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Article

Multielemental separation and determination of some heavy metals (Cu, Co, Cd and Ni) in tap water and high salinity media by CGA (colloidal gas aphron)-coflotation

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The heavy metals Cu, Co, Cd and Ni were separated by coflotation on $Fe(OH)_3$ using stearylamine (SA) CGA (colloidal gas aphron) in aqueous media of varying salinity (from tap water to synthetic sea water) and determined by atomic absorption spectrophotometry.
The separation process was optimized by the univariant and the simplex methods (COFLOT program).
The results indicate that a flotation time of less than five minutes provides about 90 % recovery when the elements are present at 10-20 ppb. The recovery of Co and Cd decreased when synthetic sea water was analyzed.

preconcentration / multielemental separation / coflotation / Colloidal Gas Aphron (CGA)

Séparation et détermination de métaux lourds (Cu, Co, Cd et Ni) dans l'eau du robinet et des milieux salins par co-flottation en présence d'une mousse colloïdale (CGA). *Cu, Co, Cd et Ni ont été séparés par co-flottation, en utilisant $Fe(OH)_3$ et une mousse colloïdale (CGA) de stéarylamine dans des milieux de salinités variées (de l'eau du robinet à une eau de mer synthétique), puis déterminés par spectrophotométrie d'absorption atomique.*
Le procédé de séparation a été optimisé par des méthodes monodimensionnelle et de simplexe (programme COFLOT).
Les résultats montrent qu'un temps de moins de 5 minutes suffit pour obtenir des taux de recouvrement d'environ 90 %, lorsque les éléments sont à des concentrations de 10 à 20 $\mu g/L^{-1}$.
Les taux de recouvrement sont plus faibles lorsque l'on analyse de l'eau de mer synthétique.

préconcentration / séparation multi-élémentaire / co-flottation / mousse colloïdale (CGA)

INTRODUCTION

CGA (Colloidal Gas Aphron) systems are built by very small gas bubbles encapsulated within a double soapy-water film which may contain up to 66 % occluded gas. The structure, properties, handling and stability of CGA have been studied in detail by Sebba *et al.* [1-4]. CGA have two main analytical features : their small size and the presence of a double layer encapsulating the gas. The resulting large surface area and stability are of great potential usefulness for separation and/or preconcentration [3, 5].

One the most promising applications of CGA is their use as an alternative to gas bubbling in conventional flotation. The use of CGA in analytical systems has received little attention, despite the fact that CGA have been used in flotation processes involving metals, dyestuffs, algae and carbon particles [5-11].

Ionic strentgh is one of the parameters that most influences flotation processes; an increase in ionic strength generally decreases the efficiency of flotation processes.

The present work investigates the optimization of a coflotation process for Cu, Co, Cd and Ni ions using $Fe(OH)_3$ and stearylamine (SA) Colloidal Gas Aphron (CGA) in media of varying salinity (tap water to synthetic sea water) [12]. The above CGA gave efficient separations even in natural waters, where conventional flotation does not work well [13]. The method was optimized by both the single-variable and simplex methods, the latter using the COFLOT computer program described previously [14]. The results obtained show that the CGA allows separation and determination of all four elements within five minutes. The recoveries were about 90 % in all cases, except Co and Cd when synthetic sea water was used. The $Mg(OH)_2$ in this solution has a large adverse effect on the flotation process.

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EXPERIMENTAL

Reagents

All the chemicals used were analytical grade, except for stearylamine (Eastman, pract.) and sodium laurysulphate (NaLS) (Scharlau, pure). 1 000 ppm Cu(II), Co(II), Cd(II) and Ni(II) stock solutions were used.

Apparatus

The experiments were carried out using the equipment described previously [10, 11]. The columns used were similar to those used in conventional flotation [15, 16]; the sintered glass porous plates of the lower part were removed since they are unnecessary because bubbles are preformed in the CGA. A system similar to that proposed by Sebba [2] was used to generate the CGA and an Eyela MP-3 peristaltic pump was used to pump the CGA.

A Pye-Unicam SP-9-800 atomic absorption spectrophotometer with an air-acetylene flame was used for both optimization and analysis of the sublates.

Concentrations were measured using calibrating graphs based on standard solutions similar to the samples using the optimum experimental conditions.

