

SPDE

VOC ANALYSIS ACCORDING TO EPA 524 USING SPDE-GC/MS

TEN TIMES MORE HEADSPACE SENSITIVITY – AT LEAST

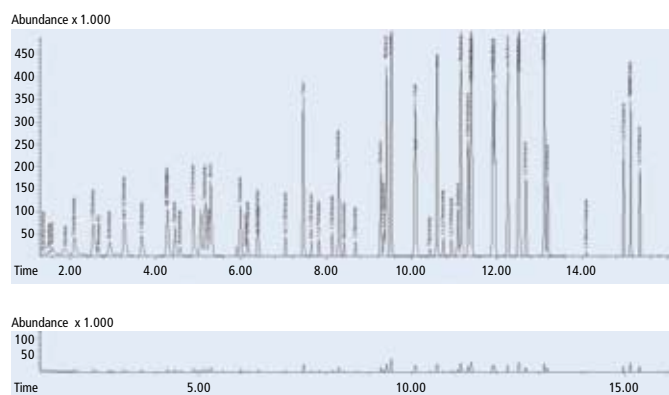
Headspace analysis of volatile compounds according to EPA 524 is routinely used in many labs worldwide. However, this established method needs lot more analytical power since the regulatory requirements got more strict over the past years.

We'll show the superior extraction power of SPDE (Solid Phase Dynamic Extraction) compared to headspace sampling. This application note consists of two parts: Part 1 demonstrates more than 10-fold sensitivity gain when switching from classical headspace to standard SPDE. Step two shows the benefit of advanced SPDE for compounds with very low boiling points. Even for Vinyl chloride you'll enter the concentration ranges of 1 ng/l and below.

10-FOLD MORE HEADSPACE SIGNAL USING SPDE WITH EXTRACTION COOLER

This is what you get when adding the CHROMTECH SPDE option plus the CHROMTECH SPDE Extraction Cooler. Both options will literally extract the headspace during the standard incubation time. Even very volatile compounds like Vinyl chloride will be enhanced. Table 1 shows the enhancement of SPDE over standard headspace. Picture 1 shows 1 µg/l EPA standard with SPDE extraction compared to static headspace analysis. Of course it's all the same scale!

Note that this is still a split injection, wasting sensitivity. Wouldn't you want to analyze all?



Picture 1: Enhancement of SPDE versus headspace technique
Top is SPDE extraction, bottom is headspace. Both derived from a standard of 1 µg/l with about 16 minutes incubation time.

