

Optimization of dimethyltin chloride determination by hydride generation gas phase molecular absorption spectrometry using a central composite design

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Abstract

A factorial design is applied to the optimization of the determination of dimethyltin chloride by hydride generation gas phase molecular absorption spectrometry (HG-GPMAS). A method is described for the determination of dimethyltin chloride after conversion into gaseous dimethyltin 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 gas phase molecular absorption spectrometry (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 these factors is performed using a central composite design. The spectra obtained over a wide range of wavelengths, 190–220 nm, allow the multivariate calibration to be studied. The parameters affecting the production and collection of the dimethyltin hydride are studied. The detection limit obtained is 3.2 ng ml^{-1} . The precision ($\text{RSD} = 4.1\%$) is calculated from a solution containing ten times the corresponding detection limit. The recoveries (99–108%) are satisfactory. A study is made of the influence of several interferent ions (hydride generators, transition metals and anions) in the presence of dimethyltin chloride. © 2000 Elsevier Science B.V. All rights reserved.

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

1. Introduction

The organometallics of general form R_2SnX_2 are used as thermal stabilisers in plastics such as PVC; species of the R_3SnX type have applications as biocides, fungicides, paint protectors and disin-

fectants [1,2]. The lipidic properties of these compounds facilitate their accumulation in marine organisms. The environmental methylation of tin, and the degradation of TBT (tributyltin) to DBT (dibutyltin) and MBT (monobutyltin) are also factors which contribute to the presence of tin organometals in the environment [3].

The derivatization by hydride generation with sodium tetrahydroborate (III) [1,4], sodium tetraethyl borate [5] or alkylation by Grignard

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reagents [6,7] are the most commonly used methods for the analysis of these compounds by conversion to volatile species. For multicomponent analysis, the separation techniques most often used are gas chromatography [8] and HPLC [9]. The compounds can be detected by atomic absorption spectrometry [4], mass spectrometry [2], atomic emission detection [10], flame photometric detection [11], or spectrofluorimetric detection [12].

GPMAS (gas phase molecular absorption spectrometry) is a widely used technique. Syty [13] introduced this method in 1973. In this technique, the volatile molecular species are generated from solutions and are transported to an atomic absorption spectrophotometer in which the atomization device has been replaced by a silica flow cell. Analytical applications of GPMAS have been independently developed by Syty [14] and by Cresser [15,16]. The use of a diode-array system as the detector permits the obtaining of the volatile species spectrum generated over a wide wavelength range. This gives a large amount of information about the changes produced in the structure of the molecule generated [17] or allows simultaneous determination of the various species involved [18–20].

This work proposes a determination system using the generation of dimethyltin hydride, carried out by continuous addition of the reducing agent and subsequent determination by GPMAS. The choice of molecular absorption spectrometry as the detector permitted the obtaining of the complete spectra of the generated volatiles, making possible their simultaneous determination and interference elimination by the application of multivariate calibration methods: PLSR [21,22], and PCR [23]. The optimization study was performed in a sequential way, presenting the results obtained for each of the stages carried out during the study. Owing to the numerous experimental factors that influence the response of the volatile species, a statistical model of the Plackett-Burmann design [24] was used to evaluate the significance of each factor. A statistical model of central composite design [25] was then used to study the influence of the interaction between variables and the optimum conditions. The spectra obtained over a wide range of wavelengths, 190–220 nm, permitted the application of

differing calibration methods (univariate, MLR and PLSR) and their comparison in the resolution of artificial samples. The work was completed with a study of the interferences involved in the determination of dimethyltin (DMT) using GPMAS.

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 peristaltic pump (Cole Parmer Instrument 7554-20), an Agitamatic Heïdolph MR 3003 with platinum probe (Heïdolph, Kelheim, Germany), a Mettler PJ 3600 Delta Range, a Dewar (2 l) Dilvac and a generator flask Schott ISO 250/1000 ml.

The generation scheme and procedure system are already described in previous papers [26]. The statistical designs were created and analyzed with the Statistica 5.0 software package [27]. For multicomponent analysis, Parvus 3.0 [28] was used.

