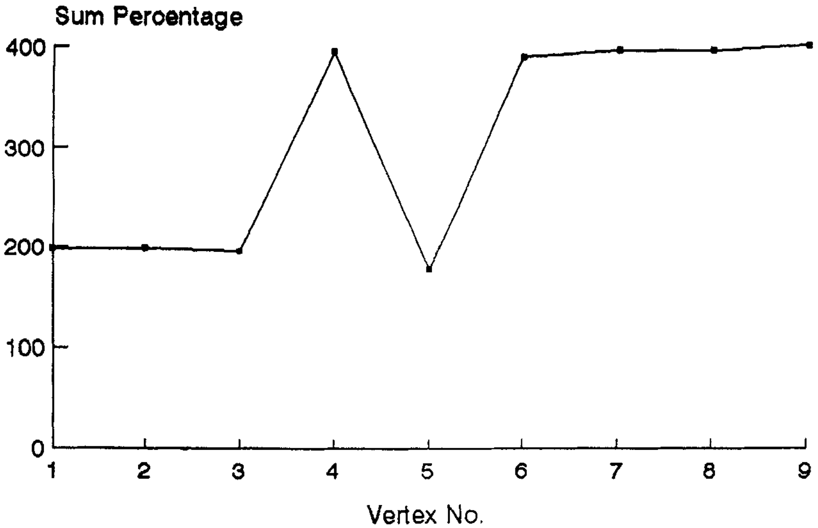

FIG. 2 Response evolution in Simplex optimization 2.

plex 1 and 9 for Simplex 2), which is especially interesting for the second case considering that the Simplex was begun from a zone of response theoretically unfavorable.

Factorial Design

In order to obtain further information on the influence of the different parameters in the flotation process, a factorial design (15) was carried out at two different levels for the same variables investigated by the Simplex Method. The levels imposed as well as the results obtained are reproduced in Tables 1 and 2. The flotation percentages obtained for each of the four elements investigated, as well as the overall sums, are reproduced in Table 3.

The values obtained for the estimates indicate that the most influential factor is the pH, followed by the coprecipitant amount and the pump position which determines the surfactant concentration in the medium and the gas flow entering the column. For Ni, Co, and Cd, pH appears to be the most influential variable. For Cu, presumably from the fact that the pH range selected falls within a zone of coflotation of Cu, pH is not the most influential variable. Considering the interaction between two factors, the most influential ones appear to be those of AC (pump position–pH), BC (mL coprecipitant–pH) and AD (pump position–induction time), with a lesser degree of interaction for AB (pump position–mL coprecipitant). Considering the elements individually, interaction AC is the most significant, followed by BC and AD which are coincident with the interaction extent considering simultaneous separation of the elements. The influence of such effects on the Cu process is nearly unnoticeable with the exception of interaction AC which presents a relatively low weight as related to the remaining elements. As regards the effects arising from the influence of three factors, the most noticeable one, considering both the elements individually or jointly (simultaneous separation), is ACD (pump position–pH–induction time).

TABLE 1
Factor Definitions and Levels

		Level	
Effect	Factor	Low (−)	High (+)
A	Pump position	5	10
B	Coprecipitant (mL)	5	10
C	pH	7.5	10
D	Induction time (minutes)	7	10

TABLE 2
Results for Factorial Design

	Flotation (%)				
Experiment	Ni	Co	Cu	Cd	Total
1	31	25	96	39	191
2	40	32	98	63	233
3	37	33	96	56	222
4	56	50	98	72	276
5	96	98	96	98	388
6	98	95	96	98	387
7	96	96	98	98	388
8	96	96	97	99	388
9	17	13	97	30	157
10	50	39	98	51	238
11	28	25	98	35	186
12	69	58	98	78	303
13	99	97	97	99	392
14	100	98	98	100	396
15	98	98	97	99	390
16	100	97	98	100	395

TABLE 3
Values of Estimates

Effect[a]	Ni	Co	Cu	Cd	Total
T	69.44	65.62	97.25	75.94	308.12
A	6.69	5.00	0.38	6.69	18.88
B	3.06	3.50	0.25	3.69	10.38
C	28.44	31.25	0.12	22.94	82.38
D	0.69	0.00	0.38	1.94	1.00
AB	1.06	1.12	0.12	0.94	3.12
AC	6.06	5.38	0.25	6.31	17.88
AD	2.94	2.38	0.00	1.56	7.00
BC	3.44	3.62	0.12	3.56	10.62
BD	0.56	0.38	0.12	0.31	1.00
CD	0.69	0.62	0.00	2.56	3.75
ABC	1.19	1.00	0.00	0.81	2.88
ABD	0.06	0.50	0.00	1.81	1.50
ACD	2.81	2.00	0.38	1.44	5.75
BCD	0.44	0.25	0.25	0.44	1.50
ABCD	0.31	0.12	0.12	1.94	1.50

[a] For an explanation of the effect coding, see Table 1.

