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Short Communication

PRECONCENTRATION AND DETERMINATION OF TRACE METALS IN SYNTHETIC SEA WATER BY FLOTATION WITH INERT ORGANIC COLLECTORS

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Summary. The preconcentration and separation of copper, cadmium, cobalt and nickel 8-quinolinolates in solutions of high salinity including synthetic sea water is studied with phenolphthalein or 2-naphthol as collector and octadecylamine as surfactant. A simplex optimization is applied. Yields >90% are achieved for Ni, Co and Cd with both collectors, but the copper yield is low. Flame atomic absorption spectrometry is used for the final measurements.

Heavy metals have received a great deal of attention in the study of marine pollution. Their low concentrations in sea water mean that preconcentration is needed during their determination. The usual preconcentration techniques, such as liquid/liquid extraction, ion-exchange, coprecipitation and evaporation, need time and large amounts of sample. These inconveniences may partly be avoided by the use of flotation techniques [1] which have proved to be of great utility [2—4] in the preconcentration of trace elements in natural [5—9], waste [6, 9—12] and marine waters [8, 13—16].

Of the flotation techniques described, co-flotation is probably most applied; numerous co-precipitants or collectors, both inorganic and organic, have been studied. In practice, however, the hydrated oxides of iron [5, 9, 10, 13—15, 17—19], indium [8, 20], aluminum [9, 10, 17], tin [21] and zirconium [22] are the compounds most used as collectors. Kuznetsov [23] and later Myasoedova [24] described the analytical use of "inert" organic collectors in separation processes. In spite of the advantages that these offer compared to classical collectors (e.g., their greater sensitivity, selectivity and ease of destruction if required before the final measurement of the collected species), they have hardly been used recently [25] and their applications as collectors in flotation processes have not been studied.

The present study describes the flotation of copper, cobalt, cadmium and nickel 8-quinolinolates in solutions of high salinity and synthetic sea water [26] with inert organic reagents (phenolphthalein or 2-naphthol) as the collector, and octadecylamine (ODA) and sodium dodecylsulfate (SDS) as the surfactants. The process was optimized by means of the COFLOT program [27].

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Experimental

Apparatus and reagents. The flotation cell has been described [28, 29]. The final measurements were made with a Pye Unicam SP9-800 atomic absorption spectrometer with an air/acetylene flame.

The reagents used were of analytical grade, except for the surfactants. Octadecylamine was from Eastman and SDS from Scharlau (pure).

Procedure for optimization. For the study of the optimum flotation conditions of the metal 8-quinolinolates with phenolphthalein or 2-naphthol, exactly 1 l of 3.5% (w/v) sodium chloride solution was placed in a beaker, and exactly 1 ml of a multistandard solution containing 1.000 μg ml^{-1} each of the metals to be studied was added. The amounts of 8-quinolinol (as a 4% w/v solution in 8% v/v acetic acid) and inert collector (10% w/v solution of phenolphthalein or 2-naphthol in ethanol) established in the optimization process were also added. The pH was adjusted by addition of ammonia or sodium hydroxide solution, and the required volume of ODA (6.0 g l^{-1} in ethanol) was added. The mixture was stirred during the induction time. The solution was placed in the flotation cell, in which the air flow had been previously adjusted to the optimum value; then 2 ml of SDS (0.01 M) was added as flotation began, and again after 2 and 5 min. Samples of ca. 5 ml were taken at 30 s, 1, 2, 4, and 10 min, in centrifuge tubes with screw tops containing 0.15 ml of concentrated hydrochloric acid. Residual concentrations in the solution of the four metals were measured by atomic absorption spectrometry (a.a.s.). The sum of the flotation percentages of all the elements was taken as the response function.

