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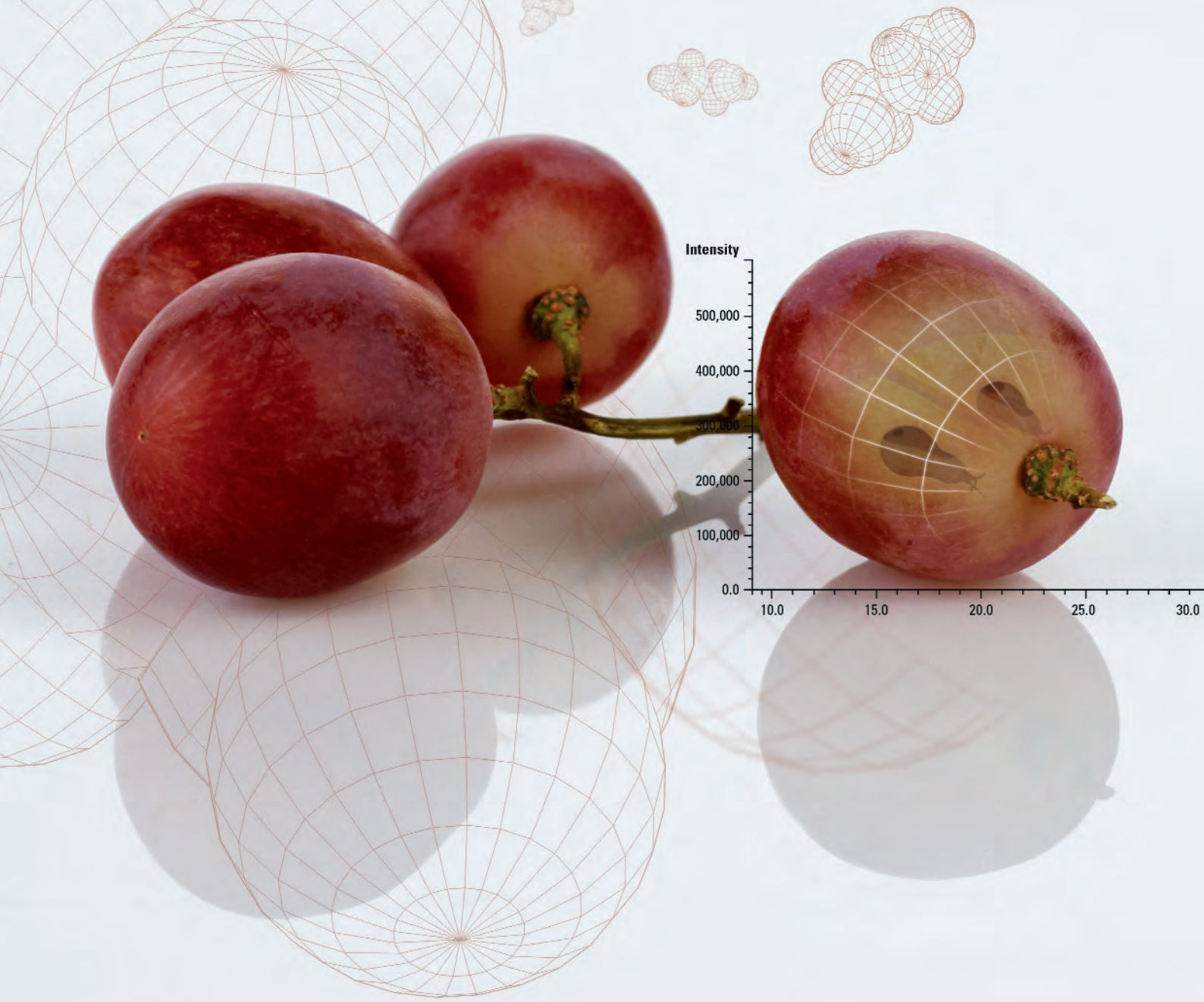
NEWS



Individually dosed – Therapeutic drug monitoring with LC/MS/MS

Bread packaging – What's hidden in plastic bread packaging?

