

SIMPLEX OPTIMIZATION OF EXPERIMENTALS  
FACTOR IN ATOMIC SPECTROSCOPY  
PART. 2 APPLICATIONS IN THE ATOMIC EMISSION  
SPECTROSCOPY

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ABSTRACT

The sequential simplex with the Nelder and Mead algorithm was applied for the multielement determination with photographic detection in A.E.S.

Function responses are presented for the study of the signal to noise density ratio or for minimizing the matrix effect by the multielement analysis. In order to avoid premature simplex contraction the expansion of the initial Simplex is recommended. Examples for the analysis of solutions and powders are given.

Se aplica el método simplex secuencial, con el algoritmo de Nelder y Mead, para la determinación de varios elementos en A.E.E. con detección fotográfica.

Se presentan funciones respuestas para el estudio de la relación señal-ruido, o para la disminución del efecto matriz, en el análisis de varios elementos. Para evitar la contracción prematura del simplex se recomienda la expansión del simplex inicial. Se brindan ejemplos en el análisis de soluciones y polvos.

#### INTRODUCTION

In Atomic Emission Spectroscopy (A.E.S.) are few the works in which optimization techniques are employed being the traditional method of varying one factor at a time the most common used.

Gradient or steepest ascent (descent) methods in A.E.S. (1-7) successfully predict the direction in which the optimum search should be directed, but the minimum number of experiments required for the determination of the next move increases when the number of variables is large, which makes this method troublesome.

In the first part of this work the sequential simplex procedure has been successfully applied in Atomic Absorption Spectroscopy (A.A.S.) according to the Nelder and Mead algorithm (8).

The aim of this paper is to evaluate the performance of the Simplex optimization procedure in A.E.S. for the multielement determination with photographic detection. In the absence of a complete theoretical solution of some problems in A.E.S., the use of optimization techniques is perhaps the best available solution for determining the optimum set of operating conditions.

#### RESPONSE IN ATOMIC EMISSION SPECTROSCOPY

It is usual to consider the density values as a response in A.E.S. A maximum value of such response doesn't mean an enhancement of detection limits. The multielement determination, or removing the matrix effect are also everyday problems in A.E.S. Thus the determination of a response function that really evaluates the system performance is of great significance in A.E.S.

To consider the difficulties in the multielement determination, a function response (9) of such a form is proposed:

$$Y_j = \sum_{i=1}^n (\bar{Y}_i - Y_{ij})^2 \alpha_i \quad (1)$$

where:

$Y_j$  is the response function evaluated in the  $j$  experiment

$\bar{Y}_i$  is the maximum value of the response

$Y_{ij}$  is the value of the response function in the  $j$  experiment for the analytical line of the  $i$  element.

$\alpha_i$  is a coefficient use to characterize the difficulty in the determination of the  $i$  element.

The value of this coefficient should be calculated from:

$$\alpha_i = \frac{N_i}{\sum_{i=1}^n N_i} \quad (2)$$

In this equation  $N_i$  is the order number of the element. Thus a successive arrangement of the elements is undertaken according to considerations concerning the limit of detection of the elements, or to a given priority order, fixed for the particular analytical procedure.

Instead of density values we used the signal to noise ratio defined by

$$R = \frac{\Delta S}{\sigma \Delta S} \quad (3)$$

where:  $\Delta S = S_L + b - S_D$  is the difference between the spectral line density value and the background ( $S_D$ ) in the vicinity. A similar equation for the line intensity can also be applied.

Equation (1) then reads:

$$R_j = \sum_{i=1}^n (R_i - R_{ij})^2 \alpha_i \quad (4)$$

The objective of the simplex optimization will be to minimize the value of  $R_j$ .

For  $R_i$  a value of 100 was fixed.

It is also clear that such a response has little significance if we have to consider matrix effects. In such a case we used as a measure of the line intensities differences an adequate quantity (10) defined as:

$$|\delta m| = \frac{1}{n} \sum_{i=1}^n |Y_{iA} - Y_{iB}| \quad (5)$$

where  $Y_{iA}$  and  $Y_{iB}$  are the intensities logarithms of the spectral line of the  $i$  element in matrices A and B respectively.

