Very-Large-Volume Sampling of Water in Gas Chromatography Using the Through Oven Transfer Adsorption Desorption (TOTAD) Interface for Pesticide-Residue Analysis

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Abstract

The Through Oven Transfer Adsorption Desorption (TOTAD) interface is used to directly introduce large volumes of water (1 mL or more) into a capillary gas chromatograph. The TOTAD interface is a greatly modified programmed temperature vaporizer injector incorporating changes that affect the pneumatics, sample introduction, solvent elimination, and operation mode. The system can easily be automated. The technique is applied to the analysis of pesticide residue in standard solutions and real water samples from the Ebro River (northeastern Spain). The speed of sample introduction was 1 mL/min, and the solvent elimination was almost complete. A nitrogen phosphorous detector is used, and the relative standard deviation varied from 5.7% to 11.7% for the absolute peak areas. The sensitivity achieved by introducing 1 mL of the sample is sufficient for most pesticide-residue analyses in water. The limits of detection ranged from 0.5 to 8.1 ng/L.

Introduction

The required detection limits for pesticide-residue analysis in aqueous samples are normally expressed in parts-per-billion. Capillary gas chromatography (GC) is the most frequently used technique in water analysis because of its high separation power and the wide range of sensitive and selective detectors that can be used. The reliable quantitation of analytes in a GC detector requires approximately 10 pg of analyte, and for the required detection limits to be reached, at least 0.1 to 1 mL of water has to be introduced into the GC system. Large-volume injection is a powerful tool because it allows for the introduction of up to several hundreds of microliters while maintaining good chromatographic characteristics (1).

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Samples have to be prepared prior to GC analysis, and the on-line coupling of sample enrichment or the cleanup processes of GC allows for automation and prevents contamination from external sources. On-line systems such as liquid–liquid extraction (LLE)–GC, solid-phase extraction (SPE)–GC, and liquid chromatography (LC)–GC require large volumes of solvent to be transferred to the GC.

In recent years, several injection techniques have been developed that allow for the injection of large volumes into a capillary GC (2). These techniques include partially concurrent solvent evaporation (PCSE) using an on-column injector (3,4), fully concurrent solvent evaporation (FCSE) using a loop-type interface (5,6), and the programmed temperature vaporizer (PTV) injection technique (7,8). Large-volume sampling using a PTV injector can be carried out in the solvent split mode in which the solvent is eliminated as vapor (evaporative mode) via the split line. The components that are retained in the liner are transferred to the column in the splitless mode. This PTV operation mode is only recommended for the determination of high-boiling solutes, because most volatile compounds are partly lost by evaporation with the solvent. Therefore, a large number of experimental parameters have to be optimized (9,10). A modification of the PTV solvent split operation mode has been described by Herraiz et al. (11) in which the capillary column is disconnected from the injector body before the sample is introduced. In this way, solvent elimination (evaporative and nonevaporative mode) is effectively performed through the bottom of the injector.

However, the introduction of a polar solvent (especially water) into a GC still presents serious problems that several methods have tried to solve. Such methods can be described as indirect and direct approaches (12).

Indirect methods involve the elimination of water by LLE or SPE prior to transferring the compounds of interest to the GC column (phase-switching methods).

Initially, direct methods would seem to present numerous advantages, but the polar nature of water creates numerous difficulties. Large volumes of water may have an adverse effect on the deactivation layer and the stationary phase of the chromatographic column. In order to protect the GC system, solvent vapor is released via a solvent exit positioned after an uncoated capillary (PCSE and FCSE techniques) or a split vent (PTV injection technique).

