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

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Abstract

This application note describes volatile organic compounds analysis in soil and sediments using the Agilent 8697 headspace sampler, 8860 GC, and 5977B GC/MSD system. The system performance in terms of repeatability, linearity, limit of detection, limit of quantitation, and method recovery rate were evaluated with good results. The area repeatability was in the range of 1.0 to 4.3%; the LOD and LOQ in the quartz sand blank was from 0.51 to 1.21 µg/kg and from 1.7 to 4.1 µg/kg, respectively. The recovery rate for the soil samples at spiked concentrations of 50 and 125 µg/kg was 78.2 to 125.9% and 71.7 to 108.7%. The linearity across the tested concentration range is excellent, with the R^2 of all components better than 0.996. The test results met or exceeded the requirements of Chinese standard HJ 642-2013.

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. In China, the soil pollution prevention law was passed by the National People's Congress on 31 August 2018 as the first comprehensive framework law for addressing soil pollution, creating new obligations and potential liabilities for land-use-rights holders. The law requires the land-use-rights holder to investigate soil conditions upon the government's identification of soil pollution risk.

Headspace and purge-and-trap methods are used for VOCs contamination measurement in soil and sediments, with the method used dependent on the sample concentration. The static headspace method features easy operation and good repeatability. It allows use of an autosampler and minimizes carryover.

Chinese standard HJ 642-2013 is an environmental protection standard for determination of VOCs in soil and sediments by headspace GC/MS. It gives guidelines for handling of VOCs in soil and sediments when using a headspace method.

The 8697 headspace sampler is a platform that can introduce VOCs in the soil and sediments to a GC or GC/MSD platform for analysis as required by HJ 642-2013 standard. The 8697 headspace sampler has smart features that are developed to improve user experience and expand its diagnostic capability. The 8697 headspace sampler connects to Agilent smart GCs, including the 8860, 8890, and Intuvo 9000 GC with integrated communication. Users can access the browser interface of the smart GC or workstation to configure or set the headspace parameters. Compared to previous headspace products, the 8697 headspace sampler has more automated diagnostic functions, which can be executed from the browser interface of the GC. With the help of this user-initiated diagnosis process, it is easy to know whether the 8697 headspace sampler is in good health and ready for sample analysis. Clear guidance on the browser interface, in text or in image formats, makes the headspace maintenance or troubleshooting more straightforward. Besides the smart maintenance and diagnosis features, the 8697 headspace sampler provides 48-vial capacity and 12-position air bath vial oven for precise temperature control of every sample throughout its equilibration time, which meet the routine sample throughput requirement in most commercial testing labs.

In this application note, VOCs in soil were analyzed on the 8697 headspace/8860 GC/5977B GC/MSD platform by following Chinese standard HJ 642-2013. The linearity, repeatability, LOD, and LOQ for the targeted 36 VOCs were evaluated to show the system's excellent performance for VOCs analysis.

Experiment

Chemicals and standards

Stock solution: A mixture of 36 volatile organic compounds (VOCs) in methanol at 1,000 mg/L; internal calibration standard of fluorobenzene, chlorobenzene-d$_5$, and 1,2-dichlorobenzene-d$_4$ in methanol at 2,000 mg/L; and 2,000 mg/L surrogate standard of toluene-d$_8$ and 4-bromofluorobenzene in methanol were used.

Matrix modifier: 500 mL of organic-free water was adjusted to pH ≤2 with phosphoric acid and saturated with analytical-grade sodium chloride.

Working solution: The VOCs and surrogate stock solutions were mixed and diluted by methanol to 10 mg/L as the working solution. The IS stock solution was diluted to 50 mg/L by methanol for later use.

Calibration standards and soil sample preparation

The quartz sand was weighed at 2 g. The sand and 5 mL matrix modifier were added to a 20 mL headspace vial. Aliquots of VOCs/surrogates and IS working solutions were spiked into the modifier solution quickly, and then the vials were sealed immediately and shaken to well mix the standard. The final calibration standards are prepared approximately at 4, 10, 20, 50, and 100 µg/L, and the internal standards were spiked with the concentration of 50 µg/L.

The soil sample was weighed at 2 g in a 20 mL sample vial. Matrix modifier of 5 mL was added then spiked with IS to 50 µg/L. The vial was then quickly sealed and shaken to mix well.

