

# Taguchi Experimental Design Study of Very Large Sample Injection of Pesticides in Capillary Gas Chromatography

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## Abstract

The use of a programmed-temperature vaporizer (PTV) in a modified solvent elimination mode for the analysis of very large volumes of a pesticide solution by direct sampling onto gas chromatography is described. A Taguchi experimental design is used to study the influence on the performance of the method of four factors, namely the length of the packing material in the glass-liner of the PTV, the temperatures of the PTV during both adsorption and desorption, and the sampling volume. Three of the possible interactions between the mentioned variables are also investigated. The described method allows the direct injection of up to a 25-mL sample volume, 1.5 mL/min being the speed of sample introduction. No special instrumentation is necessary; the methodology is not expensive and can be performed in any laboratory. This method may also be an interesting approach to the use of a PTV as an interface for liquid chromatography-gas chromatography, as experimental conditions (i.e., the sampled volume, the speed of sample introduction, and the solvent used) are suitable to fit the requirements of on-line coupling of reversed-phase liquid chromatography and gas chromatography (RPLC-GC).

## Introduction

In recent years, the concern about the pesticide contamination of the environment and foodstuffs has grown. As pesticide residues occur at low concentrations, an extraction and concentration step is usually needed prior to the chromatographic analysis itself. Liquid-liquid and solid-phase extractions are common techniques for this purpose, although these methods are time-consuming and may be a source of sample contamination and analytical errors regarding reliability and accuracy. Moreover, in some cases, relatively high volumes of hazardous solvents are required. Consequently, it is of general interest to improve analytical methods in order to avoid these drawbacks and to increase the detection limits of the overall procedure.

To achieve this aim, there have been described several approaches. One of them involves large volume sampling into gas chromatography (GC) (1-5), although the injected volumes

reported so far are rarely higher than 1 mL. Another approach is the direct coupling of liquid chromatography and gas chromatography (LC-GC). Several interfaces adequate for on-line coupling of normal-phase liquid chromatography and gas chromatography (NPLC-GC) and many successful applications have been reported (6-8). Some interfaces have also been described for reversed-phase (RP) LC-GC (9-11), but despite the developments which have already been reported in this technique, most interfaces proposed only allow the transfer of small LC fractions to GC because the flow rate in the LC-preseparation is not high enough to allow the use of some LC columns. Specifically, analysis of pesticides by direct coupling RPLC-GC is very difficult or impossible in most cases (12).

In this paper, we present a method that allows direct sampling in GC of a volume as high as 25 mL of a pesticide solution in methanol, 1.5 mL/min being the speed of sample introduction. A Taguchi experimental design was used to study some important variables involved in the method and some interactions existing between them.

Taguchi methodology is based on the employment of fractional factorial designs, that is, orthogonal arrays. Columns of the orthogonal array correspond to variables (control factors) or interactions and rows correspond to the experiments to be carried out (see Table I). The size of the orthogonal array depends on the number of variables and interactions to be studied. In order to assign each variable or interaction to a column, linear graphs are used. The selection of the linear graph and the assignment of control factors to its points must be done in such a way that the interactions of interest become placed on lines connecting these points (see Figure 1). This methodology also considers the robustness of the studied system, that is, the attainment of the best performance with the lowest possible influence of noise factors (e.g., factors whose control is either difficult or undesired). To this aim, the experiments are performed at different levels of selected noise factors (13,14). The Taguchi signal-to-noise ratio (S/N), a compromise between the extent and the variability of data obtained at each set of the control factors, is used as a response to evaluate experimental results.

The Taguchi methodology allows the study and/or the optimization of many experimental variables with only a few experiments. This methodology has been largely used in the industry

and has also been applied to chromatographic studies in the laboratory (15,16).

## Experimental

### Instrumentation

The analyses were performed using a Perkin Elmer (Norwalk, CT) model 8320 GC equipped with a programmed temperature vaporizer and a flame ionization detector. Data collection was done with 2600 Chromatography software (Perkin-Elmer Nelson Systems).

