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Introduction

The European Union (EU) directives set a maximum admissible concentration of 0.1 µg/l for each pesticide and 0,5 µg/l for the sum of all the pesticides in drinking water (1). The analytical methods must quantify a great number of pesticides at such low levels of concentration.

Large volume injection (LVI) allows to introduce in GC a volume very superior to that usually injected in GC, which permits to reach lower detection limits. The high boiling point, very large volume of vapour formed and the poor wettability of the water make especially difficult the introduction of large volume of water in GC. To this aim it is necessary to dispose of reliable interfaces which eliminate the solvent and retain analytes without causing losses and contaminations.

Our research group has developed a new interface named TOTAD (Through Oven Transfer Adsorption Desorption) for LVI and on-line coupling LC-GC (2). TOTAD interface allows LVI of polar and non-polar solvent.

A new method for the determination of pesticides in water by LVI using the TOTAD interface and mass spectrometric detection is presented. No sample pre-treatment step other than a simple filtration was needed. TOTAD interface allows the introduction of up to several millilitres of water while good chromatographic characteristics are maintained.

Experimental

1) Samples:

Water was from LabScan (Dublin, Ireland). Pesticides were dissolved in methanol (100 mg/l). This solution was used to spike water at levels from 25 µg/l to 500 µg/l of each pesticide. Real water samples were obtained from a deep channel and from an underground well.

2) Sample preparation:

Prior to LVI-GC-MS analysis, the water samples were filtered through 0,20 µm filter (Chromatography Research Supplies, Inc).

3) Instrumentation:

Manual injection valve (model 7125 Rheodyne, CA) with a volume loop of 500 µl

Quaternary pump (Konik 550) was used to push the large volume of sample into the TOTAD interface

Gas chromatograph (Konik 4000B) equipped with:
 Injector: PTV modified — **TOTAD interface**
 Liner filled with Tenax TA (1 cm length)
 Column: 30m x 0.25 mm x 0.25 µm; Methyl 5% Phenyl Silicone
 Mass spectrometric detector

4) Analysis:

The TOTAD interface (US patent 6,402,947 B1, exclusive rights assigned to KONIK-Tech, Sant Cugat del Vallés, Barcelona, Spain) was used for injecting a very large volume of sample into the GC.

The sample was introduced in the LC manual injection valve. Pump flow was 0.1 ml/min.

TOTAD interface conditions:

Temperature adsorption/desorption: 80 °C/250 °C (for 5 min)
 Operation mode has been described previously (2) (Figure 1)

GC conditions:

Injection and solvent elimination: the oven temperature was kept at 50 °C
 Oven temperature: 50 °C; 10 °C/min to 160 °C; 2 °C/min to 170 °C; 5 °C/min to 230 °C; 10 °C/min to 300 °C hold 5 min
 Carrier Gas: Helium at flow rate of 1 ml/min
 Detector: MS (MS Q12 Konik) Mass spectrometric analysis was performed in EI full-scan mode from 50 to 500 u with ion-extraction at specific m/z values

Results

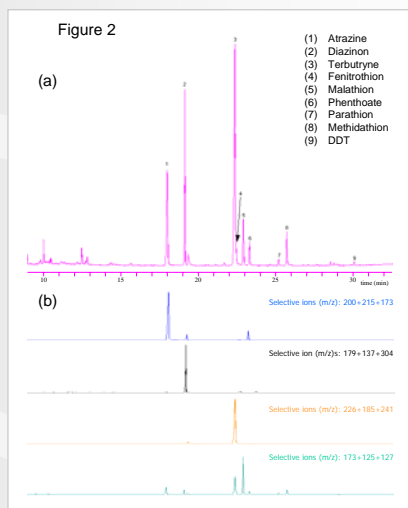


Figure 2. (a) LVI (5000 µl)-GC-MS full-scan chromatogram of a sample of water spiked at 50 µg/l of each pesticide. (b) LVI (5000 µl)-GC-MS selective ions chromatograms used for pesticide quantification.

PESTICIDE	RSD area (%)	RSD tr (%)	R2	LOD (ug/l)
Atrazine	8.6	0.04	0.99	0.05
Diazinon	5.7	0.04	0.99	0.02
Terbutryne	8.4	0.05	0.99	0.02
Fenitrothion	13.1	0.05	0.99	0.08
Malathion	16.5	0.05	0.96	0.07
Parathion	10.4	0.05	0.99	0.12
Phenthoate	19.0	0.06	0.96	0.73
Methidathion	18.3	0.07	0.97	0.04
DDT	10.8	0.05	0.99	0.77

Table 1. Relative standard deviation (RDS) from the absolute peak area and from the retention time (n=5) when 500 µl of water spiked at 50 µg/l was injected. Correlation coefficient (R²) for 500 µl of water at spiking levels ranging from 25 µg/l to 500 µg/l of each pesticide. Detection limits (LOD) when 5000 µl of water spiked at 50 µg/l was injected.

Conclusions

The present method:

- Allows the determination of organophosphorus, organochlorine and triazine pesticides in one run
- Reduces the amount of solvent used, minimizes the number of analytical steps necessary and avoids laborious and time-consuming clean-up and concentration steps.
- Gives good linearity and repeatability.
- The sensitivity wasn't good enough to ensure a reliable determination at levels lower than the MRLs established by European legislation when 500 µl was injected. A further optimization is needed.
- The sensitivity was improved by increasing the sample volume injected
- The method was applied to the analysis of pesticide residues in real water samples

References

- (1) EEC Drinking Water Guidelines; 80/779/EEC, EEC No.I.229/11-29; EEC: Brussels, Aug 30, 1980.
- (2) Perez, M., Alario, J., Vázquez, A.M., Villén, J. *Anal. Chem.* 2000, 72, 846-852

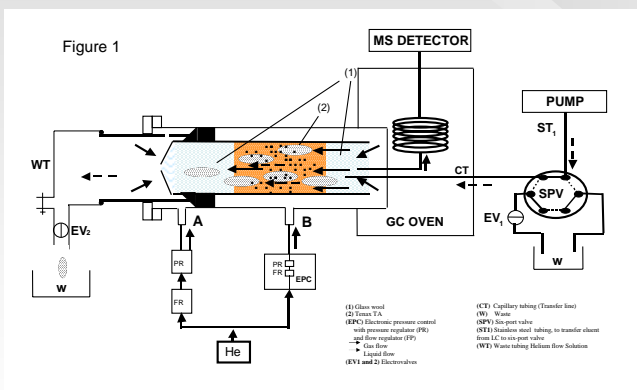


Figure 1: Scheme of the TOTAD interface during the injection step.