

Multi-element optimization of the operating parameters for inductively coupled plasma atomic emission spectrometry with a charge injection device detector for the analysis of samples dissolved in organic solvents[†]

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A multi-element optimization of the operating parameters for simultaneous ICP-AES with a CID detector for the analysis of samples dissolved in organic solvents was carried out. Some statistical experimental designs were used to evaluate the influence of the operating parameters on the effect of volatile organic solvents and to obtain the best plasma conditions for multi-element analysis. The lower limit of detection was used as the optimization criteria. A factorial study showed that nebulizer pressure is the factor that strongly affects the signal-to-root background ratio of the elements under study. The best operating conditions of the plasma for simultaneous determination were obtained using some objective functions reported in the literature. A multi-element analysis of NIST SRM 1085 a Wear Metals in Oil was accomplished using the plasma operating conditions established by the simultaneous optimization. No statistically significant differences were observed between the measurements made and the certified values. The precision of the method was in the range 1–3% expressed as RSD percentage.

Keywords: Inductively coupled plasma atomic emission spectrometry; trace metal determination; organic solvents; optimization

An organic medium is a common matrix for inductively coupled plasma atomic emission spectrometric (ICP-AES) analyses, in particular when the sample is crude oil or related products. In general, the presence of an organic solvent depresses the analyte signals. Different workers have attributed this effect to the presence of high organic vapor loadings which can absorb rf power in the plasma, thus lowering its excitation temperature and decreasing the analytical signal.^{1–14} Because of this interference, the operating parameters of the ICP must be carefully selected as it has been demonstrated that the plasma is less sensitive to matrix interferences under optimized operating conditions.^{15–17}

The optimization of simultaneous multi-element analysis in ICP-AES can be troublesome because a compromise set of instrumental operating parameters has to be selected. Sadler *et al.*¹⁸ described the optimization procedure as consisting of two distinct steps.

(i) The definition of a composite response or objective function, which is representative of all the elements under study, and will act as a measure of the over-all analytical performance of the chosen set of plasma operating conditions.

(ii) Variation of the plasma operating parameters in order to reach the optimum value of the response function. The factors to be varied in a typical ICP-AES optimization are rf forward power, argon gas flow rates, viewing height (measured

above the load coil) and the sample flow rate if a peristaltic pump is used for sample introduction.

A number of different objective functions have been proposed for multi-element optimization of ICP-AES, for example: the objective functions derived by Leary and Brokes¹⁹, (F); Moore *et al.*²⁰ (M), Werner and Friege²¹ (C_{opt}); and Kalivas²² (ACC). Some workers have reported that these objective functions are not useful in situations where the element concentration levels of the samples are unknown or the samples have different compositions.

Sadler *et al.*¹⁸ developed a response function that may be seen as an (n)-dimensional surface, where n is the number of factors to be varied during the optimization process. The response function may be written generally as:

$$R = f(Q_1, Q_2, \dots, Q_n)$$

where Q_i is a measure of the analytical performance of element i at a given factor combination. Examples of Q_i include the limit of detection, the net line signal or signal to background ratio (SBR).

The function has the form:

$$R = \prod_{i=1}^n Q_i^{w_i}$$

where Π represents the product and R is known as the geometric mean of the $Q_i^{w_i}$ values and w_i is a proportionality constant. This constant has been made element-specific so as to act as weighting parameter.

Sartoros and Salin²³ reported another approach, satisfying the conditions required for obtaining optimum compromise operation conditions: obtaining the maximum compromise SBR for all elements and emphasizing the maximization of the SBR of elements at concentrations close their limit of detection. The combined ratio method (CRM) is given by:

$$CRM = \frac{\sum_{i=1}^n (SBR)_i}{\sum_{j=1}^k R_j}$$

where n is the number of elements, k is $(n-1) + (n-2) + \dots + 1$, $(SBR)_i$ are the signal to background ratios of each element and R_j is the ratio of SBRs of two given elements (j th combination) where the maximum SBR of the two is in the numerator such that R_j is ≥ 1 .

The CRMs perform a weighted average on the sum of the SBRs and maximize the individual SBRs while minimizing the difference between these ratios (*i.e.*, minimizing ΣR_j).

The objective of the present work was to perform a multi-element optimization of the operating parameters of the ICP with a CID detector for the analysis of samples dissolved in organic solvents. The lower limit of detection was used as the optimization criteria.