TABLE 4
Optimum Values for Simplex Optimization and Factorial Design

Method	Pump position	Coprecipitant (mL)	pH	Induction time (min)
Simplex 1	8.2	5.0	10.2	1.5
Simplex 2	6.2	10.5	9.8	11.7
Simplex average	7.2	7.8	10.0	6.6
Factorial design	7.5	7.5	10.0	7.5

Discussion of Results

The optimum values taken for the variables in Simplex 1 and Simplex 2 are reproduced in Table 4. The values presented are the mean values obtained from the five best vertexes for every Simplex. Average values are also included in this table of the parameters of the experiments which furnished the best results in factorial design, as are values of the parameters obtained as mean values from the two Simplex systems which were used later on in connection with the investigation of the influence of salinity and sublate recovery. The optimum results obtained by both the Simplex Method and by factorial design show great similarity, as expected.

Influence of Salinity

Proceeding similarly as was done in connection with the optimization process, a number of flotation experiments were carried out on 500 mL samples ranging from distilled water, NaCl solutions of varying concentrations, and synthetic seawater (10). The values given to the variables were those obtained as average between the optima of each Simplex (Table 4). Each of the investigated elements was present at a 2 ppm concentration

TABLE 5
Influence of Salinity

	Flotation (%)				
		NaCl			
Element	H_2O	1.7%	2.3%	3.5%	Synthetic seawater
Ni	97	96	99	98	98
Co	100	100	100	100	100
Cu	98	98	98	97	96
Cd	98	97	98	98	81
Total	393	391	395	393	375

TABLE 6
Influence of Salts Present in Synthetic Seawater

Elements	Flotation (%)			
	No $MgCl_2$	No $CaCl_2$	No Na_2SO_4	No KCl
Ni	99	99	99	100
Co	100	100	100	100
Cu	98	97	98	98
Cd	95	88	86	86

level. Samples were taken from the side-tap of the column just before starting the coflotation process and again after 3 minutes. The results obtained for the corresponding flotation experiments are reproduced in Table 5.

The results obtained allow us to conclude that the salinity of the synthetic seawater influences the flotation percentage of Cd, thereby leading to a reduction of the overall flotation percentage. In order to disclose which of the salts present may be responsible for lowering the extent of flotation in synthetic seawater samples, a number of flotation experiments were carried out under identical conditions on 500 mL samples of synthetic seawater lacking one of the salts.

From the results obtained (Table 6), it is concluded that the presence of $MgCl_2$ brings about a slight decrease in the flotation percentage of Cd.

Recovery of Sublates

In order to investigate the analytical applicability for determination of the elements considered in the flotation process, a number of experiments were carried out using 500 mL samples in distilled water, 3.5% NaCl,

TABLE 7
Percentages on the Recovery of Sublates[a]

Element	H_2O	NaCl, 3.5%	Synthetic seawater
Ni	100.0 ± 6.9	100.8 ± 7.0	100.4 ± 6.0
Co	101.2 ± 7.7	101.9 ± 5.9	100.1 ± 7.5
Cu	101.2 ± 7.4	99.7 ± 7.5	100.0 ± 6.0
Cd	100.9 ± 7.2	99.2 ± 6.9	99.0 ± 7.5

[a] The data included in this table represent average values as obtained for four different experiments carried out with 0.5, 1.0, and 2.0 L sample volumes (average of 12 results in each case).

and synthetic seawater containing 200, 100, and 20 ppb of the elements investigated.

Experiments were carried out additionally on 1 L samples under the same medium conditions as above but containing 100, 20, and 10 ppb of the elements in question. Finally, the recovery of sublates was investigated in 2 L samples containing 20 and 10 ppb of the elements considered.

The results obtained in all cases are about or over 90% coflotation yield and exhibited acceptable reproducibility. Values for the mean recoveries obtained are reproduced in Table 7.

The experiments carried out with 2 L samples showed the need to double the amount of coprecipitant in order to obtain amounts of precipitates of suitable consistency to be carried up by the small aphron bubbles. When only 7.8 mL Fe(III) solution was used, the amount of precipitate produced was too small compared with the sample volume used.

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