Instrumentation and analytical conditions

An 8860 GC was equipped with a split/splitless inlet. The 8697 headspace sampler was used to extract and transfer the VOCs in the sample to the GC. The gas in the headspace of sample vials went through the 8697 transfer line and entered the split/splitless inlet before separation on an analytical column. The sample was then analyzed using a 5977B GC/MSD configured with an inert extraction ion source.

Agilent MassHunter Acquisition software version 10.0 was used for data collection. MassHunter Qualitative Analysis version B.08.00 and MassHunter Quantitative Analysis version B.08.00 were used for peak identification and quantitation.

The analytical conditions are listed in Table 1.

Results and discussion

According to HJ 642-2013, MSD performance should be checked daily to ensure MS data validity and reliability. The MSD was tuned, and the tune result was verified by analysis of the headspace gas in a 20 mL vial with 5 µL of 100 µg/mL BFB standard, according to the HJ 642-2013 requirements for mass spectrum quality. Table 2 shows the tune evaluation result.

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

Parameters	Setpoints
Inlet Temperature	250 °C
Liner	4 mm id Ultra Inert inlet liner, split (p/n 5190-2295), glass wool removed
Column Flow	Constant flow, 1.2 mL/min
Split Ratio	10:1
Oven Program	40 °C (2 min), 8 °C/min to 90 °C (4 min), then 6 °C/min to 200 °C (10 min)
Column	Agilent J&W DB-624 GC column, 60 m × 0.25 mm, 1.40 µm (p/n 122-1364)
MSD Transfer Line	230 °C
MS Source	280 °C
MS Quad	150 °C
Gain Factor	1
Drawout Plate	6 mm
8697 Loop Size	1 mL
Vial Pressurization Gas	He
HS Loop Temperature	100 °C
HS Oven Temperature	80 °C
HS Transfer Line Temperature	110 °C
Vial Equilibration Time	50 min
Vial Size	20 mL, 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	15 psi
Loop Fill Mode	Custom
Loop Ramp Rate	20 psi/min
Loop Final Pressure	9 psi
Loop Equilibration Time	0.1 min
Carrier Control Mode	GC carrier control
Vent After Extraction	On

Table 2. MSD Etune result conformity assessment.

Target Mass	Rel to Mass	Lower Limit %	Upper Limit %	Rel. Abn %	Raw Abn	Pass/Fail
95	95	100	100	100	96,889	Pass
96	95	5	9	7.3	7,109	Pass
173	174	--	2	0	0	Pass
174	95	50	--	64.3	62,325	Pass
175	174	5	9	7.4	4,612	Pass
176	174	95	105	96.3	60,018	Pass
177	176	5	10	6.6	3,981	Pass

The data of the calibration standards were acquired in selected ion monitoring (SIM) mode. The total ion chromatogram (TIC) in Figure 1 showed the separation and detection for the 20 µg/L standard.