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Firstly, the influence of the operating parameters on the effect of a volatile organic solvent (xylene) for atomic and ionic lines plus a combination of both types of lines was studied. Secondly, optimized operating conditions of the plasma obtained for atomic, ionic and a combination of both types of lines were compared. Finally, the performance of some objective functions when volatile organic solvent solutions were nebulized into the emission source were evaluated.

EXPERIMENTAL

Instrumentation

A Thermo Jarrell Ash (Franklin, MA, USA) Model Iris HR simultaneous spectrometer with a CID detector was used. Details of the instrument and the operating conditions used throughout this study are listed in Table 1. The spectrometer can adjust the forward power and the auxiliary (intermediate) gas flow rate in steps of 200 W (e.g., 1150, 1350, 1550 W) and 0.5 l min⁻¹ (e.g., 0, 0.5, 1 and 1.5 l min⁻¹), respectively.

Chemicals and emission lines

To evaluate the effect of an organic solvent in the plasma an oil based standard (21 element; 100 µg ml⁻¹) from Conostan (Ponca City, OK, USA), dissolved in xylene, was nebulized into the plasma discharge. A factorial design was used to evaluate the effect of the operating parameters on the effect of the organic solvent and a surface response obtained by a central composite design was used to obtain the best compromise operating conditions of the plasma. In order to evaluate the dependence of the effect of the organic solvent and optimal conditions for each parameter on the types of emission line, Al, Cu, Cr, Fe and Mg were chosen as test elements. The most sensitive lines for these elements include both atomic and ionic lines. The spectral lines of these elements along with their excitation energies are listed in Table 2.

Table 1 Instrumental and experimental parameters

Spectrometer	Thermo Jarrell Ash Model IRIS HR
Grating	Echelle grating having 36 grooves mm ⁻¹
Rf generator	27 MHz
Forward power	1350–1550 W
Nebulizer	Cross flow
Spray chamber	Scott type
Outer gas flow rate	16 l min ⁻¹
Auxiliary (intermediate) gas flow rate	0–1.5 l min ⁻¹
Nebulizer pressure	16–24 psi*
Observation height in the plasma	8 mm above load coil
* 1 psi = 6894.76 Pa.	

Table 2 Wavelengths and excitation potentials of the emission lines examined

Spectral species	Wavelength/nm	Excitation potential/eV
Al I	309.3	4.02
Cu I	324.8	3.82
Mg I	285.2	4.35
Cr II	283.6	5.93
Fe II	259.8	4.82
Mg II	280.3	4.22

RESULTS AND DISCUSSION

Influence of the operating parameters on the effect of volatile organic solvents for atomic and ionic lines

In order to evaluate the influence of the operating parameters on the effect of a volatile organic solvent for atomic, ionic and both types of emission intensities, a full two level and four factor (2⁴) factorial study was designed.^{24,25} The four factors considered were: forward power (*P*), nebulizer pressure (*N*), auxiliary (intermediate) gas flow rate (*A*) and sample uptake rate (*S*). Although, the observation height is another important parameter to be considered for the optimization, this factor was kept constant at 8 mm above load coil. In the instrumentation configuration used, the observation height is not easy to manipulate as it must be fixed manually inside the spectrometer. The *R* function with the signal-to-root background ratio, *SRBR*, was used as the response. The *SRBR* was recommended for optimization of an ICP-AES with a charge transfer device detector, as this type of response allows lower limits of detection to be obtained than the *SBR* (the common type of response used).²⁶ The four factors and their levels are listed in Table 3. The values of the levels were fixed in the range recommended by other workers when organic samples were run on an ICP-AES.^{1–14}

In Tables 4 and 5 are shown the experimental values of the *R* function and calculated effects and standard error for a 2⁴ screening design for atomic lines (Al I 309.3 nm, Cu I 324.8 nm and Mg I 285.2 nm), ionic lines (Cr II 283.6 nm, Fe II 259.8 nm and Mg II 280.3 nm) and both types of lines. It should be noticed that for atomic lines the forward power (*P*), nebulizer pressure (*N*), the sample uptake rate (*S*), and the interactions (*N* × *S*) have significant effects on the signals. The effect of power is well known^{15,16} and is indicative that the lowest possible power compatible with stable operation of the generator must be chosen. In the present case 1.350 kW is the