Table 1: Enhancement of SPDE versus Headspace technique

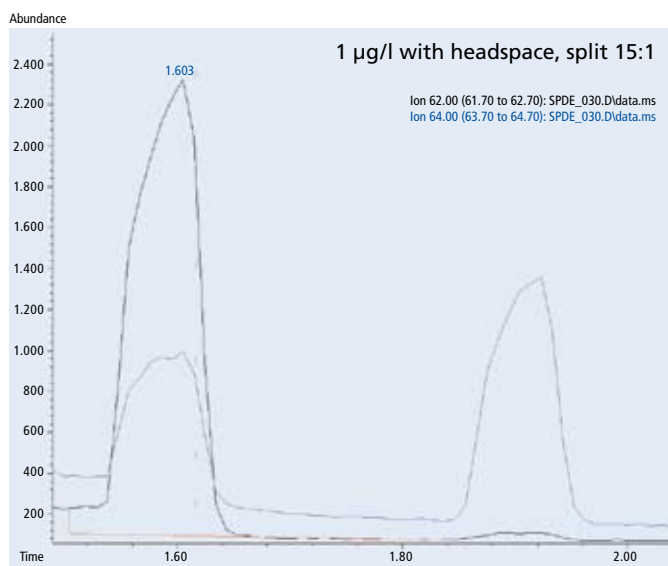
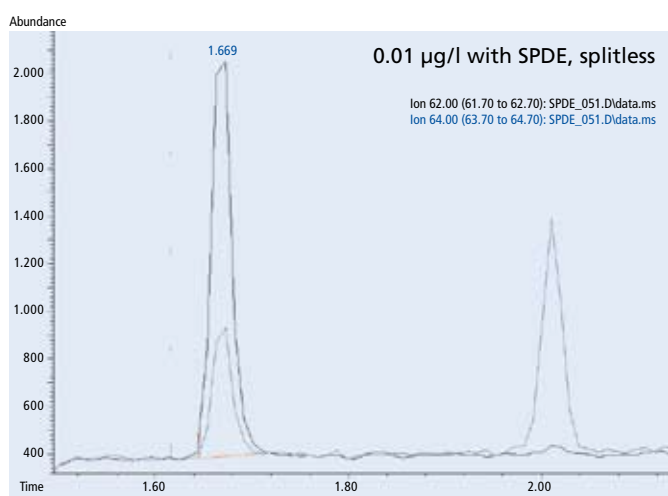
Name	Retention Time [min]	Quantitation Ion [m/z]	Enhancement by CHROMTECH SPDE [SPDE area/HS - area*]
D5-Bromethan (IS)	2.684	115	n. a.
Trifluortoluol (IS)	6.132	146	n. a.
Dichlordifluormethan	1.394	85	2 ⁺
Chlormethan	1.522	50	6 ⁺
Vinylchlorid	1.598	62	5 ⁺
Brommethan	1.866	94	8 ⁺
Chlorethan	1.919	64	4 ⁺
Trichlorfluormethan	2.120	101	6 ⁺
1,1-Dichlorethen	2.561	61	13
Dichlormethan	2.947	49	14
trans 1,2-Dichlorethen	3.287	61	16
1,1-Dichlorethan	3.690	63	13
2,2-Dichlorpropan	4.292	77	16
cis 1,2-Dichlorethen	4.299	96	14
Chloroform	4.466	83	14
Bromchlormethan	4.595	130	13
1,1,1-Trichlorethan	4.903	97	15
1,1-Dichlorpropan	5.078	75	16
Tetrachlormethan	5.177	117	16
1,2-Dichlorethan	5.261	62	13
Benzol	5.312	78	14
Trichlorethen	6.009	130	16
1,2-Dichlorpropan	6.165	63	15
Bromdichlormethan	6.400	83	14
Dibrommethan	6.427	174	13
cis 1,3-Dichlorpropen	7.062	75	15
Toluol	7.476	91	16
trans 1,3-Dichlorpropen	7.663	75	15
1,1,2-Trichlorethen	7.842	97	14
1,3-Dichlorpropan	8.149	76	14
Tetrachlorethen	8.303	166	16
Dibromchlormethan	8.433	129	13
1,2-Dibromethan	8.688	107	13
Chlorbenzol	9.289	112	15
1,1,1,2-Tetrachlorethen	9.362	131	15
Ethylbenzol	9.417	91	18
m,p-Xylol	9.416	91	19
o-Xylol	10.086	91	18
Styrol	10.114	104	20
Tribrommethan	10.438	173	12
Cumol	10.439	105	20
1,1,2,2-Tetrachlorethan	10.751	83	14
1,2,3-Trichlorpropan	10.944	75	13
Brombenzol	11.096	156	14
Propylbenzol	11.163	91	20
1-Chlor-4-methylbenzol	11.337	126	17
1,3,5-Trimethylbenzol	11.396	105	22
1-Chlor-2-methylbenzol	11.414	126	17
tert Butylbenzol	11.914	119	20
1,2,4-Trimethylbenzol	11.958	105	21
sec Butylbenzol	12.269	105	21
p-Isopropyltoluol	12.515	119	23
1,3-Dichlorbenzol	12.690	146	14
1,4-Dichlorbenzol	12.526	146	15
n-Butylbenzol	13.344	91	23
1,2-Dichlorbenzol	13.190	146	14
1,2-Dibrom-3-chlorpropan	14.109	157	12
1,2,4-Trichlorbenzol	14.975	180	14
Hexachlorbutadien	15.142	225	16
Naphthalin	15.143	128	16
1,2,3-Trichlorbenzol	15.355	180	14

*HS = headspace; *See below for additional sensitivity gain of this compound.