2.2. Reagents

All reagents used were of analytical grade quality. A stock solution of tin compound was prepared of 1000 $\mu\text{g ml}^{-1}$ of Sn as follows: dimethyltin dichloride, $\text{C}_2\text{H}_6\text{SnCl}_2$ 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), NaBH_4 from Carlo Erba (Milan, Italy) were prepared immediately prior to use. Hydrochloric acid (37% m/m, 1.186 g ml^{-1}) and acetic acid (80% m/m, 1.070 g ml^{-1}) were from Carlo Erba-RPE (Milan, Italy). Working solutions were prepared daily by diluting concentrated solutions with double-distilled water. Dried granular calcium chloride was from Carlo Erba-RPE (Milan, Italy). The

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

3. Results and discussion

3.1. Study of significant factors

The absorbance response of dimethyltin hydride by HG-GPMAS, whose absorbance spec-

trum is shown in Fig. 1, is considered as a function of the several factors. In order to identify the significant factors, a Plackett-Burman design was used. This study permitted the elimination of non-significant variables, and also the fixing of the non-continuous variables (sample volume, acid type and carrier gas). The Plackett-Burmann designs are fractional factorial designs of two levels, used to study K factors with $(K = N - 1)$ in N tests. In this experimental design, each main

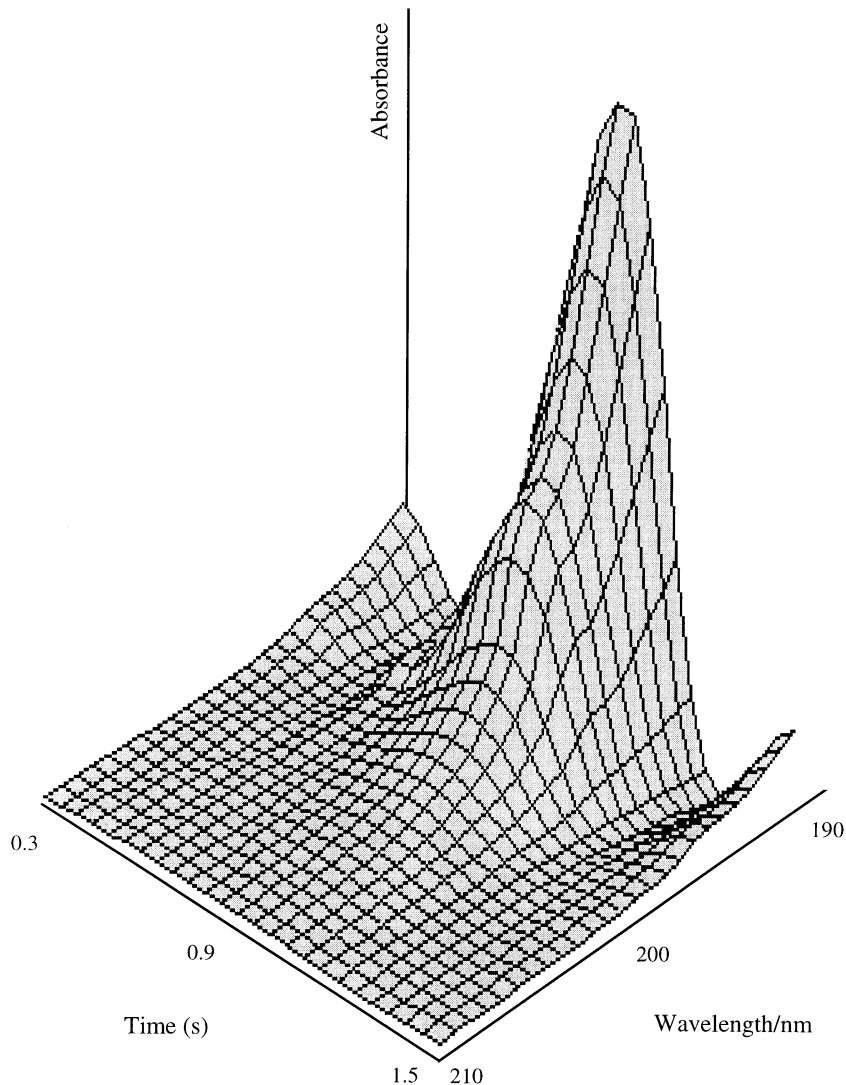


Fig. 1. Three-dimensional absorption molecular spectrum of dimethyltin hydride.

