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Optimization of Analytical Foam Flotation Separations by Means of the Simplex Algorithm

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Abstract

The simplex algorithm has been used to carry out a quick and easy optimization of co-flotation processes under consideration of the following parameters: pH, gas flow rate, amount of coprecipitant and collector, and induction time. The capacity of the simplex algorithm to establish the optimum point has been confirmed through factorial design experiments. The technique has been applied to the optimization of the co-flotation process of Cu(II) with sodium oleate as collector and iron hydroxide as coprecipitant.

INTRODUCTION

Foam flotation involves the separation of material (ionic, molecular, colloidal, or macroparticulate) from aqueous solutions through adsorption on the surface of bubbles ascending through the liquid (*1*). The analytical potential of flotation techniques has been the object of increasing attention in recent years (*2–4*). Special attention has been paid to one of the alternatives, co-flotation (adsorbing colloid flotation), which has been proposed as the basis for a number of procedures suitable for the effective separation and preconcentration of some 60 elements in different forms, at trace levels, in natural, marine, and wastewaters. Continuous methods have been proposed recently which allow the manipulation of large volumes of samples (*5*).

As a rule, the experimental devices used (*1, 3*) are extremely simple in design; therefore, no specifically designed commercial flotation cells are

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available. Consequently, the design and dimensions of the flotation cells used by different investigators vary significantly. Special difficulties are encountered in accurately reproducing the sintered glass disks which become deformed and obturated during the process of being welded to the cells.

The co-flotation processes is fundamentally affected by the following five parameters: pH of the media, amount of coprecipitants (mainly metallic hydroxides) and collectors (anionic, cationic, or chelating surfactants), gas flow rate (usually air), bubble size through the flotation cell, and induction time (stirring time prior to the strict flotation process). Some of these parameters are not independent and—depending on the nature of the species being investigated—may be of little importance (i.e., the induction time).

As a rule, the literature does not yield specific information on the development and optimization of a particular procedure. One assumes that trial-and-error methods may have been used. However, in cases where the number of parameters to be optimized is large, and especially when two or more of them may interact, it is sensible to use a formal optimization strategy (*6*).

The simplex algorithm (*7*), particularly the so-called modified simplex method (MSM) (*8, 9*), has been extensively used in connection with the formal optimization of analytical techniques and procedures as well as for separation methods (*10, 11*). To our knowledge, however, such methods have not been used in the optimization of flotation techniques.

In the present communication, data related to the applicability of the simplex algorithm to the optimization of co-flotation processes by means of a computer program specifically designed for this purpose are presented. Such a study has been carried out on the Cu(II) system, coprecipitated with iron(III) hydroxide, using sodium oleate (NaO) as the collector, which has been previously optimized through the univariate optimization strategy as described elsewhere by the authors (*12*).

EXPERIMENTAL

The general experimental procedure, described elsewhere (*12*), starts with a 500-mL distilled water sample to which 1.0 mL of a standard (1000 ppm) Cu(II) solution is added. This procedure allows accurate and easy control of the flotation system evolution throughout the process by resorting to the pertinent extraction of aliquots from the solution to be submitted for analysis by flame atomic absorption spectroscopy (AAS).