A high-performance liquid chromatography (HPLC) pump, Waters model 501 (Marlborough, MA), was connected to the PTV via a manual Rheodyne valve (model 7125, Cotati, CA), which provided a stabilized flow of the model solution during sampling. All connections were made using 0.1-mm i.d. silica capillary tubing.

### Model solution

A synthetic test mixture of organophosphorous and triazine pesticides in methanol was used. Pesticide standards were purchased from Chem Service, Inc. (West Chester, PA). Methanol was pesticide-free grade obtained from LabScan (Dublin, Ireland). A

solution containing 0.5 mg/L of each pesticide in methanol was used for the experimentation.

The pesticides contained in the solution (in elution order) were simazine, diazinon, fenitrothion, terbutryn, fenthion, parathion, fentoate, methidathion, and ethion.

### PTV operation and conditions

PTV operation has been described elsewhere (17). Tenax TA 80-100 mesh (Chrompack, The Netherlands) was selected as packing material in the glass liner of the PTV. The vaporization insert (80-mm length  $\times$  1-mm i.d.  $\times$  2-mm o.d.) was packed either with a 0.5-cm length (1.4 mg) or with a 2-cm length (5.6 mg) of the sorbent between two glass wool plugs. The packed liner was conditioned under a 600 mL/min stream of helium for 60 min at 350°C. Once the experimental run was completed, the liner was cleaned for 10 min at 350°C under the same helium stream.

Before beginning the sampling, the GC column was disconnected from the injector body, the split valve was closed, the helium flow through the vaporizing chamber was established at 600 mL/min, and the PTV was allowed to stabilize at the sampling temperature (40 or 80°C).

The sampling starts by acting the Rheodyne valve so that the solution reach the injector at a speed equals 1.5 mL/min. The previously mentioned conditions are maintained during the injection time and 3 min more in order to remove the remaining solvent from the liner. Afterwards, the helium flow is switched off, the injector temperature is allowed to go down, and the GC column is connected to the injector body.

The GC analysis is performed after opening the helium at analysis pressure, which is maintained for 3 min before heating the injector in order to remove the air entering during the connection of the column. Subsequently, the PTV is ballistically heated (14°C/s) to the desorption temperature (250°C or 350°C) so that the retained pesticides are thermally desorbed and transferred to the chromatographic column.

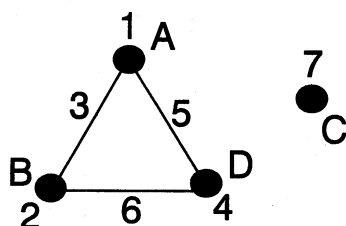
The experiment was directed to determine the effect of operating conditions on the performance of the analysis of a pesticide solution in methanol, by direct sampling on the PTV of a very high sample volume (up to 25 mL) at a high speed of sample introduction (1.5 mL/min). Experimental conditions (e.g., sample volume, speed of sample introduction, and solvent) were selected for further investigation concerning RPLC-GC analysis of pesticides.

### GC analysis

A fused-silica capillary column (30 m  $\times$  0.32-mm i.d.) coated with a 0.25- $\mu$ m layer of cross-bonded, 5% phenyl methyl silicone (DB-5, J&W Scientific, Folsom, CA) was used. After 2 min at an initial temperature of 40°C, the GC oven was heated to 170°C at 10°C/min, to 180°C at 2°C/min, and to 230°C at 10°C/min. In all analyses, detector temperature was set at 325°C. Helium at 20 psig was used as the carrier gas.

### Experimental design

Although a large number of experimental variables could have some influence on this analytical



**Figure 1.** Linear graph selected for the  $L_8(2^7)$  Taguchi orthogonal array. Numbers stand for columns of the array, letters stand for factors. Dots indicate assignments of a factor to a column and lines indicate assignments of the interactions between connected factors to a column.

**Table I.**  $L_8(2^7)$  Taguchi Orthogonal Array

Column/Factor	1	2	3	4	5	6	7
Trial	A*	B	AB	D	AD	BD	C
1	1 <sup>†</sup>	1	1	1	1	1	1
2	1	1	1	2 <sup>‡</sup>	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

\* A: Tenax Length; B: Adsorption PTV temperature; C: desorption PTV temperature; D: sampling volume; AB, AD, BD: two factor interactions.