Table 1
Factors and levels used in the Plackett-Burman design

Factors	Level	
	Low (–)	High (+)
A. Reductor flow (ml min ⁻¹)	2	10
B. Reductor concentration (%)	0.5	4
C. Acid	Acetic acid	Hydrochloric acid
D. Generation flow (ml min ⁻¹)	200	500
E. Revolatilizing temperature (°C)	60	90
F. Carried time (min)	2	5
G. Carrier gas	H ₂	N ₂
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

effect is confounded with all the interactions in which it does not participate. This optimization technique was chosen because of the excellent relation which it offers between the experimental effort needed (11 factors, 12 experiments) and the results obtained, as well as the simplicity of its approach, realization and results analysis. The application of this design was undertaken on the assumption that the interactions of second order or higher are much smaller than the principal effects.

For the proposed method, the dependent variable was the absorbance of the dimethyltin hydride measured at 192 nm. The independent variables were sample volume, pH, acid type, reductor agent flow, reductor concentration, carrier gas, gas flow generation, carried time, time at room temperature, revolatilizing time and revolatilizing temperature.

The values of the variables for each level were chosen with regard to Refs. [1,4] and our own experience [17,29] (Table 1) and were carried out with three replicates per run, to obtain a value for the experimental error. The sample amount was

413.2 µg for dimethyltin (DMT) dichloride. Table 2 gives the design matrix for this experiment, the mean response obtained and the main effects of the factor.

After the estimation of the factor's main effect, the determination of the significant factors affecting the dependent variable (absorbance) was computed by means of an ANOVA test. The sum of squares (SS) was used to estimate the significant factors. The total sum of squares was divided into the sum of squares of the factor and the sum of squares of the residuals; the *F*-ratios are the ratios of the respective mean square effect and the mean square error. When the factors have a significant effect, the variance of the data set was larger than the variance of the residuals. This was confirmed by a hypothesis test. Each ANOVA main effect had one degree of freedom, since the factors in the study had two levels. The *P*-values indicate when the main effect of each factor is statistically significant (*P* < 0.05). The results from the ANOVA study are shown in Table 3.

The significant effects were reductor agent flow, reductor concentration, acid type, gas flow generation, carried time, carrier gas, time at room temperature and sample volume. The sign of the main effects determined the experimental conditions of the next design. The acid type, sample volume and carrier gas were not continuous variables; the first gave a positive sign and the hydrochloric acid was therefore selected as the reaction medium, whereas the sample volume and carrier gas showed negative signs, and these were therefore fixed at 150 ml and hydrogen. The reductor concentration, gas flow generation, carrier time and time at room temperature were significant and positive effects, so that the region of their higher level was studied further, whereas the reductor agent flow was a significant and negative effect so that the region of its lower level was studied further. The revolatilizing time, revolatilizing temperature and pH are not significant effects. For these factors, the signal's absorbance did not increase or decrease when passing from the lower to the higher level. The values of these factors were therefore chosen,

Table 2
Design matrix, results and main effects for the Plackett-Burman design

Runs	Factors											DMT response (192 nm)
	Reductor flow (ml min ⁻¹)	Reductor (%, w/v)	Acid	Generation flow (ml min ⁻¹)	Revolatilizing temperature (°C)	Carried time (min)	Carrier gas	Time of room temperature (min)	Revolatilizing time (min)	Sample volume (ml)	pH	
7	+1	-1	+1	-1	-1	-1	+1	+1	+1	-1	+1	0.1725
3	+1	+1	-1	+1	-1	-1	-1	+1	+1	+1	-1	0.2037
5	-1	+1	+1	-1	+1	-1	-1	-1	+1	+1	+1	0.1811
1	+1	-1	+1	+1	-1	+1	-1	-1	-1	+1	+1	0.3107
4	+1	+1	-1	+1	+1	-1	+1	-1	-1	-1	+1	0.2031
10	+1	+1	+1	-1	+1	+1	-1	+1	-1	-1	-1	0.4657
9	-1	+1	+1	+1	-1	+1	+1	-1	+1	-1	-1	0.4527
2	-1	-1	+1	+1	+1	-1	+1	+1	-1	+1	-1	0.1230
11	-1	-1	-1	+1	+1	+1	-1	+1	+1	-1	+1	0.4906
6	+1	-1	-1	-1	+1	+1	+1	-1	+1	+1	-1	0.0400
12	-1	+1	-1	-1	-1	+1	+1	+1	-1	+1	+1	0.1578
8	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	0.2284
Calculated effects	-0.040	0.050	0.064	0.090	-0.004	0.134	-0.122	0.033	0.009	-0.166	0.000	

within the interval studied, to be the most useful in terms of later applications of simultaneous determinations with other analytes. These were fixed at 90°C, 30 s and pH 1, respectively.

