Volatile Organic Compounds Analysis in Soils Using the Agilent 8697 Headspace Sampler

Jie Zhang
Life Science and Applied Markets Group
Agilent Technologies, Inc.
412 Yinglun Road, 200131
Shanghai, China

Agilent
Trusted Answers

Introduction

Volatile organic compounds (VOCs) are widely used in many industries as solvents or chemical intermediates. VOCs leaked or emitted into industry waste pollute the soil and sediments that the wastewater flows through. Considering that many VOCs have adverse environmental effects and soil remediation is costly, decisions regarding the significance of contamination and cleanup must be based on accurate VOC measurement. Headspace is one of the sample introduction techniques used for VOCs contamination measurement in soil and sediments. The static headspace method features easy operation and good repeatability. It allows use of an autosampler and minimizes carryover.

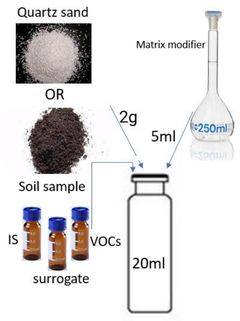
The Agilent 8697 headspace sampler communicates directly with the Agilent 8890, 8860, and Intuvo 9000 GCs. This integrated technology provides a true systems approach to GC analysis, allowing users to view status information from the headspace sampler directly on the GC interface. Integrated intelligence also allows the Agilent GC and headspace sampler to work better together for optimized sequence throughput.

In this work, VOCs in quartz sand and soil were analyzed on the 8697 headspace-8860 GC/5977B GC/MSD platform. The linearity, repeatability, method recovery and quantitation limit for 36 VOCs were evaluated to show the system's excellent performance for VOCs analysis in soil samples.

Experimental

Calibration standards and soil sample preparation

The quartz sand or soil sample was weighed and added to a 20 mL headspace filled with 5ml matrix modifier. For calibrants preparation, aliquots of VOCs standards, surrogates and IS working solutions were spiked into the modifier solution, then the vials were sealed immediately. For soil samples, only IS working solution was spiked.



Matrix modifier: organic-free water was saturated with analytical-grade sodium chloride (pH ≤2).

VOCs standard: 10mg/L of 36 VOC components in methanol.

Internal calibration standard: 50mg/L fluorobenzene, chlorobenzene-d5 , and 1,2-dichlorobenzene-d4 in methanol

Surrogates: 10mg/L toluene-d8 and 4-bromofluorobenzene in methanol.

8697 headspace-8860GC-5977B GC/MSD system

Instrumentation

The Agilent 8697 headspace sampler was connected to the Agilent 8860 GC-5977B MSD system via split/splitless inlet. MSD performance was checked by BFB standard to ensure MS data validity as required by measurement method (China HJ 642-2013 method).

Table 1. Analytical conditions of the Agilent 8697 headspace sampler / 8860-5977B GC/MSD system

Parameters	Setpoints
Inlet temperature	250^{0}C
liner	4-mm id Ultra Inert, split (p/n 5190-2295), glass wool removed
Column flow	Constant flow, 1.2ml/min
Split ratio	10:1
Oven program	40^{0}C (2min), 8^{0}C /min to 90^{0}C (4min), then 6^{0}C /min to 200^{0}C (10min)
column	J&W DB-624 GC Column, 60 m, 0.25 mm, 1.40 µm (p/n 122-1364)
MSD transfer line	230^{0}C
MS source	280^{0}C
MS Quad	150^{0}C
Gain factor	1
Draw out plate	6mm
8697A loop size	1ml
Vial pressurization gas	He
HS loop temperature	100^{0}C
HS oven temperature	80^{0}C
HS transfer line temperature	110^{0}C
Vial equilibration time	50min
Vials size	20ml, PTFE/silicone septa, (p/n 8010-0413)
Vial shaking	Level 7, 136 shakes/min with acceleration of 530 cm/ S^2
Vial fill mode	Default
Vial fill pressure	15psi
Loop fill mode	Custom
Loop ramp rate	20psi/min
Loop final pressure	9psi
Loop equilibration time	0.1min
Carrier control mode	GC carrier control
Vent after extraction	On

Table 2. MSD tune result conformity assessment

Target Mass	Rel To Mass	Lower Limit %	Upper Limit %	Rel. Abn %	Raw Abn	Pass/Fail
95	95	100	100	100	96889	Pass
96	95	5	9	7.3	7109	Pass
173	174	--	2	0	0	Pass
174	95	50	--	64.3	62325	Pass
175	174	5	9	7.4	4612	Pass
176	174	95	105	96.3	60018	Pass
177	176	5	10	6.6	3981	Pass

Chromatograms---acquired in selected ion monitoring (SIM) mode.