The instrument repeatability was verified based on the analyte absolute response. System linearity performance was verified based on analytes' quantitated concentrations instead of absolute area response, because HJ 642-2013 uses ISTD method for quantitation. Six vials of 20 µg/L calibrants were run for repeatability assessment. The response RSD% of the 38 VOCs (i.e., 36 analytes and 2 surrogates) are in the range of 1.0 to 4.3% (Figure 2), which demonstrated excellent sampling and detection precision. Instrument linearity were evaluated from 4 to 100 µg/L in 5 mL of matrix modifier with 2 g of quartz sand as control matrix, corresponding to 10 to 250 µg/kg analytes in real samples. All targeted components showed good linearity, with correlation coefficients (R^2) of regression formula better than 0.996. The calibration curves of four representative compounds eluting at the early, middle, and late part of the chromatogram are shown in Figure 3. The linearity results were achieved on the 6 mm MSD drawout plate. When using a 3 mm drawout plate, there were several compounds with R^2 less than 0.99, which did not meet the HJ standard requirement.
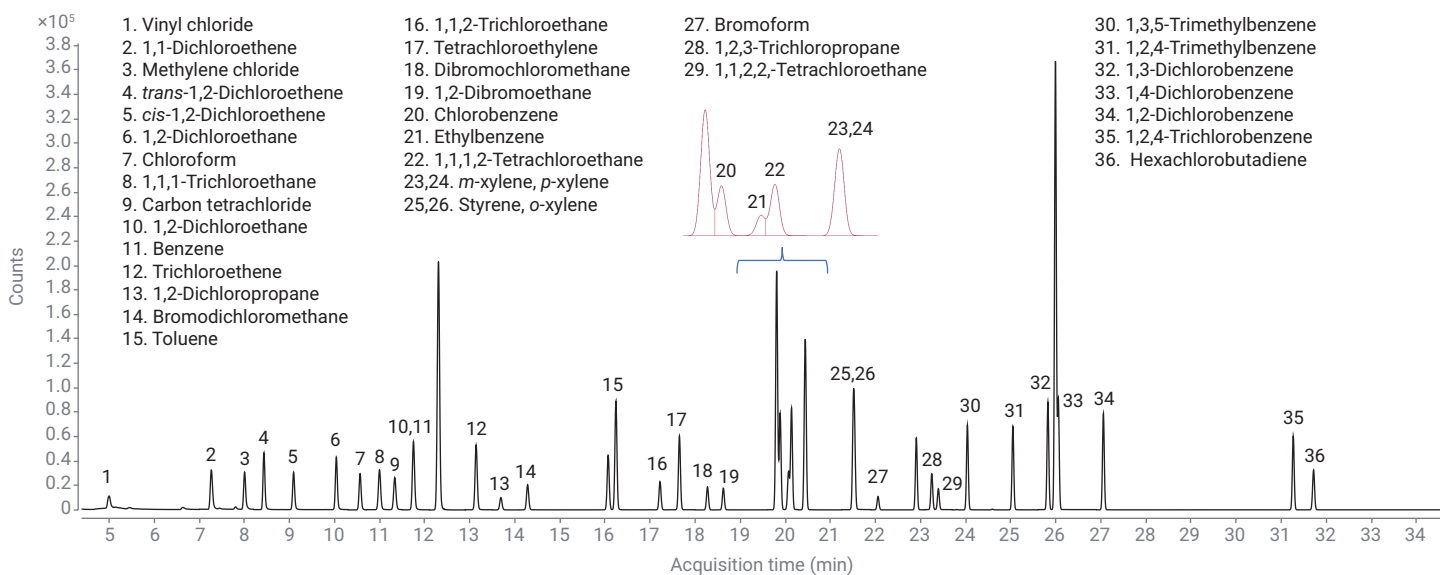