Procedure

i) Optimization of the coflotation process

2 mL of the standard solution containing 1 000 ppm Cu, Cd, Co and Ni was diluted with 1 L 3.5 % NaCl solution. To this was added the Fe(III) (0.05 M $FeCl_3$) established by the optimization process selected (univariant or simplex) and the pH was adjusted by careful addition of NH_3 and/or NaOH. The solution was stirred continuously throughout the induction time and the solution was poured into the flotation column. The CGA was generated from an SA solution as described by Sebba [2]. The CGA was pumped into the column through the lower tap at the desired flowrate. The flotation process was initiated 1-2 min later. 1 mL NaLS solution (2 g/L) was added to give consistency to the foam [13, 17, 18]. Samples (10 mL) were taken after 2 and 5 minutes of initiation of flotation using glass tubes containing 0.5 mL 12 M HCl and having screw-on caps.

The sum of the percent flotations of the four elements was used for optimization with the single-variable and the simplex methods.

ii) Recovery of sublates

Fe(III) solution (8 mL) was added to sample volumes from 0.5 L to 2 L, and the pH was adjusted to 10.0 + 0.1 with NH_3 and NaOH. The solution was stirred gently for five minutes and transferred to the flotation column. The CGA was pumped in at 30 mL/min using the peristaltic pump. NaLS solution (1 mL) was added 1 and 2 min after the beginning of the flotation and the process was concluded after five minutes.

It was necessary to wait 2-3 minutes when sea water was used and the CGA flow was restarted for about 3 minutes. At the end of the process, the liquid was discharged through the lower tap of the column and both the precipitate and the built foam were treated with about 15 mL of a MIBK : Ethanol HCl (4:4:2) solution. The column was washed with 15-20 mL of this solution and the washings were collected together with the liquid resulting from the treatment of the precipitate and the foam, and were made up to 50 mL in a volumetric flask.

RESULTS AND DISCUSSION

Process optimization

The process was optimized by the isolated variable and the simplex methods. A factorial design was used to study the influence of the variables on the process and to verify that the optimum range agreed with that obtained by previous methods.

a) Optimization by the univariate method

The variables selected were : pH, amount of the coprecipitating species (mL of Fe(III) solution), induction time, CGA flow entering into the flotation column, SA concentration generating the CGA, and flotation time. Ionic strength is an important variable in processes of this type. However all the experiments were carried out in 3.5 % NaCl (similar to sea water) since the present work also aimed to establish a simple and quick method for determining trace elements in media of varying salinity.

Optimum pH

A number of experiments were carried out at different pH values by adding 4 mL of the Fe(III) solution generating the CGA with 1 g/L HCl · SA in 30 % ethanol. NaLS (1 mL) was added 1 and 2 minutes after the beginning of the process and the CGA pumped at 30 mL/min. The induction time was 5 minutes and the process was finished after 3 minutes. The results (Fig. 1a) indicate that the optimum pH for the separation is 10.

Amount of Fe(III)

The influence of the amount of the Fe(III) on the separation process was investigated at pH 10. The results (Fig. 1b) from variations in the volume of Fe(III)

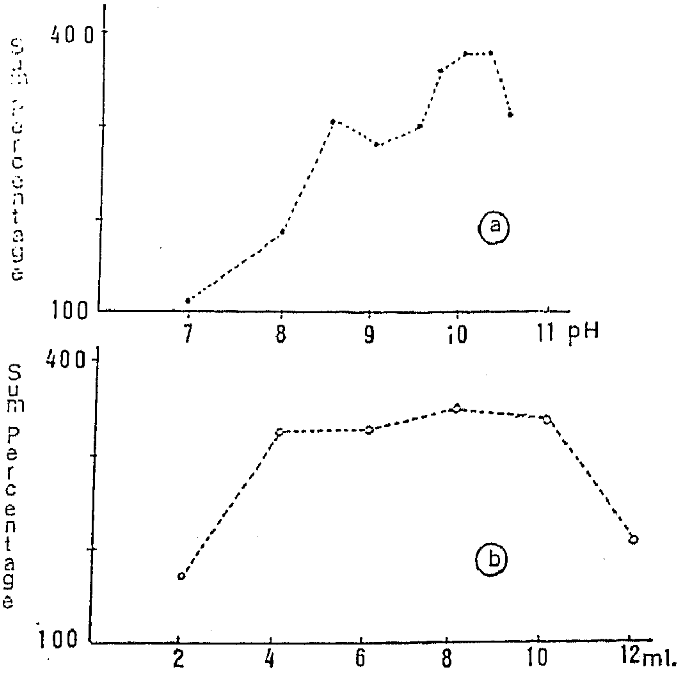

Fig 1. Influence of experimental variables on the CGA coflotation of Cu(II), Cd(II), Co(II) and Ni(II). a) pH of the mother solution. b) Amount of Fe(III) coprecipitant.

solution from 6 to 10 mL had little effect. A volume of 8 mL was used in all subsequent procedures.

Induction time

The effect of induction time was tested at pH 10 and 8 mL Fe(III) solution. The results indicate that 5-10 minutes is sufficient to provide good separation of elements.

