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Chromatography Technical Note No AS99

Parts per trillion determination of volatile organic compounds in water using automated headspace extraction with the Gerstel MPS and CTS-2 cryofocusing unit on an Agilent GC-MS

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Introduction

Static headspace extraction with gas chromatography-mass spectrometry (HS-GC/MS) is an established technique for the determination of volatile organic compounds (VOCs) in drinking water and waste water. Analysis in the concentration range 1 to 100 µg/L is well established. However, it might not deliver sufficient sensitivity at sub µg/L levels (i.e. parts per trillion) particularly for gases such as dichlorofluoromethane and vinyl chloride. This is often because the gases are not adequately trapped/refocused at the head of the analytical column at ambient temperatures.

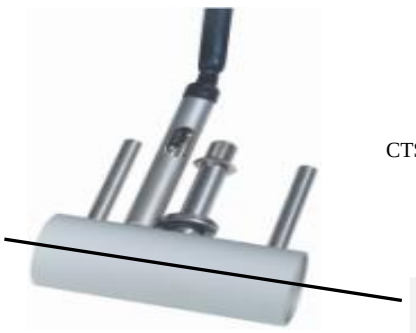
Cryogenic cooling focuses volatile compounds in a tight band at the front of the capillary column. This concentration technique is more common with purge and trap methods than with headspace extraction.

This application note describes the use of a Gerstel MPS with CryoTrapSystem (CTS2) to improve headspace method sensitivity. The solution is fully automated using the MPS. By refocusing the headspace extract, it is possible to improve sensitivity without loss of peak shape. Limits of detection are in the order of 0.01 µg/L (10 parts per trillion) for the compounds listed opposite, including some difficult to analyse compounds such as gases and petroleum additives (oxygenates).

This solution delivers a method with high sensitivity and a good dynamic range. It will be of interest to water, environmental and food laboratories to enhance their capability to meet legislative demands and to satisfy customers who need much lower detection limits than those generally in use.

Instrumentation

GERSTEL Multi-Purpose Sampler (MPS 2XL) Prepstation configured for headspace analysis with 2.5 ml gastight syringe.
GERSTEL MAESTRO software
GERSTEL CryoTrapSystem (CTS2)
Pictured below: combines a cooling and heating unit for liquid nitrogen cryogenic trapping and subsequent thermal desorption. The capillary column is inserted through the CTS2 and it does not need to be removed or reconfigured when cryofocusing is not needed



GERSTEL Controller C506
Liquid nitrogen adaptor
Self-pressurising liquid nitrogen dewar
Agilent 7980N Gas Chromatography with 5975C inertXL MSD.
Agilent ChemsStation
Anatune XLR8R
Anatune cooling accessory

Compound List

Internal Srandards

Pentaflurobenzene	1,4 Diflurobenzene
Chlorobenzene d5	1,4 Dichlorobenzene d4

System Monitoring Compounds

1,2 Dichloroethane d4	Toluene d8
4-Bromofluorobenzene	

Target Compounds

Dichlorofluoromethane	1,3 Dichloropropane
Chloromethane	Dibromochloromethane
Vinyl chloride	1,2 Dibromoethane
Bromomethane	Chlorobenzene
Chloroethane	1,1,2,2 Tetrachloroethane
Trichlorofluoromethane	Ethylbenzene
1,1 Dichloroethene	M & P Xylene
Carbon disulfide	O xylene
Dichloromethane	Styrene
MTBE	Bromoform
Trans 1,2 Dichloroethene	Isopropylbenzene
1,1, Dichloroethane	1,1,2,2 Tetrachloroethane
ETBE	Bromobenzene
2,2 Dichloropropane	1,2,3 Trichloropropane
Cis 1,2 Dichloroethane	N Propylbenzene
Bromochloromethane	2 Chlorotoluene
Chloroform	3 Chlorotoluene
1,1,1 Trichloroethene	Tert Butylbenzene
Carbon Tetrachloride	1,2,4 Trimethylbenzene
1,1 Dchloropropene	Sec Butylbenzene
Benzene	1,3 Dichlorobenzene
1,2 Dichloroethane	P Isopropyltoluene
TAME	1,4 Dichlorobenzene
Trichloroethene	1,2,3 Trimethylbenzene
1,2 Dichloropropane	N Butylbenzene
Dibromomethane	1,2 Dichlorobenzene
Bromodichloromethane	1,2 Dibromo-3-chloropropane
Cis 1,3 Dichloropropene	1,3,5 Trichlorobenzene
Toluene	1,2,4 trichlorobenzene
Trans 1,3, Dichloropropene	Hexachlorobutadiene
1,1,2 Trichloroethane	Naphthalene
Tetrachloroethene	1,2,3 Trichlorobenzene

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Methodology

Crimp-capped round-edged vials were charged with a salting out agent and filled with clean water. The aqueous sample was spiked with internal standard, surrogate mixture and the target analytes in order to build a calibration from 0.01 to 10 µg/L. The vial was capped and loaded onto the MPS for incubation and sampling using the PrepAhead function prior to analysis on an Agilent 5975 MSD operating in selected ion monitoring (SIM).