3.2. Optimization of the experimental conditions

The variables considered in the optimization process were reductor agent flow, reductor concentration, gas flow generation, carried time and time at room temperature. A fractional factorial central 2^{5-1} + star rotatable ($\alpha = 2$) composite design with three central points was performed. In this design, each of the variables had five coded levels, $-\infty$, -1 , 0 , $+1$ and $+\infty$, and required a total of 29 experimental runs and three central points, which were carried out with three replicates per run.

Due to the very high number of experiments, a 2^{5-1} fractional factorial design was used. This design is a fraction of the full factorial 2^5 design which allows a reduction in the number of experiments while maintaining the statistical ability to identify the influence of each parameter and the interactions between factors. In this experimental design, the main effects were confounded with four-way interactions, normally not significant, whereas the interactions of order two were confounded with the interactions of order three. The star points are located at $+\infty$ or $-\infty$ from the

centre of the experimental domain and the value of ∞ , as well as the number of central points, depended upon the design criterion (rotatability). In our design three central points were carried out. To find the values of the factors corresponding to these points, the average was calculated between the $+$ and $-$ levels of each factor. The levels of the variables were chosen according to the result of the Plackett-Burman design. Table 4 show the design matrix and response values. The sample amount was 75.2 μg for dimethyltin chloride.

This design gave the surface response; the experimental data were fitted to the polynomial mathematical model:

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

(with i and j ranging from A to E) where β_{ii} and x_i^2 are the quadratic regression coefficients and the quadratic settings, respectively. These are the coefficients used for the prediction of each response for new factor values. The results from the ANOVA study are shown in Table 5. The analysis of the results showed that all the lineal terms have significant effects and that several interactions and quadratic terms were significant. The coefficient of multiple determination (r^2) is 0.9167, indicating that the variables explain the data fairly well.

Table 3
ANOVA for the Plackett-Burman design

Source of variation	Sum of squares	Degrees of freedom	Mean square	F-ratio	P-value
A. Reductor flow	0.01417	1	0.01417	44.0804	0.00000
B. Reductor	0.02233	1	0.02233	69.4622	0.00000
C. Acid	0.03651	1	0.03651	113.5480	0.00000
D. Generation flow	0.07246	1	0.07246	225.3772	0.00000
E. Revolatilizing temperature	0.00012	1	0.00012	0.3851	0.54074
F. Carried time	0.16230	1	0.16230	504.8090	0.00000
G. Carrier gas	0.13369	1	0.13369	415.8346	0.00000
H. Time at room temperature	0.00974	1	0.00974	30.3024	0.00001
I. Revolatilizing time	0.00067	1	0.00067	2.0843	0.16174
J. Sample volume	0.24836	1	0.24836	772.4879	0.00000
K. pH	0.00000	1	0.00000	0.0037	0.95205
Error	0.00772	24	0.00032		
Total SS ^a	0.70807	35			

^a Sum of squares.

Table 4
Design matrix and response of fractional factorial central composite design

Runs	Factors					DMT response (192 nm)
	A	B	C	D	E	
	Reductor flow (ml min ⁻¹)	Reductor (%, w/v)	Generation flow (ml min ⁻¹)	Carried time (min)	Time at room temperature (min)	
8	6.5	6.0	625	5	4	0.1157
28	6.5	6.0	625	3	2	0.1349
24	6.5	6.0	375	5	2	0.1387
1	6.5	6.0	375	3	4	0.0984
26	6.5	2.0	625	5	2	0.1098
13	6.5	2.0	625	3	4	0.1136
15	6.5	2.0	375	5	4	0.1025
5	6.5	2.0	375	3	2	0.1392
25	2.5	6.0	625	5	2	0.1369
18	2.5	6.0	625	3	4	0.1471
27	2.5	6.0	375	5	4	0.1056
17	2.5	6.0	375	3	2	0.1483
20	2.5	2.0	625	5	4	0.1232
21	2.5	2.0	625	3	2	0.1119
12	2.5	2.0	375	5	2	0.1178
11	2.5	2.0	375	3	4	0.1113
7	4.5	4.0	500	4	3	0.1355
10	4.5	4.0	500	4	3	0.1328
19	0.5	4.5	500	4	3	0.1252
9	8.5	4.5	500	4	3	0.1256
3	4.5	0.5	500	4	3	0.1016
6	4.5	8.5	500	4	3	0.1334
22	4.5	4.0	250	4	3	0.1199
23	4.5	4.0	750	4	3	0.1321
29	4.5	4.0	500	2	1	0.1297
16	4.5	4.0	500	6	5	0.1358
4(C)	4.5	4.0	500	4	3	0.1304
14(C)	4.5	4.0	500	4	3	0.1118
2(C)	4.5	4.0	500	4	3	0.1388