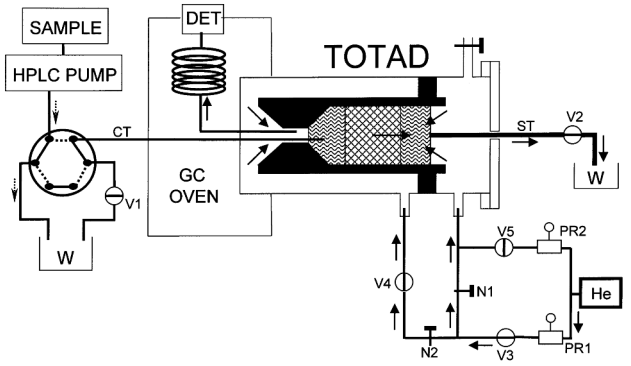

Figure 1. Scheme of the TOTAD interface used as an injector in this study. Valves are positioned for LC separation, interface stabilization, and cleaning steps. (N) needle valve, (V) on–off valve, (PR) pressure regulator, (TT) stainless steel tubing used to transfer from LC to GC, (CT) silica capillary tubing, (ST) stainless steel tubing to allow for the exit of liquids and gases, and (W) waste.

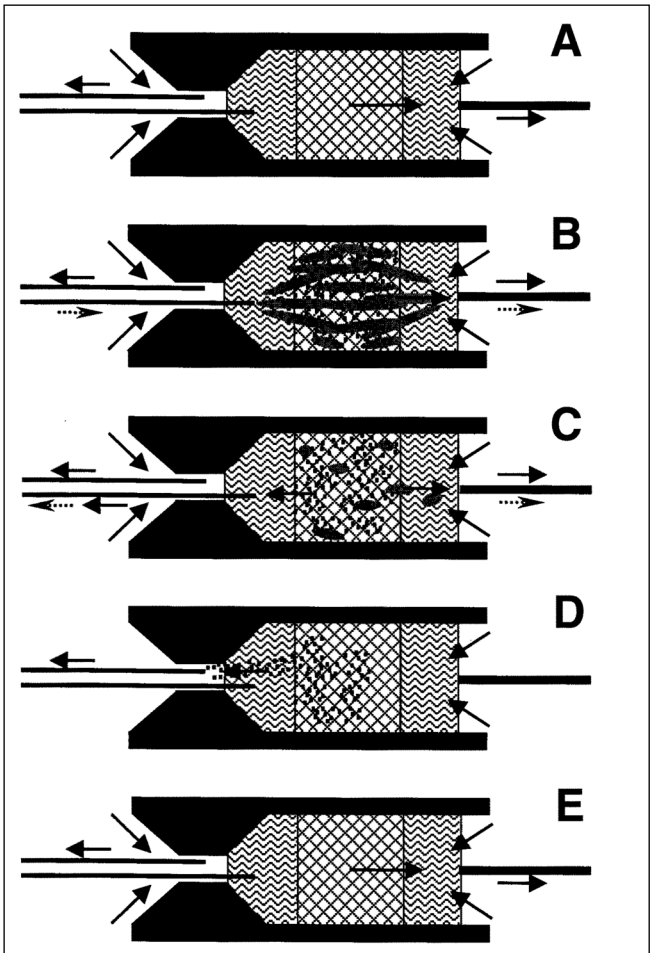

Figure 2. Drawing of the glass liner during the five steps of the operation mode: (A) stabilization, (B) transfer, (C) solvent elimination, (D) thermal desorption, and (E) cleaning.

The poor water wettability of uncoated columns and the destruction of the deactivation layer of the retention gap are serious problems for on-column injection. The wetting characteristics of the water used can be improved by adding an organic solvent with a boiling point higher than water or one that forms an azeotropic mixture with water. When FCSE is used with a loop-type injector, there is no need for good wettability of the solvent. However, because of the high temperatures needed for the FCSE of water and the very large volume of vapor formed, even fairly high boiling analytes are lost. Grob and Li have determined the presence of atrazine in water using this procedure (13).

The low evaporation rate of water makes the injection of a large volume by means of a PTV in solvent-vent mode time-consuming because of the speed of sample introduction, which should be equal to the rate of solvent elimination (9). Water can be prevented from entering the GC column by modifying the carrier gas supply in order to apply a counterflow from the GC column to the injector.