CGA flow

The pumping flow of the CGA to the flotation column is a critical parameter since the amount of surfactant agent introduced and the flow of gas through the column influences the separation. Experiments were carried out under the optimum experimental conditions by varying the flowrate (17, 24 and 30 mL/min). The results indicated that 30 mL/min produced sufficient foam.

SA · HCl

The amount of SA · HCl influences both the amount of surfactant agent introduced and the stability of the aphron system. The results indicate that the optimum concentration is 1 g/L.

Flotation time

The process was run for 12 minutes under optimum experimental conditions to establish the time needed to attain a good separation. The results indicate that 5 minutes is sufficient to finish the process.

Influence of salinity

The effect of salinity was investigated under optimum conditions. The results clearly indicate that salinity has little influence on the process. Thus effective separation can be obtained under conditions of widely varying salinity.

b) Optimization by the simplex method

Once the influence of each parameters had been established by the method of isolated variables, the method was optimized by the simplex method using the CO-FLOT program [11, 13, 14, 17, 19]. Two simplexes were run beginning within response zones which were considered in principle sufficiently different and the four most important variables were selected to maintain the optimization process within reasonable time limits. The parameters chosen were : CGA flow, mL Fe(III), pH and induction time. Other variables, such as the concentration of SA generating the CGA and the flotation time, were not considered as they had little influence on the process. As a result all the experiments were finished in five minutes after initiating the process and the SA solution generating the CGA was 1 g/L.

Figs. 2 and 3 show the changes in the two simplexes and the sum flotation for all the elements investigated. Both simplexes were ended when the response function reached values above 380 and flotation percents greater than 90 % for the four elements considered. In both cases the optima were reached with a relatively small number of experiments (15 and 12, respectively).

c) Factorial design

The factorial designs gave information on the optimum response zone and on the influence of the variables and the interactions among them. Therefore a four-variable factorial design was used, as for the optimization by the simplex method.

The factorial design was centered on vertix n° 10 of simplex n° 1 which provided an average flotation percent of 99 % for the elements investigated. The levels imposed on the factors are indicated in Table I. The results obtained and the corresponding estimates are shown in Tables II and III.

We conclude that the most important variable is the pH, followed by the pH-induction time interaction.

The pH and the pH-induction time interaction are the most important for the determination of Ni.

For Cd and Co, the CGA flow rate and the amount of Fe(III) are also important. But the estimation of Cu was not appreciably influenced by any particular variable or any interaction between variables, presumably because the high (+) and low (–) values selected for Cu in the factorial design have no practical influence on the separation of Cu (Table II).

d) Analysis on the results

Table IV shows the optimum results for each variable obtained by the two optimization precesses used. The simplex method data are given for the average values corresponding to vertexes n° 6, 8, 10 and 13 for simplex n° 1 and vertexes n° 2, 5, 6 and 12 for simplex n° 2. For the factorial design, the average values correspond to experiments n° 5, 6, 7, 8, 15 and 16.

The results show a satisfactory agreement between the methods of optimization used, indicating that an optimum response zone was reached. The analysis shows that pH is the variable which most influences the efficiency of the process, since all the optimization process give similar values.

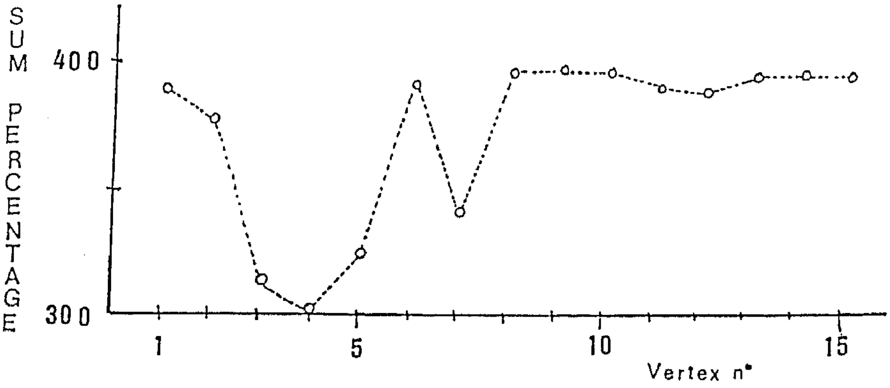

Fig 2. Response evolution in simplex optimization n° 1.

