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INTRODUCTION

Pesticides constitute a very important group of organic pollutants regulated by governments all over the world owing to their high toxicity and their extended use in agriculture practice. Determination of pesticides in environmental and food samples is mainly performed by gas chromatography (GC) with selective detectors or GC-MS. Classical methods for analysis of these compounds in these matrixes require the use of sample preparation steps where manipulation of the sample is mandatory and can cause contaminations and losses of analytes.

In this work, a new application of the patented TOTAD® interface for on-line coupling HPLC x HRGC-MS (KONIK Pestilizer® system) is presented. The interface allows the direct analysis of pesticides in edible oils and environmental samples. The sample is directly injected into the HPLC system and the fraction of interest is transferred to the HRGC through the interface. With the addition of the KONIK Robokrom HPLC Autosampler and the full control through the Konikrom® Software, the complete analysis can be easily automated, limiting the use of solvents while protecting sample integrity. Moreover, the use of selective detector such as MS working in EI (+) mode allows unequivocal identification of pesticides and avoids interferences from matrix working in single ion monitoring mode (SIM).

INSTRUMENTATION AND SYSTEM CONDITIONS

The innovative KONIK Pestilizer® system marries in synergy the separation and fractionation potential of normal or reversed HPLC to the separation and selective detection of HRGC-MS system.



LC-GC Transfer

The flow diagram (Figure 1) describes the interface operating principles. This patented interface allows the trapping of pesticides in the trap, which is held at the chosen temperature while a digitally controlled continuous flow of Helium maintains the column flow and eliminates the solvent from the trap.

Figure 1-a Stabilization step

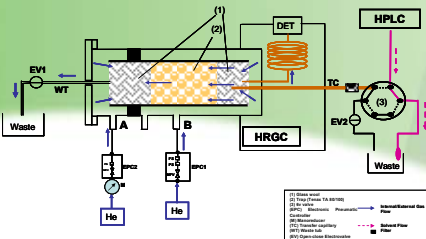
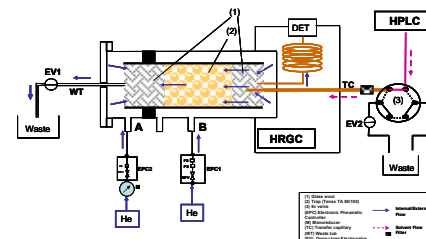


Figure 1-b Transfer step



Stabilization:

Helium enters the packed liner through both external (500 ml/min) and internal flow (500 ml/min) (A and B in Figure 1). Eluent coming from HPLC pump is sent to waste. K2 injector temp. stabilizes at 70°C (water) and 90°C (oil). Oven temp. is set at 40°C. EV1 is opened and EV2 is closed.

Transfer:

The solvent with pesticides reaches the liner at 0.5 ml/min (water analysis) and 0.1 ml/min (olive samples). Helium pushes the solvent through the adsorbent. Analytes are retained, and the solvent is vented to waste through the waste tubing (WT in Figures 1 and 2).

Remaining solvent elimination:

LC solvent coming from the pump is sent to waste. Helium pushes the remaining solvent in the capillary tubing to waste for 2 min to complete elimination of the solvent. EV2 is closed. EV1 is opened.

Thermal desorption:

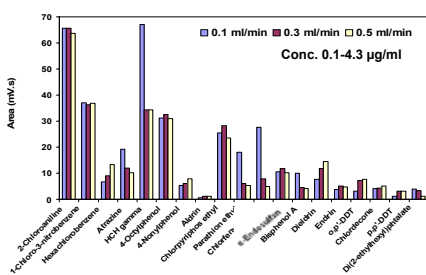
Helium enters only through the external gas inlet (A in figure 1) to the column. K2 interface is heated for 3 min and the retained pesticides are desorbed and transferred to the capillary GC column. EV1 and EV2 are closed.

RESULTS

ANALYSIS OF PESTICIDES IN WATER

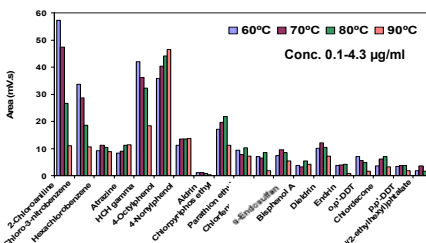
a- Optimisation of transference step for water

Transfer HPLC flow: 1 ml transferred; Ads. Temp. 70°C



✓ For 1 ml of water, the best responses were obtained for slower transfer flow, i.e. 0.1 ml/min. Nevertheless, for transference of high volumes of water (for instance 10 ml), 0.5 ml/min were chosen for reasons of rapidity.