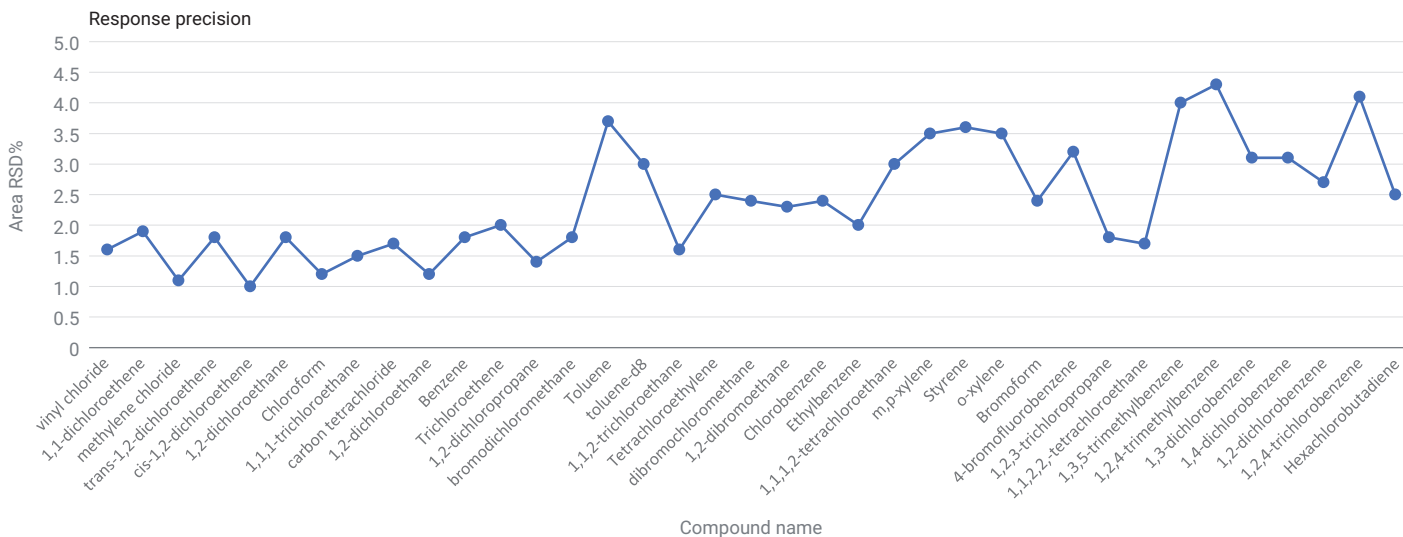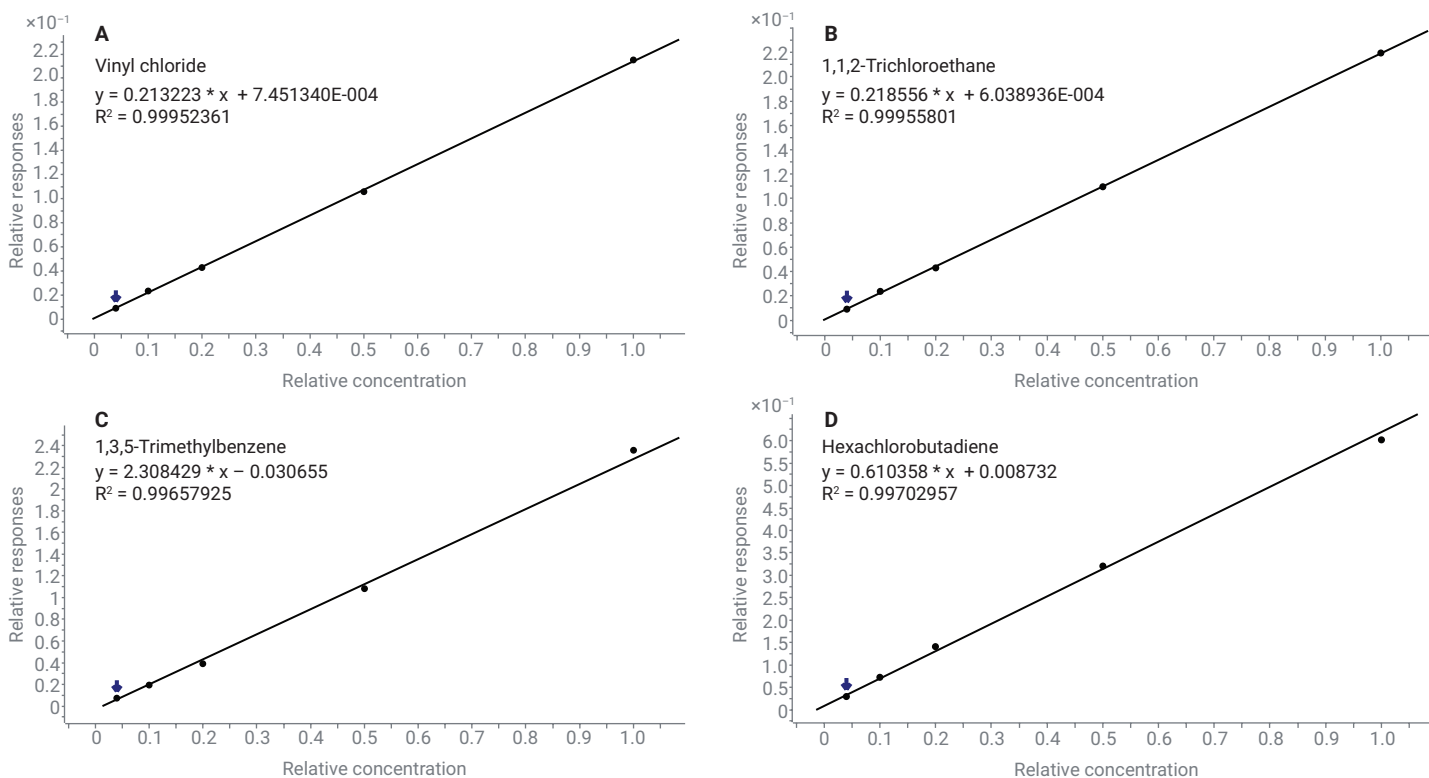**Figure 1.** TIC SIM of 20 µg/L VOCs standard in 5 mL matrix modifier.