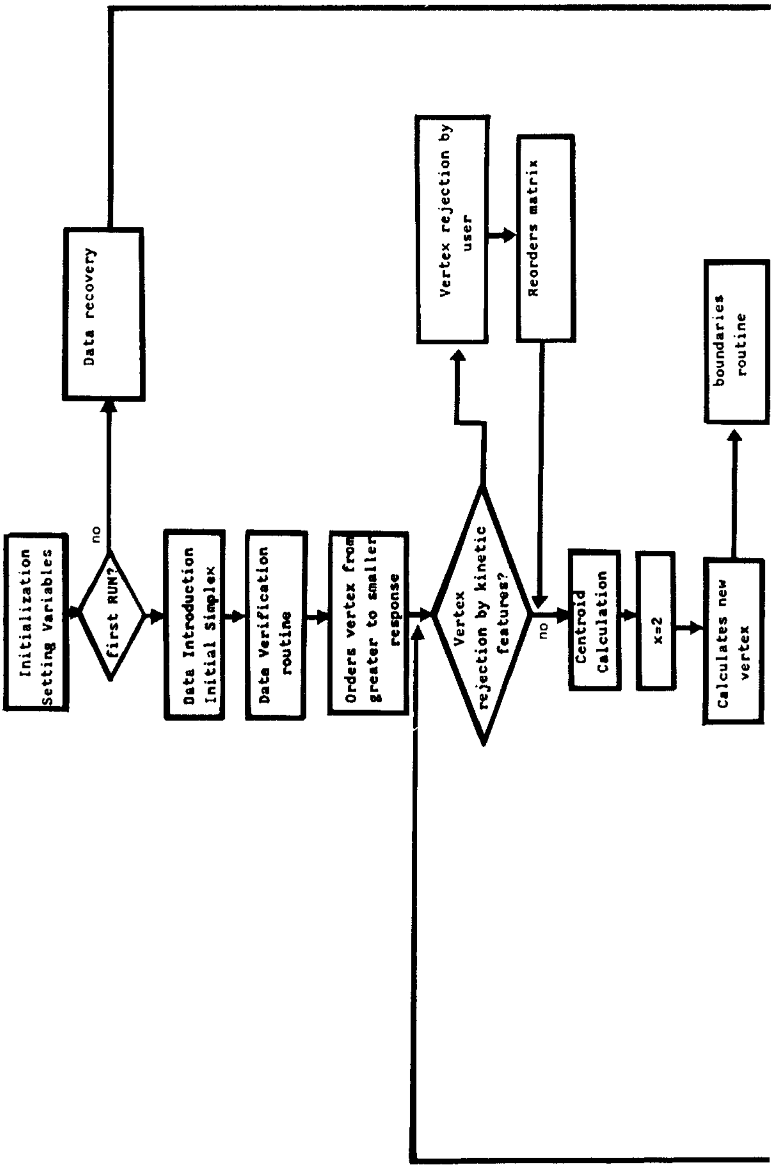
The necessary amount of 0.05 *M* $FeCl_3$ solution is then added (as established by means of the simplex algorithm, SA) followed by the necessary amount (also determined by the SA) of sodium oleate (NaO) solution (2.6 g/L in 50% ethanol). The pH is adjusted to the value established by the SA through careful addition of NH_3 or HCl. Then the mixture is stirred during the induction time established by the SA. The resulting solution is transferred into the flotation cell (design and size as described elsewhere (*12, 13*)) to which 2.0 mL ethanol has been added in order to ensure an appropriate bubble size. The air flow rate is adjusted (as established by the SA) to allow the flotation process to run for 15 min, and then samples of about 3 mL are taken in stoppered centrifuging tubes containing 0.15 mL concentrated HCl. Samples are taken at 0, 0.5, 1, 2, 4, 8, and 15 min flotation times in order to monitor both the co-flotation yield and kinetics during the entire process by analytical measurements (AAS) of the Cu(II) residual solution concentration.

The AAS measurements were made with a PYE-Unicam model SP9-800 atomic absorption spectrophotometer (air-acetylene flame) by means of a calibrating curve obtained with standard Cu(II) solutions for the 0.1-2.0 ppm range under the same acidity and NaO concentration conditions as contained in the samples taken.

Optimization Strategy

A computing program (Applesoft) called COFLOT has been created for the optimization process. Its flow chart is schematically depicted in Fig. 1. The program permits a maximum of eight parameters to be optimized, of which five are preestablished (flow rate, coprecipitant, surfactant, pH, induction time) while the remaining three can be established by the user, if needed. At the beginning of optimization, the data of the initial simplex (resulting from six experiments run in the usual way when dealing with the simplex algorithm (*9, 14, 15*)) are introduced as experimental data. The vertices are ordered from major to minor response (percent flotation extent after 15 min) and the program is then ready for the elimination of the vertex with the worst response in order to calculate the simplex centroid and the new reflected vertex. However, when an objective function is used with only the percent flotation for a given time (15 min in our case) considered, no information about the process kinetics is obtained.