A typical MPS build for analysis of 240 VOC samples is shown below. Optional automatic spiking of internal standards and surrogates can be done using the vials on the right hand side of the photograph. Note that the CTS2 is housed inside the GC oven.

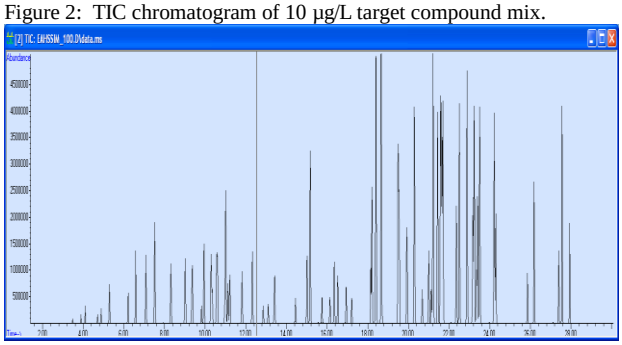
Figure 1. Typical build for MPS for analysis of 240 VOC samples with optional automatic spiking of internal standards and surrogates.

The CTS2 uses liquid nitrogen to cryogenically trap analytes at -150ºC at the head of the GC column. It could also be used to trap compounds in a precolumn or in the first column of a GC multidimensional system. When trapping is complete, accurate temperature-controlled thermal desorption ensures that the trapped analytes are introduced in a very sharp band. This provides good peak shape and improved detection limits.
For even lower detection limits multiple headspace sampling could be used.

Results

A TIC chromatogram of the 10 µg/L calibration standard is shown.

Figure 2: TIC chromatogram of 10 µg/L target compound mix.

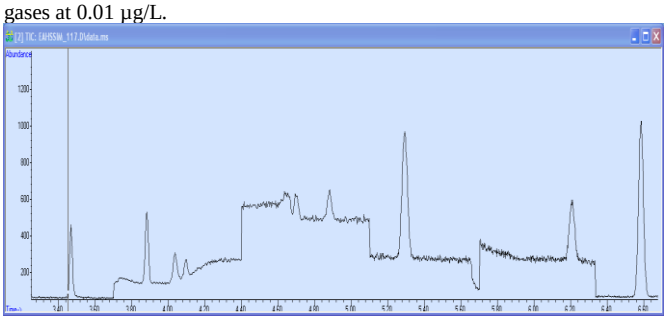


The gases can be clearly seen in the early part of the chromatogram

Figure 3 shows the TIC for the 0.01 µg/L standard. The raised baseline between about 4 and 6 minutes is due to water from the headspace sample.

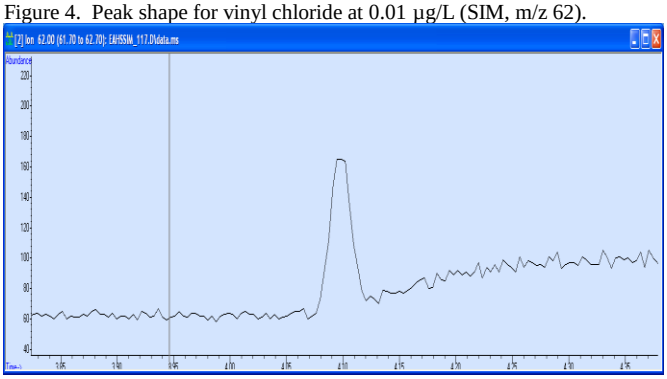
However, peak shapes for the gases are not affected significantly by the presence of water and the signal-to noise ratio even at 0.01 µg/L is greater than 40:1 for vinyl chloride.

Figure 3: SIM TIC of expanded region showing acceptable peak shape for gases at 0.01 µg/L.



