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SIMPLEX OPTIMIZATION OF EXPERIMENTALS FACTORS IN ATOMIC SPECTROSCOPY. (part. 1)

J. González
Ministerio de Educación Superior
F. Berti
Centro Nacional de Investigaciones Científicas
J. L. Lamazares
Centro de Investigaciones para la Industria Minero Metalúrgica

RESUMEN

Se presentan los fundamentos del método Simplex de optimización. Se muestran los diagramas de flujo para la determinación del mínimo o el máximo de una respuesta.

Se discuten ejemplos de la aplicación del método en la Espectroscopía de Absorción Atómica. Se destaca que el método simplex resulta apropiado para la optimización de los factores experimentales en E.A.A.

ABSTRACT

The principles of the simplex optimization method are presented. The information flow charts for the determination of the minimun or maximun of a response are shown.

Examples for the application of the method in Atomic Absorption Spectroscopy are discussed. It is pointed out that the simplex method is useful for the optimization of the experimental factors in A.A.S.

1. INTRODUCTION

Simplex method (1) may be considered among the most efficient optimization techniques in term of the number of experiments and the ease of calculation. The method was presented by Spendley (2). Later was modified by Nelder and Mead (3), introducing the flexible simplex with expansions or contraction in the proper direction. In Analytical Chemistry was applied for the first time by Ernst (4). Others authors (5) have argued the possibility of applying this method to chemical systems, in particular to Analytical Chemistry (6,7), and in relation to the selection and preprocessing of factors (8). The difficulties in the application of simplex optimization to analytical chemistry have been also discussed (9).

In the present work, we will introduce our experiences in the application of Simplex to Atomic Absorption Spectroscopy (A.A.S.). In this field are relatively few the works in wich optimal conditions are determined with the aid of optimization methods (10,11,12,13,14,15).

2. BASIC PRINCIPLES OF THE SIMPLEX METHOD

Factor is an independent variable in an experimental system, (for example air flow rate, lamp current or burner height in A.A.S.). Response is that function of the observed system imputs and outputs used to evaluate system performance (for example, absorbance as system output in A.A.S.).

The simplex is the geometric figure defined by a number of points equal to one more than the number of factors (n) to be optimized.

The objective of the method is to conduct the simplex toward the optimum region and the concerned decisions will be determined by five basic rules (6).

Simplex great advantage lies precisely in the fact that one only realize n + 1 experiments in order to determine the departure points. A move is made after each observation of the response. The progression into that adjacent simplex is obtained by discarding the point of the current simplex, corresponding to the least desirable response and replacing it with its mirror image across the hyperface of the remaining points. This allows all the possible factors to be included without increasing in a considerable manner the number of experiments.

In order to make easier the application of the method, Figures 1 and 2 present the information flow charts, for calculating the minimun and maximun of n factors for a given response.

As bi (i = 1,2, ... n + 1) are defined the n + 1 vertex of the simplex in the n dimensional space.

The best (subindex b) and the worst (subindex w), response (ϕ) for the bi vertex are determined in correspondence with the optimization strategy. Three operations are utilized reflection(subindex r)contraction(subindex c) and expansion(subindex e). These are calculated according to:

$$br = (1 + \alpha)c - \alpha bW \qquad (1)$$

where α is the reflection coefficient, generally $\alpha = 1$.

$$be = br + (1 - \gamma)c \qquad (2)$$

being $\gamma = 2$ the expansion coefficient.

$$bc = \beta bw + (1 - \beta)c \qquad (3)$$

with $\beta = 0{,}5$ as the contraction coefficient.

The operations are calculated for the centroid (c) of the simplex, wich is defined excluding the point of worst response in correspondance with:

$$c = \frac{1}{n} \sum_{i=1}^{n} bi \qquad (4)$$

for all the values of $bi \neq bw$

For determining, if the optimum has been reached, we recommend to utilize, the criterium that.

$$\sqrt{\sum_{i=1}^{n+1} (\phi_i - \bar{\phi})^2 / n} \leq E \qquad (5)$$

where: ϕ_i - values of the response for each one of the Simplex vertex

$\bar{\phi}$ - mean value of the ϕi values

E - a given number, selected by the investigator.