As a rule, only the yield of the co-flotation process is of interest in the preliminary optimization stages, but as the simplex reaches the vicinity of the optimum, the process yields become similar ($\geqslant$90%) and the kinetics


Initialization
Setting Variables
first RUN?
no
Data recovery
Data Introduction
Initial Simplex
Data Verification routine
Orders vertex from greater to smaller response
Vertex rejection by kinetic features?
no
Vertex rejection by user
Reorders matrix
Centroid Calculation
x=2
Calculates new vertex
boundaries routine

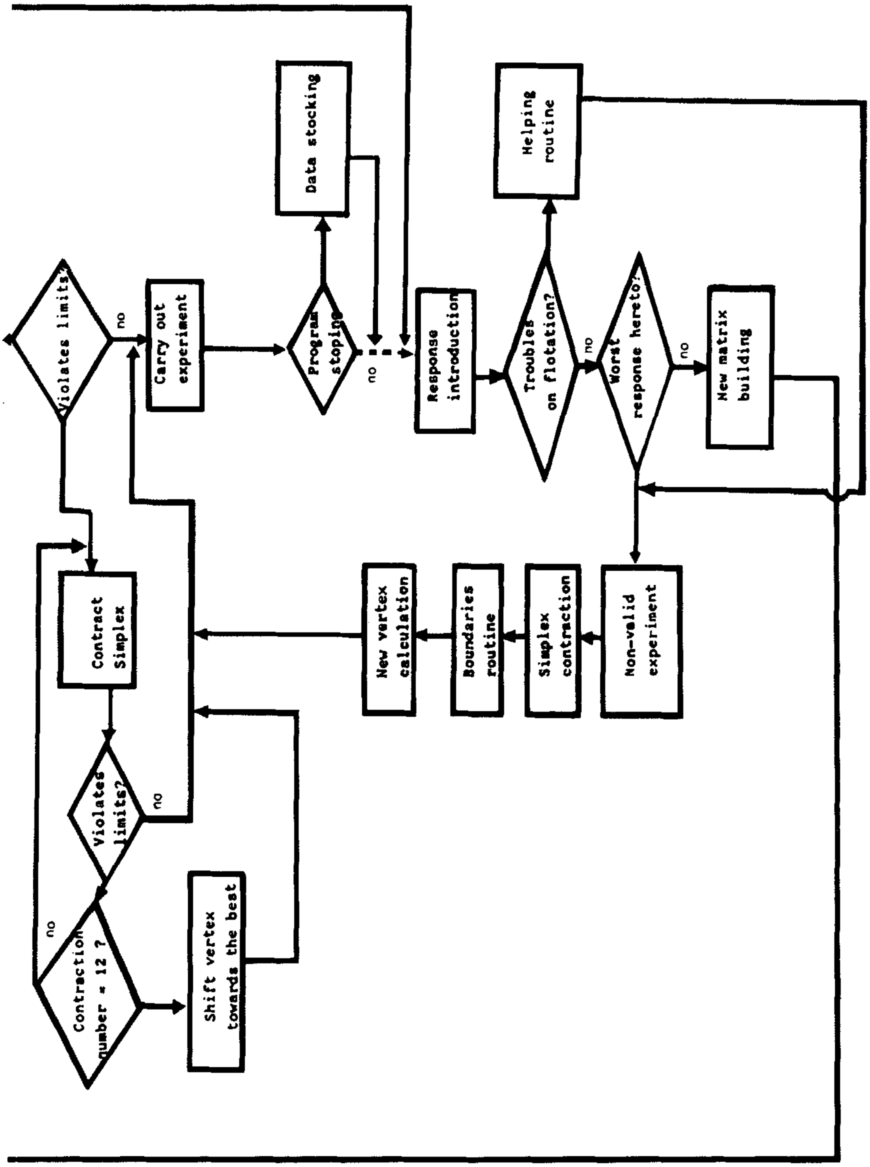


FIG. 1. Flow chart of COFLOT program.

may become the deciding factor when the time comes to make a decision about the vertex to be eliminated. For this reason, the program has been established in such a way that before carrying out the automatic elimination of the worst response vertex, an option is offered to the operator to decide which vertex is to be eliminated. Furthermore, this option allows use of the so-called "Rule 3" of the simplex algorithm: "If, on making the vertices of the next simplex, the newly created vertex is the worst one, then reject the next-to-worst vertex."