The elimination of vapor through the bottom of the PTV injector requires removing and installing the GC column for each run. This system cannot be automated.

The Through Oven Transfer Adsorption Desorption (TOTAD) interface for on-line rapid-phase LC–GC has been used by our research group in previous studies (14,15). The interface is a modified PTV injector. The modifications allowed for solvent elimination similar to what occurs through the bottom of the PTV injector, but in this case, automation was possible. The changes made in the PTV injector affected the pneumatics, sample introduction, and solvent elimination. In this study, the TOTAD interface was used to directly inject water samples (as large as 1 mL or more) into the capillary GC. The technique was applied to the analysis of pesticide residues in standard solutions and real water samples from the Ebro River (Northeast of the Iberian Peninsula).

Experimental

Materials

Pesticide standards were obtained from Chem Service Inc. (West Chester, PA). The pesticides used for the experiment were

Table I. Quantitative Data of the Analysis for Each Pesticide

Compound	Absolute peak areas %RSD*	Absolute peak areas $R^{2\dagger}$	Normalized areas %RSD*	Phenthoate as internal standard $R^{2\dagger}$	LOD (ng/L)
Diazinon	8.1	0.958	4.1	0.994	0.51
Fenitrothion	11.7	0.992	10.7	0.993	8.06
Fenthion	5.7	0.979	0.7	0.999	0.47
Parathion	6.7	0.984	5.7	0.997	0.63
Phenthoate	9.4	0.983	6.0	–	5.68

* $n = 5$.
† Measured for the linearity interval.

diazinon, fenthion, parathion, phenthoate, and fenitrothion. Methanol was obtained from LabScan (Dublin, Ireland). Water was collected from a Milli-Q water purification system (Millipore, Milford, MA). Real water samples were collected from the Ebro River. The pesticides were dissolved in methanol (1 mg/mL), and aliquots of these solutions were added to water–methanol (90:10) in order to give standard solutions at a concentration ranging from 10 ng/L to 10 µg/L. Methanol was added up to 10% to the real water sample and then was spiked in order to give a final concentration of 0.5 µg/L of each pesticide.

Tenax TA 80-100 mesh (Chrompack, Middelburg, The Netherlands) was used as the packing sorbent in the glass liner of the interface. The packed liner was conditioned under a helium stream by heating it to 300°C at 50°C/min and holding it for 5 min and then programming it to rise to 350°C at 5°C/min and hold for 90 min.

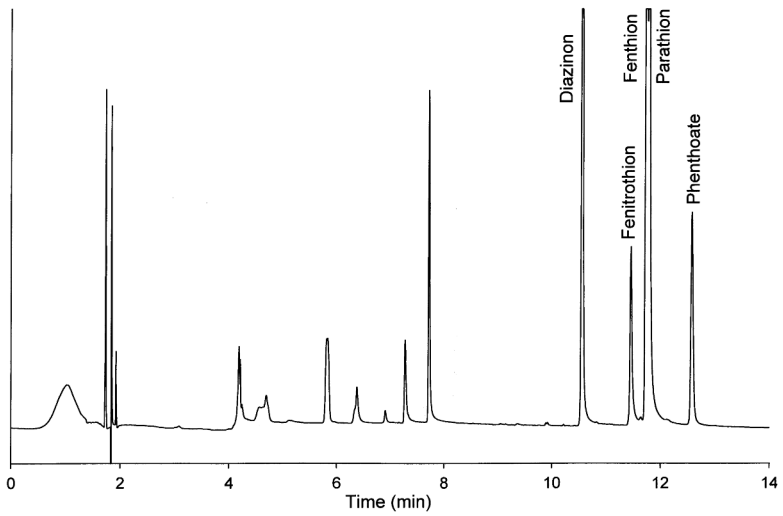

Figure 3. Chromatogram obtained by sampling 1 mL of a standard solution containing 10 µg/L of each pesticide in methanol–water (10:90). The full scale was 2 V.