As practical rule for determining the value E we recommend that when the convergency of the response is observed, near the optimum, the experiments should be repeated and the concerned error be calculated. Even better, the latter can be determined previously within the experimental rank desired. In the practice the investigator without additional experiments should be able to set value of E according to the possible error of the response.

3. EXPERIMENTAL PART

For determining the optimum operation parameters in A.A.S. an spectrophotometer PYE - UNICAM SP 1900 was used. The Co spectral line 240.7 nm was selected and solutions of this element present as chloride in 5 and 10 ppm concentration were utilized. Values of absorbance were taken as response.

Figure 3 enables us to observe simplex application for the optimization of two variables: air and acetylen flow rate. No contractions, or expansions were employed, and a lector not trained in the method can follow simplex progression towards maximun values of absorbance.

Observe point b7 and b8. These lie outside the boundaries of the factors. No experimental observation was made and a very undesirable response was assigned.

If the reflected point has the least desirable response in the new simplex, the reflexion will be made for the vertex with the second undesired value. This rule unables simplex continue oscillation between two points. This is, for example the case in simplex b4 b5 b6 and b5 b6 b7. In this, latter, can be observed that the reflexion is developed for b5.

The rules force the simplex to circle around point b6 (maximum absorbance value).

In table I is shown the slit width and burner height optimization, according to the flow chart in Fig. 2. The first subindex of b indicates the operation (reflection, expansion or contraction) and the second, the number of time that the operation has been realized.

Finally, in table II is showed the optimization of four factors with 11 experiments.

CONCLUSIONS

Simplex method has been successfully applied to A.A.E. Its development is efficient in term of the number of experiments and easy to learn, even for undergraduate persons.

The flow charts given in this paper allow and efficient

application of the method. According to our experience it should be particularly observed:

- to identify the constraints for the factors. The experimental region will be defined als the region lying within the constraints. To those simplex vertex beyond the experimental region a very undesirable response is assigned.
- to applied equation (5) as criterium for determining if the optimum has been reached.
- to reevaluate each vertex, retained in n+1 succesive simplexes.

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TABLE I

	Exp. No.	Simplex Points	Factors x_1	x_2	(b_i)
	1	b_1	0,05	2	0,361
	2	b_2	0,10	2	0,332
	3	b_3	0,08	6	0,287
	4	br_1	0,07	-2	W_1
	5	bc_1	0,10	4	0,379
óptimo	6	br_2	0.05	4	0,385
	7	be_1	0,02	5	W_2
	8	br_3	0,10	6	0,322
	9	bc_2	0,06	3	0,382

X_1 - Slit width 0,05 - 0,3 - mm.

X_2 - Burner height 0 - 40 mm.

TABLE II

Exp. No.	Simplex Points	Factors				(b_i)
		x_1	x_2	x_3	x_4	
1	b_1	800	2	0,05	10	0,222
2	b_2	1200	4	0,08	12	0,288
3	b_3	900	8	0,08	12	0,354
4	b_4	900	4	0,15	12	0,254
5	b_5	900	4	0,08	14	0,267
6	br_1	1000	8	0,15	15	0,315
7	br_2	1100	8	0,05	15	0,398
8	be_1	1500	8	0,05	16	0,390
9	br_3	1200	10	0,10	13	0,348
10	br_4	900	13	0,11	16	0,274
11	bc_1	1100	6	0,09	13	0,314

1 - Acetylem Flow rate 500 - 2000 cc/mm.

2 - Burner height 2 - 20 mm.