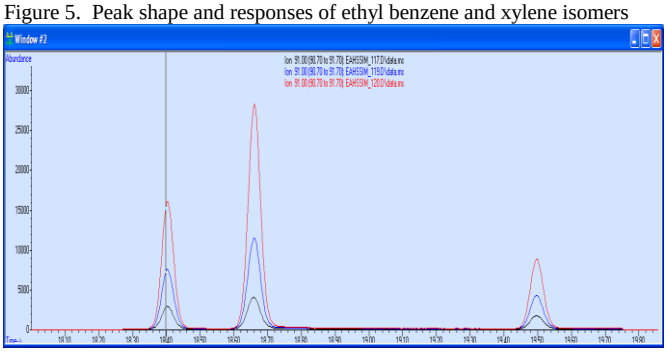
At 0.01 µg/L, peak shape for vinyl chloride using m/z 62 is good and will enable precise quantification, as seen below.

Figure 4. Peak shape for vinyl chloride at 0.01 µg/L (SIM, m/z 62).



Overlays of the extracted ions for ethyl benzene, m/p-xylene and o-xylene at concentrations of 0.01 µg/L (black), 0.05 µg/L (blue) and 0.1 µg/L (red) are shown in figure 5. Peak shape is Gaussian and response increases linearly with concentration.

Figure 5. Peak shape and responses of ethyl benzene and xylene isomers



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Figures 6, 7 & 8 show the calibration curves for vinyl chloride, methyl tert butyl ether (Mtbe) and benzene over the range 0.01 to 10 µg/L.

Figure 6. Calibration curve for vinyl chloride over range 0.01 to 10 µg/L

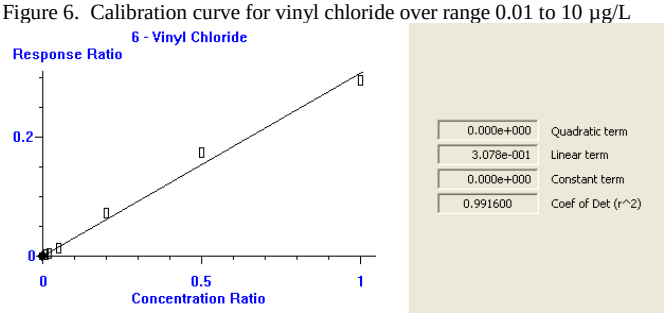


Figure 7. Calibration curve for Mtbe over range 0.01 to 10 µg/L

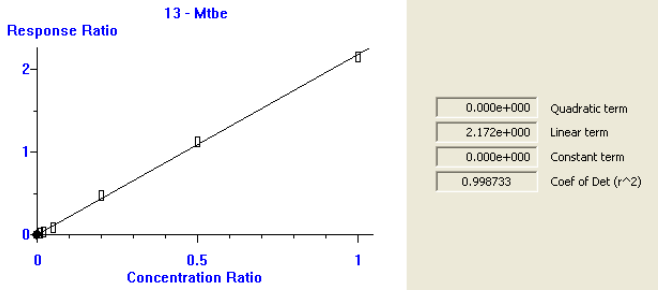
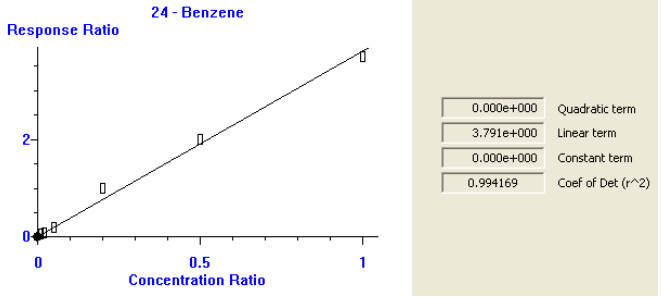


Figure 8. Calibration curve for benzene over range 0.01 to 10 µg/L



Conclusions

Quantification of low parts per trillion concentrations of VOC priority pollutants can be achieved using headspace sampling. This is accomplished by using the MPS and cryofocusing the headspace sample on the front of the analytical column using a CryoTrapSystem (CTS2).

Peak shape even at trace levels is good and quantification using selected ion monitoring (SIM) produces a linear calibration over 3-orders of magnitude.

A real benefit of the system to analytical laboratories is that the analytical column does not need to be removed from the CTS2 and its presence does not affect chromatography performance or resolution when cryogenic cooling is not needed.

References

Anatune Application Notes:
AS15: High Throughput Screening of VOCs in Wastewaters
AS17: Rapid Quantitation of VOCs in Soil & Water by HS-GC-MS
AS28: Rapid Analysis of VOCs in Soil & Water, to 1-ppb, by HS-GC-MS to MCERTS Criteria
AS33: Rapid Sub-ppb Headspace Analysis of Selected Red List Solvents & THMs in Water using the Agilent 5975 GC-MS
AS55: Automated Spiking of Internal Standards and Surrogates to build Calibration Curves using the GERSTEL MPS PrepStation
AS74: A Summary of the Anatune Environmental VOC System

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