<sup>†</sup> Level 1 conditions: tenax length, 0.5 cm; adsorption PTV temperature, 40°C; desorption temperature, 250°C; sampling volume, 10 mL.

<sup>‡</sup> Level 2 conditions: tenax length, 2cm; adsorption PTV temperature, 80°C; desorption temperature, 350°C; sampling volume, 25mL.

methodology, our previous experience (17) suggest that the tenax length (factor A), the PTV temperature during both adsorption (factor B) and desorption (factor C), and the sampled volume (factor D) show high effects. Interactions between some of these factors have also been previously reported (18,19).

In order to investigate the mentioned four factors and three presumably important interactions, the experimentation was designed according to a  $L_8(2^7)$  Taguchi orthogonal array. Table I shows the orthogonal array in the control factors (inner array) together with the respective experimental values at both the low "1" and high "2" levels. Each factor and interaction was assigned to a column according to the linear graph selected (Figure 1). With the purpose of investigating the need of establishing an additional HPLC stabilization time to avoid (or at least, minimize) the influence on the performance of the method of possible adsorption/desorption of components in any part of the system, the required stabilization time of the HPLC pump before starting the analysis was considered to be a noise factor, with level 1 = 3 min and level 2 = 20 min. Therefore, the complete inner array given in Table I was run once at each noise factor level. The 16 runs were performed at random, except for the tenax length because this factor takes the greatest time to change, so that it should be changed the least. That is why the mentioned factor was assigned to the column 1. The first eight experiments were performed using the 0.5-cm length of tenax (low level), and experiments 8 to 16 correspond to a plug length equal to 2 cm (high level).

Initially, the sensitivity (peak area) of each of the investigated compounds and the sum of all of them were the selected responses. However, as ghost peaks were observed during experimentation (probably because of tenax or pesticide degradation products), the ratio of the sum of peak areas for the investigated compounds to the sum of peak areas for the three highest ghost peaks was also considered as an additional response.

## Results and Discussion

Table II shows the response values obtained in the experimental runs at each noise factor level. The individual pesticide peaks

(simazine, fenthion, and ethion) included in Table II were selected as representative for the discussion because of their different chemical structures and the wide volatility range covered by their elution times.

Also included in Table II is the Taguchi signal-to-noise ratio, expressed in decibels, obtained according to Equation 1 where the so-called "larger-the-better case" is considered in order to select the experimental conditions providing maximal sensitivity and, consequently, to develop an analytical method suitable for trace compounds analysis.

$$S/N = -\log_{10} [(1/y_1^2 + 1/y_2^2)/2] \quad \text{Eq 1}$$

where  $y_1$  and  $y_2$  are the response values at the two noise factor levels.

The effect of each factor or interaction on the response (d in Table III) is obtained from the absolute value of the difference between the mean S/N of the runs performed at level 1 of the corresponding column in the orthogonal array and those performed at level 2. The control factors with larger effects (underlined in Table III) were selected to define an empirical model, and those levels yielding the highest S/N values are recommended as the most suitable operating conditions. The interactions with larger effects (underlined in Table III) were also included in the model.

In order to check the empirical model, the estimated response at the recommended levels of the control factors was calculated, then a confirmatory experiment was performed at these levels, and finally the estimated and the measured responses were comparatively evaluated.

Data obtained for the different responses investigated (e.g., sum of peak areas, simazine area, fenthion area, ethion area, and sum of peak areas/degradation) are discussed subsequently.

### Sum of peak areas

The mean values of responses at the two noise levels,  $\bar{y}_1$  and  $\bar{y}_2$  (Table II), show no noticeable difference (less than 1.5%). This indicates that the noise factor seems not to affect the results, so that an additional stabilization time of the HPLC pump is not necessary under the experimental conditions described.

