

# Experimental design methodologies to optimize monobutyltin chloride determination by hydride generation gas phase molecular absorption spectrometry

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## Abstract

A hydride generation gas phase molecular absorption spectrometry (HG-GPMAS) method for the determination of butyltin compound is optimized by experimental design. This method is based on the conversion of the butyltin chloride into gaseous monobutyltin hydride by adding a sodium tetrahydroborate (III) solution. The hydride generated is collected in a liquid nitrogen cryogenic trap. This is revolatilized, driven to the quartz flow cell and measured with GPMAS with diode array detection. A Plackett–Burmann design is used for the study of the factors that influence the absorption signal. The optimization of the parameters affecting the production and collection of the monobutyltin hydride is achieved using a central composite design. Partial least square (PLS), multiple linear regression (MLR) and univariate calibration are applied to the spectra obtained. The quality parameters (detection limits and precision) for the butyltin chloride are reported. An interference study is made. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydride generation; Gas phase molecular absorption spectrometry; Butyltin chloride; Factorial design

## 1. Introduction

One of the most important steps in the development of a new analytical method is its optimization: the study of those factors which have an influence on the analytical signal, and selection of the values that produce the best results for the analytical method. In the traditional strategy of

one variable at a time, only one variable is changed while all the others remain constant. This approach requires a large number of experiments and does not allow the study of any response changes which may occur when two or more factors are modified simultaneously.

Experimental design is an alternative to this strategy. It allows a large number of factors to be screened simultaneously to determine which of them has a significant effect on the analytical signal; in addition, the factors can be optimized to give the best possible results with a relatively low

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number of experiments. This methodology also allows for sequential experimentation, in such a way that each group of experiments is based on the previous group.

A variety of analytical techniques have been described for the determination of organotin compounds. Many of these are based on separation via high performance liquid–liquid chromatography (HPLC) [1,2] or more often using gas chromatography (GC) [3–5]. The derivatization by hydride generation with sodium tetrahydroborate (III) [1,6], sodium tetraethyl borate [5,7] and alkylation by Grignard reagents [8] are the most commonly used methods for the analysis of these compounds by conversion to volatile species. Several detection techniques have been coupled to GC and HPLC for the determination of derivatized organotin compounds. These include atomic absorption spectrometry (AAS) [9], atomic emission spectrometry (AES) [4], mass spectrometry (MS) [10], flame photometric detection (FPD) [11] and microwave-induced plasma atomic emission spectrometry (MIP-AES) [5,12].

Gas phase molecular absorption spectrometry (GPMAS) is a consolidated technique; analytical applications of GPMAS have been independently developed by Syty [13] and by Cresser [14] since 1973. The technique is based on the measurement of the absorption of molecular species in the gas phase, generated at room temperature. Its application has focused on sulphur compounds [15], nitrogenated compounds [16], halides [17], covalent hydride volatiles [18] and more recently, arsenic and tin organo-metals [19]. The introduction of a diode-array system as the detector has widened the technique's application range. Obtaining the volatile spectrum generated over a wide wavelength range allows the study of the changes produced in the structure of the molecule generated [20] or the simultaneous determination of the various analytes involved [21].

The aim of this study was to establish the best possible experimental conditions for the determination of monobutyltin chloride using the generation of monobutyltin hydride, carried out by continuous addition of the reducing agent and subsequent determination by GPMAS. The optimization study was performed in a sequential

way. Owing to the numerous experimental factors that influence the response of the analyte, a statistical model of the Plackett–Burmann [22] design was used to evaluate the significance of each factor. A statistical model of central composite design [23] was then used to study the influence of the interaction between variables and the optimum conditions.

## 2. Experimental

### 2.1. Apparatus

All measurements were made with a Hewlett-Packard (model HP 8451) diode-array Spectrophotometer equipped with an HP 98155A keyboard, an HP 9121 disk drive for bulk data storage, an HP Thinkjet printer and an HP 7475A graphics plotter. A Hellma 174QS 1 cm quartz flow cell was used, together with a Masterflex peristaltic pump Ref. E07523-37 (Cole-Parmer, USA), a Heidolph MR 3003 agitomatic (Heidolph, Kelheim, Germany) with platinum probe, a Mettler PJ 3600 Delta Range, a Dilvac Dewar (2 l) and a Schott ISO 250/1000 ml generator flask.

For mathematical treatment, a Hewlett-Packard Vectra VL was used; the statistical designs were created and analyzed with the Statistica 5.0 software package [24]. For multicomponent analysis, Parvus 3.0 [25] was used.

### 2.2. Reagents

All reagents used were of analytical grade quality. Double distilled water was used.

A stock solution of tin compound was prepared, of  $1000 \mu\text{g ml}^{-1}$  of Sn as follows: butyltin trichloride,  $\text{C}_4\text{H}_9\text{SnCl}_3$  from Aldrich (Sigma–Aldrich, USA) dissolved in double-distilled water. Working standards were prepared by serial dilution of the stock solutions with double-distilled water, immediately before use.

Aqueous solutions of sodium tetrahydroborate (III),  $\text{NaBH}_4$  from Carlo Erba (Milan, Italy) were prepared immediately prior to use.

Hydrochloric acid (37% m/m,  $1.186 \text{ g ml}^{-1}$ ) and acetic acid (80% m/m,  $1.070 \text{ g ml}^{-1}$ ) from

Carlo Erba-RPE (Milan, Italy). Working solutions were prepared daily by diluting concentrated solutions with double-distilled water.

Dried granular calcium chloride from Carlo Erba-RE (Milan, Italy).

The carrier gases were nitrogen and hydrogen (C-50 Carbuos Metálicos).