Hair in your soup? Microchip electrophoresis can help

Acid Test – TOC determination in concentrated hydrochloric acid

2/2012

Headspace-Cold Trap Samp

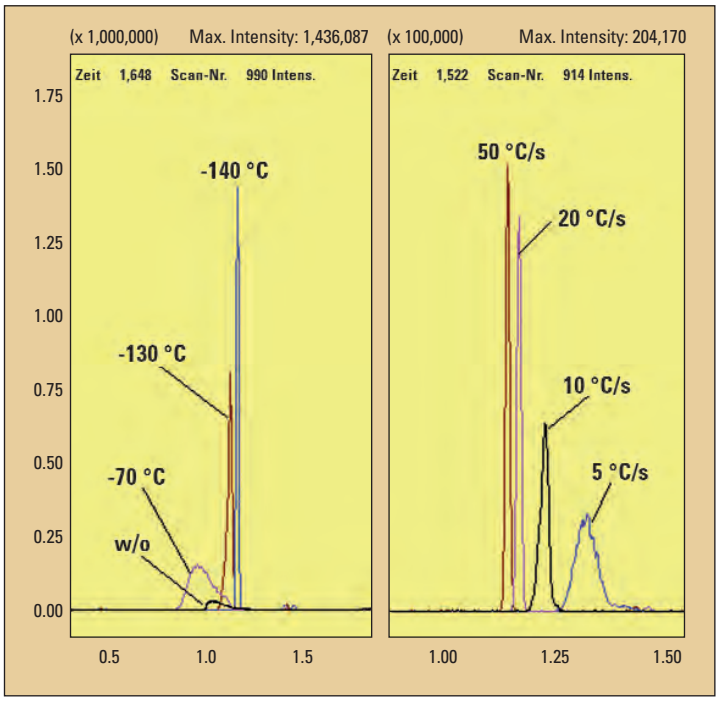


Figure 1: Left: Peak of m/z = 62 (vinyl chloride) for different cryofocus temperatures (without cryofocus, -20 °C, -70 °C, -130 °C and -140 °C). Right: Peak of m/z = 62 for different heating rates of the cryofocus after refocusing.

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Analysis of EPA624 regulated volatile organic compounds in drinking and wastewater is usually performed with headspace or purge and trap technique using a so-called 624 phase with 30 m, 0.25 mm and 1.4 µm. Reducing analysis time (fast GC) but maintaining chromatographic resolution has been applied successfully using narrow bore columns in various fields. However, the reported results were based mainly on liquid injection techniques.

In headspace analysis the transfer of sample from the insert to the column is quite slow as small split ratios are normally used in favor of sensitivity. The spatial distribution of analyte molecules in the glass insert cannot therefore be refocused easily, and fast GC approaches are difficult. A cold trap (cryofocus, ATASGL, The Netherlands) was therefore mounted at the top of the column directly under the injector, cooling the first part of the column in order to refocus volatile compounds showing a broad band during passage through the injector liner. The cooling was established by direct transfer of liquid nitrogen to the trap.

Instrumentation used was a Shimadzu GCMS-QP2010 Ultra with an AOC-5000 Plus headspace sampler. As the column is surrounded by the directly cooled cryofocus, refocusing takes place inside the column. In this study, the inner diameter of the chosen column was 0.18 mm. Length and film thickness were 20 m and 1 µm respectively. Split ratio was 5:1 and the linear velocity was

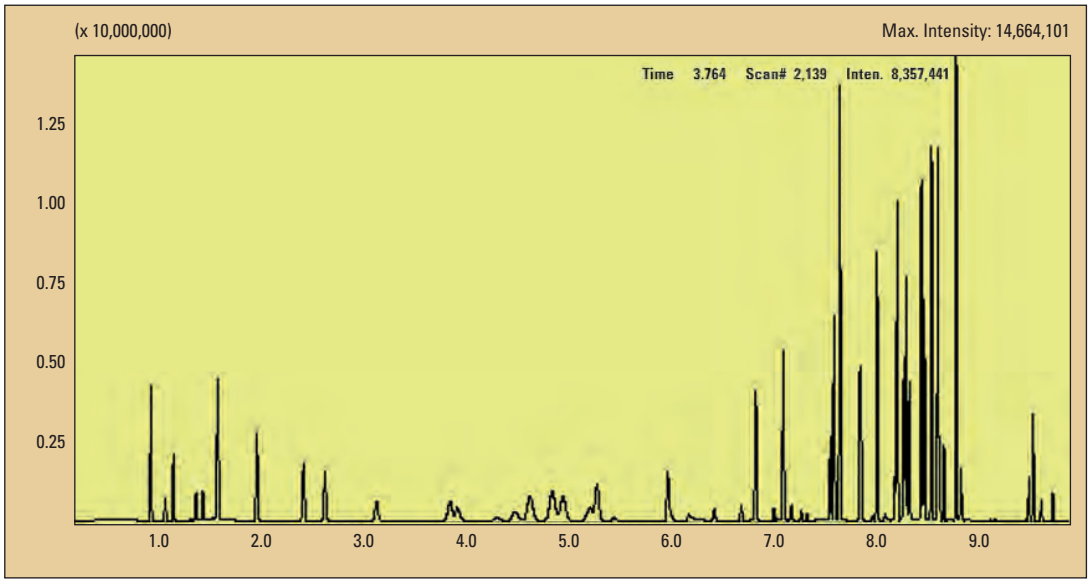

Figure 2: Full scan chromatogram (TIC) of 60 volatile compounds

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Fast GCMS analysis of VOCs in water