Strictly speaking, only the coincidence of working curves must be regarded as a conclusive criterium for the exclusion of matrix effects, but we have found that the applications of equation (5) allows an efficient optimization of the spectral buffer concentration with a reduced number of experiments.

## Experimental part

### Analysis of solutions

As a first example we present the estimation of optimum operating conditions for the analysis of the dry residue of solutions, according to Silberstein (10).

We decide the simultaneous optimization of arc current intensity, of carrier concentration ( $C_a(\text{NO}_3)_2$ ) and exposure time. The signal to noise ratio for the density

values of the spectral lines of 14 elements. (Mg, B, Ni, Co, Cr, Mn, Sn, Fe, Au, Cd, Pb, Zn, As and Hg) was chosen according to equation (4). The apparatus and operating conditions were:

Spectrograph: PGS-2 Carl Zeiss Jena

Diffraction grating: 650 grooves/mm.

Blaze 560 nm

Slit width: 20 m  $\mu$

Electrodes: Flat: 6 mm diameter. Johnson Matthey Grade I electrodes

Analytical gap: 3,0 mm

Emulsion: Spectral plattes ORWO WU3.

Microphotometer: Rapid densitometer GII. Carl Zeiss Jena

Table 1 shows in detail the optimization of the three given parameters.

The response value of each simplex move is an average over 8 spectrograms.

For determining if the optimum has been reached the concerned error (E) was determined previously within the experimental range. An appropriated stop criterium was presented in the first part of this article.

The simplex should be halted when the differences in response approach some predetermined value (E = 300 R units).

By the determination of the initial Simplex, the importance of the investigator previous experience should

not be undervaluated. When the initial Simplex is fixed between the maximum values of the experimental parameters the simplex rules, force the contraction inside the experimental region (see Table 1). Boundary violations are handled by assigning a poor response to the vertex whose locations violates the boundary constraint

Atomic emission spectroscopy with protographic detection is not a noise-free environment. We have found in this field the reluctance of the Simplex procedure (according to Nelder and Mead algorithm) to approach the boundary constraints. This failure is in dependence of the initial Simplex size.

In table 2 is possible to see the failure of the Simplex near a boundary constraint. According to the stop criterium the Simplex is halted in the first contraction (Experiment No. 8). The initial Simplex size was selected between 5 and 6 % carrier concentration. This is very unfavourable and causes an irregular evaporation. The  $R_j$  values are too high and only a local optimum is founded.

#### *Analysis of powders*

The simplex method was also applied for the optimization of five experimental parameters (exposure time, direct current intensity, slit width, buffer-probe dilution and buffer concentration) for the cualitative determination of Ni, Co, Cr, Sn, Mo, V, Ti, Al and Mn in the

residual products from the nickel minerals processing industry. For the solution of this analytical problem is necessary to take account of the possible matrix effects.

The chemical composition of the two different matrices is showed in Table 3. The samples were prepared by dilution in the matrices and with spectral pure oxides of the analytical elements. Standart samples with concentrations of 0,3 Al and Cr, and 0,03 of Sn, Ni, Co, Mn, Ti, V and Mo were used in the optimization process.

The spectrograph, illumination system, analytical gap, emulsion and microphotometer experimental conditions were similar to the mentioned by the analysis of solutions.

Twenty mg of the standard samples were excited in graphite electrodes, with 3 mm diameter, 6 mm deep and 1 mm wall widths.

A response function according to equation (5) was employed. The error for this response function was  $\pm 0,02$  and the same stop criterium was utilized as for the minimization of  $|\delta_m|$ . The response value of each experiment is an average over 10 spectrograms.

The simplex movement is presented in Table 4. Observe the boundary violations for experiments 7 and 15. Optimal values were founded in the experiments 2 and 13. To decide among these experimental conditions, the signal to noise ratio was evaluated for the spectral lines. In this

case experiment No. 13 allowed a higher signal to noise density values ratio for all the spectral lines involved.

The matrix effect was minimized with minimum dilution buffer-probe. It is also evident the advantages of the simplex method over the traditional method of varign one factor at a time generally used for the establishment of "optimum" operating conditions in A.E.S.. In this case a proper exploration of the response surface was achieved with only 15 experiments for 5 experimental factors.