### 2.3. System description. Basic procedure

The system used for the generation and measurement of the butyltin hydride is shown in Fig. 1; the scheme consists of: (i) the hydride generator; (ii) the trapping section; (iii) the revolatilizing section; and (iv) UV detection.

A volume of the acidified standard solution was added to the generation vessel, the peristaltic pump introduced the reducing agent and a gas flow was applied through the solution. Once the reducing agent was consumed, the gas flow was maintained for some minutes more. The volatiles generated were condensed in the U-tube immersed in liquid nitrogen.

The U-tube was then removed from the liquid nitrogen and left for a short period at room temperature. Volatilization of the hydrides was achieved by a controlled heating of the trap. The trap was connected to the flow cell with a Teflon tube. The butyltin hydrides were detected using the BASIC program as given in the experimental procedure; a time overlap was obtained of the

volatile absorbance spectra from 190 to 220 nm every 0.2 s for 7 s (enough time for the absorbance to fall to zero).

Using the determination system selected, the total absorbance spectrum of monobutyltin hydride, shown in Fig. 2, was obtained.

## 3. Results and discussion

### 3.1. Study of significant factors

In order to achieve the significant factors, a Plackett–Burman design was used. This experimental design allows a large number of factors to be screened simultaneously to determine which of them has a significant effect on the response. This design supposes that only the principal effects influence the absorbance signal; the interactions among the variables are not considered.

Several variables could potentially affect the absorbance signal: reducing agent flow, reductor concentration, acid type, gas flow rate during hydride generation, revolatilizing temperature, carried time, carrier gas type, time at room temperature, revolatilizing time, sample volume and pH. Each variable was studied at two levels; these levels were selected on the basis of previous results [19], in function of the bibliography found [1,6], and taking into account the limitations of the experimental system. The levels of control are

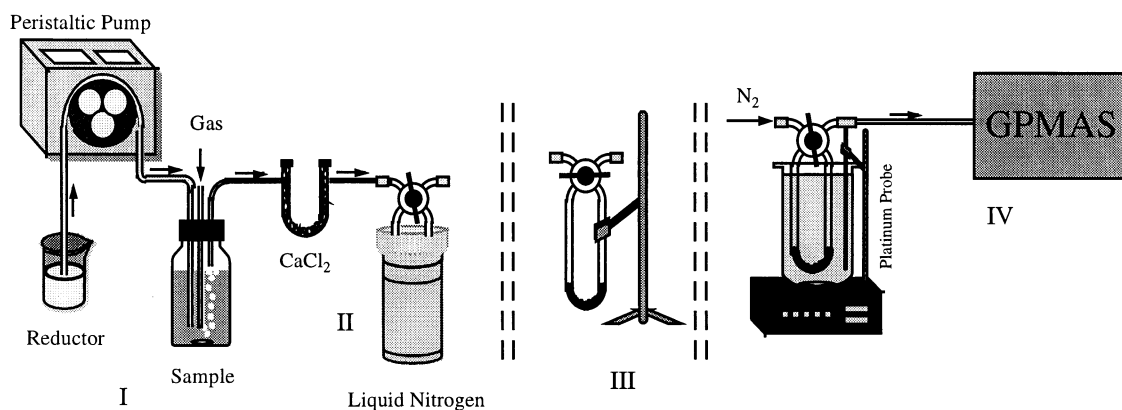


Fig. 1. Schematic diagram of the determination system. (i) The hydride generator; (ii) the trapping section; (iii) the revolatilizing section; (iv) UV detection.

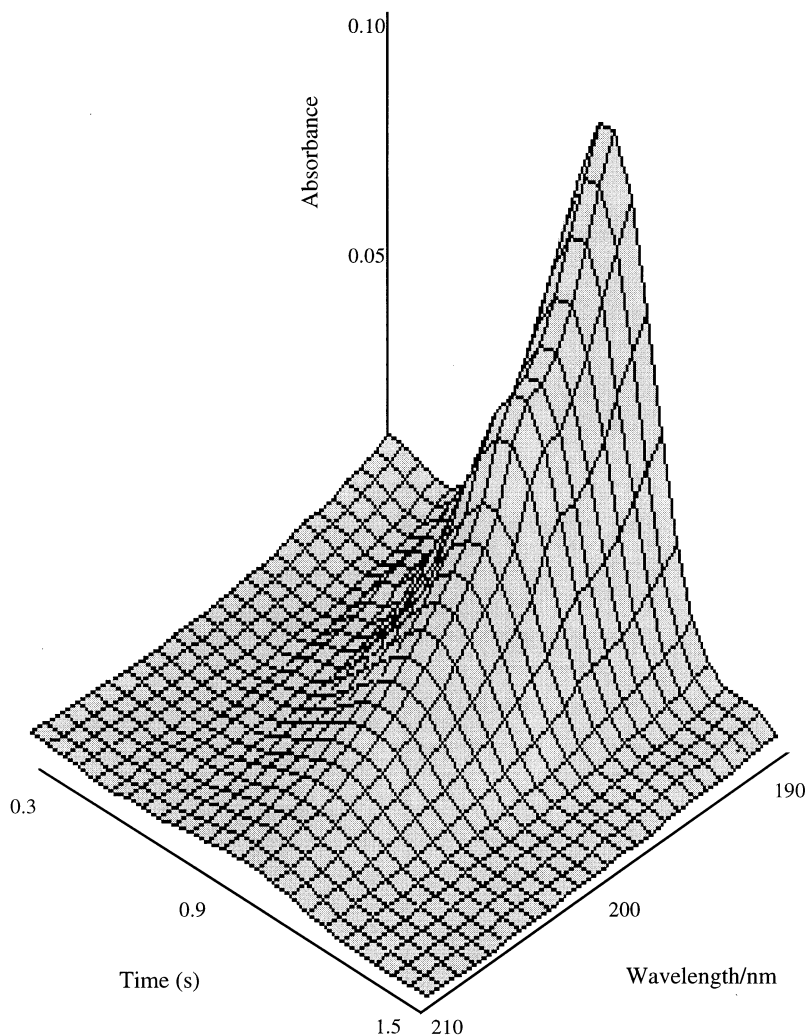


Fig. 2. Three-dimensional absorption molecular spectrum of monobutyltin hydride.