Upon calculation of the new vertex by using an expansion coefficient $x = 2$, we enter into a routine of boundary checking. Table 1 shows such boundaries for the five parameters predetermined in the program. The remaining limits must be established by the user, but the program has a default value of 0 (low) and 25 (high). Should the new vertex violate the established boundaries, the program carries out a simplex contraction by testing for values of $x = 1$, 0.5, 0.25, and −0.5, making certain in every instance that the new vertex does not violate the established limits. Should none of the attempted contractions exceed the established criteria as related to boundary violations, the vertex is shifted to a position approaching the best vertex obtained so far.

The operator has to carry out the next experiment under the conditions furnished by the program. Should the computer have to be used for other purposes during this time, the program allows for it because it is provided with a routine for storing data and parameters which have to be recalled when the process is reinitiated.

Once the experiment has been completed, the yield calculated, and the co-flotation kinetic data obtained, the response result of the experiment is introduced and the optimization process is carried further after making sure that it does not correspond to the worst response obtained so far. The experiment is then accepted as valid.

In this part of the program a helpful routine has been provided to assist inexperienced operators. It offers a twofold advantage since it is interactive and can be used for teaching. Such a routine can provide expansions or contractions of the simplex as a function of eventual problems observed by the operator in the course of the experiments; for instance, the absence of froth formation, excess froth formation which may run over the flotation cell, and foam coalescence.

RESULTS AND DISCUSSION

The co-flotation process of trace levels of Cu(II) with iron hydroxide as the coprecipitant and with NaO as the collector has been studied

TABLE 1
Optimization Parameters and Boundary Constraints

Parameter	Units	Boundaries	
		Low	High
Air flow rate	mL/min	0	300
Coprecipitant	mL ($FeCl_3$ solution)	0	20
Surfactant	mL (NaO solution)	0	25
pH		0	14
Induction time	Minutes	0	30

previously by resorting to the trial-and-error method (*12*). As a matter of fact, should some preliminary information be available concerning the operational conditions, the simplex vertices are placed in the neighborhood of the response surface corresponding to the pertinent conditions. Obviously, the closer to the optimum the initial simplex is placed, the less the number of experiments (vertices) that will be needed to accomplish the location of the optimum. In cases where this information is not available, it is possible to make use of the approximate data gathered by Hiraide and Mizuike (*3*) which correspond to the limits of the different parameters used by most authors.

In our case the question concerned the establishment of the ability of the simplex method to locate the optimum no matter what zone of the response surface was selected to start the process nor the method followed to establish the initial simplex.

The first experiment was carried out by establishing the initial simplex in the vicinity of the optimum on the basis of previously available data (*12*). Figure 2(a) depicts the evolution of the response of the simplex obtained where the proximity of the initial simplex to the optimum can be clearly observed in that only three experiments (Vertex 9) allow one to attain 99% flotation. Thereafter, it is apparent that we have simplex convergence. Table 2 shows all pertinent data corresponding to this experiment, including the vertices obtained in each case, the expansion coefficient used for the establishment of each vertex, and the values corresponding to all the parameters considered.

Additionally, two new experiments were carried out involving two new simplexes which were initiated in zones rather far away from the response surface, exhibiting varying sizes and configurations for the initial simplex. Table 3 shows the data corresponding to the initial simplexes for each of these experiments compared with those obtained for the first one as well as with the data of the optimum obtained through