SPDE

ADVANCED SPDE ALLOWS SPLITLESS INJECTION EVEN FOR HIGHLY VOLATILES (VINYL CHLORIDE)

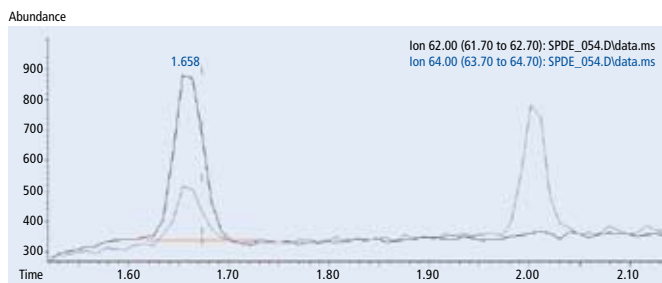
By adding a cold trap to the SPDE system we are able to obtain good peak shape even in splitless injection mode. Picture 2 shows some results of advanced SPDE: Comparing bottom and top trace, you'll realize the excellent peak shape for Vinyl chloride in the top trace. This advanced SPDE mode gives an additional sensitivity gain for the highly volatile compounds marked in table 1.



Picture 2: Vinyl chloride in advanced SPDE mode (top) versus standard headspace (bottom). Note that the SPDE (top) trace derived from a 100 fold lower standard (0.01 µg/l = 10 ng/l).

HOW LOW CAN WE GO?

By adding a cold trap to the SPDE system we will obtain excellent peak shapes even in splitless injection mode of headspace compounds. Comparing picture 2 bottom and top you'll realize the difference in concentration. The upper trace derived from 10 ng/l Vinyl chloride. Picture 3 shows 4 ng/l Vinyl chloride. Obviously there is enough sensitivity to enter the region of 1 ng/l and below. The advanced SPDE method has the potential to enter the pg/l range by a negligible extension of the extraction time (only 16 min in this application).



Picture 3: 4 ng/l of Vinyl chloride in advanced SPDE mode. Note that only 16 minutes extraction time was used. Further extension of the extraction time will allow you to enter the sub-ng/l range.

Method Setup for SPDE and Headspace extraction procedure

Agilent GC-MSD 7890A/5975C is combined with CTC Combi PALxt equipped with CHROMTECH SPDE Option with Extraction Cooler and GC cold trap

Column	Restek RTX Volatiles 30 m x 250 µm x 1 µm. Flow 1.6 ml/min
Oven	40°C (3 min), 15°C/min > 65°C (0 min); 10°C/min > 132°C (1 min); 25°C/min > 170°C (0 min); 35°C/min > 250°C (0 min)
Injector	250°C, Split see below; Septum Purge 3 ml/min
MS Parameters	Interface: 270°C, SIM groups for the EPA 524 compounds
PAL Settings	2.5 ml HS Syringe: max speed: 2 ml/sec and min volume: 50 µl

SPDE Parameters

SPDE Needle Temperature	- 25°C
Pre Incubation Time	3 min
Syringe Temperature	35°C
Incubation Temperature	45°C
Extraction Stroke Speed	30 µl/sec
Extraction Strokes	15
Pullup Delay	5 sec
Desorption Volume	100 µl
Pre Desorption Time	0 sec
Desorption Flow Speed	100 µl/sec
GC 7890A Split Injector	split 3:1

Headspace Parameters

Incubation Temperature	75°C
Incubation Time	15 min
Syringe Temperature	110°C
Agitator Speed	500 rpm
Fill Speed	1.000 µl/sec
Fill Strokes	0
Pullup Delay	1.000 ms
Injection Speed	800 µl/sec
Pre Inject Delay	0 sec
Post Inject Delay	0 sec
Flush Time	2 min
GC Runtime	60 sec

Advanced SPDE (with Cold Trap)

GC Trap Column	30 cm, 0.530 mm i.d., 2.4 µm film DB5 column
GC Trap Temperature	- 55°C for 40 sec, then start GC and heat up to 250°C
GC 7890A Split/splitless Injector	splitless time 0.01 min (results in splitless time of 40.01 sec)