listed in Table 1. The experiments were carried out with three replicates per run, to obtain a value for the experimental error. Randomization was used in order to obtain a random distribution of unknown systematic errors. The sample amount was 208.5  $\mu\text{g}$  for butyltin chloride. Table 2 gives the design matrix for the Plackett–Burman design, the mean response obtained (absorbance of the monobutyltin hydride measured at 192 nm) and the main effects of the factors.

The analysis of the results given in Table 2 produced the bar chart shown in Fig. 3. In this chart, the bar lengths are proportional to the

absolute value of the estimated main effects; those which exceed the reference line, corresponding to the 95% confidence interval (CI), are significant as regards to the response.

The factors which gave significant effects on the signal were reductor concentration, gas flow rate during hydride generation, carried time, carrier gas type, time at room temperature, revolatilizing time and sample volume. The sign of the main effects showed whether the response would be improved or decreased on passing a given factor from the lower level to the higher level, and determined the new experimental domain to be

Table 1  
Factors and levels used in Plackett–Burman design

Factors	Level	
	Low (–)	High (+)
(A) Reductor flow (ml min <sup>-1</sup> )	2	10
(B) Reductor concentration (%)	0.5	4
(C) Acid	Acetic acid	Hydrochloric acid
(D) Generation flow (ml min <sup>-1</sup> )	170	500
(E) Revolatilizing temperature (°C)	60	90
(F) Carried time (min)	2	5
(G) Carrier gas	H <sub>2</sub>	N <sub>2</sub>
(H) Time at room temperature (min)	1.5	3
(I) Revolatilizing time (min)	0.5	1.5
(J) Sample volume (ml)	150	750
(K) pH	1	4

explored to obtain response optimization. The sample volume and carrier gas type were not continuous variables and showed negative signs, and these were therefore fixed as 150 ml and

hydrogen gas. The reductor agent concentration, gas flow rate during hydride generation, carried time, time at room temperature and revolatilizing time were significant and positive effects, so that the region of their higher level was studied further. The reducing agent flow, acid type, revolatilizing temperature and pH were not significant effects and these were fixed at the values of 2 ml min<sup>-1</sup>, hydrochloric acid, 90°C and pH 1. The results of this first study led to the elimination of four variables of the sequential optimization (reducing agent flow, acid type, revolatilizing temperature and pH) and also allowed the fixing of those variables which were non-continuous (carrier gas type, acid type and sample volume).

### 3.2. Optimization of the experimental conditions

A second-order polynomial function was postulated with the aim of obtaining a response map. A five level central composite design with three central points was carried out. This design gave the surface response; the experimental data were fitted to the polynomial mathematical model:

$$y_{\text{pred.}} = \beta_0 + \sum \beta_i x_i + \sum \beta_{ij} x_i x_j + \sum \beta_{ii} x_i^2 + \varepsilon$$

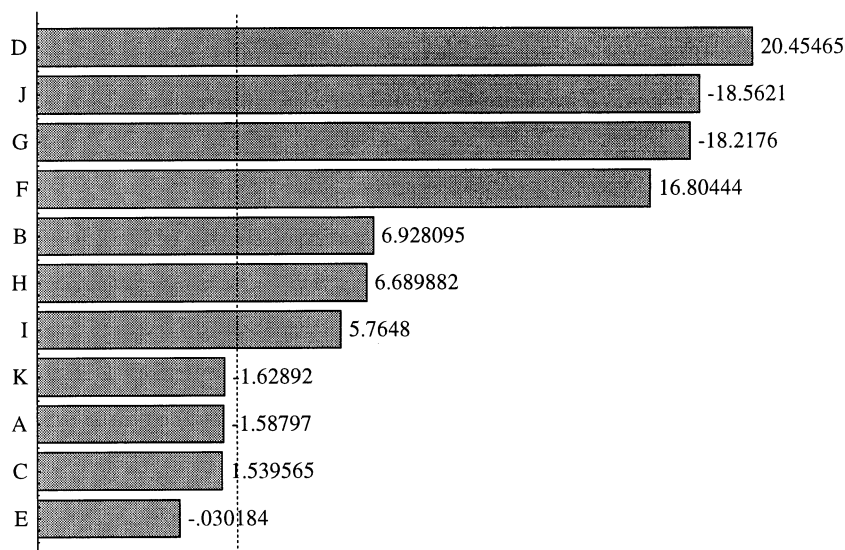


Fig. 3. Graphic analysis of the main effects obtained from the Plackett–Burman design. The vertical line defines the 95% confidence interval (CI).