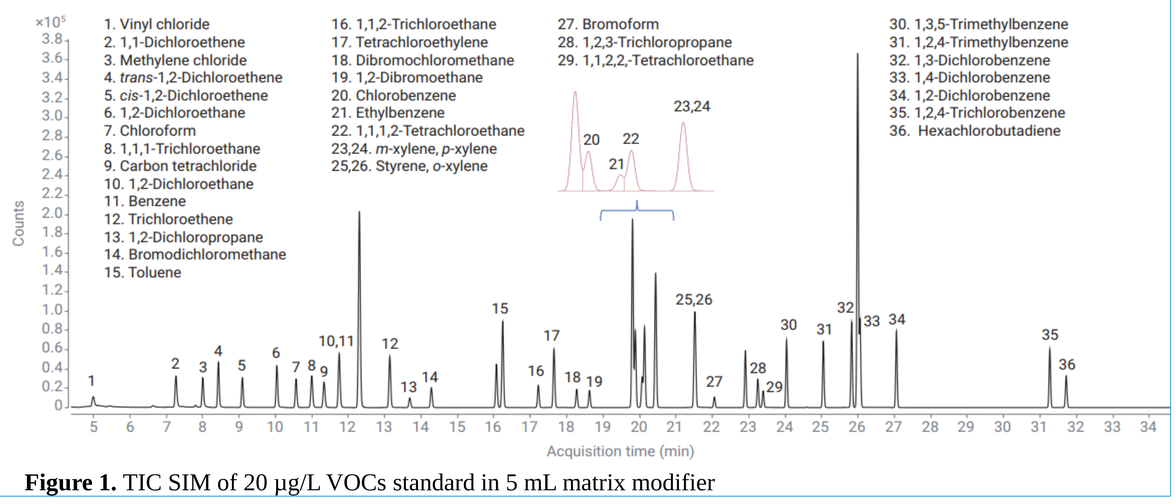


Figure 1. TIC SIM of 20 µg/L VOCs standard in 5 mL matrix modifier

Instrument performance

- The instrument repeatability was verified based on response precision of 20 µg/L calibrants in six vials. (Figure 2)
- System linearity performance was verified based on analytes relative response factors. All tested components showed good linearity in the range of 4 to 100 µg/L with correlation coefficients (R^2) better than 0.996. (Figure 3)
- The method recovery was evaluated on 2g of real soil samples spiked with 20 and 50 µL 10 mg/L calibration standards (corresponding to 50 and 125 µg/kg VOCs in soil sample). (Figure 4 and Figure 5)
- The instrument detection limits (IDL) for 36 targeted VOCs and two surrogates were calculated based on quantitation precision of 4 µg/L standards in eight vials. Method LOD and LOQ (in the unit of µg/kg) in blank quartz sand were calculated based on IDLs. They were in the range of 0.51 to 1.21 µg/kg and 1.7 to 4.1 µg/kg, respectively.