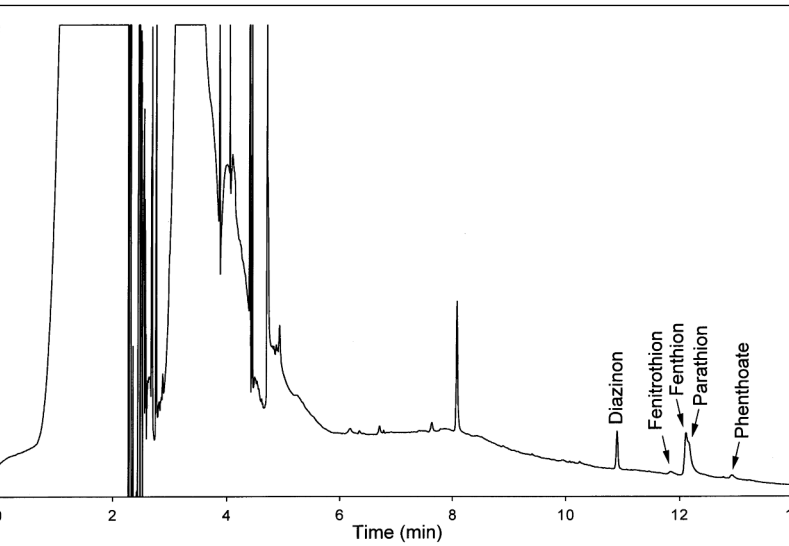

Figure 4. Chromatogram obtained by sampling 1 mL of a standard solution containing 10 ng/L of each pesticide. The full scale was 0.2 V.

Instrumentation

A Varian 3400 CX GC equipped with a PTV injector and nitrogen phosphorous detector (NPD) was used. The GC column was 30-m × 0.32-mm i.d. and 5% phenyl methyl silicone (d_f = 0.25 µm). The PTV injector was substantially modified (as shown in Figure 1) in order to construct the TOTAD interface. The modifications made to the PTV have been extensively described in previous studies (14,15).

A high-performance liquid chromatographic (HPLC) isocratic pump (HP 1050) was used to push the large-volume samples into the TOTAD interface. A six-port valve (Rheodyne 7000) was positioned between the HPLC pump and the TOTAD interface.

Star 4.5 chromatography software (Varian, San Fernando, CA) was used to acquire the LC and GC data.

Operation mode

The operation mode involved five steps (Figure 2 shows what happens inside the glass liner during each of these steps):

Stabilization (Step A)

Helium enters the packed liner through both the oven side (1800 mL/min) and the opposite side (900 mL/min) and then leaves through stainless steel tubing. The solution propelled by the HPLC pump is sent to waste. The TOTAD interface temperature stabilizes at 80°C. The oven temperature is set to 40°C.

Transfer (Step B)

The solution reaches the glass liner at 1 mL/min. The helium pushes the solution through the sorbent. Analytes are retained, and the solvent is vented to waste through stainless steel tubing.

Remaining solvent elimination (Step C)

The LC solution from the pump is sent to waste. Helium pushes the remaining solution in the transfer silica capillary tubing to waste. These conditions are maintained for 0.25 min in order to achieve complete elimination of the solvent.

Thermal desorption (Step D)

The on–off valves are switched (valve V5 open and all other valves closed) so that helium can be allowed to enter only through the usual gas inlet in order to reach a PTV injector and exit only through the GC column. The TOTAD interface is heated to 250°C and maintained at this temperature for 5 min in order to achieve the thermal desorption of the retained solutes and the subsequent transfer of these solutes to the capillary column. The oven temperature is maintained at 40°C for 3 min and is then programmed to 200°C at 20°C/min for the GC analysis.

Cleaning (Step E)

The interface is maintained under the helium stream for 5 min at 325°C. Afterwards, it is cooled to 80°C so that step A can begin again.