3 - Slit width 0,05 - 0,3 um

4 - Lamp current 10 - 20 mA

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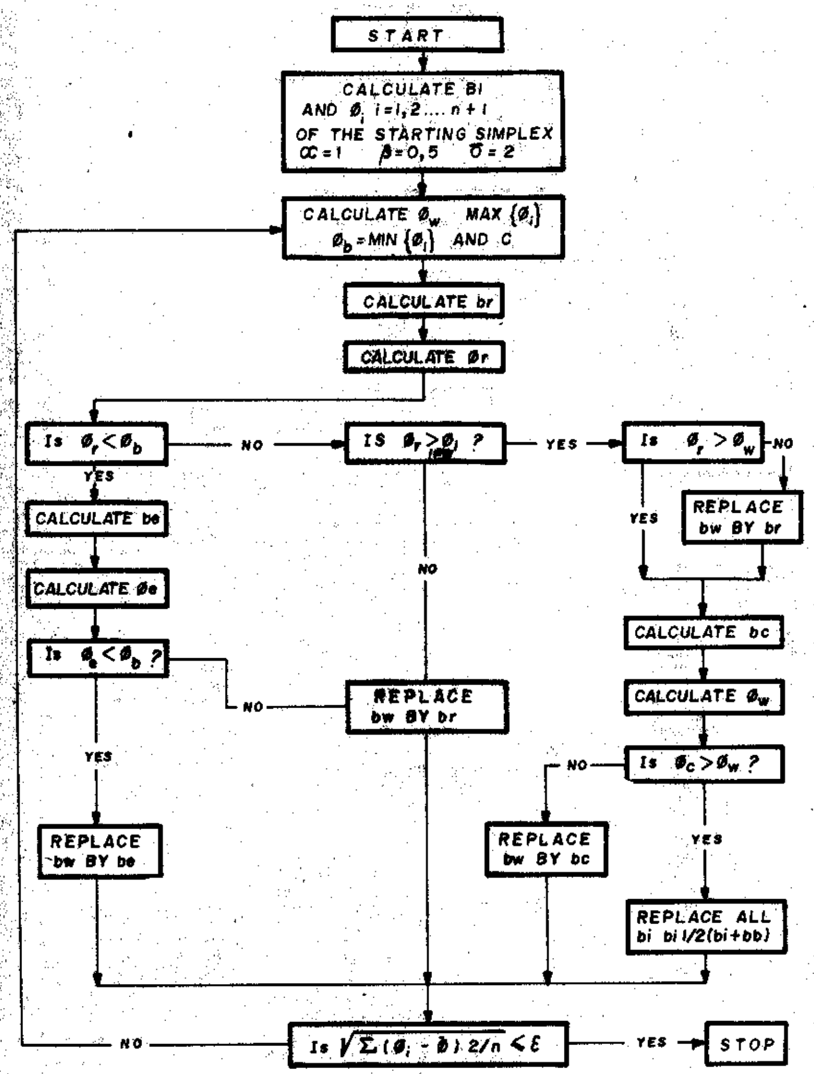