Table 3 Factor levels for the two-level screening design

Factor	Level	
	-1	1
Power/kW (<i>P</i>)	1.35	1.55
Auxiliary (intermediate) gas flow rate/l min ⁻¹ (<i>A</i>)	0.5	1.5
Nebulizer pressure/psi (<i>N</i>)	18	25
Sample uptake rate/ml min ⁻¹ (<i>S</i>)	1.6	2.1

Table 4 Experimental values obtained for the *R* function¹⁸ obtained for atomic, ionic and a combination of both types of lines in the screening design

Run	Factor				Response		
	<i>P</i>	<i>N</i>	<i>S</i>	<i>A</i>	<i>R</i>	<i>R</i>	<i>R</i>
					atomic	ionic	all lines
1	-1	1	1	-1	31.69	119.97	61.66
2	1	-1	-1	-1	11.66	88.19	32.07
3	1	1	1	-1	28.03	129.4	60.23
4	-1	1	-1	-1	25.35	130.6	57.56
5	1	-1	1	1	14.47	100.9	38.21
6	-1	1	1	1	28.52	78.25	47.24
7	1	1	1	1	27.40	97.48	51.68
8	1	1	-1	1	24.99	102.7	50.66
9	1	1	-1	-1	23.77	125.5	54.61
10	1	-1	1	-1	12.70	96.29	34.96
11	-1	1	-1	1	28.11	90.22	50.36
12	-1	-1	1	-1	14.04	100.6	37.6
13	1	-1	-1	1	14.30	88.81	35.64
14	-1	-1	-1	-1	14.67	99.32	38.16
15	-1	-1	1	1	16.79	106.8	42.35
16	-1	-1	-1	1	14.91	101.7	38.94

Table 5 Calculated effects and standard error for a 2⁴ screening design for atomic, ionic and both types of lines

Effect	Estimate ± standard error		
	Atomic	Ionic	All lines
Average	20.7 ± 0.3	104 ± 1	45.8 ± 0.5
<i>Main effects—</i>			
<i>P</i>	-2.1 ± 0.7	0.2 ± 2.1	-2.0 ± 1.1
<i>N</i>	13.0 ± 0.7	11 ± 2.1	17.0 ± 1.1
<i>S</i>	2.0 ± 0.7	0.3 ± 2.1	2.0 ± 1.1
<i>A</i>	1.0 ± 0.7	-15.4 ± 2.1	-2.7 ± 1.1
<i>Two factor interactions—</i>			
<i>P</i> × <i>N</i>	-0.3 ± 0.7	8.8 ± 2.1	2.1 ± 1.1
<i>P</i> × <i>S</i>	-0.2 ± 0.7	4.4 ± 2.1	1.0 ± 1.1
<i>P</i> × <i>A</i>	0.3 ± 0.7	3.0 ± 2.1	1.3 ± 1.1
<i>N</i> × <i>S</i>	1.4 ± 0.7	-6.3 ± 2.1	-0.1 ± 1.1
<i>N</i> × <i>A</i>	-0.9 ± 0.7	-18.8 ± 2.1	-5.8 ± 1.1
<i>S</i> × <i>A</i>	-0.8 ± 0.7	-0.3 ± 2.1	-1.0 ± 1.1

minimum power that can be used in this instrument when organic solvents are introduced.

In the case of ionic lines, *N*, *A* and the interaction of *N* with the others factors have a significant effect on the emission signal. The most significant effect is caused by the auxiliary (intermediate) gas flow rate (*A*), which has a strong depressing effect on the ionic lines. This effect can be explained by decreases in the excitation temperature with increasing auxiliary (intermediate) gas flow rate.⁷ It is well known that changes in the excitation temperatures affect ionic lines more as these lines are mainly excited by thermal mechanisms.^{14,16}

When routine analyses are carried out, ionic and atomic lines are involved, and a compromise set of instrumental operating parameters has to be used to obtain the best instrument performance for both types of lines. This can be appreciated when both types of lines are considered in the response function *R* (see Table 5). The results obtained in the factorial design when both types of lines are considered show that all factors have an effect on the signal. The nebulizer

Table 6 Factor levels for the central composite design: forward power 1.35 kW; and auxiliary (intermediate), gas flow rate 0.5 l min⁻¹

Codified number	Factor	
	Nebulizer pressure/psi	Sample uptake rate/l min ⁻¹
1.414	25.7	2.8
1	24	2.5
0	20	2.1
-1	16	1.5
-1.414	14.3	1.3

