



Application Note SP303e

Determination of Pesticides in Drinking Water with SPDE-GC/MS

Introduction

In agriculture, pesticides are used extensively against insects, moulds and weeds. Some pesticides are suspected as endocrine disruptors. Due to the good water solubility in combination with the high persistence of some pesticide compounds an increased danger for groundwater and drinking water exists.

The Netherlands National Institute of Public Health and Environmental Protection (RIVM, 1992) concluded that "groundwater is threatened by pesticides in all European states. This is obvious both from the available monitoring data and calculations concerning pesticide load, soil sensitivity and leaching... It has been calculated that on 65% of all agricultural land the EC standard for the sum of pesticides (0.5; μ g/l) will be exceeded. In approximately 25% of the area this standard will be exceeded by more than 10 times..."

The environmental hazard potential resulting from this is kept as low as possible by an appropriate legislation. This is the reason why drinking water must be continually monitored to determine the trace levels of these pesticides.

Regardless of the analytical detection method (UV, MS, ECD,...), the quantitation of pesticides in drinking water requires extraction and enrichment of the sample to minimize matrix related problems. Therefore the determination of pesticides in drinking water close to the detection limit requires appropriate analytical equipment.

Due to the combination of fully automated **CHROMTECH SPDE**-Option followed by mass spectrometric detection (**SPDE-GC/MS**)

the determination of pesticides in water down the low ppt range is possible in routine analysis.

In this application note we report the suitability of **SPDE-GC/MS** with pesticide spiked drinking water.

Methods

GC-Conditions: *Agilent 6890N*. Column: *Varian VF-5MS*, 30 m x 0.25 mm x 0.25 μ m. 70°C (1 min), 15°C/min $\Rightarrow$ 320°C (10 min). S/SL-Injector (250°C), 1 min splitless, 30 mL/min Purge Flow. Helium (1,2 mL/min).

MS-Conditions: *KODIAK 1500* with GC Interface (280° C). EI at -70 eV, 150 μ A, 230° C. SIM with 300 ms Scan time and 0.7 u SIM Width; 1250 amu/sec.

SPDE-Conditions: *CHROMTECH SMM* (Single Magnet Mixer) on *CTC CombiPAL*. 20 ml Headspace vials; Temperature (Syringe and Oven): 50° C; 500 rpm Agitator Speed; 40 mm Sample Penetration; 90 Extraktion Strokes à 1 ml; 1 ml Desorption Gas Volume with 50 μ L/s Flow Speed; 60 s Pre Desorption Time

Results and Discussion

Figure. 1 shows the total ion current (TIC) of the Pesticide Mix (2.5 ppm) scanned from m/z 50-550. The performed scan was used for identification of the pesticides and the determination of their retention times.

Table 1 illustrates the retention times of the analytes and the respective SIM ions that were used for the following analyses.

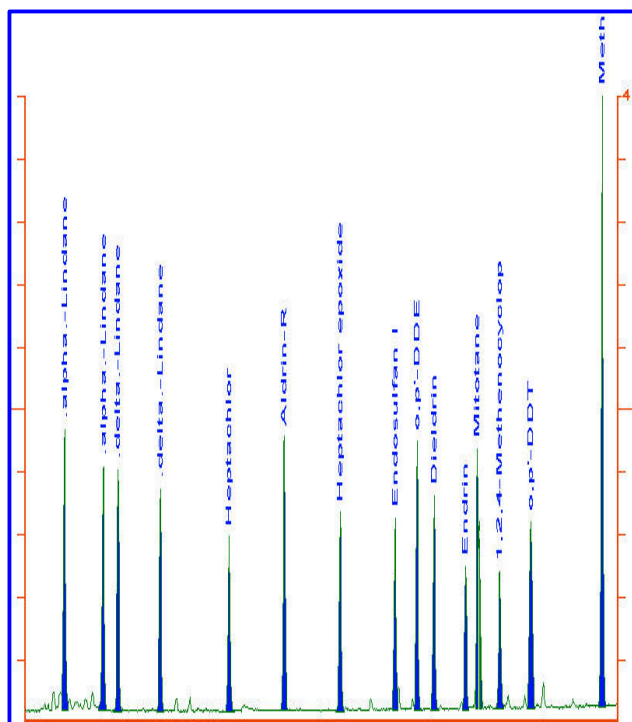


Abb. 1: TIC (m/z 50-550) of the Pesticide Mix (2.5 ppm)