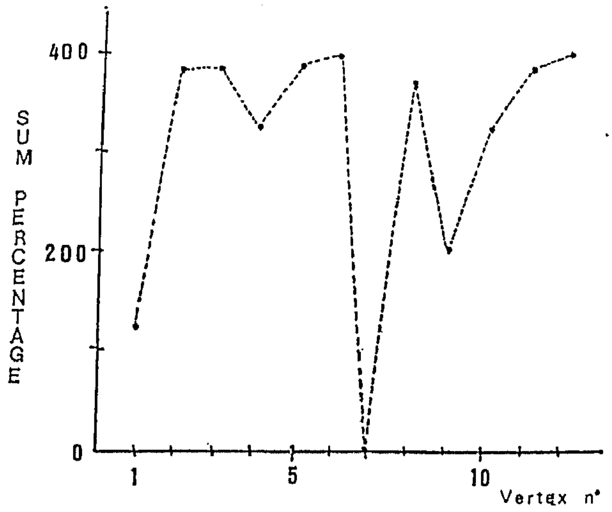

Fig 3. Response evolution in simplex optimization n° 2.

Table II. Results for factorial design.

Experiment	% flotation				
	Ni	Cd	Cu	Co	Total
1	32	19	88	38	177
2	56	47	91	69	263
3	38	34	94	54	220
4	72	56	91	80	299
5	91	97	92	100	380
6	97	97	94	100	388
7	96	97	92	100	385
8	96	98	92	99	385
9	59	97	81	54	291
10	82	26	95	74	277
11	90	52	87	67	296
12	90	55	90	62	297
13	90	59	96	89	334
14	89	89	84	91	353
15	97	99	97	99	392
16	98	99	99	99	395

Table III. Values of estimates.

Effect	Ni	Cd	Cu	Co	Total
T	79.19	70.56	91.44	79.69	320.70
A	5.81	3.94	0.56	4.56	11.37
B	4.69	5.19	1.31	2.81	12.87
AB	0.69	1.94	0.31	2.06	1.00
C	14.31	25.81	1.81	17.44	55.75
AC	4.31	4.81	1.56	4.44	7.62
BC	2.94	3.56	0.44	0.69	0.13
ABC	0.94	2.81	1.81	1.69	2.00
D	6.94	2.56	0.31	0.31	8.62
AD	2.19	2.31	0.31	2.44	10.25
BD	1.44	2.19	0.82	0.44	2.75
ABD	1.19	1.19	0.69	1.31	0.88
CD	8.44	3.19	1.06	2.31	16.62
ACD	2.19	1.44	1.81	2.81	2.81
BCD	0.69	0.56	1.44	2.81	9.50
ABCD	2.94	2.06	1.31	1.18	1.88

Table I. Factor definition and levels.

			Levels	
Effect	Factors	Units	Low (–)	High (+)
A	Coprecipitant	mL	4	10
B	Pump Position		5	10
C	pH		8	10
D	Induction time	minutes	0	10

Table IV. Optimum values for the optimization and factorial design.

	Pump flow	mL Fe(III)	pH	Induction time	% flotation				
					Cu	Cd	Co	Ni	Total
Univariant Method	10.0	8.0	10.0	5.0	99	98	95	98	390
Simplex n° 1	8.6	8.3	10.0	0.5	99	99	99	99	396
Simplex n° 2	8.3	15.1	9.8	7.6	99	99	96	98	391
Factorial design	7.0	8.4	10.0	3.3	99	94	98	96	387

Table V. The recovery of sublates.

	Tap water (1)	Tap water (2)	3.5 % NaCl solutions (2)	Synthetic sea water (2)
Element	ppb found	ppb found	ppb found	ppb found
Cu	4.1 ± 0.8	12.6 ± 0.7	9.3 ± 0.9	10.2 ± 1.9
Cd	0.5 ± 0.4	8.5 ± 0.4	9.2 ± 0.9	7.1 ± 1.2
Co	0.5 ± 0.4	8.2 ± 0.3	8.4 ± 9.5	8.1 ±.3
Ni	2.4 ± 0.8	9.9 ± 0.6	8.2 ± 0.9	10.8 ± 0.7

(1) Direct determination

(2) Average values of 5 standard addition (10 ppb).

Sublate recovery. Analysis of real samples

The optimized process for 3.5 % NaCl was used to test recovery of the elements in the sublates. The test solution was a 2 L 3.5 % NaCl solution containing 10 ppb of each of element. The results, after subtraction of blanks, are shown in Table V. This table also includes an analysis of tap water containing 10 ppb of each elements. The presence of $Mg(OH)_2$ in the synthetic sea water strongly interfered with the separation. However, a good separation could be obtained if the solution was let to stand for 2-3 minutes followed by pumping of CGA flow for about another 3 min. The results for the 10 ppb of each of the four elements, after subtraction of the blank values, are shown in Table V. Acceptable recovery values were obtained, except for Co and Cd.

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