As can be seen in Table III, the PTV adsorption temperature (factor B) has the most important effect and gives the best perfor-

**Table II. Responses Obtained in the Taguchi Experimental Design at Each Noise Level ( $y_1 = 3$  min;  $y_2 = 20$  min) and Signal-to-Noise Ratio (S/N)**

Trial	Sum of peak areas			Simazine area			Fenthion area			Ethion area			Sum of peak areas/degradation		
	$y_1$	$y_2$	S/N	$y_1$	$y_2$	S/N	$y_1$	$y_2$	S/N	$y_1$	$y_2$	S/N	$y_1$	$y_2$	S/N
1	75534	60631	96.50	11925	9188	80.25	76168	5335	75.82	1601	1090	62.10	4.81	4.19	13.00
2	207062	201288	106.19	40240	37095	91.72	25648	26351	88.30	6621	7401	76.87	5.58	6.08	15.29
3	165242	162483	104.29	39050	38897	91.81	20335	18057	85.62	7549	6258	76.67	7.25	5.78	16.11
4	444316	443989	112.95	102684	106813	100.40	55361	57784	95.05	39101	33536	91.13	20.18	16.42	25.11
5	39437	40448	92.03	7404	6904	77.07	2273	2144	66.87	1017	1122	60.55	2.88	2.97	9.32
6	108126	118722	101.06	24371	25801	87.98	9345	10080	79.73	1081	1431	61.73	5.92	6.39	15.77
7	165571	160689	104.25	33611	33686	90.54	17491	17359	84.82	4806	4753	73.59	11.61	10.94	21.03
8	387171	381931	111.69	104475	96180	100.01	36678	35649	91.16	28588	26526	88.79	11.98	11.34	21.32
Mean	199057	196273	103.62	45470	44320	89.97	21843	21595	83.42	11295	10265	73.93	8.78	8.01	17.12

mance at the high level (80°C). However, as it has been previously reported (20), solid-phase extraction on tenax gives usually better performance at lower temperatures as the solute-sorbent affinity is then increased, but, on the other hand, higher temperatures during sampling allow higher solvent evaporation rate, which must be a more important effect in this analysis.

The sampled volume (factor D) has also an important effect and shows the best performance at the level 2 (25 mL) (Table III). It is interesting to underline that the retention power of the packing material is satisfactory even working with such high sample volumes and a 0.5-cm plug length. Actually, the sensitivity achievable from an injection of a 25-mL volume is approximately 2.5 times higher than that obtained with 10 mL (compare sum of peak areas of trials 2 and 1, 4 and 3, 6 and 5, or 8 and 7 at any noise level in Table II).

The effect of the tenax length (factor A) is not as important as those observed for the PTV adsorption temperature and the sampled volume. It is clear from Table III that experimentation performed at level 1 (0.5 cm) gives the highest sensitivity. Apparently, this is a con-

tradictory observation because in solid-phase extraction systems an increase of the sorbent material amount usually results in an increase of the retention power, so that higher sensitivity is finally achievable. In this respect, it should be taken into account that solvent elimination is carried out simultaneously in both the evaporative and non-evaporative modes. Consequently, solvent elimination is achieved by using (a) the PTV injector operated in the solvent split mode and (b) the sorption properties of the packing material placed in the glass-liner (solid-phase extraction mode).

From Figure 2 and Table III, it is also clear that the improvement of the sensitivity when increasing the PTV adsorption temperature is different at the two tenax lengths. The best performance is obtained at the level A<sub>1</sub>B<sub>2</sub>, specifically low tenax length and high adsorption temperature, which also turned out to be the recommended values for the mentioned factors when considered individually.

The desorption temperature (factor C) has no influence on the performance of the analysis (Table III), so it can be concluded that 250°C is a temperature high enough to produce the desorption of pesticides from tenax. As an increase of the temperature may bring about experimental problems (e.g., a shorter sorbent lifetime), operation at 250°C is recommended. On the other hand, the effects of the interaction of the sample volume with both the tenax length (interaction AD) and the adsorption temperature (interaction BD) are not important.

