CHROMTECH

SPDE™
the Magic Needle

Application Note SP404e

Automated Extraction and Detection of VOC with *SPDE*™-GC/MS, *SPDE*™ *Extraction Cooler* and Split-/Splitless Injector

Introduction

VOC (Volatile Organic Compounds) form a class of diverse organic substances only related by their volatility. One commonly used analytical approach is headspace extraction followed by GC/MS separation and detection. Since detection limits have decreased over the last few years, it turns out that the extraction process itself is the crucial step in VOC analysis.

SPME™ has been shown to have a good concentration factor, but it lacks robustness when a high number of samples have to be calibrated and analyzed under routine conditions. Another factor contributes to SPME™-related limitations in VOC analysis: Trapping of VOCs

Fig. 1: Automated *SPDE* Extraction with *Extraction Cooler*: The analyte is purged through the *SPDE* needle at a temperature of -15° C. Meanwhile the sample is constantly heated to 50° C. So the sample is heated while the SPDE-needle is cooled during the extraction process.

has to be carried out at elevated temperatures to force the VOCs' transfer from water to the headspace phase. At this elevated temperature, the trapping efficiency of SPME™ for highly volatile compounds is reduced.

Introducing the fully automated *CHROM-TECH SPDE* option, which in combination with a cooling device (*SPDE Extraction Cooler*), selectively cools down the trapping part of the whole extraction system, thus enabling the user to get analytical access to the highly volatile VOCs (fig. 1 shows a schematic view).

In this application note, we report the suitability of *SPDE GC/MS* and the *SPDE Extraction Cooler* for the analysis of VOC-spiked drinking water. This approach runs on a standard Split/Splitless Injector. In another application note (SP405e), even higher sensitivity is obtained by using a PTV Injector.
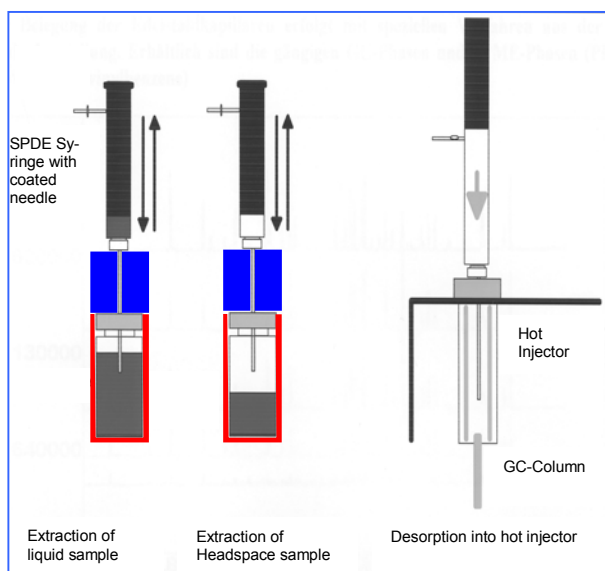
Methods

GC-Conditions: *Agilent 6890N*. Column: BGB CKW, 50 m x 0.32 mm x 2.00 µm. 40°C (10 min), 10°C/min $\Rightarrow$ 200°C (5 min). S/SL-Injector (250°C), split 5:1. Helium (2 mL/min).

MS-Conditions: *KODIAK 1500* mit GC Interface (250° C). +EI at -70 eV, 150 µA, 200° C. SIM method with 12 timeslices (see. tab. 1).

SPDE-Conditions: *CHROMTECH SMM* (Single Magnet Mixer) with *SPDE Extraction Cooler* on a *CTC Combi PAL*. SPDE syringe PDMS/AC 50 µm x 72 mm, -15° C needle temperature. 10 mL sample in 20 mL headspace vials; temperature (Syringe/Oven): 35°/50° C; 750 rpm agitator speed; 20 mm sample penetration; 40 extraction strokes with 1 mL sample volume; 200 ml desorption gas

volume at 400 µL/s flow speed; 0 s pre desorption time. Needle cleaning: 10 min at 250°C.