Table 2  
Experimental matrix and results for Plackett–Burman design

Runs	Factors											BT response
	A	B	C	D	E	F	G	H	I	J	K	
7	+	–	+	–	–	–	+	+	+	–	+	0.0398
3	+	+	–	+	–	–	–	+	+	+	–	0.1666
5	–	+	+	–	+	–	–	–	+	+	+	0.0466
1	+	–	+	+	–	+	–	–	–	+	+	0.1541
4	+	+	–	+	+	–	+	–	–	–	+	0.1023
10	+	+	+	–	+	+	–	+	–	–	–	0.2164
9	–	+	+	+	–	+	+	–	+	–	–	0.2301
2	–	–	+	+	+	–	+	+	–	+	–	0.0366
11	–	–	–	+	+	+	–	+	+	–	+	0.2992
6	+	–	–	–	+	+	+	–	+	+	–	–0.0010
12	–	+	–	–	–	+	+	+	–	+	+	0.0373
8	–	–	–	–	–	–	–	–	–	–	–	0.0746
Effect	–0.008	0.033	0.007	0.096	–0.000	0.078	0.085	0.032	0.027	–0.087	–0.007	

(with  $i$  and  $j$  ranging from  $A$  to  $E$ ) where  $\beta_{ii}$  and  $x_i^2$  are the quadratic regression coefficients and the quadratic settings respectively.

Time limitations on the great number of experiments potentially involved led to the selection of a minimum set of experiments to estimate the model coefficients. In this case, the number of experiments was reduced by running a fractional factorial design,  $2^{5-1}$ . In this design, the main effects were confused with four-way interactions, normally not significant, whereas the interactions of order two were confused with the interactions of order three. The central composite design consisted of the points of fractional factorial design augmented with ten star points. These star points were located at  $+\alpha$  and  $-\alpha$  from the centre of the experimental domain. An axial distance ( $\alpha$ ) was selected with a value of 2 in order to establish the rotatability condition.

On the basis of the previous results, the experimental domain for the remaining variables was adjusted as follows: reductor agent concentration (A): 1–5 (%), gas flow rate during hydride generation (B): 250–750 ( $\text{ml min}^{-1}$ ), carried time (C): 2–6 (min), time at room temperature (D): 2–4 (min) and revolatilizing time (E): 0.5–2.5 (min). The sample amount was 88  $\mu\text{g}$  for butyltin chloride. Due to anticipated problems of overpressure in the system as a result of an excessive quantity of gas, it was not possible to investigate reductor agent concentration of over 5% or carried time of over 6 min. The results obtained are shown in Table 3, together with the corresponding matrix design. The experimental runs were randomized and were carried out with three replicates per run.

Variance analysis (ANOVA) was used to estimate the significance of the main effects and interactions (Table 4). In this table, the sum of squares (SS) is the information that was used to estimate the F-ratios ( $F$ ), which are the ratios of the respective mean square effect and the mean square error. The  $P$ -values indicate when the effect of each factor is statistically significant ( $P < 0.05$ ) or statistically not significant ( $P > 0.05$ ).

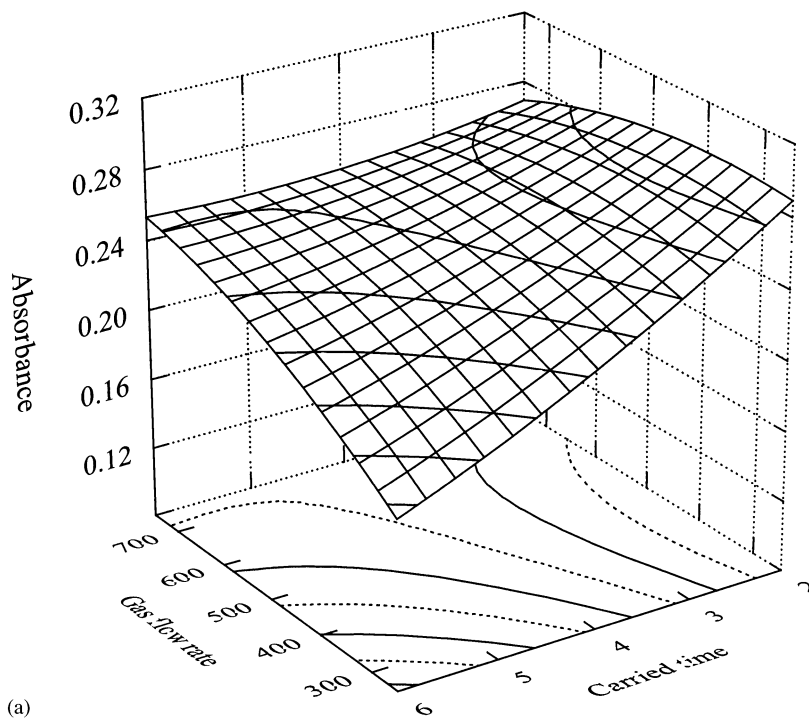
The analysis of the results showed that, out of all the factors studied in this experimental design, the reductor concentration and the revolatilizing time had the highest influence on the response.

Several interactions and quadratic terms were also significant.