According to the Taguchi methodology, the underlying empirical model is a linear model in which the response is the grand mean plus the deviations due to the effects included in the model. The estimated S/N response at the recommended level of the factors is given by

$$S/N_{\text{est}} = \bar{T} + (\bar{A}_1 - \bar{T}) + ((\bar{A}_1\bar{B}_2 - \bar{T}) - [\bar{A}_1 - \bar{T}] - (\bar{B}_2 - \bar{T})) + [\bar{B}_2 - \bar{T}] + [\bar{D}_2 - \bar{T}] = 112.98 \text{ dB} \quad \text{Eq 2}$$

where  $\bar{T}$  is the mean value of the eight S/N obtained (the grand mean),  $\bar{A}_1$  is the mean S/N value of the

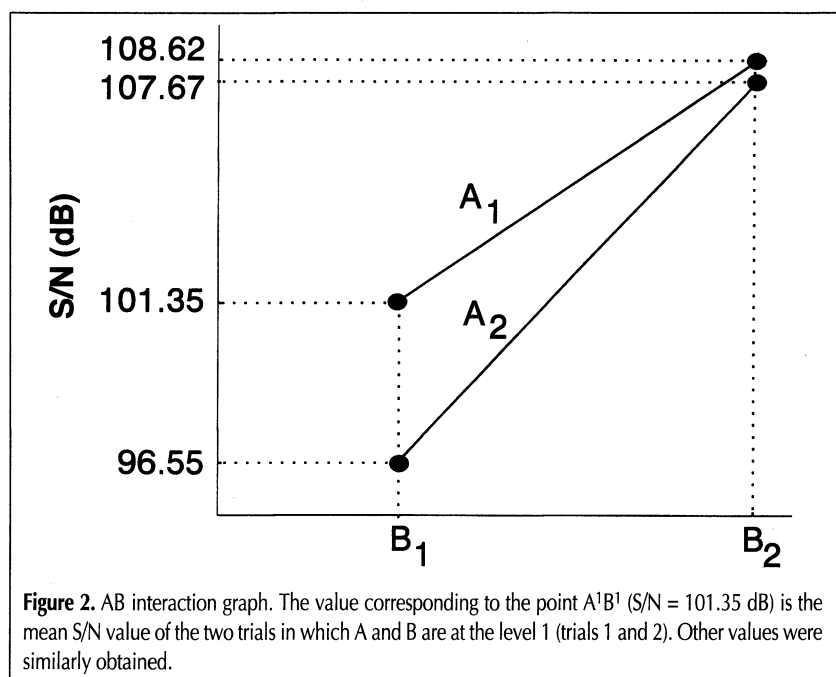


Table III. Mean S/N of the Runs Performed at Each Level and Effect (d) of the Control Factors and Interactions

Factor	Sum of peak areas			Simazine area			Fenthion area			Ethion area			Sum of peak areas/degradation		
	Level 1*	Level 2*	d <sup>†</sup>	Level 1*	Level 2*	d <sup>†</sup>	Level 1*	Level 2*	d <sup>†</sup>	Level 1*	Level 2*	d <sup>†</sup>	Level 1*	Level 2*	d <sup>†</sup>
A <sup>‡</sup>	104.98	102.26	<u>2.72</u> <sup>§</sup>	91.05	88.90	2.15	86.19	80.65	<u>5.54</u> <sup>§</sup>	76.69	71.16	<u>5.53</u> <sup>§</sup>	17.38	16.86	0.52
B <sup>‡</sup>	98.95	108.29	<u>9.34</u> <sup>§</sup>	84.26	95.69	<u>11.43</u> <sup>§</sup>	77.68	89.16	<u>11.48</u> <sup>§</sup>	65.31	82.54	<u>17.23</u> <sup>§</sup>	13.34	20.89	<u>7.55</u> <sup>§</sup>
C <sup>‡</sup>	103.69	103.55	0.14	89.80	90.15	0.35	83.85	82.99	0.86	72.14	75.72	3.58	18.73	15.51	<u>3.22</u> <sup>§</sup>
D <sup>‡</sup>	99.27	107.98	<u>8.71</u> <sup>§</sup>	84.92	95.03	<u>10.11</u> <sup>§</sup>	78.28	88.56	<u>10.28</u> <sup>§</sup>	68.23	79.63	<u>11.40</u> <sup>§</sup>	14.87	19.37	<u>4.50</u> <sup>§</sup>
AB <sup>‡</sup>	104.66	102.58	<u>2.08</u> <sup>§</sup>	90.63	89.31	1.32	85.02	81.81	<u>3.21</u> <sup>§</sup>	75.34	72.52	2.82	17.66	16.58	1.08
AD <sup>‡</sup>	103.39	103.86	0.47	90.01	89.93	0.08	83.08	83.76	0.68	72.32	75.53	3.21	16.55	17.69	1.14
BD <sup>‡</sup>	103.29	103.95	0.66	89.43	90.51	1.08	82.22	84.62	2.40	75.64	72.21	3.43	17.19	17.05	0.14