Results and Discussion

Figure 1 illustrates the principle of operation for *SPDE* in combination with the **SPDE Extraction Cooler**. Using this method, the VOCs of the heated sample could be enriched inside the cooled **SPDE** needle and thereafter injected directly into the split-/splitless injector of the GC/MS. The enrichment process needs a little more time than the GC analysis.
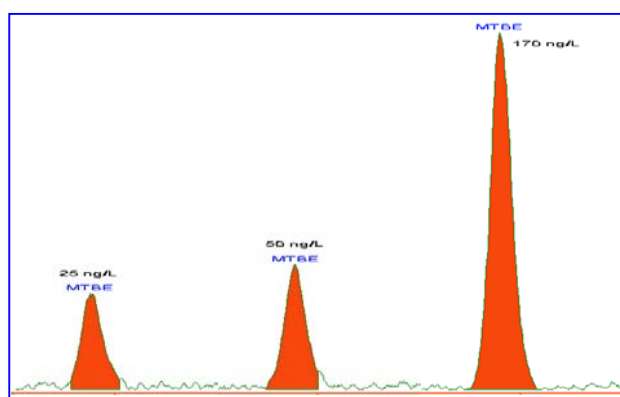
Therefore it is possible to establish a continuous extraction/analysis process. Figure 3 shows the three lower calibration points for MTBE (methyl tertiary-butyl ether). In table 1, the results of 18 VOCs are listed. Special attention should be given to the signal/noise value calculated from the lowest calibration level. In essence, a concentration down to 10 ng/L is possible with the combination of **CHROMTECH SPDE + CHROMTECH Extraction Cooler + Agilent Split/Splitless Injector**. In another application note (SP405e), we show that it is possible to reach a tenfold higher sensitivity by using a longer extraction time (more strokes) and a PTV injector.
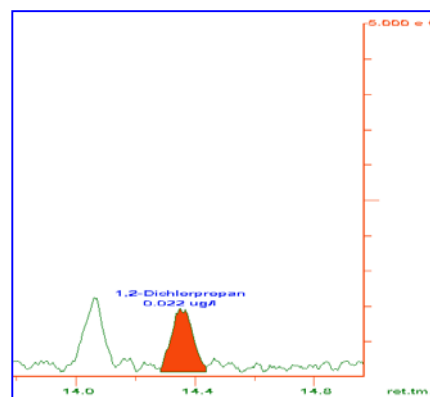

Fig. 2: MTBE at the lower 3 calibration points (SIM m/z 73; scale $5*10^6$, see fig 3). Signal/noise for the lowest concentration is higher than 100:1 for a concentration of 25 ng/L.

Fig. 3: 1,2-Dichloropropane at the lowest calibration point (20 ng/L, SIM m/z 63, signal/noise 45:1).

Substance	Ion [m/z]	RT [min]	r²	s/n** bei L0	L0** [ng/L] n=2	L1 [ng/L] n=2	L2 [ng/L] n=2	L3 [ng/L] n=2	L4 [ng/L] n=1	L5 [ng/L] n=1
MTBE	73	6.4	0.9924	110	25	50	170	850	1.700	3.380
Trichloromethane	83	10.1	0.9863	1000	25	50	170	850	1.700	3.410
1,1,1-Trichloroethane	97, 99	11.2	0.9871	370	15	30	100	480	960	1.910
Tetrachloromethane	119	12.0	0.9896	120	15	35	115	570	1.140	2.280
1,2-Dichloroethane	62, 64	12.2	0.9851	60	25	50	160	800	1.610	3.220
Benzene	78	12.3	0.9853	260	45	90	310	1.560	3.120	6.240
1,2-Dichloropropane	63	14.3	0.9891	45	20	50	150	740	1.490	2.970
Bromodichloromethane	83, 85	14.8	0.9883	160	15	30	110	570	1.140	2.270
Toluene*	91	16.7	0.9626	700	25	50	190	930	1860	3.720
Chlorobenzene	112	19.2	0.9824	500	15	30	110	550	1.100	2.210
1,1,1,2-Tetrachlorethane	131	19.3	0.9809	110	15	30	110	570	1.140	2.280
Ethylbenzene*	91	19.4	0.9729	900	50	110	370	1.860	3.720	7.430
m-Xylene + p-Xylene*	91	20.2	0.9494	770	25	50	180	870	1.720	3.460
o-Xylene	91	19.6	0.9725	330	55	110	370	1.860	3.730	7.460
1,3-Dichlorobenzene	146	22.9	0.9830	1300	55	110	370	1.870	3.730	7.460
1,2-Dichlorobenzene	146	23.6	0.9852	1600	55	110	370	1.840	3.680	7.360
HCBD	225, 227	26.5	0.9786	190	15	30	100	480	0.950	1.900

* The higher concentrations result in saturation of the MS detector.
** The numbers are rounded.

Tab. 1: Composition of the VOC standard mixture and results. The s/n values are indicated for the lowest concentration. In fig. 3, the lowest occurring s/n of 45 is shown to give the reader an impression of the corresponding peak shapes for higher s/n ratios.