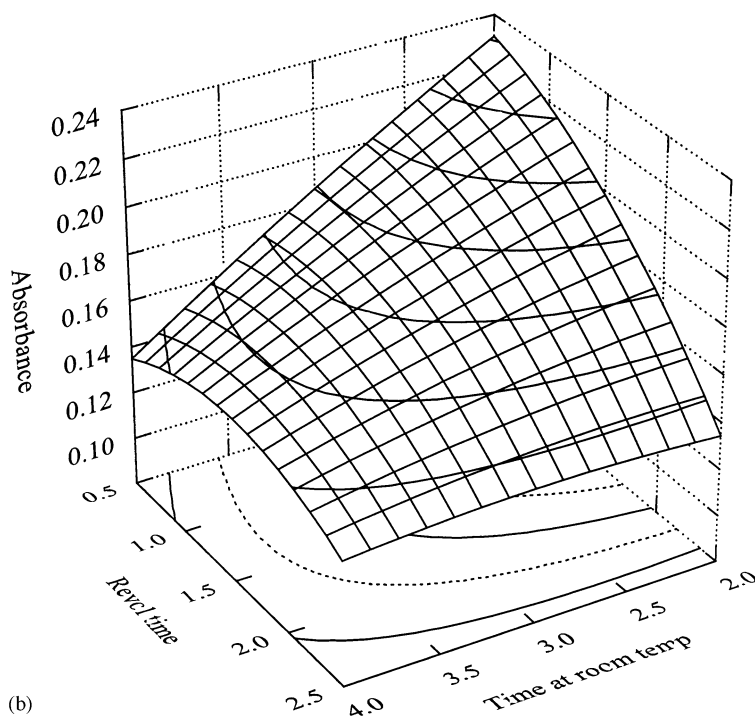
The design allows the obtaining of the response surface. This is an effective way of locating the optimum and for the interpretation of the most influential interactions if a mathematical relationship between the variables is known. Fig. 4 shows the response surfaces including the significant interactions. Fig. 4(a) shows the response surface function developed by the model for gas flow rate during hydride generation and carried time. The response obtained showed a maximum between 200 and 600  $\text{ml min}^{-1}$  when the carried time was at its lowest level. Fig. 4(b) shows the response surface function developed by the model for revolatilizing time and time at room temperature; the response obtained was greatest when the two factors were at their lowest levels; when one of the two factors was at its highest level and the other at its lowest level, the response was minimum. The response was inversely proportional to the two factors. Fig. 4(c) shows the function for carried time and time at room temperature. In this case, the function showed a maximum when the two factors were at the lowest or the highest level.

Fig. 4(d) shows the function for reductor concentration and time at room temperature; the response obtained was a maximum when the first factor was at its high level and the other at its low level. The response is directly proportional to the reductor concentration. Fig. 4(e) shows the response surface function developed by the model for revolatilizing time and carried time. The function was at a maximum when the two factors were at their lowest levels. Fig. 4(f) shows the function for revolatilization time and gas flow rate during hydride generation. As can be seen, the response surface presents a maximum for high flows and low times.

It can be seen that these results confirm those obtained in the above study. Of all the factors investigated, the reductor concentration and the revolatilization time are those which most affect the response. This design completes the previous study, since it permits the obtaining of the interactions between the factors and the optimum working conditions. The most important interactions were seen between the parameters affecting the



(a)



(b)

Fig. 4. Response surfaces estimated from the central composite design for (a) carried time vs gas flow rate, (b) time at room temperature vs revolatilizing time, (c) time at room temperature vs carried time, (d) reductor agent concentration vs time at room temperature, (e) revolatilizing time vs carried time, and (f) revolatilizing time vs gas flow rate.



