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Fast GCMS Analysis of 60 VOC Compounds Using Headspace-Trap Sampling

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Introduction

The analysis of EPA624 regulated volatile organic compounds in drinking and waste water is usually done with headspace or purge and trap technique using a so called 624 phase with 30 m, 0.25 mm, 1.4 µm according to the EPA method 624. Reducing analysis time (fast GC) but maintaining chromatographic resolution has been successfully applied using narrow bore columns in various fields. In Headspace analysis the transfer of sample from the insert to the column is quite slow as normally small split ratios are used in favour of sensitivity which has been in contradiction to fast GC approaches. This paper deals with fast GC approach in combination with Headspace sampling. Helium and Hydrogen was used as carrier gas.

Experiments

A cold trap (cryofocus, Atas GL The Netherland) was mounted here at the top of the column directly under the injector cooling (direct LN2).The first part of the column was cooled in order to refocus the volatile organic compounds (VOC). The trap cooling was done by a flow of liquid nitrogen from a pressurised LN2 dewar. The maximum heating rate of this trap was 50°C/sec. The column used was a RTX-624 20 m, 0.18 mm, 1 µm. Figure 1 shows a Chromatogram (MS:SIM) of 60 VOC (table 1) compounds with Helium as carrier gas.

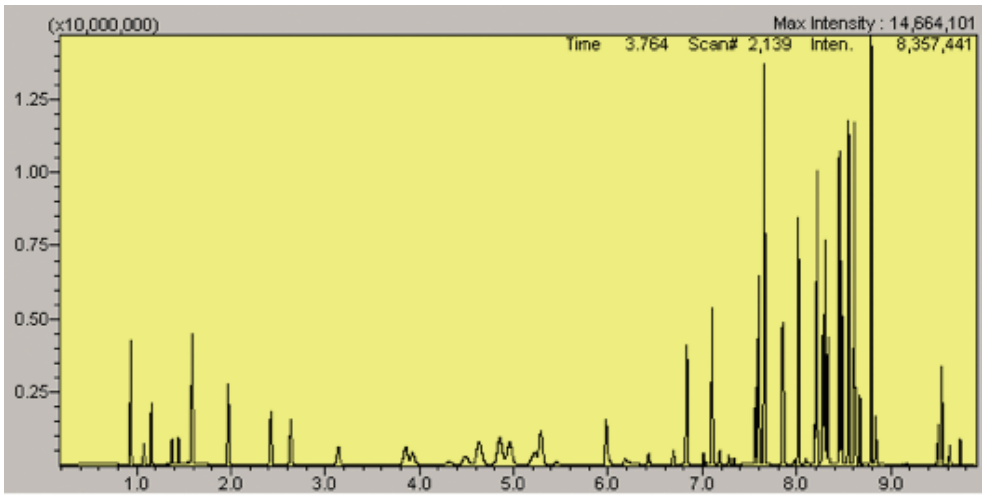

Fig. 1 Chromatogram (SIM) of 60 volatile compounds.

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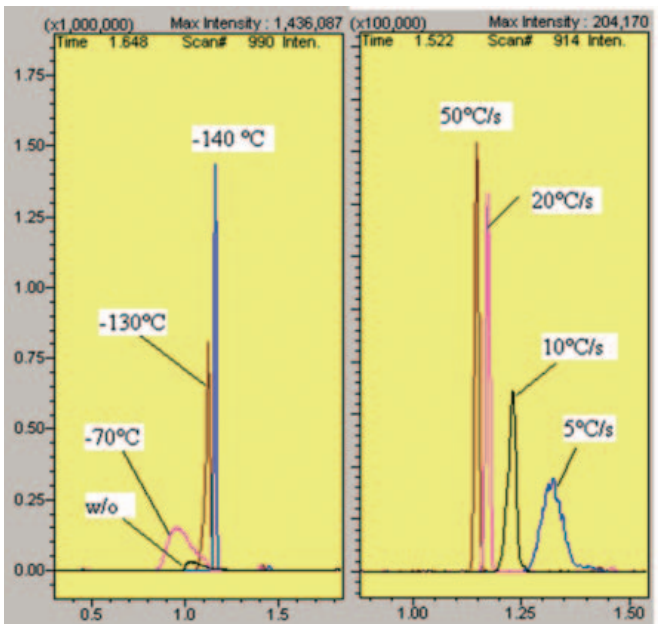
The water samples (5 mL) were placed into 20 mL headspace vials. The sample volume injected was 1 mL (AOC-5000 Plus, GCMS-QP2010 Ultra. The split ratio was 5:1 and the linear velocity was set to 45 cm/sec (He). The GC oven temperature started at 40°C, 5 min and then ramped with 50°C/min to 120°C, 30°C/min to 170°C, 60°C/min to 220°C. Different cold trap temperatures were selected. Fig. 2 shows peak profiles of vinyl chloride at different Trap cold/heating rate temperatures.