Table 7 Experimental values obtained for *R* objective function¹⁸ obtained for atomic, ionic and both types of lines in the central composite design

Run	Factors		Objective function <i>R</i>		
	<i>F</i>	<i>S</i>	Atomic	Ionic	All lines
1	0	0	341.9	743.6	470.9
2	-1.41421	0	228.9	654.4	361.8
3	1	1	286.6	532.5	424.1
4	-1	-1	242.8	668.6	376.6
5	-1	1	281.2	701.0	414.9
6	0	0	346.6	751.2	476.9
7	0	-1.41421	286.0	725.6	425.7
8	1	-1	381.0	656.3	467.4
9	0	1.41421	357.1	762.8	487.8
10	1.41421	0	369.0	434.8	374.3
11	0	0	354.1	649.1	448.1

pressure has the major effect. The auxiliary (intermediate) gas flow rate and forward power have a depressing effect on the signal. Because of this, they must be set up at the minimum tolerable values. Nebulizer pressure and the sample uptake rate are the factors that must be carefully optimized. It is important to note that results obtained in the factorial design with a combination of all types of lines do not have a physical explanation because the design show only the average effect between the atomic and ionic lines.

Optimization of plasma operating conditions for atomic and ionic lines

The compromise conditions for atomic, ionic and a combination of both types of lines were studied. Hence, a surface response for atomic and ionic lines was obtained using a central composite design.^{24,25} The *R* objective function of Sadler *et al.*¹⁸ was used as the response. Nebulizer pressure and sample uptake rate were the factors considered. Forward power and auxiliary (intermediate) gas flow rate were held constant at 1.350 kW and 0.5 l min⁻¹, respectively. The levels of the factors were listed in Table 6.

Shown in Fig. 1 are the response surfaces obtained for atomic (Fig. 1A) and ionic lines (Fig. 1B) and a combination of both types of lines (Fig. 1C). It can be appreciated that the response surfaces obtained for atomic lines were fairly different from those obtained for ionic lines. In the first case, a maximum in the response was not obtained, the best values were obtained for higher values of nebulizer pressure and sample uptake rate. For ionic lines, the maximum values of the responses were obtained for lower values of the two factors when compared with those values obtained for atomic lines. It can also be appreciated that when the responses for ionic and atomic lines were considered, the objective function was really a set of compromise conditions for atomic and ionic lines. The best values of *R* were obtained for intermediate values of the considered factors.

Comparison of the compromise conditions obtained with some objective functions

The compromise conditions given by some of the objective functions were compared. Six separate multi-element response surfaces were constructed from the data, based on: (i) the *F* function reported Leary *et al.*,¹⁹ (ii) the modified *F* function, *SBR* replaced by *SRBR*; (iii) the *R* function reported Sadler *et al.*¹⁸ with *SBR*; (iv) the *R* function with *SRBR*; (v) the *CRM* function reported Sartoros and Salin;²³ and (vi) the modified *CRM* function, *SBR* replaced by *SRBR*. The response surfaces were obtained using a central composite design.^{24,25} The levels of the factors are listed in Table 7. For each of the of the six surfaces, the optimum compromise conditions were taken as the combination of the nebulizer pressure and sample uptake rate that maximized the response function. Three atomic lines and three ionic lines were used (see Table 2). The values obtained for each response are listed in Table 8 and the response surfaces obtained for each objective function are shown in Fig. 2. It can be appreciated that each objective function generates different surface responses. Also, it can be seen that a maximum response was only obtained when the *F* and *R* objective functions were used with the *SRBR*.

To evaluate the performance of each objective function to determine the best compromise instrument operating conditions, the detection limits for each one of the studied elements were determined under the best conditions generated by each response surface, as shown in Table 9. The basic equation for the detection limit, *C_L*, using the *SBR*-*RSD* approach derived by Boumans¹¹ was used. The *RSD_b* was determined by using multiple measurements of the background signal at the analyte