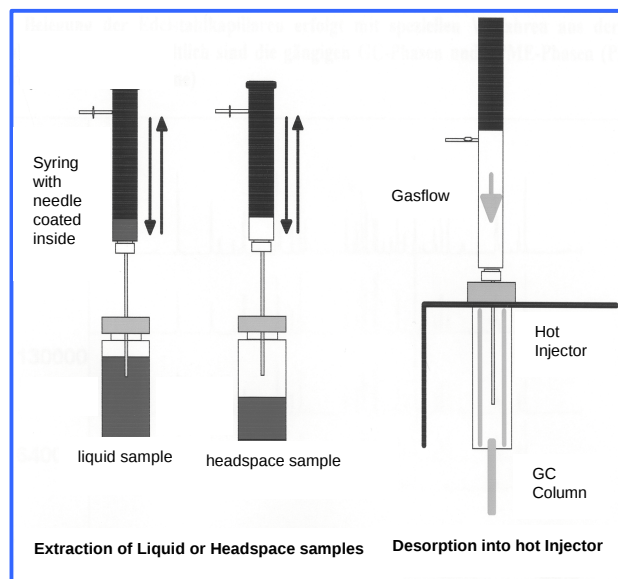


Abb. 2: Principle of the automated SPDE extraction. The analyte is enriched by controlled pumping through the specially coated syringe needle.

Table 1

Nr.	Name	RT (min)	SIM Ion (m/z)	SIM Group
1	α -Lindane	13.66	219	1
2	β -Lindane	14.01	219	1
3	χ -Lindane	14.14	219	1
4	δ -Lindane	14.53	219	1
5	Heptachlor	15.15	100	2
6	Aldrin	15.66	66	3
7	Heptachlorepoxyde	16.17	81	4
8	Endosulfan I	16.67	195	5
9	o,p-DDE	16.87	176	6
10	Dieldrin	17.03	79	6
11	Endrin	17.31	81	7
12	o,p-DDD	17.42	235	7
13	Endosulfan II	17.44	235	7
14	Endrin aldehyde	17.63	67	8
15	o,p-DDT	17.91	387	8
16	Methoxychlor*	18.56	227	9

* Methoxychlor has the fourfold amount in all mentioned standards and dilutions.

The following illustrations 3 to 6 represent in each case the TIC of the SIM traces, with decreasing concentrations of the standard Pesticide Mix. The number of piston strokes of the SPDE syringe during the extraction was always 90 strokes. The spiked water samples were agitated during the extraction with a magnetic stir bar at 500 rpm.

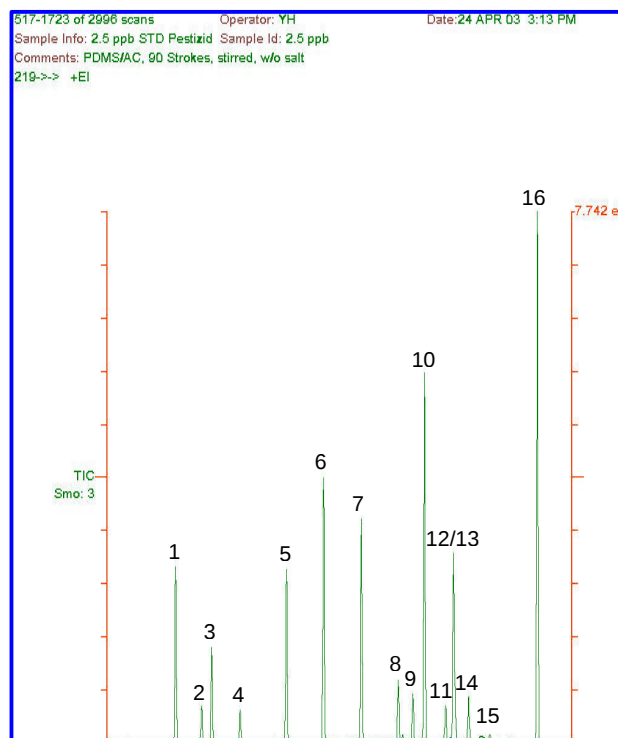


Abb.3: TIC of the SIM traces (comp.Tab.1); 25 ppb (µg/L), 90 strokes, agitated; PDMS/AC.