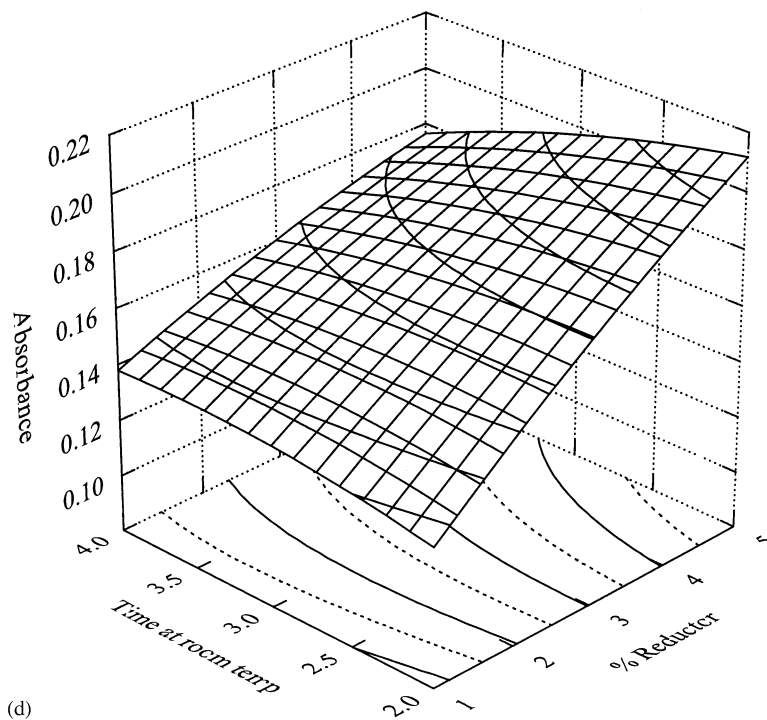
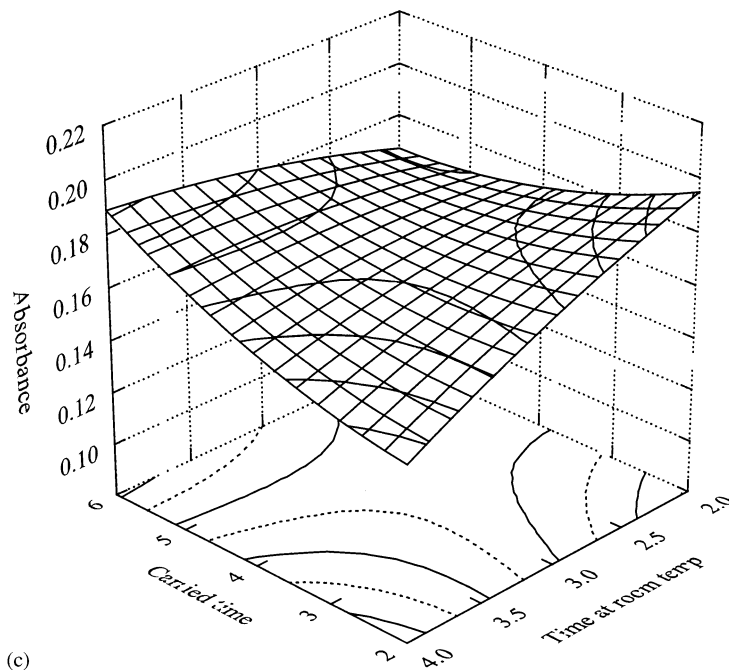
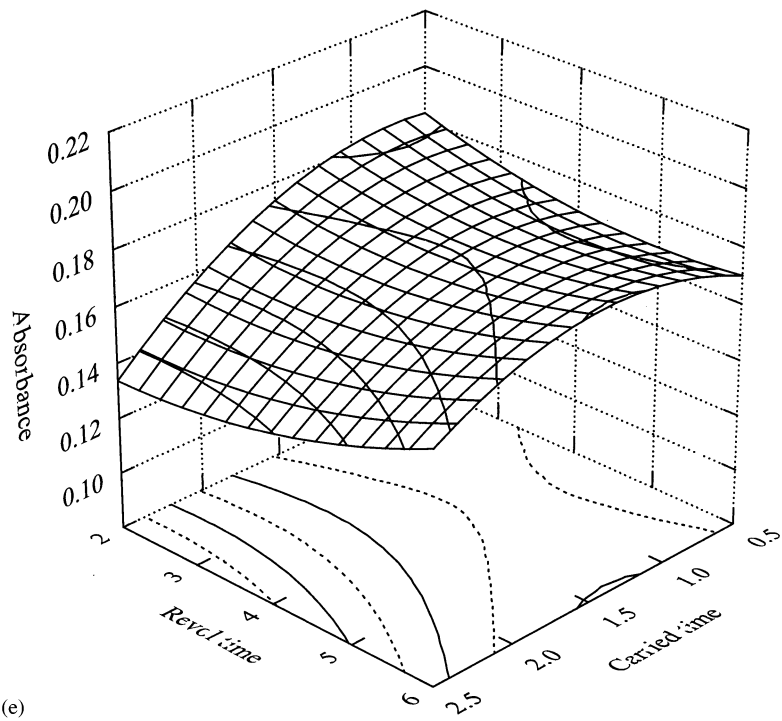
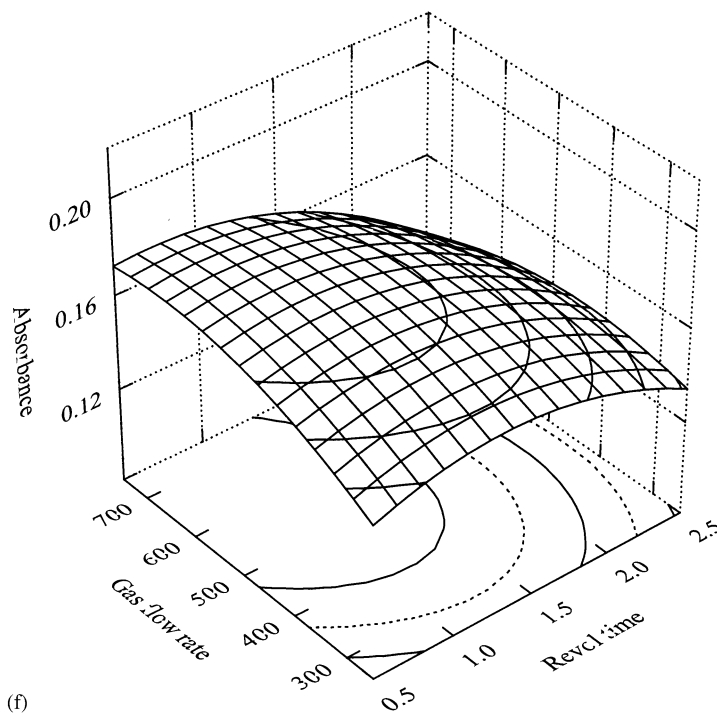


Fig. 4. (Continued)



(e)



(f)

Fig. 4. (Continued)

Table 3  
Design matrix and response of fractional factorial central composite design

Runs	Factors					BT response (192 nm)
	Reductor (%)	Gas flow rate (ml min <sup>-1</sup> )	Carried time (min)	Time room $T^a$ (min)	Revol. time (min)	
1	+	+	+	+	+	0.1774
2	+	+	+	-	-	0.1575
3	+	+	-	+	-	0.1537
4	+	+	-	-	+	0.1700
5	+	-	+	+	-	0.1381
6	+	-	+	-	+	0.1188
7	+	-	-	+	+	0.1474
8	+	-	-	-	-	0.1244
9	-	+	+	+	-	0.1967
10	-	+	+	-	+	0.1578
11	-	+	-	+	+	0.1617
12	-	+	-	-	-	0.2025
13	-	-	+	+	+	0.1612
14	-	-	+	-	-	0.1590
15	-	-	-	+	-	0.1339
16	-	-	-	-	+	0.1372
17	$-\alpha$	0	0	0	0	0.1568
18	$+\alpha$	0	0	0	0	0.1141
19	0	$-\alpha$	0	0	0	0.1053
20	0	$+\alpha$	0	0	0	0.1948
21	0	0	$-\alpha$	0	0	0.1338
22	0	0	$+\alpha$	0	0	0.1483
23	0	0	0	$-\alpha$	0	0.1598
24	0	0	0	$+\alpha$	0	0.1650
25	0	0	0	0	$-\alpha$	0.1654
26	0	0	0	0	$+\alpha$	0.1344
27	0	0	0	0	0	0.1659
28	0	0	0	0	0	0.1643
29	0	0	0	0	0	0.1659

volatile's generation (carried time and gas flow rate during hydride generation) and those affecting the revolatilization (time at room temperature and revolatilizing time).