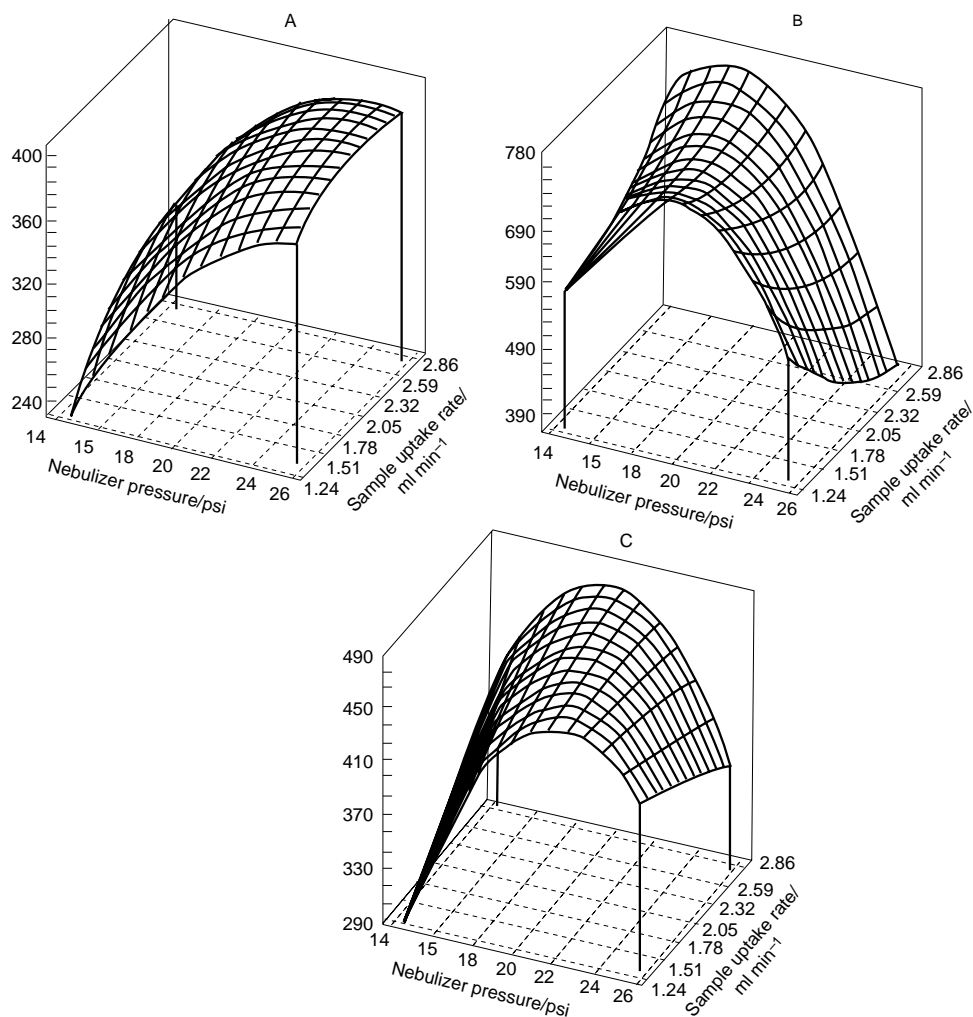


Fig. 1 Response surfaces obtained for: A, atomic lines; B, ionic lines; C, combination of both types of lines.

wavelength from different exposures of a blank solution. For those objective functions that do not give a maximum in the response surface, the higher values of N and S were used as the best conditions. The detection limits obtained are shown in Table 10. It can be appreciated that for all the lines studied, the lower detection limits were obtained with the R objective function. Also, the best detection limits were obtained when the $SRBR$ were used for all the objective functions studied. Hence, it is recommend that the R objective function with

$SRBR$ is used for the simultaneous determination of analyses in samples dissolved in organic solvents.

Reliability of the method

A multi-element analysis of NIST SRM 1085 a Wear Metals in Oil was carried out to evaluate the accuracy of the method. The optimized operating conditions of the plasma obtained as a result of the present work were used: forward power, 1350 W;

Table 8 Experimental values obtained for some objective functions considering atomic and ionic lines in the central composite design

Run	Level of factors		Objective function					
			R^*		F^\dagger		CRM^\ddagger	
			SBR	$SRBR$	SBR	$SRBR$	SBR	$SRBR$
1	0	0	49.12	470.9	28.51	236.33	6.72	3.63
2	-1.41421	0	39.15	361.8	21.77	171.18	4.86	2.48
3	1	1	60.32	424.1	37.45	230.83	9.21	5.31
4	-1	-1	42.03	376.6	23.61	179.47	5.33	2.70
5	-1	1	43.80	414.9	26.11	205.82	6.22	3.00
6	0	0	50.29	476.9	29.07	238.77	6.83	3.68
7	0	-1.41421	46.77	425.7	24.95	201.82	5.46	3.12
8	1	-1	61.97	467.4	36.70	248.84	8.67	5.30
9	0	1.41421	51.18	487.8	29.95	248.22	7.01	3.89
10	1.41421	0	66.86	374.3	41.50	208.16	10.17	6.40
11	0	0	53.29	448.1	31.42	231.18	7.33	4.13

* Ref. 18. † Ref. 19. ‡ Ref. 23.