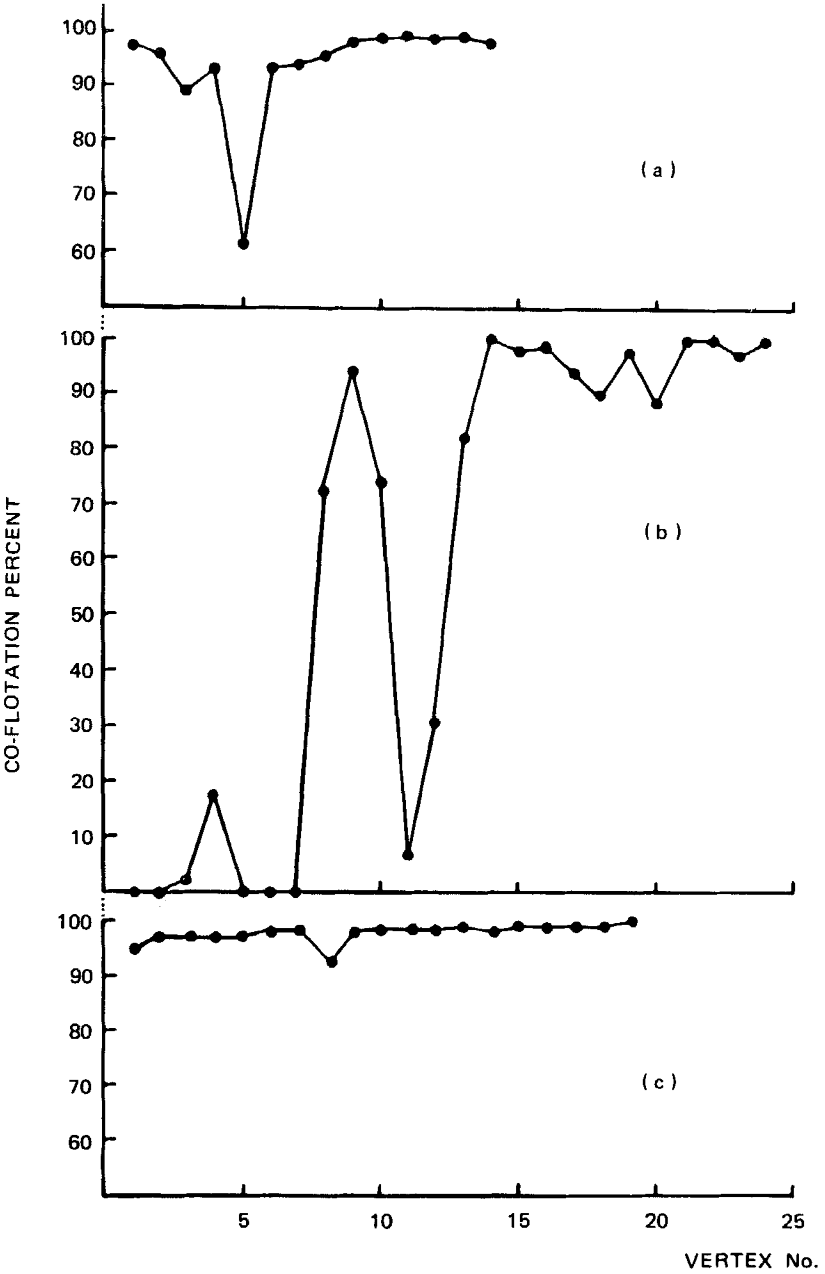


FIG. 2. Response evolution in simplex optimization of Cu(II) co-flotation: (a) Experiment I; (b) Experiment II; (c) Experiment III, see Table 2.

TABLE 2

Data and Results of Simplex Evolution in Experiment 1[a]

Vertex no.	Vertices retained	x	Flow rate (mL/min)	Coprecipitant (mL)	Collector (mL)	pH	t_{ind} (min)	Co-flotation (%)
1			40	4.0	2.0	10.0	8	97.5
2			60	4.0	2.0	10.0	8	95.6
3			40	2.0	2.0	10.0	8	88.9
4			40	4.0	4.0	10.0	8	92.9
5			40	4.0	2.0	8.1	8	61.3
6			40	4.0	2.0	10.0	15	93.6
7	1, 2, 3, 4, 6	0.25	45	3.5	2.5	10.5	9.7	93.7
8	1, 2, 4, 6, 7	2	55	7.7	3.5	10.3	13.2	96.1
9	1, 2, 4, 6, 8	2	51	7.2	3.1	9.2	11.8	98.5
10	1, 2, 6, 8, 9	1	58	6.8	1.0	9.8	14.5	99.0
11	1, 2, 8, 9, 10	2	79	9.8	3.0	9.6	3.3	99.6
12	1, 2, 9, 10, 11	1	60	5.0	0.95	9.2	5.0	99.0
13	2, 9, 10, 11, 12	1	83	9.1	2.0	9.1	9.0	98.9
14	9, 10, 11, 12, 13	0.5	69	9.4	2.0	9.05	9.1	98.1

[a] Vertices 7, 8, and 1 were rejected because they had the worst kinetic features.