Table 5
ANOVA for the fractional factorial central composite design

Source of variation	Sum of squares	Degrees of freedom	Mean square	F-ratio	P-value
<i>A</i>					
Reductor flow (L)	0.00031	1	0.00031	14.3280	0.00033
Reductor flow (Q)	0.00060	1	0.00060	27.4618	0.00000
<i>B</i>					
Reductor (L)	0.00319	1	0.00319	144.9473	0.00000
Reductor (Q)	0.00167	1	0.00167	76.0668	0.00000
<i>C</i>					
Generation flow (L)	0.00039	1	0.00039	17.9398	0.00007
Generation flow (Q)	0.00061	1	0.00061	27.9788	0.00000
<i>D</i>					
Carried time (L)	0.00027	1	0.00027	12.4015	0.00078
Carried time (Q)	0.00006	1	0.00006	2.5321	0.11633
<i>E</i>					
Time at room temperature (L)	0.00314	1	0.00314	142.7643	0.00000
Time at room temperature (Q)	0.00106	1	0.00106	48.0101	0.00000
AB	0.00055	1	0.00055	25.0395	0.00000
AC	0.00027	1	0.00027	12.1738	0.00087
AD	0.00004	1	0.00004	2.0340	0.15853
AE	0.00072	1	0.00072	32.5438	0.00000
BC	0.00065	1	0.00065	29.6733	0.00000
BD	0.00002	1	0.00002	0.7390	0.39309
BE	0.00069	1	0.00069	31.5123	0.00000
CD	0.00002	1	0.00002	1.0500	0.30925
CE	0.00314	1	0.00314	142.7757	0.00000
DE	0.00001	1	0.00001	0.5700	0.45296
Error	0.00145	66	0.00002		
Total SS ^a	0.01742	86			

^a Sum of squares.

If a mathematical relationship between the variables is known, response surface mapping is an effective method for locating the optimum and for the interpretation of the most influential interactions. Fig. 2 shows the response surfaces for the significant interactions; as can be seen, the maxima zones are well defined. Fig. 2(a) shows the response surface function developed by the model for reductor agent flow and reductor concentration; the response showed a maximum at 3 ml min⁻¹ and 6%, respectively. Fig. 2(b) shows the response surface function developed by the model for gas flow generation and reductor agent flow, giving a maximum for reductor agent flow of 3 ml min⁻¹ and for gas flow generation, 600 ml min⁻¹. Fig. 2(c) shows the function for time at

room temperature and reductor agent flow; in this case, the function showed a maximum between 3 and 6 ml min⁻¹ and 1.5 and 2.5 min, respectively.

Fig. 2(d) shows the function for reductor concentration and gas flow generation; the response obtained was maximum when the first factor was at 6% and the other at 600 ml min⁻¹. The response is directly proportional to the reductor concentration. Fig. 2(e) shows the response surface function developed by the model for reductor concentration and time at room temperature. The function gave a maximum when the two factors are at 6% and 1.5 min; Fig. 2(f) shows the function for gas flow generation and time at room temperature. As can be seen, the function is max-

imum when the two factors are at their lowest levels or highest levels.

The results obtained made it possible to demonstrate the interactions between the factors studied. Interactions were seen between the parameters which affect the volatile's generation (concentration and flow of the reducing agent and flow of the carrier) in that a high concentration of reducing agent makes necessary a low carrier flow, to

allow control of the reaction's speed and avoid problems of overpressure. The gas flow generation has to be high enough to guarantee the correct drawing through of the volatiles to the liquid nitrogen trap.