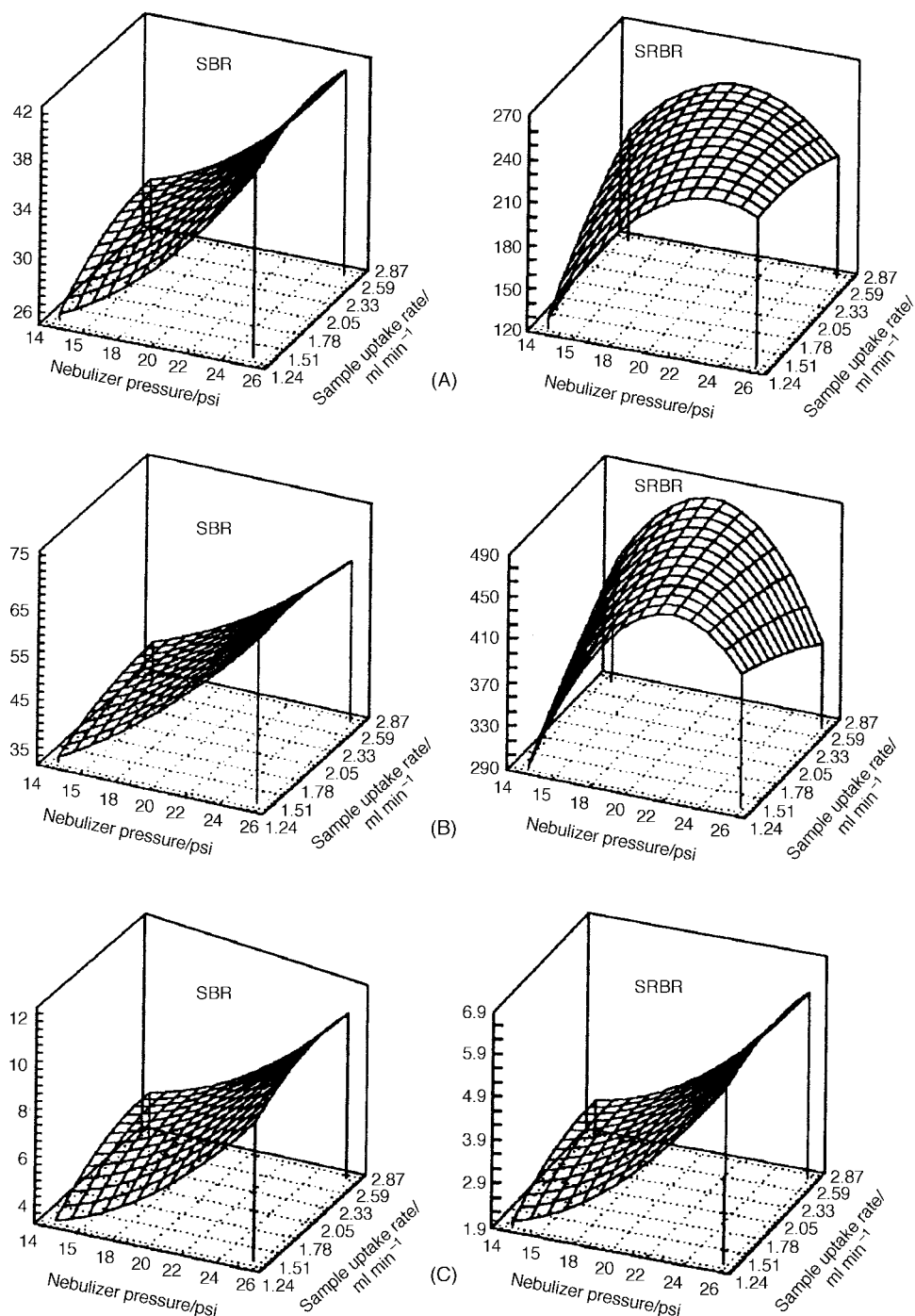


Fig. 2 Multi-element response surfaces obtained by using some objective functions: *F* function (Fig. 2A); *R* function (Fig. 2B); *CRM* function (Fig. 2C).