Recommended procedure. Under the optimum conditions established for the two collectors (air flow-rate 100 ml min^{-1}, 5 or 10 ml of 8-quinolinol solution, 7.5 ml of phenolphthalein solution or 5 ml of 2-naphthol solution, pH 7.0, 7.5 or 5 ml of surfactant and 10-min induction time), experiments were done with 1.5-l samples of 3.5% sodium chloride solution and synthetic sea water, to which a concentration of 16.6 μg l^{-1} of each of the metals had been added. After 10 min flotation, the air stream was stopped and the mother liquor was sucked out, first through the side-drain of the column and finally under vacuum through the sintered-glass plate at the bottom of the column. The precipitate was dissolved in 20 ml of methyl isobutyl ketone/ethanol/6 M hydrochloric acid (40:40:20 by volume). The resulting solution, together with the rinsing liquid, was placed in a 50-ml volumetric flask, and made up to volume with the above solvent. The trace metal concentrations in this solution were determined by a.a.s., with use of a standard additions method.

Results and discussion

Optimization of flotation of metal 8-quinolinolates with phenolphthalein or 2-naphthol. During the optimization process, it was necessary to add a surfactant to make the foam more consistent and to inhibit its coalescence, thus avoiding re-entry of the floated material into the solution. The use of

TABLE 1

Data and results of simplex optimization for the complex formation with 8-quinolinol (8-HQ) and collection with phenolphthalein (PP)[a]

Test	Vertices retained	Air	ODA	PP	pH	Time	8-HQ	Recovery (%)				
								Ni	Co	Cu	Cd	Total
Experiment 1												
1		80	5.0	1.5	6.0	8.0	4.0	97	95	64	80	336
2		40	5.0	1.5	6.0	8.0	4.0	97	90	57	73	317
3		80	8.0	1.5	6.0	8.0	4.0	98	96	88	90	372
4		80	5.0	0.6	6.0	8.0	4.0	96	98	82	77	353
5		80	5.0	1.5	8.0	8.0	4.0	96	93	60	85	332
6		80	5.0	1.5	6.0	0.0	4.0	98	91	58	76	323
7		80	5.0	1.5	6.0	8.0	8.0	100	97	71	85	353
8	1, 3, 4, 5, 6, 7	160	6.5	1.1	7.0	4.0	6.0	94	97	61	90	342
9	1, 3, 4, 5, 7, 8	120	7.2	0.8	7.2	22.0	7.0	93	87	75	88	343
10	3, 4, 5, 7, 8, 9	140	8.4	0.5	8.2	13.0	8.5	94	85	73	90	342[b]
11	3, 4, 7, 8, 9, 10	140	8.4	0.5	5.6	13.0	8.5	93	78	82	70	323
12	3, 4, 7, 8, 9, 10	125	7.5	0.8	6.2	11.8	7.4	95	95	72	95	357
13	3, 4, 7, 8, 9, 12	42.5	2.9	2.1	2.9	4.9	1.2	—	—	—	—	—
14	3, 4, 7, 8, 9, 12	75	4.7	1.6	4.7	7.6	3.6	92	50	81	—	238
15	3, 4, 7, 8, 9, 12	91	5.6	1.3	5.5	8.9	4.8	91	89	61	46	287
16	3, 4, 7, 8, 9, 12	99.3	6.1	1.2	6.0	9.6	5.4	90	92	65	90	337
17	3, 4, 7, 5, 9, 12	103	6.3	1.1	6.2	9.9	5.7	95	92	62	89	338
Experiment 2												
1		80	5.0	1.5	6.0	8.0	4.0	97	93	62	80	332
2		150	5.0	1.5	6.0	8.0	4.0	97	94	58	67	316
3		80	1.0	1.5	6.0	8.0	4.0	97	96	84	37	314
4		80	5.0	5.0	6.0	8.0	4.0	99	95	75	77	346
5		80	5.0	1.5	4.0	8.0	4.0	98	57	53	19	227
6		80	5.0	1.5	6.0	15.0	4.0	96	91	65	76	328
7		80	5.0	1.5	6.0	8.0	1.0	94	80	76	46	296
8	1, 2, 3, 4, 6, 7	115	3.0	3.2	10.0	11.5	2.5	31	50	81	70	232
9	1, 2, 3, 4, 6, 7	68	5.7	0.9	2.0	6.8	4.5	—	—	—	—	—
10	1, 2, 3, 4, 6, 7	80	5.0	1.5	4.0	8.0	4.0	94	56	52	4	206
11	1, 2, 3, 4, 6, 7	86	4.7	1.8	5.0	8.6	3.8	100	86	62	6	254