On carrying out the generation, it was seen that the gas from the generator contained a quantity of water vapor, which varied as a function of the reductor concentration, the reductor agent flow

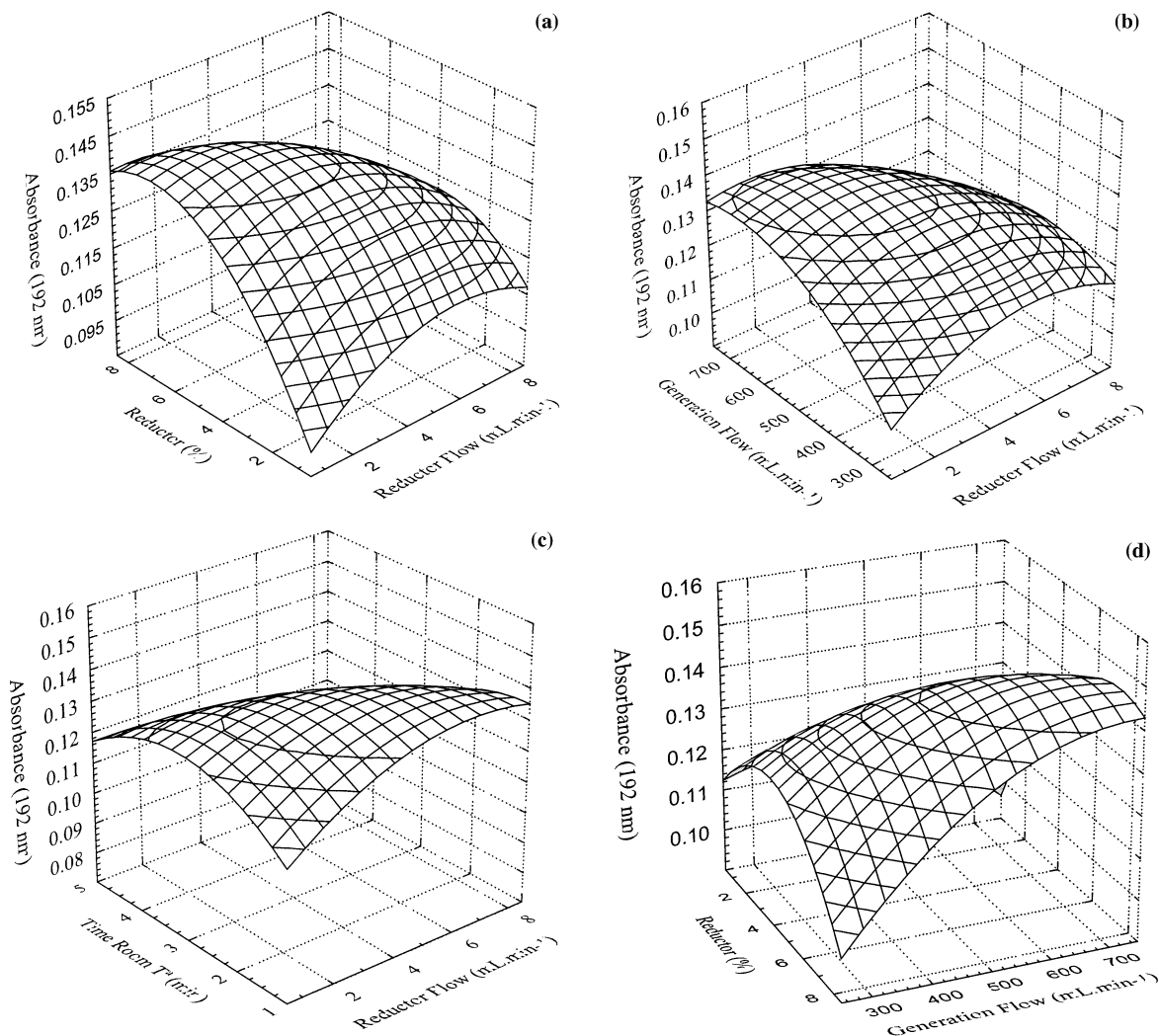


Fig. 2. Response surfaces estimated from the central composite design. (a) Reductor flow versus Reductor concentration. (b) Reductor flow versus Generation flow. (c) Reductor flow versus Time at room temperature. (d) Generation flow versus Reductor concentration. (e) Reductor concentration versus Time at room temperature. (f) Time at room temperature versus Generation flow.