Results and Discussion

Figure 3 shows the chromatogram obtained by sampling 1 mL of the standard solution containing 10 µg/L of each pesticide in methanol–water (10:90). The speed of sample introduction was 1 mL/min, thus this large volume was introduced in only 1 min. This rate of sample introduction was possible because of the combination of two mechanisms (solvent evaporation and SPE) that were used to eliminate the solvent.

The same analysis was repeated five times in order to calculate the precision. Table I shows that the relative standard deviations (RSDs) varied from 5.7% to 11.7% for the absolute peak areas, and an improvement of the RSD up to 0.7–10.7% could be achieved if normalized areas were considered. It should be stressed that these data give the precision of the whole analysis because there were no other steps involved.

In order to test the linearity interval, solutions containing 10 µg/L, 1 µg/L, 0.1 µg/L, and 10 ng/L of each pesticide were sampled in the same conditions as described previously. The determination coefficients (R^2) of the logarithm plot of the absolute area versus the logarithm of the concentration for each compound are shown in Table I. The values of R^2 ranged from 0.958 to 0.992 when the absolute peak areas were considered. It can be initially observed that these values may not be considered to be very good even though they include the whole analysis. However, if one pesticide is taken into consideration as the internal standard, a great improvement in the R^2 values is achieved. The values of R^2 obtained by considering Phenthoate as the internal standard are also listed in Table I. These range from 0.993 to 0.999 (which are very good values); therefore, the use of an internal standard is advisable. The chromatogram corresponding to a 10-ng/L concentration of each pesticide analyzed is shown in Figure 4.

Table I also shows the limits of detection (LODs) of the solution sampled, which was calculated as the amount of product giving a signal equal to five times the background noise (S/N = 5). The LODs were calculated from the chromatogram in Figure 4 and ranged from 0.5 to 8.1 ng/L. These LODs can be considered very good because they are between ten and a hundred times lower than 0.1 µg/L, which is the maximum concentration allowed for drinking water by European Union legislation (16).

The addition of methanol to water samples before the SPE step may improve the retention of pesticides. Taking into consideration that SPE was a mechanism implied in the sample introduction system used, it was thought that the addition of methanol to the water sample may improve the method's sensitivity. For this reason, methanol was added to water up to 10%, but its influence on sensitivity was not statistically tested.

The chromatograms depicted in Figures 3 and 4 showed such a small solvent peak that it may be claimed that solvent elimination was almost complete. Therefore, it is possible to use a detector that is very sensitive to water (such as the NPD) in order to obtain good quantitative data. However, the small amount of water that reaches the NPD damages its bead power in such a way that it must be changed after 3–6 months of use. A slight distortion of the detector signal as a result of water can be observed in some chromatograms together with the solvent peak (see Figures 3 and 4). However, it may be possible to overcome this problem by using another type of detector (i.e., a flame photometric detector) that is not so sensitive to water, but this would not provide such low LODs.

Figure 5 shows the chromatogram corresponding to the analysis of a real water sample from the Ebro River. Methanol was added to water up to 10%, and the sample was fortified up to 0.5 µg/L of each pesticide. The analysis was carried