\* Level 1 and level 2: Mean S/N obtained from analysis performed at level 1 or level 2, respectively, of the corresponding control factor or interaction (column in the orthogonal array).

<sup>†</sup> Absolute value of the difference between levels 1 and 2. Selected control factors are underlined (see text for further details).

<sup>‡</sup> Control factors: A, tenax length; B, adsorption PTV temperature; C, desorption PTV temperature; D, sampling volume; AB, AD, BD, two factor interactions.

<sup>§</sup> Control factors with larger effects selected to define an empirical model.

runs performed at the level 1 of the control factor A (tenax length), etc. A confirmatory experiment carried out at  $A_1B_2C_1D_2$  gives  $y_1 = 441301$  and  $y_2 = 485987$ , so that  $S/N = 113.29$  dB, which is a similar value to that previously estimated from Equation 2. Taking into account that experiment 4 was carried out under the same experimental conditions, it is interesting to note that the  $S/N$  value obtained (112.95 dB) is an additional confirmatory result.

To illustrate the capabilities of the method, Figure 3 shows the chromatogram obtained from the pesticide solution at the recommended level of the control factors.

As far as the precision of the analysis is concerned, it should be mentioned that, under the experimental conditions recommended, the mean value of the relative standard deviations (RSD) of the absolute peak areas is 8.2% ( $n = 3$ ).

### Area of individual peaks

As previously mentioned, three peaks (e.g., simazine, fenthion, and ethion) were selected as representative of the studied compounds because of its differences in volatility and chemical structures. The results show a different influence of the experimental variables on the area achievable for each compound.

If the fenthion area is considered, the selected control factors and the recommended levels were the same as those obtained for the sum of peak areas, and the importance of the effects was similar (Table III).

As far as simazine is concerned, only two control factors were selected because of its important effect: PTV adsorption temperature and sampling volume (Table III). In both cases, the recommended levels were the same as those for the sum of peak areas.

On the other hand, the very high value of the effect of the PTV adsorption temperature on the ethion area must be emphasized

(Table III). The tenax length and the sampling volume have also important effects. The recommended levels for these control factors are the same as those for the sum of peak areas, although the effect of the interaction AB is not important in the case of ethion.

The estimated responses at the recommended levels of the control factors can be obtained from Equation 2 for fenthion area, thus resulting an estimated  $S/N$  value equal to 95.47 dB. Equations 3 and 4 give, respectively, the estimated response for simazine and ethion peak areas.

$$S/N_{\text{est}} = \bar{T} + (\bar{B}_2 - \bar{T}) + (\bar{D}_2 - \bar{T}) = 100.75 \text{ dB} \quad \text{Eq 3}$$

$$S/N_{\text{est}} = \bar{T} + (\bar{A}_1 - \bar{T}) + (\bar{B}_2 - \bar{T}) + (\bar{D}_2 - \bar{T}) = 91.00 \text{ dB} \quad \text{Eq 4}$$

The obtained  $S/N$  values in the confirmatory experiments are 95.02 dB for fenthion area, 101.25 dB for simazine area, and 91.07 dB for ethion area. As can be seen, the similarity existing between the mentioned values and those previously estimated is satisfactory.

### Sum of peak areas/degradation

As a measure of tenax or pesticide degradation products, sum of peak areas for the three highest ghost peaks (peaks 1, 2, and 3 in the chromatogram, Figure 3) was considered. This response was optimized in order to obtain both a high sensitivity and small peak areas corresponding to degradation products.