Table 9 Compromise conditions of nebulizer pressure (*N*, psi) and sample solution uptake rate (*S*, ml min⁻¹), determined by each of the objective functions using *SRB* and *SRBR* as responses. Rf power and intermediate gas flow rates were held constant at 1.35 kW and 0.5 l min⁻¹, respectively

	<i>F</i> function*		<i>R</i> function†		<i>CRM</i> function‡	
	<i>SBR</i>	<i>SRBR</i>	<i>SBR</i>	<i>SRBR</i>	<i>SBR</i>	<i>SRBR</i>
Atomic line—						
<i>N</i>	26.06	26.06	26.06	24.80	26.06	26.06
<i>S</i>	1.75	2.20	2.19	2.16	2.33	2.39
Ionic line—						
<i>N</i>	15.00	20.06	21.03	20.06	20.00	20.40
<i>S</i>	2.87	2.98	2.87	2.87	2.87	2.87
Atomic and ionic lines—						
<i>N</i>	27.06	22.41	27.06	21.06	27.06	27.06
<i>S</i>	2.19	2.87	2.37	2.19	2.27	2.87

* Ref. 19. † Ref. 18. ‡ Ref. 23.

Table 10 Detection limits (ng ml⁻¹) for studied elements optimized by some objective functions employing both *SBR* and *SRBR* as the response

Element	<i>F</i> function*		<i>R</i> function†		<i>CRM</i> function*	
	<i>SBR</i>	<i>SRBR</i>	<i>SBR</i>	<i>SRBR</i>	<i>SBR</i>	<i>SRBR</i>
Al I	4571	881	5439	845	5384	4510
Cu I	873	176	1070	175	1052	886
Mg I	448	98	541	91	521	449
Fe II	6603	521	7846	288	7815	5142
Cr II	5197	476	6692	270	6930	5208
Mg II	284	35	354	25	349	282

* Ref. 19. † Ref. 18. ‡ Ref. 23.

Table 11 Multi-element determination in NIST SRM 1085a

Element	Experimental value/ $\mu\text{g g}^{-1}$	Certified value/ $\mu\text{g g}^{-1}$
Al	104.3 ± 1.8	104*
Ag	102.6 ± 2.3	101.4 ± 1.5
Cr	101.3 ± 1.3	98.3 ± 0.8
Cu	100.9 ± 1.3	100.0 ± 1.9
Fe	100.7 ± 1.6	98.9 ± 1.4
Mg	101.7 ± 1.2	99.5 ± 1.7
Mo	101.8 ± 0.7	100.3 ± 1.4
Ni	100.8 ± 3.4	99.7 ± 1.6
Pb	102.0 ± 2.3	101.1 ± 1.3
Sn	96.9 ± 0.9	97.2 ± 2.6
Ti	101.8 ± 2.3	100.4 ± 3.8
V	96.4 ± 2.9	95.9 ± 9.4
Si	102.4 ± 1.2	103*

*No certified value.

auxiliary intermediate gas flow rate, 0.51 min⁻¹; nebulizer pressure, 21 psi; and sample uptake rate, 2.0 ml min⁻¹. The optimal values for the nebulizer pressure and sample uptake rate were obtained with the objective function employing *SRBR* as the response. ASTM Method D 5185 for the determination of metals in used lubricating oils was used.²⁷ The results are presented in Table 11. Significance tests (*t*- and *F*-tests) at a confidence level of 95% indicated that results for the reference material were in very good agreement with the certified values.

CONCLUSIONS

The influence of the organic solvent influence in ICP-AES is strongly dependent on the type of emission line used: atomic or ionic lines. The results obtained in the factorial design showed that nebulizer pressure has a major effect on both types of lines. Also, ionic lines were affected most when the plasma operating conditions were changed in the presence of a volatile organic solvent. For this reason, the nebulizer pressure is the factor that must be carefully optimized.

It is recommend to use the *R* objective function reported by Sadler *et al.*¹⁸ with *SRBR* for simultaneous determinations in samples dissolved in organic solvents, as the set of operation conditions, obtained by using this function, show the best performance for all the lines studied.

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