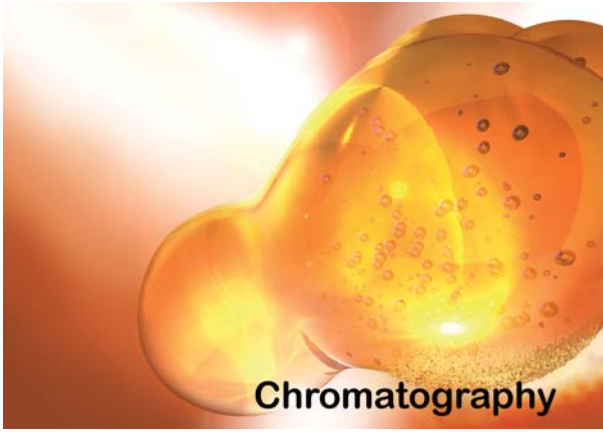
Application Note



Determination of Organic Volatiles in Water by Headspace GCMS

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Introduction

The static headspace technique was applied to analyse organic volatiles in wastewater. Traditionally the dynamic headspace technique (purge and trap) is used for this application. This technique however suffers from several disadvantages. First of all in the purge and trap technique several switching valves are used. These valves are typical spots where adsorption of analytes can occur. Furthermore decomposition of the trapping materials during thermal desorption can lead to ghost peaks and wrong results. Especially in the case of Tenax, this can give to high values in the determination of Benzaldehyde. The heated sample transfer-line, from purge and trap to GC, is very fragile and difficult to replace.
The slow thermal desorption step always makes it necessary to include a cryo focussing step prior to sample injection on to an analytical separation column.
All these disadvantages are history when the headspace technique is used. No switching valves, no adsorption material degradation peaks and, when the sample volume is accurately chosen, no cryo focussing is needed.
A fast method development was carried out to determine the rough detection limits and the linearity for this analysis.

Instrument Set-up

In this method a QP-5050A Gas Chromatograph Mass Spectrometer was used equipped with an OCI-17 Multipurpose Programmable Temperature Vaporisation injector. The Headspace pre-treatment part was done using a AOC-5000-HS. This

includes a heated sample incubator and a heated headspace syringe.

Materials

1 % (= 10000 ppm) stock solution (concentration of each volatile is about 1 % in methanol w/v):

- Trichloromethane: 1.0744 g
- Trichloroethane: 1.2001 g
- Dichloroethane 1,2: 1.0122 g
- Trichloroethene: 1.0627 g
- Toluene: 1.1087 g
- Tetrachloroethene : 1.2271 g
- Ethylbenzene: 1.1948 g
- Xylene m: 1.1748 g
- Xylene o: 1.0601 g
- Xylene p: 1.0781 g
- Methanol: 69.4760 g (density = 0.8 g/ml)
- Total: 100 ml

Calibration samples

- 10000 ppm standard: stock solution
- 100 ppm standard: 1 ml stock solution in 100 ml methanol
- 1 ppm (1000 ppb) standard: 1 ml 100 ppm standard in 100 ml water (milli Q or Spa blauw)
- 10 ppb (10000 ppt) standard: 1 ml 1 ppm standard in 100 ml water
- 400 ppt standard: 4 ml 10 ppb standard in 100 ml water
- 100 ppt standard: 1 ml 10 ppb standard in 100 ml water

To prepare those standards very clean glassware is needed.

Method description

Sample preparation:
A 10 g water sample is weight in a 20 ml headspace vial. 5 g NaCl is added to the same headspace vial. The vial is closed and the sample is shaked well manually.

Injection:
The headspace vial is heated for 10 minutes at 60 °C in the headspace autosampler oven. 1000 µl from this gaseous phase is injected into the GC-MS system (injection speed = 500 µl/s). Needle temperature = 120 °C.