#### CONCLUSIONS

The sequential simplex with the Nelder and Mead algorithm was applied for the multielement determination with photographic detection in A.E.S. The utilization of this approach has not been reported in this field.

According to our results it should be pointed out:

- The function responses presented in this paper allow the optimization of multielements determination in A.E.S. The reproducibility error of these functions should be determined. The simplex should be halted when the response differences approach this value. A similar stop criterium as that employed in A.A.S. can be used in A.E.S.
- When the simplex size and starting location of the simplex is randomly chosen, the Nelder and Mead procedure failed to locate the true optimum in its search because

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- When the simplex size and starting location of the simplex is randomly chosen, the Nelder and Mead procedure failed to locate the true optimum in its search because

of premature contraction of the simplex size. In order to avoid this effect we recommend to expand the initial Simplex between the maximum values of the experimental parameters. The Nelder and Mead algorithm forces then the contraction inside the experimental region and a proper exploration of the response surface is possible.

TABLE 1

Optimization in the analysis of solutions

Exp. No.	Simplex Points	Factors			Response R <sub>j</sub>
		X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	
1	b <sub>1</sub>	8,0	1,0	20	7836
2	b <sub>2</sub>	6,0	0,2	10	8932
3	b <sub>3</sub>	4,0	0,0	5	9471
4	b <sub>4</sub>	10,0	6,0	30	9406
5	b <sub>r1</sub>	8,0	2,1	20	8138
6	b <sub>r2</sub>	7,0	1,0	17	8520
7	b <sub>r3</sub>	8,0	1,4	19	8060

X<sub>1</sub> Direct current intensity (4 - 10A)

X<sub>2</sub> Carrier concentration  
% (Ca(NO<sub>3</sub>)<sub>2</sub>) (0 - 6 %)

X<sub>3</sub> Exposure time (5 - 30S)

TABLE 2

Failure of the simplex

Exp. No.	Simplex Points	Factors			Response R <sub>j</sub>
		X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	
1	b <sub>1</sub>	10	6	30	9406
2	b <sub>2</sub>	8	5,8	25	8922
3	b <sub>3</sub>	9	5,0	25	8279
4	b <sub>4</sub>	9	5,8	20	9082
5	b <sub>r1</sub>	7	5,1	17	9422
6	b <sub>c1</sub>	8	5,3	20	9390

TABLE 3

Chemical composition of the matrices (%)

	Probe 1	Probe 2
Fe <sub>2</sub> O <sub>3</sub>	70	90
Si O <sub>2</sub>	18	7
Mg O	12	3

TABLE 4

Optimization in the analysis of powders

Exp. No.	Simplex Points	Factors					Response $S_m$
		X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	
1	b <sub>1</sub>	90	16	10	0,09	0,40	0,07
2	b <sub>2</sub>	110	14	14	0,11	0,50	<u>0,06</u>
3	b <sub>3</sub>	130	12	18	0,14	0,20	0,09
4	b <sub>4</sub>	150	10	22	0,20	0,10	0,08
5	b <sub>5</sub>	170	8	26	0,20	0,30	0,12
6	b <sub>6</sub>	190	6	30	1,00	0,60	0,14
7	b <sub>r1</sub>	70	18	6	-0,65	0	W <sub>1</sub>
8	b <sub>c1</sub>	160	9	24	0,59	0,45	24
9	b <sub>g</sub>	110	14	14	0,11	0,50	0,09
10	b <sub>10</sub>	100	15	12	0,10	0,45	0,07
11	b <sub>11</sub>	120	13	16	0,13	0,35	0,07
12	b <sub>12</sub>	130	12	18	0,16	0,30	0,07
13	b <sub>13</sub>	140	11	20	0,22	0,40	<u>0,06</u>
14	b <sub>14</sub>	150	10	22	0,56	0,65	0,11
15	b <sub>15</sub>	90	16	40	-0,27	0,15	W <sub>2</sub>

X<sub>1</sub> Exposure time (90-190S)X<sub>2</sub> Current intensity (4-20 potentiometer steps, 4-12A)X<sub>3</sub> Slit width (10-30 μm)X<sub>4</sub> Dilution probe-buffer (1:1-1:11)X<sub>5</sub> Buffer concentration (10-60% Ba CO<sub>3</sub>)

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