TABLE
Initial Simplex Data and Final Results of Simplex

	Initial simplex					
Expt. no.	Flow rate (mL/min)	Coprecipitant (mL)	Collector (mL)	pH	t_{ind} (min)	Co-flotation (%)
I	40	4.0	2.0	10.0	8.0	97.5
	60	4.0	2.0	10.0	8.0	95.6
	40	2.0	2.0	10.0	8.0	88.9
	40	4.0	4.0	10.0	8.0	92.9
	40	4.0	2.0	8.1	8.0	61.3
	40	4.0	2.0	10.0	15.0	93.6
II	100	0.5	4.0	2.0	5.0	0.0
	143	2.0	6.0	3.6	10.0	0.0
	120	3.0	8.0	5.6	15.0	1.6
	300	10.0	10.0	6.6	7.5	17.5
	80	10.0	6.0	5.0	5.0	0.0
	261	2.0	4.0	5.0	5.0	0.0
III	70	1.0	2.5	9.25	4.0	94.0
	60	2.5	1.0	9.7	14.0	98.6
	30	1.5	3.0	8.8	6.0	97.0
	20	3.5	1.5	9.0	10.0	96.9
	40	3.0	2.0	10.0	8.0	96.9
	50	2.0	3.5	9.5	12.0	97.9

Univariate search procedure (according to Ref. 12): No. of experiments = 30

[a] Vertex where convergence was detected.

[b] Vertex with the best response through the optimization process.

application of the trial-and-error method (*12*). In the right-hand part of Table 3 we include the vertex data wherever the simplex search showed a clear convergence (to indicate the speed of the simplex search for the optimum) as well as for the vertex for which the optimum flotation percent was obtained (on the basis of the yield obtained or the kinetic features). Figures 2(b) and 2(c) depict the evolution of the responses corresponding to these two additional experiments.

As can be easily inferred from the data of Table 3, the initial simplex of Experiment II is located in a region of the response surface very far away from the optimum, where only 17.47% flotation efficiency is obtained for the best initial vertex. On the other hand, this initial simplex was built in such a way that the parameter variation is arbitrary. Therefore, it departs from a regular simplex, as was the case for Experiment I.

3
Search through the Flotation Response Surface

	Final conditions					
Vertex	Flow rate (mL/min)	Coprecipitant (mL)	Collector (mL)	pH	t_{ind} (min)	Co-flotation (%)
9	51.0	7.2	3.1	9.2	11.8	98.5[a]
11	78.6	9.8	3.0	9.6	3.3	99.6[b]
21	74.3	12.6	17.5	9.4	27.4	100.0[a,b]
9	29.0	3.1	1.9	9.3	10.6	98.6[b]
19	53.3	2.7	1.3	9.6	14.7	99.6[c]
	50.0	18.0	1.17	9.2	10.0	92.0

Obviously, more vertices are needed to reach the optimum (yield $\geqslant$99%).

Experiment III refers to a simplex initially situated in the vicinity of the optimum, the size of which is intermediate between the two considered before. It exhibits vertices built using a random table. Convergency is quickly attained, so it is easily seen that the structure of the initial simplex does not have a practical influence on the rate of advance toward the optimum.

Optimization by the trial-and-error method implies an average of 5–7 experiments for the optimization of each factor, so the advantages resulting from the simplex method can be clearly appreciate as regards the number of experiments needed even in cases where optimization is carried out in regions of the response surface which are very far away from the optimum.