Fig.1_ DETERMINATION OF THE MINIMUN OF Ø

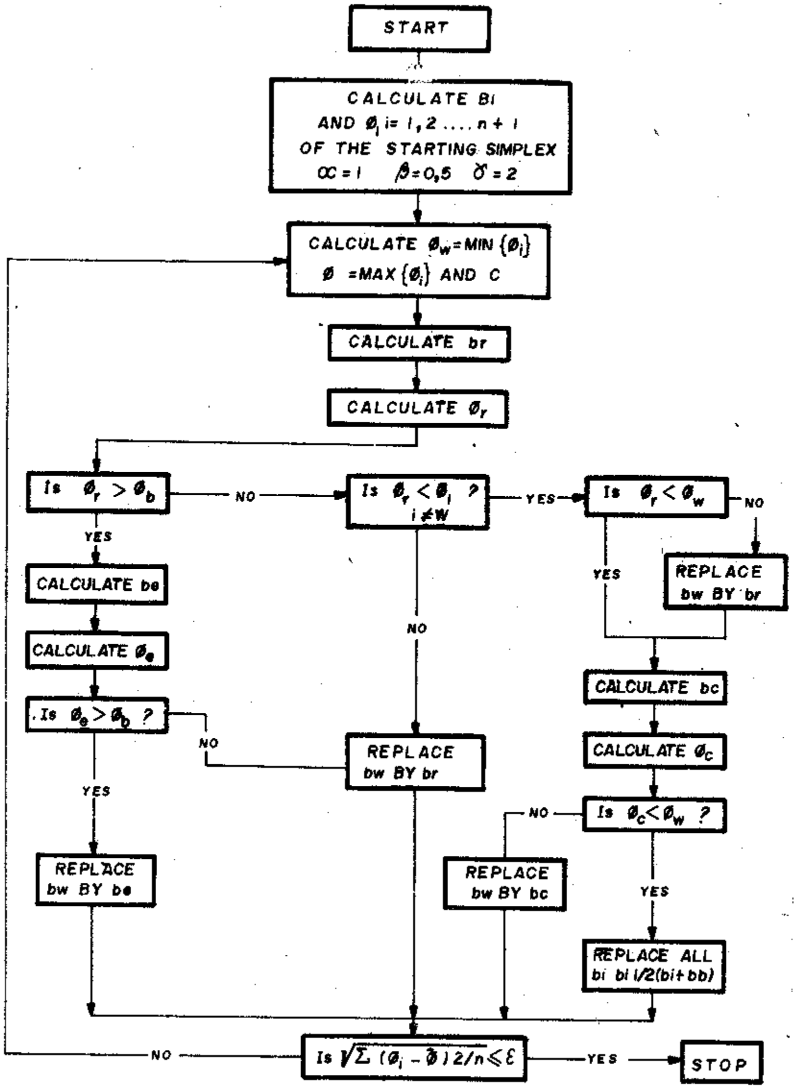

Fig.2_ DETERMINATION OF THE MAXIMUN OF Ø

SIMPLEX MOVEMENT FOR THE OPTIMIZATION OF AIR AND ACETYLEN FLOWRATE IN A.A.S.

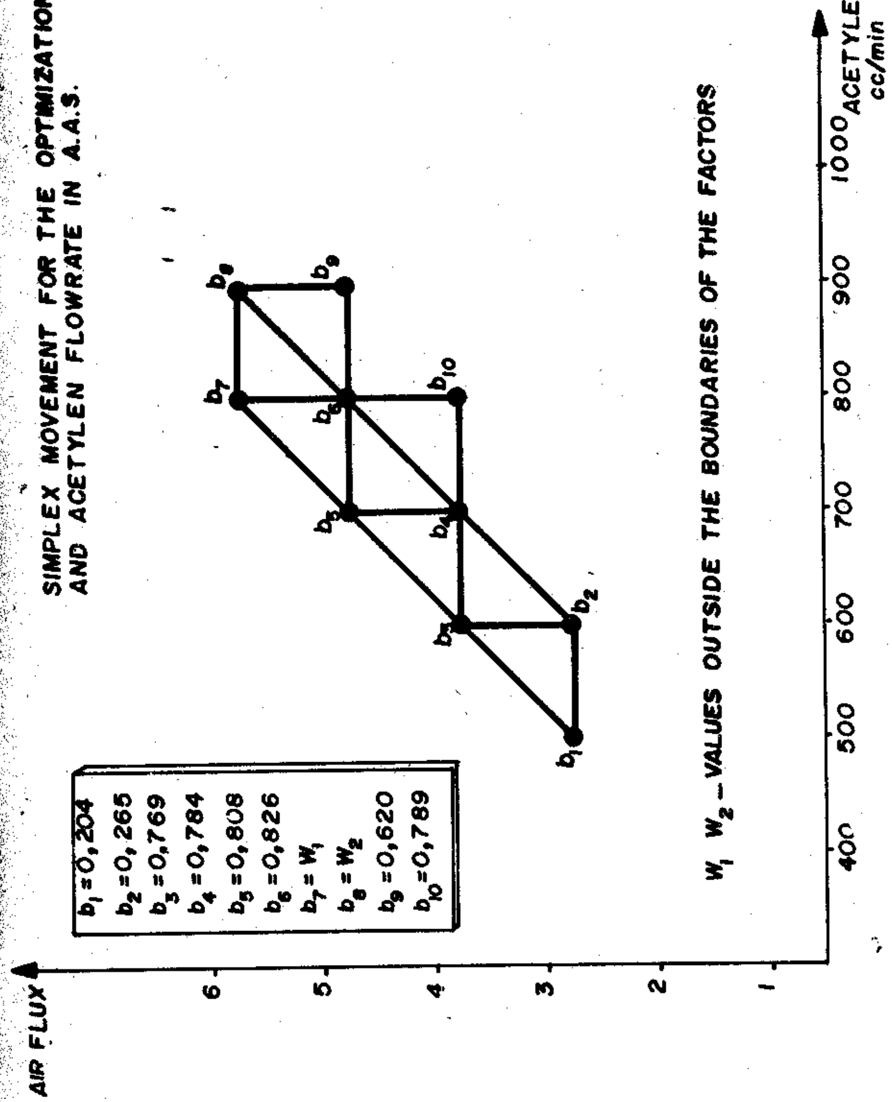

Fig. 3