FAST ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOC) IN WATER WITH HEADSPACE – CRYOFOCUS GCMS

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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.

Experiments

A cold trap (cryofocus, ATASGL The Netherland) was mounted here at the top of the column directly under the injector cooling (direct LN2) the first part of the column 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.

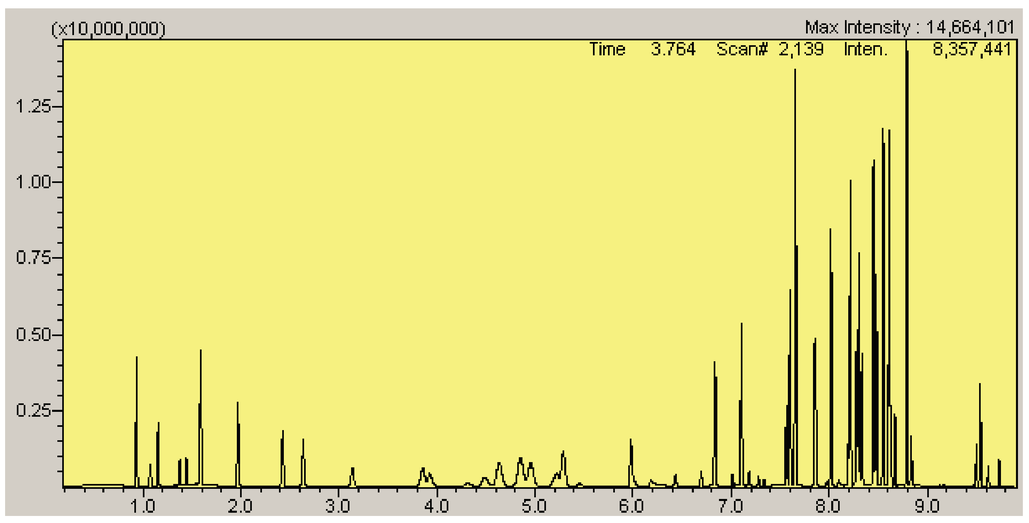
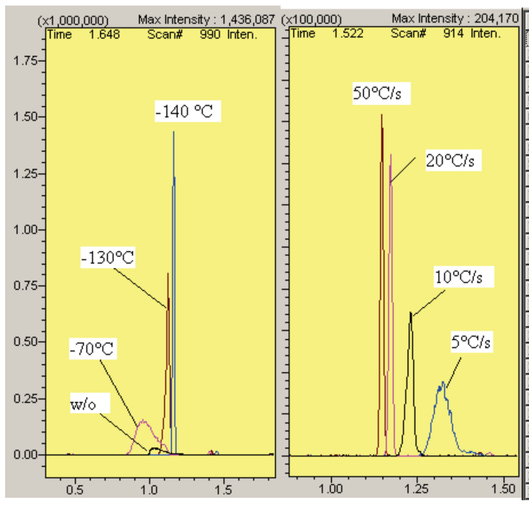


Figure 1: Chromatogram (SIM) of 60 volatile compounds

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. 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. Figure 2 shows peak profiles of vinyl chloride at different Trap cold/heating rate temperatures.



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

Figure 2 (incl. table 1 with 60 compounds)
(left): Peak of m/z 62 (vinyl chloride) for different cryofocus temperatures (without cryofocus , -20, -70, -130 and -140 ºC)
(right): Peak of m/z 62 for different heating rates of the cryofocus after refocusing

The LOD for Benzene and vinyl chloride turned out to be below 0.005 µg/L and 0.001 µg/L, respectively. Figure 3 shows calibration curves between 0.001 and 1 µg/L. In figure 4 tetrachloroethene and 1,1,2 trichloroethane is shown recorded with a sample taken from Rhine river.