TABLE 1 (continued)

Test	Vertices retained	Air	ODA	PP	pH	Time	8-HQ	Recovery (%)				
								Ni	Co	Cu	Cd	Total
12	1, 2, 3, 4, 6, 7	103	3.7	2.7	8.0	10.3	3.0	91	95	80	91	357
13	1, 2, 3, 4, 6, 12	127	2.3	3.8	7.0	12.7	9.5	91	83	70	89	333[c]
14	1, 3, 4, 6, 12, 13	33	2.3	3.8	7.0	12.7	5.5	91	92	75	89	347
15	1, 4, 6, 12, 13, 14	92	9.7	6.2	8.0	17.3	7.0	69	64	51	75	259
16	1, 4, 6, 12, 13, 14	88	6.8	4.6	7.3	14.2	6.0	60	72	51	83	265
17	1, 4, 6, 12, 13, 14	86	5.3	3.8	7.0	12.7	5.5	86	84	63	84	317

[a] The air flow rate is given in ml min^{-1}; time (i.e., induction time) is given in minutes. For ODA, PP and 8-HQ, the optimized parameter is the volume (ml) of the solution at the concentration given in the text. [b] Vertex 5 rejected because of the worse kinetic features. [c] Vertex 2 rejected because of the worse kinetic features.

non-ionic [30] or ionic [31] surfactants such as SDS has been recommended. The proportions of the surfactant are never critical, so it was not necessary to include this parameter in the optimization algorithm.

From the data on coprecipitation with phenolphthalein [32], two simplexes were initiated in zones close to those for optimum collection of the selected 8-quinolinolates. Their evolution, as well as the percentages flotation obtained for each ion, appears in Table 1. In both simplexes the search for optimum conditions was considered to be complete after 17 experiments because, with the exception of copper, the elements showed flotation at or above 90%. The values of the variables at the optima obtained in each case are similar, indicating that the global optimum has probably been achieved. The mean value of both vertices was chosen as the global optimum.

Flotation with 2-naphthol [32] was optimized in a similar way. The optimum conditions were very similar to those for phenolphthalein, and mean optimum recoveries were 94% (Ni, Co, Cd). Results for copper were unreliable.

Recovery of floated material. To study the analytical applicability of coflotation with inert collectors, a series of experiments was carried out with 1.5 l of 3.5% sodium chloride solution and synthetic sea water, spiked with 16.6 μg l^{-1} of each of the elements to be studied. The results obtained are shown in Table 2. From these results, several conclusions can be drawn. First, there are clear differences between the effectiveness of the collectors at such low concentrations of metal ions. Phenolphthalein gives greater recoveries than 2-naphthol, comparable with those for hydrated metal oxides as collectors [31]. Secondly, if these results are compared with those in Table 1, the difficulty of achieving complete multi-elemental separations with such

TABLE 2

Recoveries in highly saline and synthetic sea-water samples

Element	Recovery (%)[a]			
	Phenolphthalein		2-Naphthol	
	NaCl (3.5%)	Sea water	NaCl (3.5%)	Sea water
Cu	66 ± 11	70 ± 12	—	—
Co	81 ± 13	82 ± 6	40 ± 22	39 ± 29
Cd	91 ± 11	83 ± 6	74 ± 8	61 ± 20
Ni	89 ± 4	79 ± 12	78 ± 9	58 ± 19

[a] Mean ± standard deviation ($n = 6$) for 16 $\mu g\ l^{-1}$.

collectors becomes evident, especially for copper, although conditions do exist under which recoveries approaching 100% are achieved for some of the ions investigated. This behaviour is to be expected, taking into account the higher selectivity of the inert organic collectors as compared with the inorganic collectors.

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