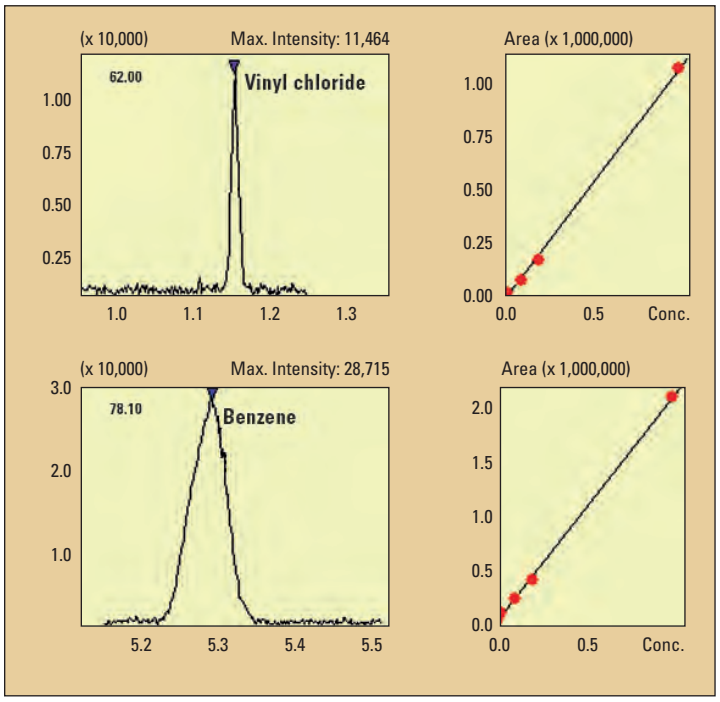

Figure 3: Calibration curves for benzene and vinylchloride

set to 45 cm/s. The GC oven temperature began at 40 °C for 5 min and then ramped with 50 °C/min to 120 °C, 30 °C/min to 170 °C, 60 °C/min to 220 °C. Injection volume was 1 mL headspace from a 20 mL vial filled with 5 mL water matrix. Different cold trap temperatures were set. The mass spectrometer was operated in scan and selected ion monitoring (SIM) mode for highly sensitive analysis.

Good peak shapes at 50 °C/s

Figure 1 (left) shows the m/z 62 relative to vinyl chloride for different cryofocus temperatures. The largest effect of refocusing monitored by measuring the peak profile at the end of the column in the mass spectrometric detector was observed at -140 °C cold trap temperature and subsequent heating to 250 °C at a rate of 50 °C/s. Figure 1 (right) shows the influence of different heating rates for vinyl chloride indicating that 50 °C/s ensures that the releasing process is fast enough to obtain good peak shapes. The peakwidth at half maximum is 8 sec and 0.5 sec for cryofocus temperatures of 0 °C and -140 °C, respectively. The peak height is increased drastically, with considerable improvement to the limit of detection (LOD). The complete chromatogram is shown in figure 2 and the compounds are listed in table 1.

Analysis within ten minutes

Analysis time for 60 volatile compounds was less than ten minutes. Calibration was performed between 0.001 and 1 µg/L. The regression coefficient R showed values of better than 0.998 for all compounds, indicating the high method precision. Two curves are shown in figure 3.

The LOD for benzene and vinyl chloride was determined as 0.005 µg/L and 0.001 µg/L respectively. In figure 4, the selected ion mass traces for tetrachloroethene and 1,1,2-trichloroethane of a real sample (the Rhine River water) is shown. Both concentrations were determined as 0.02 µg/L.

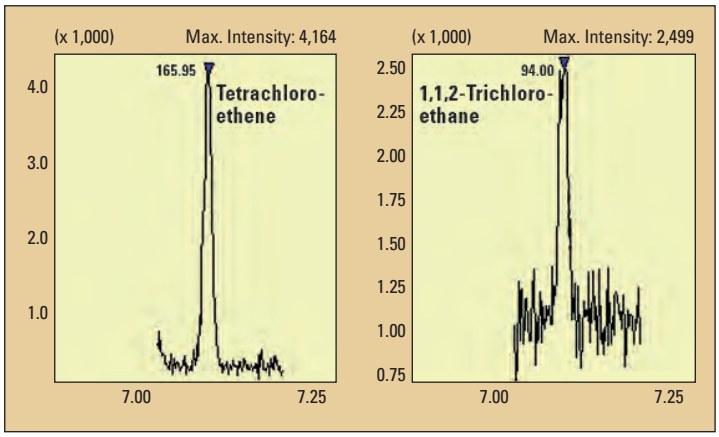

Figure 4: Peaks of tetrachloroethene and 1,1,2-trichloroethane measured for a water sample taken from the Rhine River

ID#	Name	Ret.Time	ID#	Name	Ret.Time
1	Dichlorodifluoromethane	0.945	31	1,2-Dibromoethane	7.319
2	Chloromethane	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	Chloroethane	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-Dichloroethene	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	1,2,3-Trichloropropane	8.216
14	Trichloromethane	4.521	44	n-Propylbenzene	8.200
15	1,1,1-Trichloroethane	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

Table 1: List of volatile compounds and retention times in minutes