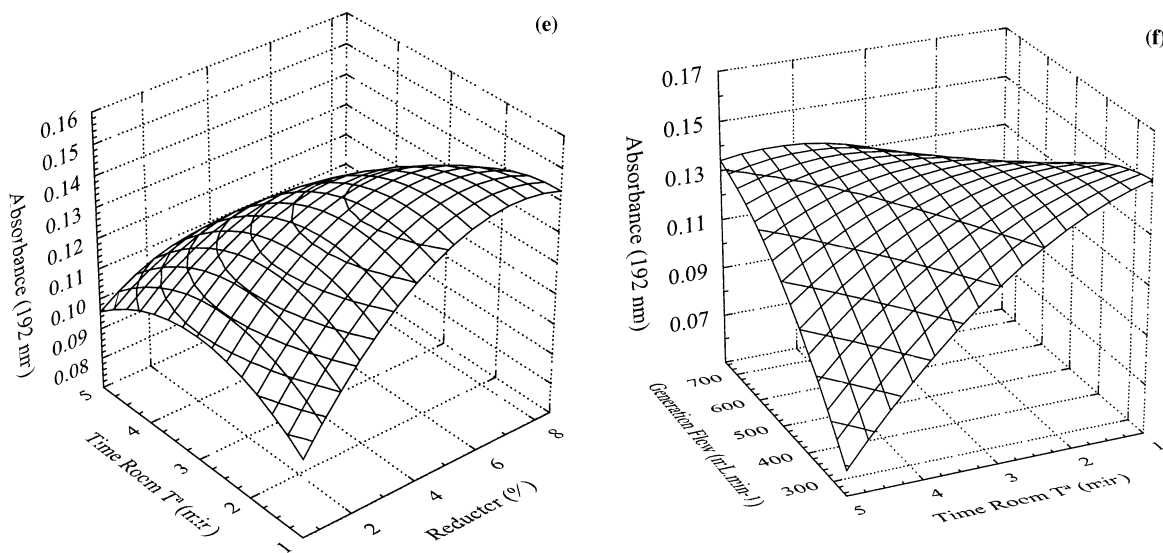


Fig. 2. (Continued).

and the gas flow generation. To avoid this vapor reaching the liquid nitrogen trap, a water trap was added; this was filled with anhydrous calcium chloride. However, it was observed that the water vapor was not completely eliminated under certain experimental conditions (such as a high reductor concentration). This circumstance may be due to the increase in the amount of vapor or to the greater velocity of passage through the water trap. The physical presence of ice was confirmed in the nitrogen trap, which affected the revolatilization produced at the 'time at room temperature' stage. This phenomenon could explain the interaction of the above factors with the factor which principally affects the revolatilization ('time at room temperature'), probably due to the dissolution of the volatile species in the aquatic phase, thus favoring its revolatilization.

Within the factors studied, the carried time did not show any interaction with the other factors, although it did have a significant effect on the signal; this indicates that the signal was not affected on varying the carrier time from 2 to 6 min, possibly due to this range not being sufficiently wide to show variations in this factor having a significant effect on the other factors.

Resulting from this study, the optimum working conditions to obtain the highest absorbance responses were selected. Table 6 shows the opti-

imum conditions for the determination of dimethyltin chloride by GPMAS.

3.3. Analytical characteristics

Under the instrumental and chemical conditions obtained in the experimental section, calibration studies were made for the dimethyltin 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

Table 6
Optimum conditions for the determination of dimethyltin chloride by GPMAS

Factor	Value
Acid	HCl
pH	1
Carrier gas	H ₂
Sample volume	150 ml
Revolatilizing temperature	90°C
Revolatilizing time	0.5 min
Reductor flow	3 ml min ⁻¹
Reductor concentration	6% (w/v)
Generation flow (H ₂)	600 ml min ⁻¹
Carried time	2.5 min
Time at room temperature	1.5 min

Table 7
Statistical parameters of the calibration

	Univariate	MLR	PLSR
R^2	0.9991	0.9994	0.9989
RMSD	0.0082	0.0090	0.0103

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 (190, 192 and 193 nm). For PLS, a cross-validation method, leaving out one sample at a time, was used to select the number of factors.

The detection limit of 3.2 ng ml⁻¹ was calculated according to the IUPAC; the value reported is the mean of five replicates. The RSD value for precision, calculated from 20 determinations from a solution containing ten times the corresponding detection limit and taken on different days, was 4.1%.

Table 7 shows the RMSD and R^2 of the calibration model. The root mean square difference (RMSD) is an indication of the average error in the analysis

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

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

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

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 there are no significant differences between the values found from the three regression models. All the models are valid for the quantitative determination of DMT using GPMAS in the experimental conditions studied.