Equipment:
- Autosampler: AOC-5000 for liquid- and headspace injection
- GCMS: Shimadzu QP-5050A GCMS (with EI)
- Column: WCOT Fused silica 30m x 0.25mm ID, coating CP-Sil 8CB low bleed / MS Df = 0.25 µm

Chromatographic conditions:
- (PTV) injector temperature: 300 °C isothermal
- Column oven: initial 40 °C for 3 minutes, 20 °C/min to 100 °C (kept for 5 minutes)
- Carrier gas (helium) flow: 1 ml/min, constant flow
- Split: 1:14

Con Centration (ppt)		Tri chloro methane	Tri chloro ethane	Di Chloro ethane 1,2	Tri Chloro ethene	Toluene	Tetra Chloro ethene	Ethyl benzene	m,p-Xylene	o-Xylene
	Rt (min)	2.55	2.78	2.89	3.53	4.53	5.1	5.84	5.95	6.25
400		111	57	139	437	419	59	443	736	425
400		111	66	135	419	397	59	418	731	408
10000		2981	2001	3349	1645	10193	1387	11799	18933	10045
10000		2686	1799	3006	1496	9211	1268	10601	16976	8970
10000		2859	1927	2963	1572	9860	1339	11388	18373	9677
1000000		294144	229677	294887	141219	1086932	165951	1300519	2055209	1040329
1000000		293584	229513	293524	140988	1082946	163924	1286052	2031151	1026856
1000000		284820	225995	296577	137616	1060242	160958	1261651	1994012	1007568

Table 1: Areas (headspace GC-MS) for the different volatiles in water standards

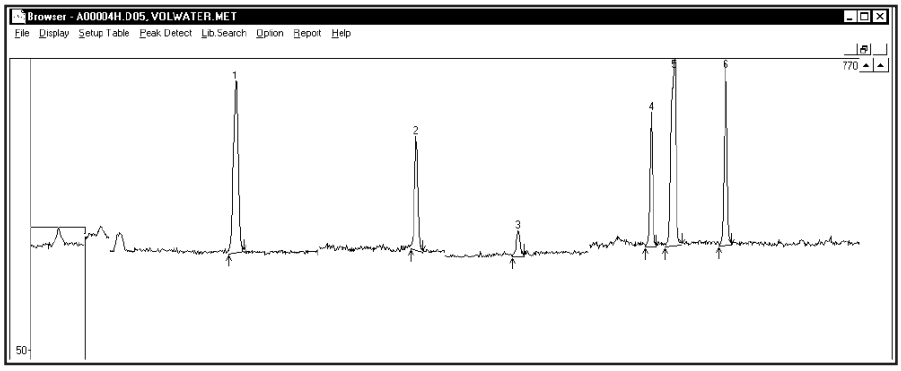

Figure 1: Chromatogram of the 100 ppt volatiles standard (1: Trichloroethene, 2: Toluene, 3: Tetrachloroethene, 4: Ethylbenzene, 5: m,p-Xylene, 6: o-Xylene).

Results

For 400 to 1000000 ppt the calibration curves for the volatiles in water are linear. For the lower concentrations a separate standard series needs to be made. Regression coefficients are still in the range of 0.999. The chromatogram of 100 ppt volatiles in water standard is included. (Signal to Noise calculations were performed for Toluene (m/z = 91), sample 100 ppt, and this was 30. The minimal detection limit is 10 ppt.

Conclusions

The static headspace is a good alternative as a sample introduction technique for the analysis of volatiles in water. Especially for the more 'heavy' compounds (from toluene onwards) detection limits of 10 - 100 ppt can easily be achieved. The developed analytical method is linear from 100 to 1000000 ppt (toluene)! The S/N ratio for 100 ppt toluene was 30. The minimal detection limit is 10 ppt.
For aromatic compounds like toluene up to naphthalene further optimisation efforts (e.g. sample amount, splitless injection, injection with high pressure pulsation) will have a good chance to be successful in increasing the linearity and optimising the detection limit.

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