On the other hand, from a comparison of the values of the different parameters considered in the vertices corresponding to the optimum of all the experiments carried out, it can be easily concluded that the pH of the matrix solution is the main critical factor. As a matter of fact, the simplex method does not yield information about the relative importance of the different factors considered in the optimization process, but the results of several simplexes initiated in different zones of the response surface can yield clear information on this question, in addition to confirming the optimum location and its dimensions. We can see from the data of Table 3 that pH is the factor exhibiting a smaller variation in the different experiments. Among the other factors, flow rate seems to be of least significance on the basis of its variation in the optimum. The values of the collector/colligend ratio vary between 0.01 and 0.23 *M* and, with the exception of Experiment II, show reasonable agreement.

On the other hand, the existence of interactions between such factors as flow rate/collector amount or collector/colligend can be reasonably assumed, a fact that suggests that one may resort systematically to multivariable optimization techniques of the type proposed in the present paper.

To get more information about the significance order of the different factors as well as about their possible interactions, experiments were carried out by means of a complete factorial design considering five factors and two levels. This results in 32 experiments centered on vertex number 2 of the simplex of Experiment I (see Table 2). Table 4 indicates the factors and levels considered in such a factorial design. Table 5 includes data obtained through application of Yate's algorithm (*16, 17*) to the results (% flotation) obtained in the 32 experiments. From this it becomes possible to calculate *F* values (9th column in Table 5) which, when compared with those tabulated elsewhere (*16, 17*), allow the significance of each factor as well as the factor interaction to be established.

TABLE 4
Factor Levels in the Complete Factorial Design

Factor	Parameter	Units	Levels	
			Low (−)	High (+)
A	Air flow rate	mL/min	30	90
B	Coprecipitant	mL ($FeCl_3$ solution)	2	8
C	Collector	mL (NaO solution)	0.2	1.8
D	pH		8.0	10.4
E	Induction time	Minutes	0	10

Thus, for a significance level of 99% (*F*-tab = 7.56), the factors of greatest significance are the amount of NaO and the pH value together with collector/pH interactions, collector/pH/induction time, colligend/collector, colligend/induction time, flow rate/pH, colligend/pH/induction time, colligend/collector/pH, and pH/induction time. With a 95% significance level (*F*-tab = 4.17) or a 90% significance level (*F*-tab = 2.9), it is necessary to consider further interactions as indicated in the last column of Table 5 in addition to the interactions listed above.

These data clearly show the existence of significant interactions between the variables involved. Difficulties in detecting the correct optimum location are to be expected when the optimization process is carried out by means of trial-and-error procedures. As a matter of fact, the best yield achieved in our case (see Table 3) by this alternative amounted to only 92%.

The results obtained through factorial design indicate that the most significant factor is the amount of collector, not the pH, as expected from the experiments carried out using the simplex algorithm. In principle, the factorial design furnishes this type of information with greater reliability than the simplex repetition, but the importance attached to each factor in the establishment of the upper and lower limits on the results of the factorial design (*16*) should be borne in mind. As a matter of fact, the lower limit assigned in this case to the C factor is 0.2 mL NaO solution which, due to its low value, can eventually alone condition the flotation results. In order to check such an implication, a partial factorial design centered over vertex number 11 of the simplex corresponding to Experiment I was traced in order to increase the lower and upper limits of sodium oleate.

The data and results corresponding to such a factorial design (2^{5-2}) can be seen in Table 6. The calculation of b_i for each of the factors (*16, 18*) is shown in the lower part of Table 6 which, as a matter of fact, leads to the conclusion that the most significant factor is the pH value, as could be anticipated.

CONCLUSIONS

The results obtained in the present study demonstrate unambiguously the convenience of using a multivariate technique for the optimization of analytical flotation procedures. The simplex method is a suitable means to achieve such a purpose by carrying out a limited number of experiments, especially where preliminary information is available (as is usually the case), taking into account the actual state of development of the flotation techniques.