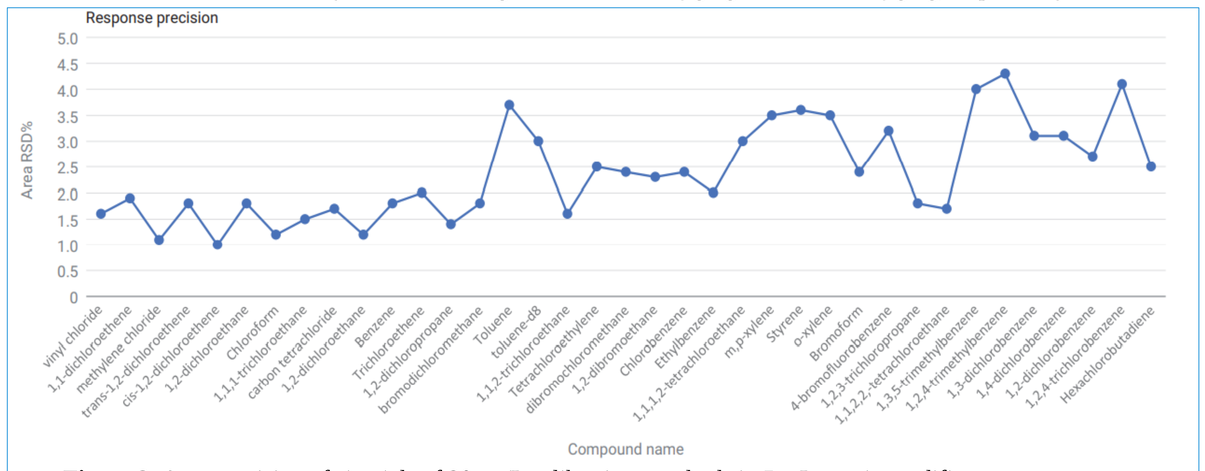


Figure 2. Area precision of six vials of 20 µg/L calibration standards in 5 mL matrix modifier

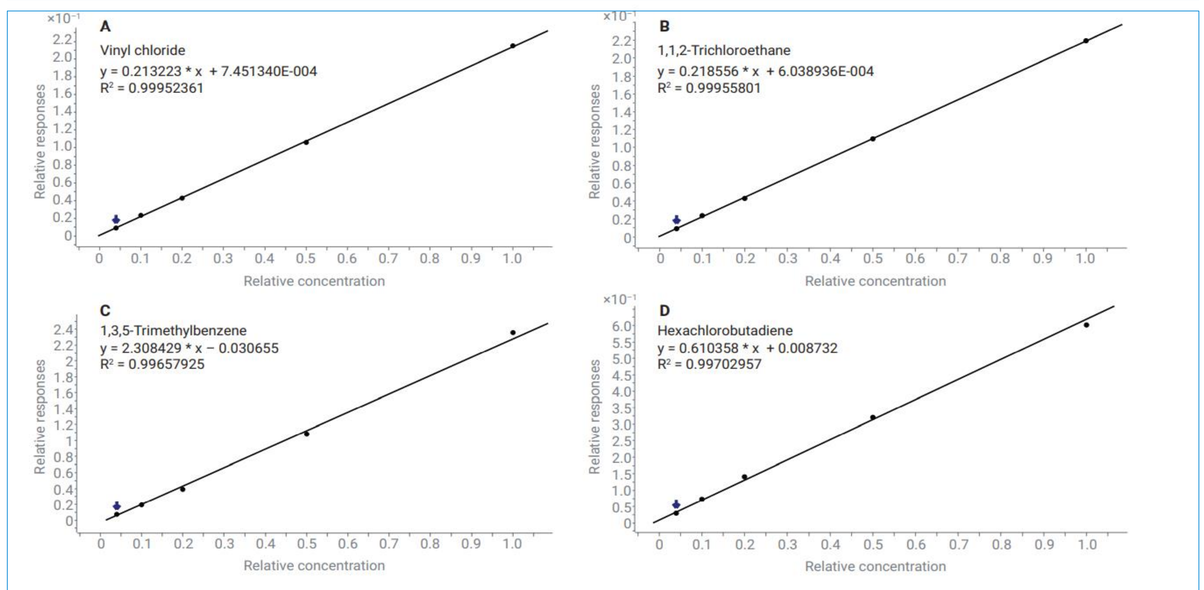


Figure 3. Calibration curves for representative compounds: (A) Vinyl chloride with R2 = 0.9995; (B) 1,1,2-trichloroethane with R2 = 0.9995; (C) 1,3,5-trimethylbenzene with R2 = 0.9965; (D) hexachlorobutadiene