ID#	Name	Ret. Time	ID#	Name	Ret. Time
1	Dichlorodifluoromethane	0.945	31	1,2-Dicbromomethane	7.319
2	Chlormethane	1.077	32	Chlorobenzene	7.547
3	Vinyl Chloride	1.156	33	Ethylbenzene	7.582
4	Bromomethane	1.375	34	1,1,1,2-Tetrachloroethane	7.586
5	Chloromethane	1.443	35	p-Xylene	7.639
6	Trichlorofluoromethane	1.587	36	m-Xylene	7.639
7	1,1-Dichloroethene	1.970	37	O-Xylene	7.835
8	Methylene chloride	2.432	38	Styrene	7.849
9	Trans-1,2-Dichloroethane	2.645	39	Tribromomethane	7.957
10	1,1-Dichloroethane	3.163	40	Isopropylbenzene	8.002
11	2,2-Dichloropropane	3.890	41	Bromobenzene	8.177
12	Cis-1,2-Dichlorethen	3.967	42	1,1,2,2-Tetrachloroethane	8.186
13	Bromochloromethane	4.346	43	1,1,3-Trichloropropane	8.216
14	Trichloromethane	4.521	44	n-Propylbenzene	8.200
15	1,1,1-Trichloromethane	4.683	45	2-Chlorotoluene	8.262
16	Tetrachloromethane	4.900	46	1,3,5-Trimethylbenzene	8.286
17	1,1-Dichloropropene	5.005	47	4-Chlorotoluene	8.319
18	Benzene	5.313	48	Tert-Butylbenzene	8.438
19	1,2-Dichlorethan	5.475	49	1,2,4-Trimethylbenzene	8.466
20	Trichloroethene	6.000	50	Sec-Butylbenzen	8.538
21	1,2-Dichloropropane	6.197	51	4-Isopropyltoluene	8.599
22	Dibromomethane	6.284	52	1,3-Dichlorobenzene	8.616
23	Bromodichloromethane	6.414	53	1,4-Dichlorobenzene	8.658
24	Cis-1,3-Dichloropropene	6.675	54	n-Butylbenzene	8.780
25	Toluene	6.813	55	1,2-Dichlorobenzene	8.825
26	Trans-1,3-Dichloropropene	6.992	56	1,2-Dibromo-3-chloropropane	9.159
27	Tetrachloroethene	7.084	57	1,2,4-Trichlorobenzene	9.489
28	1,1,2-Trichloroethane	7.084	58	1,1,2,3,4,4-Hexachloro-1,3-b	9.532
29	1,3-Dichloropropane	7.165	59	Naphthalene	9.612
30	Dibromochloromethane	7.260	60	1,2,3-trichlorobenzene	9.724

Fig. 2 (incl. table 1 with 60 compounds)
(left): Peak of *m/z* 62 (vinyl chloride) for different cryofocus temperatures (without cryofocus, -70, -130 and -140°C)
(right): Peak of *m/z* 62 for different heating rates of the cryofocus after refocusing

The LOD for Benzene and vinyl chloride for example turned out to be below 0.005 µg/L and 0.001 µg/L, respectively. In figure 3 tetrachloroethene and 1,1,2 trichloroethane are shown recorded with a sample taken from Rhine river.