Three control factors were selected because of their important effects (Table III): adsorption PTV temperature, desorption PTV temperature, and sampling volume. The recommended levels are 2, 1, and 2, respectively.

Taking into account that the tenax length (factor A) has no important effect when considering sum of peak areas/degradation

as response, whereas, as previously mentioned, higher values for the sum of peak areas are obtained if experimentation is performed at the low level for factor A, it seems to be clear that the use of a shorter tenax length increases the sensitivity but also increases the ghost peak areas. On the other hand, it is also clear that higher temperatures of the PTV during desorption produce larger ghost peaks.

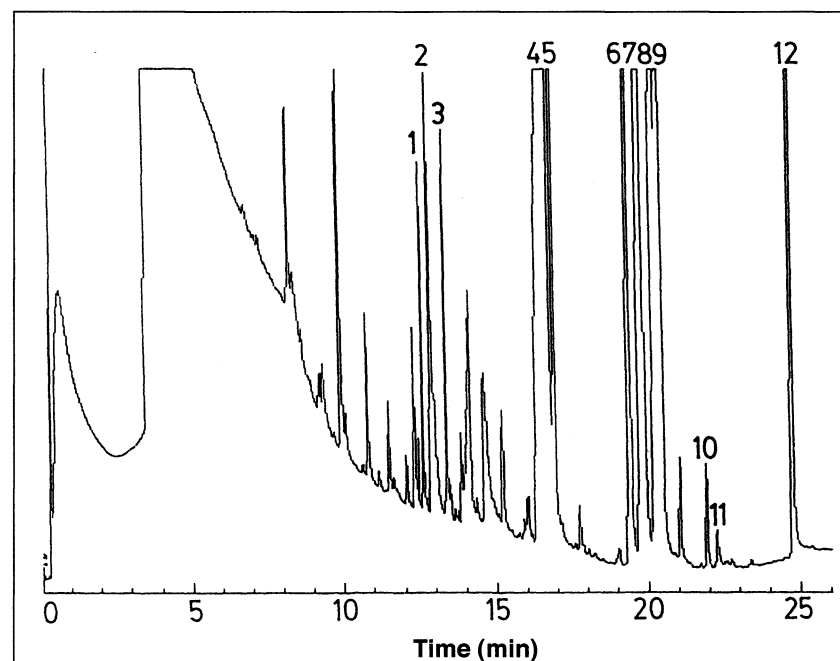
The estimated response at the recommended level is

$$S/N_{\text{est}} = \bar{T} + (\bar{C}_1 - \bar{T}) + (\bar{B}_2 - \bar{T}) + (\bar{D}_2 - \bar{T}) = 24.75 \text{ dB} \quad \text{Eq 5}$$

The obtained value in a confirmatory experiment is  $S/N = 24.38$  dB, which is close to the value previously estimated.

### Conclusion

The experimental conditions that provide the best performance of the analysis (e.g., higher sensitivity and lower degradation) are as follows: tenax length, 0.5 cm; PTV temperatures during



**Figure 3.** Chromatogram of a 0.5 ppm pesticide solution in methanol performed by direct injection in a PTV. Experimental conditions: tenax length, 0.5 cm; PTV temperature during adsorption, 80°C; PTV temperature during desorption, 250°C, sampling volume, 25 mL. Peak identification: 1, 2, and 3, ghost peaks considered in the study; 4, simazine; 5, diazinon; 6, fenitrothion; 7, terbutryn; 8, fenthion; 9, parathion; 10, fentoate; 11, methidathion; and 12, ethion.

adsorption and desorption, 80°C and 250°C, respectively; sampling volume, 25 mL.

The effect of the control factors on the sensitivity is different for each compound analyzed, and occasionally the interaction between the tenax length and the PTV adsorption temperature is noticeable.

The described method allows the direct sampling of up to a 25-mL volume of a pesticide solution in methanol, 1.5 mL/min being the speed of sample introduction. Although further experimentation is necessary, mainly concerning problems brought about by the online treatment of large volume of aqueous samples for GC analysis, the methodology presented in this work opens the possibility of pesticide residue analysis by direct coupling reversed-phase LC–GC while using a PTV as interface.

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