Adsorption Temp.: 1 ml transferred at 0.5 ml/min



✓ In general, adsorption Temp. of 70°C and 80°C were the best choice as a compromise situation between all the compounds.

b-KONIK PESTILIZER® quality parameters

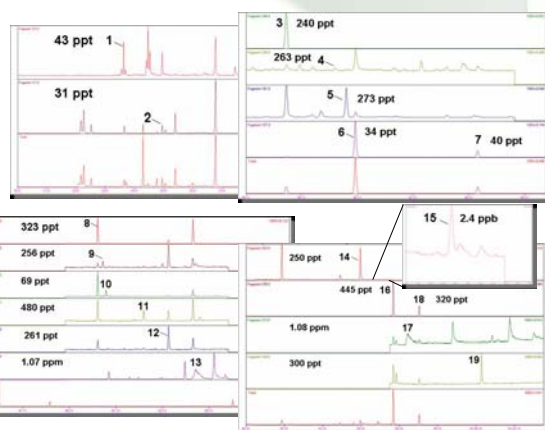
Table 2: LOD for the selected pesticides in water subjected to KONIK Pestilizer®

Peak n°	Compound	LOD ^a (ng/l)
1.	2-Chloroaniline	1.0
2.	1-Chloro-3-nitrobenzene	0.2
3.	Hexachlorobenzene	0.2
4.	Atrazine	295
5.	Lindane	9.5
6.	4-Octylphenol	0.02
7.	4-Nonylphenol	0.1
8.	Aldrin	2.0
9.	Chlorpyrifos ethyl	15.0
10.	Parathion ethyl	6.5
11.	Chlorfenvinphos	22 ^b
12.	α-Endosulfan	5.5
13.	Bisphenol A	40 ^c
14.	Dieldrin	1.5
15.	Endrin	460 ^d
16.	o,p'-DDT	0.5
17.	Chlordecone	58 ^d
18.	p,p'-DDT	4.5
19.	Di(2-ethylhexyl)phthalate	8.0

^a S/N = 3 for 10 ml of water, SIM mode; ^b ng/ml; ^c LOD 64 ng/l for m/z 81; ^d sum of ions m/z 272+274

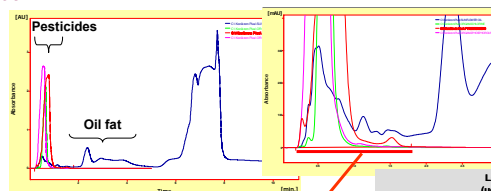
c-Sample analysis by KONIK PESTILIZER®

Tap water spiked at different pesticide levels (10 ml)



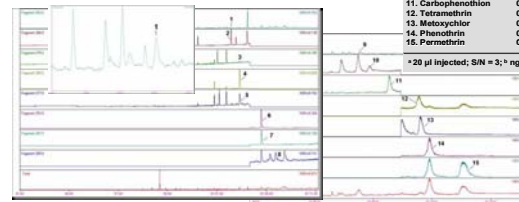
ANALYSIS OF PESTICIDES IN EDIBLE OILS

a- HPLC separation of pesticides from sunflower oil matrix



b- Sunflower oil analysis

Sunflower oil spiked at 1 µg/ml level (20 µl injected)



CONCLUSIONS AND FUTURE WORK

- The multidimensional KONIK K2 HPLCxHRGC-MS system (KONIK Pestilizer®) allows to analyse automatically without previous sample pretreatment different types of pesticides in water and oil samples.
- The KONIK Pestilizer® that uses MS allows unambiguous identification of the pesticides in water by EI(+) working in full-scan mode and good sensitivity working in SIM mode (down to ppt in water samples). Moreover, LODs can be improved if necessary by injection of higher sample volumes for both types of samples, water and oil.
- The applicability of the technique to real samples has been successfully demonstrated.
- Nowadays, optimisation of other parameters such as PDMS trap, HPLC composition for oil analysis and determination of quality parameters is under study.

ACKNOWLEDGEMENTS

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