TABLE 5
Results of 2^5 Complete Factorial Design (defining contrast = ABCDE) by Yate's Method

Effect	Response (% flotation)	(1)	(2)	(3)	(4)	(5)	Mean squares	*F* (calc)	Observations[a]
T	86.4	157.3	310.6	676.5	1,040.9	22,511	—	—	
A	70.9	153.3	365.9	364.4	1,184.2	−6.9	1.49	2.9	++
B	92.2	178.6	35.1	649.5	11.7	113.1	399.7	7.2	+
AB	61.1	187.3	329.3	534.7	−18.6	−78.1	190.6	3.4	+++
C	83.1	16.1	281.6	−45.9	60.1	561.3	9,845.5	176	++
AC	95.5	19.0	367.9	57.6	−173.2	110.5	381.6	6.8	+++
BC	99.5	138.4	204.6	−56.7	−80.3	243.3	1,715.5	31	
ABC	87.8	190.9	330.1	38.1	2.2	−36.3	41.2	2.9	+++
D	0.0	155.4	−46.6	4.7	149.5	−462.9	5,695.1	102	+++
AD	16.1	126.2	0.7	55.4	211.8	198.3	1,228.8	22	
BD	7.6	185.7	19.9	−31.7	65.1	57.1	101.9	2.9	
ABD	11.4	182.2	37.7	−141.5	45.4	11.1	3.8	2.9	+++
CD	52.7	174.5	−42.8	−39.7	62.3	278.1	2,416.9	43	
ACD	85.7	30.1	−13.9	−40.6	172.0	−41.9	54.9	2.9	+++
BCD	93.1	163.6	10.8	−4.9	−24.5	159.5	795.0	14.2	

ABCD	97.8	166.5	27.3	7.1	−11.8	27.3	23.2	2.9	
E	90.7	−15.5	−4.0	55.3	−312.1	143.3	641.7	11	+++
AE	64.7	−31.1	8.7	294.2	−114.8	−30.3	28.7	2.9	
BE	71.5	12.4	2.9	186.3	103.5	−233.7	1,706.7	30	+++
ABE	54.7	−11.7	52.5	125.5	94.8	82.5	212.7	3.8	+
CE	92.8	16.1	−28.2	47.3	50.7	−137.7	592.5	10.6	+++
ACE	92.9	3.8	−3.5	17.8	−109.8	−19.7	12.1	2.9	
BCE	98.1	33.0	−144.4	28.9	−0.9	−109.7	376.0	6.7	++
ABCE	84.1	4.7	2.9	16.5	12.0	12.7	5.0	2.9	
DE	84.0	−26.0	−15.6	12.7	238.9	197.3	1,216.5	22	+++
ADE	90.5	−16.8	−24.1	49.6	39.2	−8.7	2.4	2.9	
BDE	12.9	0.1	−12.3	24.7	−29.5	−160.5	805.0	14.4	+++
ABDE	17.2	−14.0	−28.3	147.3	−12.4	12.9	5.2	2.9	
CDE	77.3	6.5	9.2	−8.5	36.9	−239.7	1,795.5	32	+++
ACDE	86.3	4.3	−14.1	−16.0	122.6	17.1	9.2	2.9	
BCDE	74.1	9.0	−2.2	−23.3	−7.5	87.7	229.5	4.1	+
ABCDE	92.4	18.3	18.3	11.5	34.8	42.3	55.9	—	
Error	—	—	—	—	—	—	55.9	—	

[a] Significance levels: +++, significant at 99%; ++, significant at 95%; +, significant at 90% intervals.

TABLE 6

Results for Fractional Factorial Design (2^{5-2}) and Values for Estimated Coefficients Associated with the Factors

Fractional Factorial Design

Experiment no.	Factors					Response (% flotation)
	A	B	C	D	E	
1	−	−	−	−	−	97.7
2	+	−	−	+	−	96.7
3	−	+	−	+	−	98.2
4	+	+	−	−	+	99.5
5	−	−	+	+	+	93.8
6	+	−	+	−	−	99.2
7	−	+	+	−	−	99.1
8	+	+	+	+	+	99.2

Factors Definition and Levels

Effect	Factor	Units	Levels		Estimated coefficients (b_i)
			Low (−)	High (+)	
A	Flow	mL/min	54	104	1.45
B	Coprecipitant	mL ($FeCl_3$ solution)	5	15	0.82
C	Collector	mL (NaO solution)	1.5	4.5	0.20
D	pH		9.0	10.2	1.90
E	Induction time	Minutes	0	7	0.75

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Listings of the COFLOT program (Applesoft) are available on request from the authors.

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