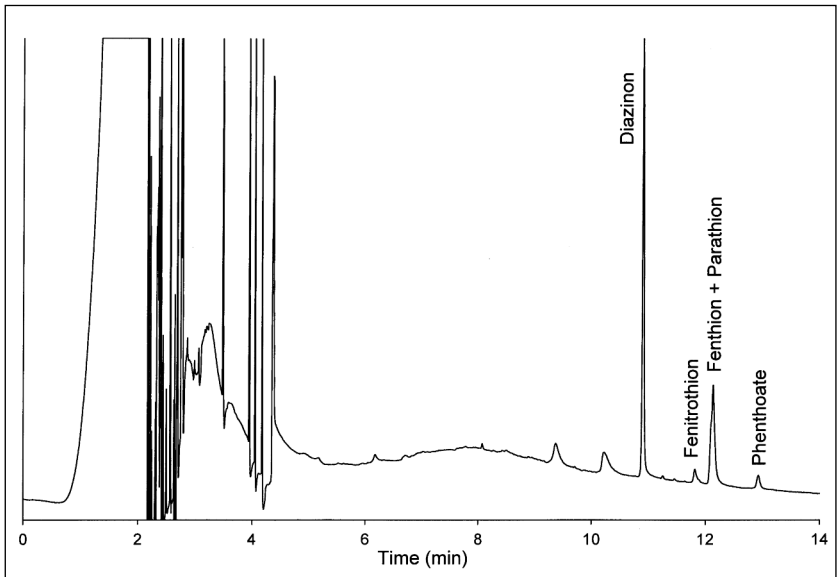

Figure 5. Chromatogram of a real water sample from the Ebro River. The full scale was 0.2 V.

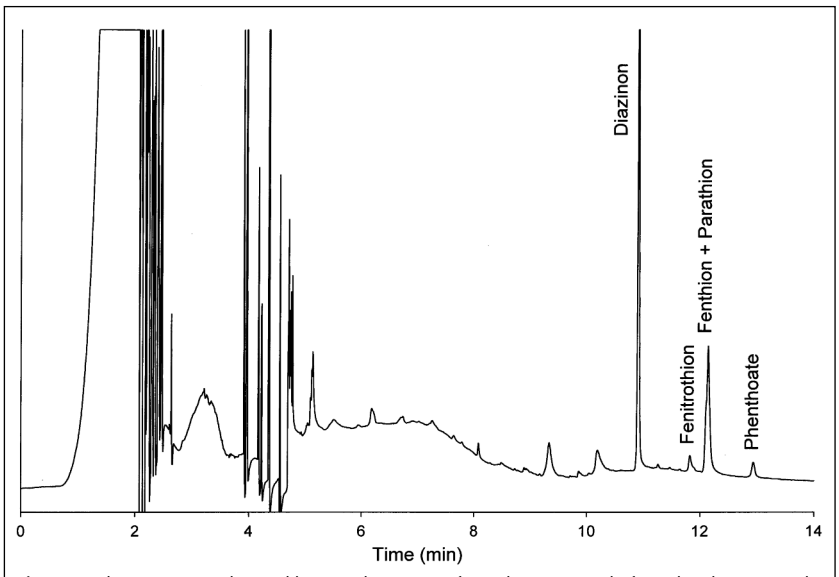

Figure 6. Chromatogram obtained by sampling 2 mL of a real water sample from the Ebro River. The full scale was 0.2 V.

out in the same conditions as those described for the standard solutions (i.e., 1 mL was injected at a rate of 1 mL/min) (Figures 3 and 4).

The TOTAD interface used was manually operated because it was developed in our laboratory and was still being tested in these initial experiments. However, it could easily be automated by simply changing the manual valves to automatic valves, as can be done with most GC apparatus manufactured today.

The sensitivity achieved by introducing 1 mL of the sample was sufficiently high for most pesticide residue analyses in water, but it should be emphasized that a much larger amount of water can be sampled by the TOTAD interface if greater sensitivity is needed. For example, Figure 6 shows the GC corresponding to the introduction of 2 mL of the same real sample injected using the same conditions as those in Figure 5. The solvent peak and distortion of the bead power by water was similar in both chromatograms, meaning that the amount of solvent remaining in the injector is the same when 1 or 2 mL are sampled. The sensitivity of the analysis can therefore be increased by increasing the sample volume introduced.

In summary, the TOTAD interface is useful for injecting very large volumes of water samples in GC. It can easily be automated. Sensitivity of the analysis is excellent and can easily be improved by increasing the sample volume. The precision is not very good when absolute areas are considered, but it can be improved by considering normalized areas. The response was linear in the wide range tested, but R^2 was not very good. Although an NPD can be used, this is probably not the best choice.

Acknowledgments

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