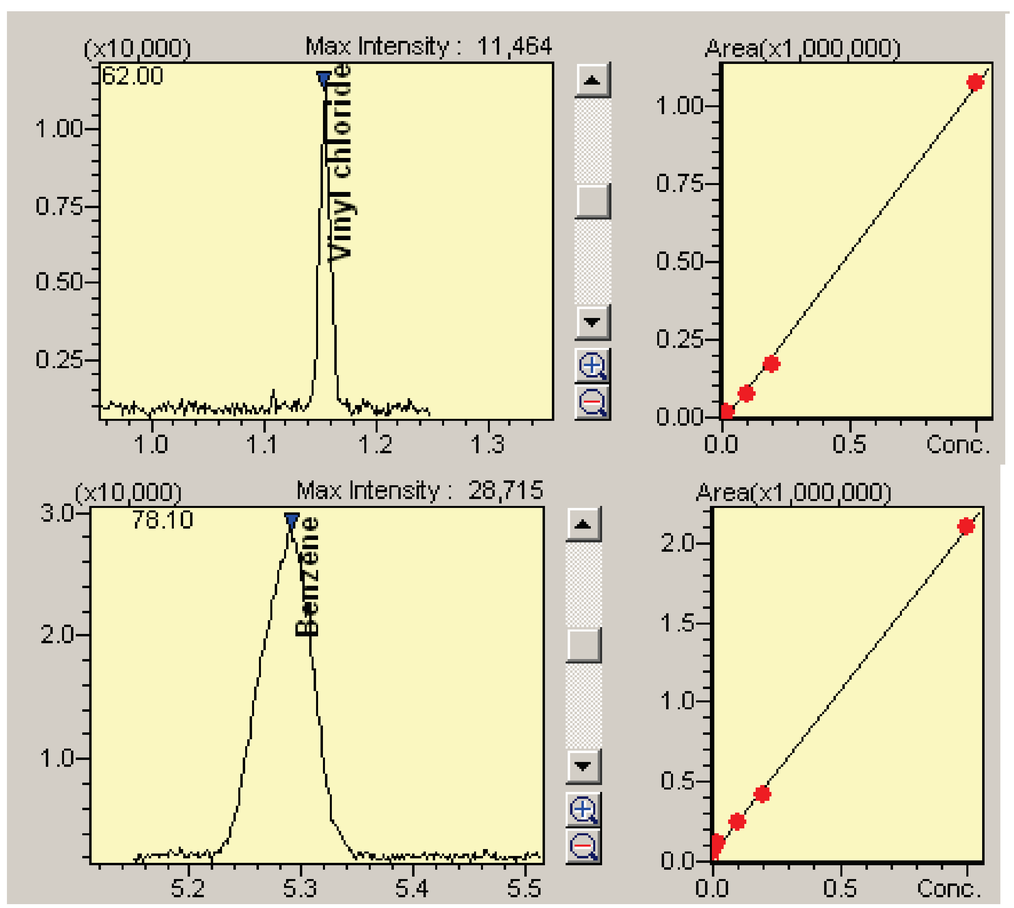


Figure 3: Calibration curves for benzene and vinylchloride. Calibration range 0.001-1 µg/L. LOQ vinyl chloride and Benzene 0.001 µg/L and 0.005 µg/L, respectively

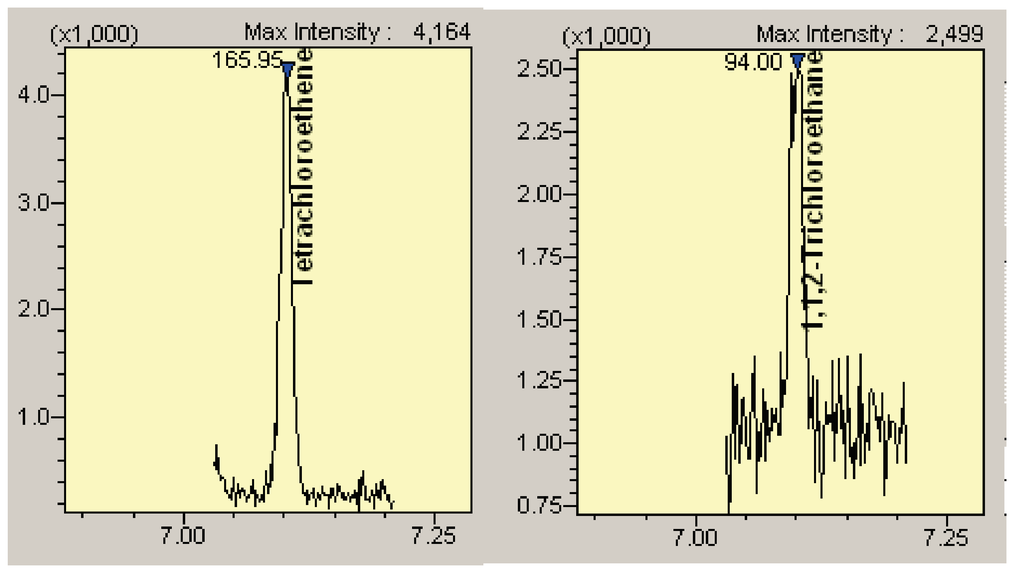


Figure 4: Peaks of tetrachloroethene and 1,1,2 trichloroethane measured for a water sample taken from the Rhine River (0.02 µg/L)

Conclusion

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).

The precision of the method is indicated by high regression coefficient of the calibration curves. Run time and limit of detection has been drastically reduced.

The peak widths specially for the early elution peaks were drastically reduced using the cryofocus which leads to decreased limits of detection far below European drinking water regulations.