During the volatile generation, a displacement of water vapor from the generator was seen. To ensure that this vapor was not carried to the four-way valve, a CaCl<sub>2</sub> U-tube was used; however, it was seen that the elimination of the vapor was not complete in some experimental conditions (high reducer concentration or high gas flow during hydride generation). This circumstance could be due to the increase in water vapor in the gas or to the higher velocity of the gas passing through the water trap. To avoid overpressure problems in

the system, the gas flow rate during hydride generation had to be sufficiently high to guarantee the correct carrying of the volatiles to the liquid nitrogen trap; a low carried time allows for control of the movement of water vapor without causing volatile loss.

The effect of the water vapor carried to the four-way valve explains the interaction between the factors which affect the revolatilization. In the optimum conditions found for the generation, a displacement of water vapor to the four-way valve is seen, in such a way that short times at room temperature and of revolatilization act against the dissolving of the analyte in the aqueous phase, thus favoring its revolatilization.

Resulting from this study, the optimum working conditions to obtain the highest absorbance responses were selected. There are: revolatilizing time 0.5 min; reductor agent concentration 5%; carried time 2 min; gas flow rate during hydride generation 550 ml min<sup>-1</sup>, and time at room temperature 2 min.

### 3.3. Analytical characteristics

Under the instrumental and chemical conditions obtained in Section 2, calibration studies were made for the butyltin chloride. The regression equation was obtained by simple linear regression, multiple linear regression (MLR) and partial least square regression (PLSR). The absorbance was obtained on a wavelength interval from 190 to 220 nm. For the univariate regression, the wavelength selected was 192 nm; the MLR results were obtained after reducing by stepwise selection the total set of 20 predictors to an optimum subset (192 and 214 nm). For PLS, in

order to select the number of factors, a cross-validation method, leaving out one sample at a time, was used.

The detection limit of 5.6 ng ml<sup>-1</sup> was calculated according to the IUPAC; the value reported is the mean of five replicates, using the absorbance signal measured at the peak height at 192 nm. The relative standard deviation (RSD) value for precision, calculated from 20 determinations from a solution containing ten times the corresponding detection limit and taken on different days, was 5.1%.

Table 5 shows the root mean square difference (RMSD) and  $R^2$  of the calibration model. The RMSD is an indication of the average error in the analysis

$$\text{RMSD} = \left[ \frac{1}{N} \sum_{i=1}^N (\hat{y}_i - y_i)^2 \right]^{0.5}$$

and the square of the correlation coefficient ( $R^2$ ) is an indication of the quality of fit of all the data to a model:

Table 4  
Analysis of variance (ANOVA) for the fractional factorial central composite design

Source of variation	Sum of squares	Degrees of freedom	Mean square	F-ratio	P-value
(A) Reductor (L)	0.02379	1	0.02379	320.48	0.0000
(AA) Reductor (Q)	0.00008	1	0.00008	1.06	0.3078
(B) GAS FLOW RATE (L)	0.00052	1	0.00052	7.02	0.0100
(BB) GAS FLOW RATE (Q)	0.00084	1	0.00084	11.37	0.0012
(C) CARRIED TIME (L)	0.00036	1	0.00036	4.82	0.0315
(CC) CARRIED TIME (Q)	0.00035	1	0.00035	4.72	0.0332
(D) TIME ROOM $T^A$ (L)	0.00115	1	0.00115	15.53	0.0002
(DD): TIME ROOM $T^A$ (Q)	0.00009	1	0.00009	1.15	0.2881
(E) REVOL. TIME (L)	0.00541	1	0.00541	72.82	0.0000
(EE): REVOL. TIME (Q)	0.00173	1	0.00173	23.28	0.0000
(AB)	0.00020	1	0.00020	2.71	0.1041
(AC)	0.00029	1	0.00029	3.96	0.0507
(AD)	0.00052	1	0.00052	7.02	0.0100
(AE)	0.00000	1	0.00000	0.02	0.8981
(BC)	0.00259	1	0.00259	34.94	0.0000
(BD)	0.00027	1	0.00027	3.63	0.0609
(BE)	0.00035	1	0.00035	4.74	0.0329
(CD)	0.00135	1	0.00135	18.20	0.0001
(CE)	0.00045	1	0.00045	6.02	0.0167
(DE)	0.00243	1	0.00243	32.80	0.0000
Error	0.00512	69	0.00007		
Total SS <sup>a</sup>	0.04794	89			

<sup>a</sup> Sum of squares.

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y})^2}$$

where  $y_i$  is the standard concentration of analyte in the sample  $i$ ,  $\hat{y}_i$  is the estimated concentration of the analyte in the sample  $i$ ,  $\bar{y}$  represents the mean of standard concentrations and  $N$  is the total number of samples. It can be seen that the best results were obtained using MLR, which gave the best correlation coefficient and the lowest RMSD.

The proposed simple linear regression, MLR and PLS methods applied to the absorption spectra allowed the resolution of drinking waters fortified with butyltin compound. In Table 6, the results obtained for the determination of the butyltin in the synthetic samples of butyltin chloride are shown. It can be seen that the RSD values were significantly lower when multivariate methods were used. The accuracy values obtained for the MLR and PLS methods were greater than for the univariate regression; within this group, the best results were obtained using PLS.

### 3.4. Interference study

The effect of several ions on a monobutyltin chloride standard of  $0.30 \text{ mg ml}^{-1}$  Sn are shown in Table 7. Solutions containing butyltin chloride (BT) and various concentrations of the potential interferents, one at a time, were subjected to the generation and determination procedure and the signals obtained by this method were compared with the signals obtained without the interference. All experiments were performed in triplicate.