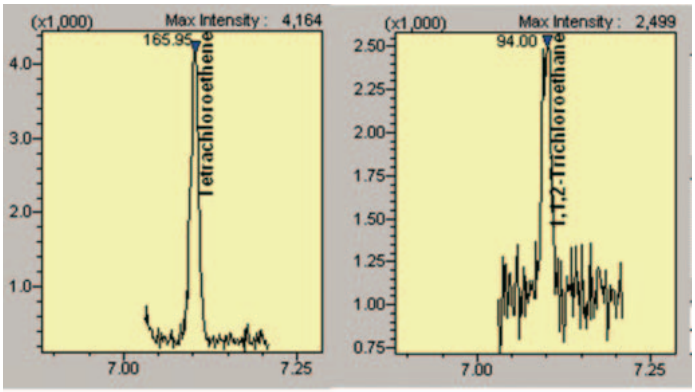


Fig. 3 Peaks of tetrachloroethene and 1,1,2 trichloroethane measured for a water sample taken from the Rhine River (0.02 µg/L).

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A comparison was done between He and H_2 as carrier gas. Figure 4 shows the mass trace 62 (vinyl chloride) for He (45 cm/s) and H_2 (65 cm/s). The retention time of that compound is observed at 1.1 min (He) and 0.82 min (H_2), respectively.

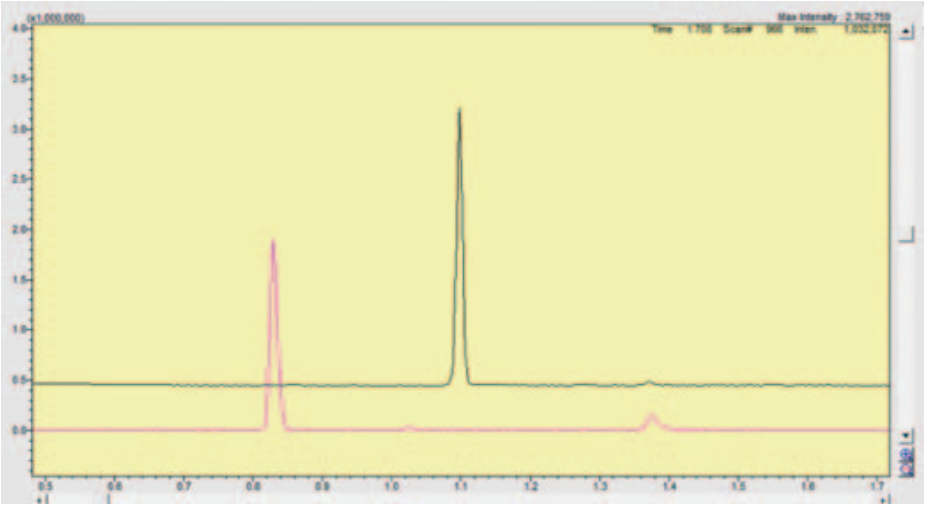

Fig. 4 *m/z* = 62 (vinyl chloride) with carrier gas He (45 cm/s, black) and H_2 (65 cm/s, purple).

A decrease in intensity is observed when using Hydrogen compared to He. Table 1 shows the difference in response for selected compounds at a concentration of 10 µg/L.

Table 2 Average signal to noise (5 injections each) of selected compounds with He and H_2 as carrier gas

	S/N		
	He	H_2	H_2/He
Vinyl Chloride	7394	5022	0,68
Chloromethane	1872	850	0,45
1,3,5-Trimethylbenzene	5781	1496	0,26
1,2,4-Trichlorobenzene	2587	735	0,28

Conclusions

Fast GC with headspace sampling can be performed when using a cold trap to refocus target compound molecules at the top of the column. Temperatures down to -140°C were necessary for volatile compounds like vinyl chloride. In order to release the refocused compounds from the trap a high trap ramp rate has to be used (50°C/sec). Hydrogen as carrier gas can be used in GCMS analysis however the sensitivity is reduced compound dependent.

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