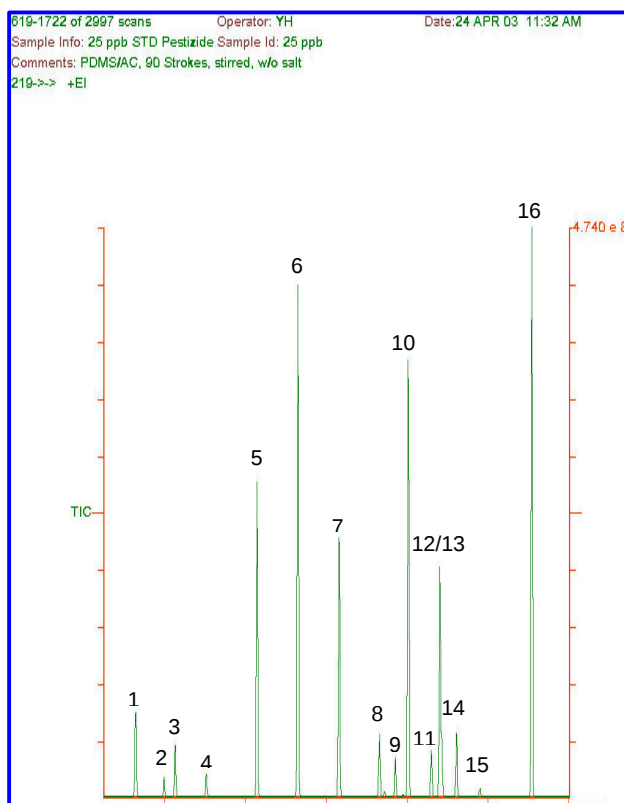


Abb.4: TIC of the SIM traces (comp.Tab.1); **2.5 ppb (µg/L)**, 90 strokes, agitated; PDMS/AC.

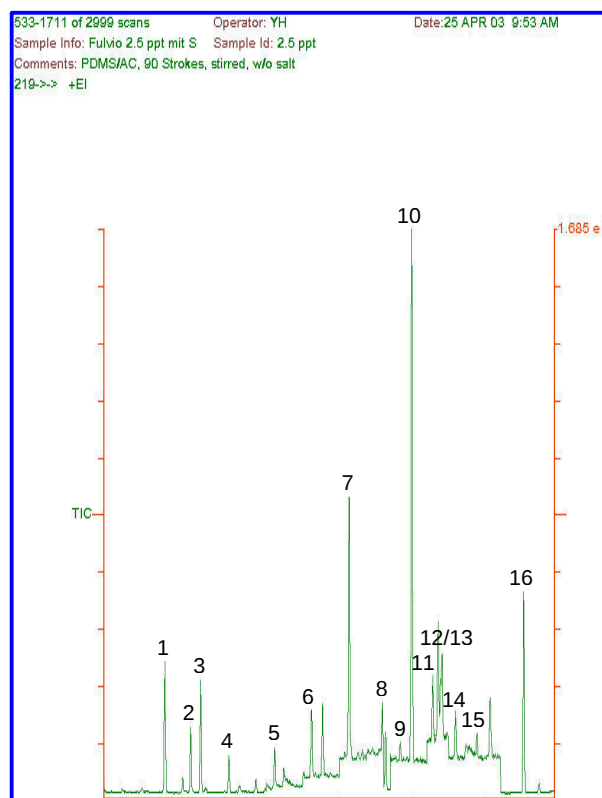


Abb.6: TIC of the SIM traces (comp.Tab.1); **2.5 ppt (ng/L)**, 90 strokes, agitated; PDMS/AC.

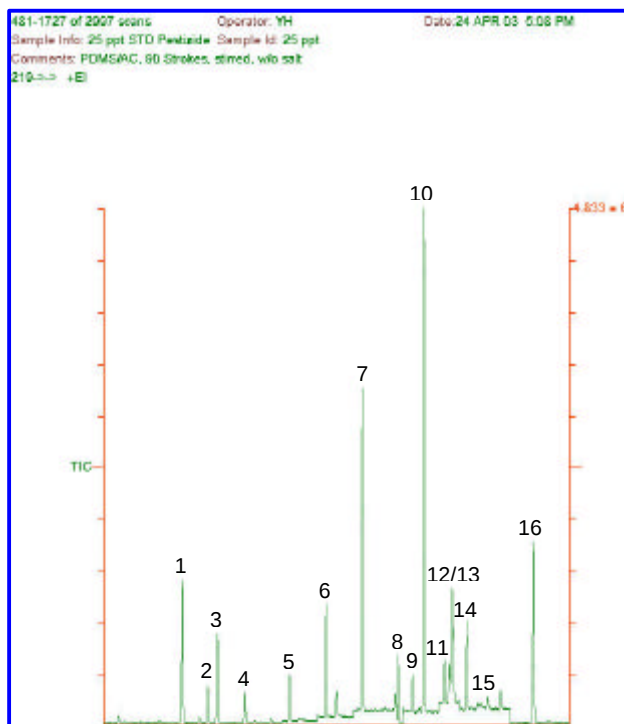


Abb.5: TIC of the SIM traces (comp.Tab.1); **25 ppt (ng/L)**, 90 strokes, agitated; PDMS/AC.

The presented results show very clearly that identification and quantitation of pesticides is possible in drinking water by means of **SPDE-GC/MS** even in the ppt range. The **SPDE** technique is characterised by complete automation and highest sensitivity. Compared to other extraction procedures only a small quantity of sample (10-20 mL water) and no toxic solvent is needed. The system is based on the **CTC CombiPAL** sampler, so no further laboratory space is needed. Due to the above mentioned advantages **SPDE** could be the method of the choice for the routine analysis of these pesticides in water.