No effects were observed for up to  $200 \text{ } \mu\text{g ml}^{-1}$  of Na (I), K (I), Ca (II), Ba (II), Sr (II), Mg (II), Mn (II), Hg (II), Cd (II), Zn (II), V (V), Mo (VI), Al (III), Cr (III),  $\text{NH}_4^+$ , Te (VI), Sn (IV), Bi (III), Pb (II), Ge (IV),  $\text{MnO}_4^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$  and  $\text{I}^-$ ; up to

$1000 \text{ } \mu\text{g ml}^{-1}$  of chloride, sulphate and nitrate did not interfere. Those elements which gave rise to a signal depression of less than 1 S.D. of the expected response were deemed not to interfere.

Depression of the signal was observed in the presence of Co (II), Ni (II), Cu (II), Ag (I), Fe (II), Fe (III) and Cr (VI).

Significant interference effects were seen from the sulphite ion and the elements which form volatile hydrides under the generation conditions. Sb (III), Sb (V), Sn (II), As (III), As (V) and the  $\text{S}^{=}$  anion caused a quantitative increase in the absorbance signal which can be used for the simultaneous determination of mixtures of several elements. The Se (IV) showed a different behavior: for low interferent/analyte ratios, the error was almost the same, but when the  $[\mu\text{g ml}_{\text{int}}^{-1} / \mu\text{g ml}_{\text{BT}}^{-1}]$  ratio increased, the interference increased also. This behavior may be due to the equilibria which becomes established between the butyltin chloride and the selenium species in the liquid or gas phase.

## 4. Conclusions

With the Plackett–Burman design used in this work, the variables which affect the determination of butyltin chloride by HG-GPMAS were identified: reductor agent concentration, gas flow rate during hydride generation, carried time, time at room temperature and revolatilizing time. This design allows a reduction in the number of factors to be studied, from 11 to 5, and establishes a new region to study.

The proposed experimental design methodology allows the finding of the optimal conditions for the determination of butyltin chloride by HG-GPMAS, together with an identification of the interactions between the factors studied, parameters which cannot be obtained when optimization of one factor at a time is used. It can be concluded that the most influential parameters on the response are reductor agent concentration, revolatilizing time and the interactions between carried time and gas flow rate during hydride generation and between time at room temperature and revolatilizing time.

Table 5  
Statistical parameters of the calibration

	Univariate	MLR	PLS
$R^2$	0.9991	0.9991	0.9989
RMSD	0.2178	1.7166	0.8651

Table 6  
Results obtained from the resolution of the artificial samples of butyltin chloride

Added (ng ml <sup>-1</sup> )	Univariate			MLR			PLS		
	Found <sup>a</sup> (ng ml <sup>-1</sup> )	Recov. (%)	RSD <sup>a</sup> (%)	Found <sup>a</sup> (ng ml <sup>-1</sup> )	Recov. (%)	RSD <sup>a</sup> (%)	Found <sup>a</sup> (ng ml <sup>-1</sup> )	Recov. (%)	RSD <sup>a</sup> (%)
42.9	45.8	107	8.3	42.6	99	1.9	43.2	101	1.1
53.6	54.8	102	5.9	53.1	99	1.4	54.1	101	1.8
74.3	68.9	92	7.8	74.5	100	1.4	74.4	100	0.89
148.6	140.2	94	12.9	145.8	98	1.6	147.9	99	0.95

<sup>a</sup> Mean of three independent determinations.

Table 7  
Results from the interference study

Interferent	Ratio [Int.]/[BT] <sup>a</sup>	% Error	Interferent	Ratio [Int.]/[BT] <sup>a</sup>	% Error
Co (II)	10	–	Sb (III)	0.1	17.56
	25	–20.61		0.2	50.85
	75	–45.25		0.3	88.02
	125	–73.27		0.5	151.7
	200	–96.3		1	257.1
Ni (II)	10	–44.05	Sb (V)	0.25	24.15
	25	–57.18		0.5	42.56
	100	–90.9		1	106.21
	150	–98.02		1.5	178.25
Cu (II)	10	–34.01	As (III)	0.25	67.66
	50	–71.25		0.5	101.49
	100	–80.74		0.75	135.32
	250	–88.06		1	202.98
Ag (I)	5	–21.96	As (V)	0.25	67.79
	25	–40.3		0.5	134.2
	50	–70.67		0.75	179.55
	100	–98.5		1	265.32
Fe (II)	10	–	Se (IV)	0.25	74.2
	25	–38.28		0.5	71.38
	75	–51.07		1.5	69.28
	150	–78.16		3.5	87.59
	300	–91.58		5	102.8
Fe (III)	25	–	Sn (II)	5	28.3
	75	–13.8		10	100.14
	150	–25.11		25	240.65
	300	–75.74		50	322.7
	400	–95.97			
Cr (VI)	5	–	NO <sub>2</sub> <sup>–</sup>	10	–38.23
	25	–46.37		25	–49.44
	75	–67.2		75	–58.69
	125	–77.42		100	–98.23
	325	–86.84	S <sup>=</sup>	0.25	99.25
		0.5		120.59	
		1		161.9	
			2	254.14	

<sup>a</sup> [ $\mu\text{g ml}_{\text{int}}^{-1}$ ]/ $\mu\text{g ml}_{\text{BT}}^{-1}$ (as Sn)].

The use of a diode-array molecular absorption spectrophotometer as the detector allows the spectra of generated volatiles to be obtained over a wide wavelength range, making possible the application of a multivariate calibration system. Fur-

thermore, the different effects that the various interferences present on the analytical signal can be observed. The spectra obtained for the interfering compounds allows, in some cases, the simultaneous determination of several compounds.

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