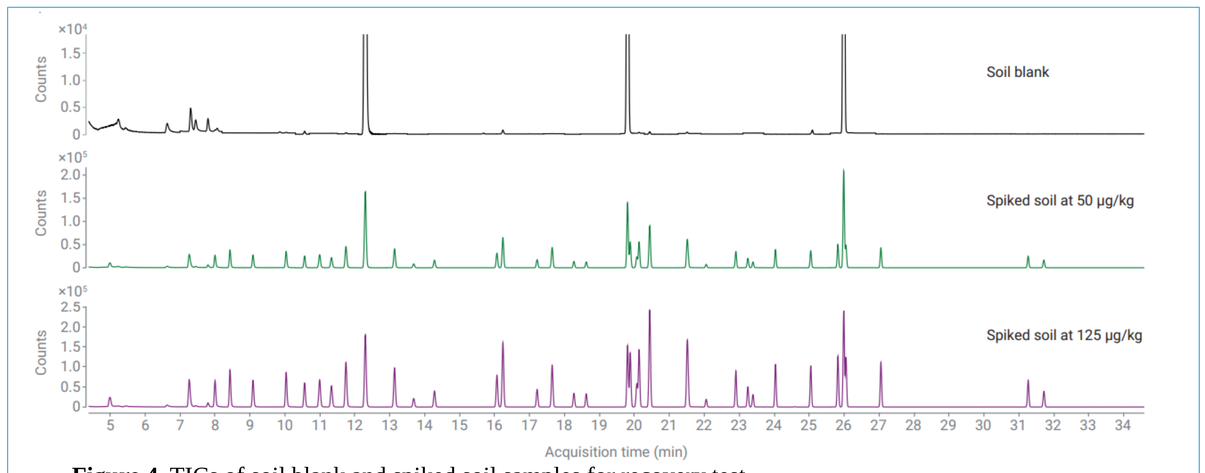


Figure 4. TICs of soil blank and spiked soil samples for recovery test.

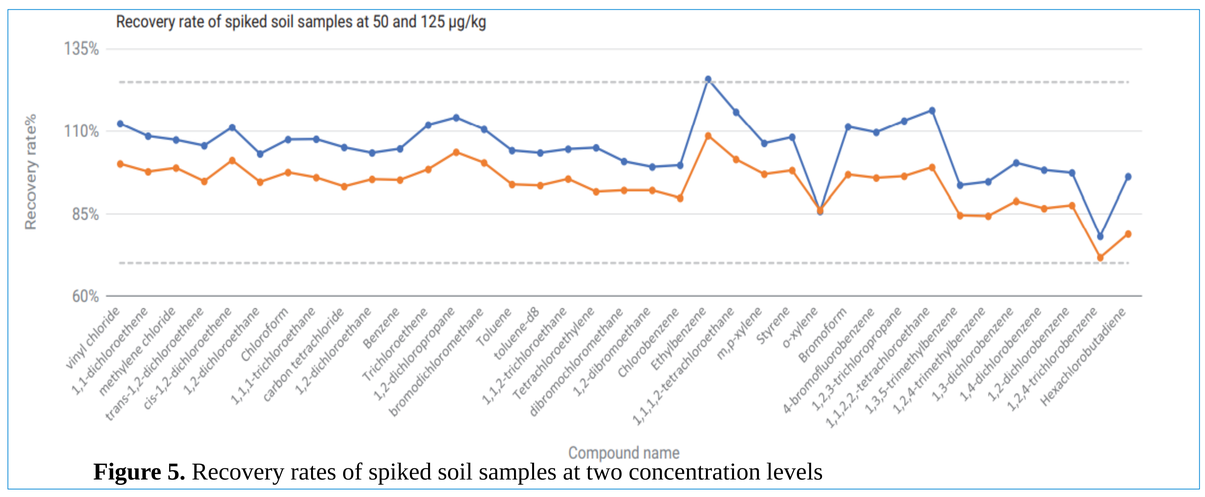


Figure 5. Recovery rates of spiked soil samples at two concentration levels

Conclusions

- The Agilent 8697 headspace sampler coupled with 8860 GC-5977B GC/MSD system can deliver excellent repeatability and linearity performance.
- The method recovery rates at two tested concentration levels were from 78.2% to 125.9% and from 71.7% to 108.7%. , showing the effectiveness of the described method on real sample analysis.
- With the excellent repeatability, sensitive detection and validated methods, the Agilent 8697 headspace sampler and 8860-5977B GC/MSD was demonstrated as a reliable platform for VOCs analysis in soils.