The proposed simple linear regression, MLR and PLS methods, applied to the absorption spec-

tra, allow the resolution of the artificial samples. In Table 8, the results obtained in the resolution of the synthetic samples of dimethyltin chloride are shown. It can be seen that the RSD values were significantly lower when multivariate methods were used. In the same way, the accuracy values obtained for the MLR and PLS method were greater than for the univariate regression; within this group, the best results were applied using PLS.

3.4. Interference study

The effect of several ions on a 0.30 µg ml⁻¹ dimethyltin chloride standard are shown in Table 9. Solutions containing DMT 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 µg 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), NH₄⁺, Te (VI), Sn (IV), Bi (III), Pb (II), Ge (IV), MnO₄⁻, Br⁻, F⁻ and I⁻; up to 1000 µg 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 sulphide ion and the elements which form volatile hydrides under the generation conditions. This group causes a quantitative increase in the absorbance signal at low concentrations which can be used for the simultaneous determination of mixtures of several elements. Within the group of elements which form volatile hydrides, Se (IV) shows a different behaviour: as the (µg ml_{Int.}⁻¹/µg ml_{DMT}⁻¹) ratio increases, the interference decreases. This is due to the interaction between the DMT and selenium species in the liquid or gas phase.

Table 8
Results obtained for the resolution of the artificial samples of dimethyltin chloride

Added (ng ml ⁻¹)	Univariate			MLR			PLS		
	Found ^a (ng ml ⁻¹)	Recovered (%)	RSD ^a (%)	Found ^a (ng ml ⁻¹)	Recovered (%)	RSD ^a (%)	Found ^a (ng ml ⁻¹)	Recovered (%)	RSD ^a (%)
21.5	23.2	108	5.23	22.7	106	1.20	22.4	100	0.58
43.8	46.4	106	5.23	45.5	104	1.21	44.8	102	0.58
65.0	66.1	102	6.45	65.1	100	1.69	65.8	101	1.34
107	106	99	4.39	107	100	2.35	108	101	1.57

^a Mean of three independent determinations.

4. Conclusions

With the Plackett-Burman design used in this work, the variables which affect the determination of dimethyltin chloride by HG-GPMAS were identified: reductor agent flow, reductor concentration, gas flow generation, carried time, and time at room temperature.

This design allows a reduction in the number of factors to be studied, from 11 to five, and establishes a new region to study.

The proposed experimental design methodology allows the finding of the optimal conditions for the determination of dimethyltin 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 concentration, time at room temperature and the interaction between reductor agent flow and time at room temperature.

Table 9
Results from the interference study

Interferent	Ratio (Int.)/(DMT) ^a	% Error	Interferent	Ratio (Int.)/(DMT) ^a	% Error
Sn (II)	5	7	Ag (I)	10	–
	15	80		50	–26
	30	160		75	–43
	60	225		100	–74
Se (IV)	0.25	60	Co (II)	10	–
	0.5	57		30	–24
	1.5	55		75	–33
	4.5	70		150	–62
As (III)	5	160	Cu (II)	250	–96
	0.25	46		10	–
	0.5	81		50	–22
	1.5	108		150	–31
As (V)	3	162	Ni (II)	300	–38
	0.25	45		10	–18
	0.5	107		30	–47
	0.75	143		75	–63
Sb (V)	1	211	Fe (II)	150	–80
	0.5	33		10	–
	1	50		50	–8
	1.5	121		100	–15
Sb (III)	3	204	Fe (III)	200	–46
	0.2	20		400	–58
	0.3	57		10	–
	0.5	99		50	–33
NO ₂ [–]	1	170	Cr (VI)	100	–47
	10	–		175	–79
	25	–8		350	–95
	75	–32		10	–
	150	–56		40	–18
S ⁼	300	–99	80	–27	
	0.25	67	150	–62	
	0.75	102	400	–89	
	1.5	133			
	2	202			

^a ($\mu\text{g ml}_{\text{Int}}^{-1}/\mu\text{g ml}_{\text{DMT(as Sn)}}^{-1}$).

The use of a diode-array molecular absorption spectrometer 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.

The study of the effect which the various interferences have on the analytical signal and the obtaining of the complete spectrum will permit the application of multivariate techniques for the elimination of interferences, or the simultaneous determination of several compounds.

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