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 R^2 = 0.9995; (B) 1,1,2-trichloroethane with R^2 = 0.9995; (C) 1,3,5-trimethylbenzene with R^2 = 0.9965; (D) hexachlorobutadiene with R^2 = 0.9970.

The method recovery performance was tested on 2 g 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). The soil sample without spiking was tested as blank, and the difference between the spiked sample and the blank was used for recovery rate calculation. The chromatograms of one soil blank and two spiked soil samples are shown in Figure 4. The surrogate's recovery rate was:

– 103.5% for toluene-d_8 and 109.7% for 4-bromofluorobenzene at 50 µg/kg

– 93.6% for toluene-d_8, and 95.9% for 4-bromofluorobenzene at 125 µg/kg

This met the standard requirements on surrogate recovery rate in real sample. The recovery rates of 36 target VOCs were between 78.2 to 125.9% at 50 µg/kg and between 71.7 to 108.7% at 125 µg/kg (Figure 5). The recovery rates demonstrated equivalent performance to the reference results in HJ 642-2013 standard.

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. The translated method LOD and LOQ (in the unit of µg/kg) in blank quartz sand based on IDL were shown in Table 3 (Appendix) as a reference of the LOD and LOQ in real soil or sediments sample. The LOD and LOQ for VOCs in quartz sand was between 0.51 to 1.21 µg/kg and 1.7 to 4.1 µg/kg, good enough to detect the targeted VOC compounds at the single-digit µg/kg level as specified by the HJ 642-2013 method.
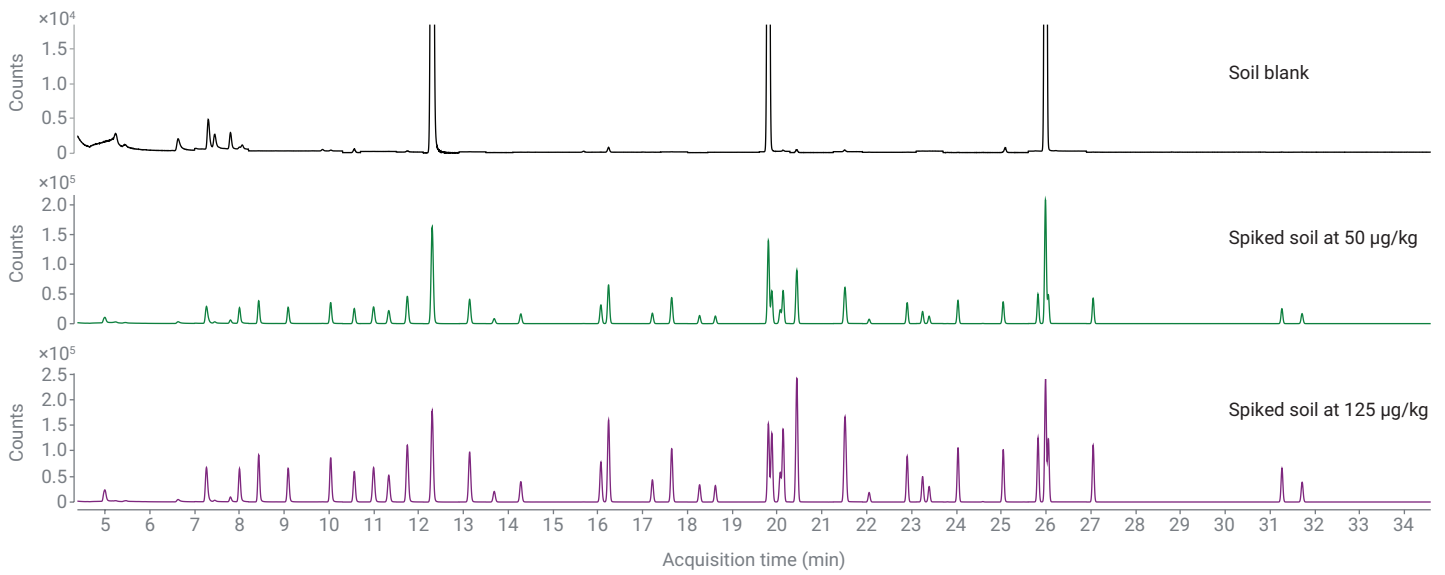
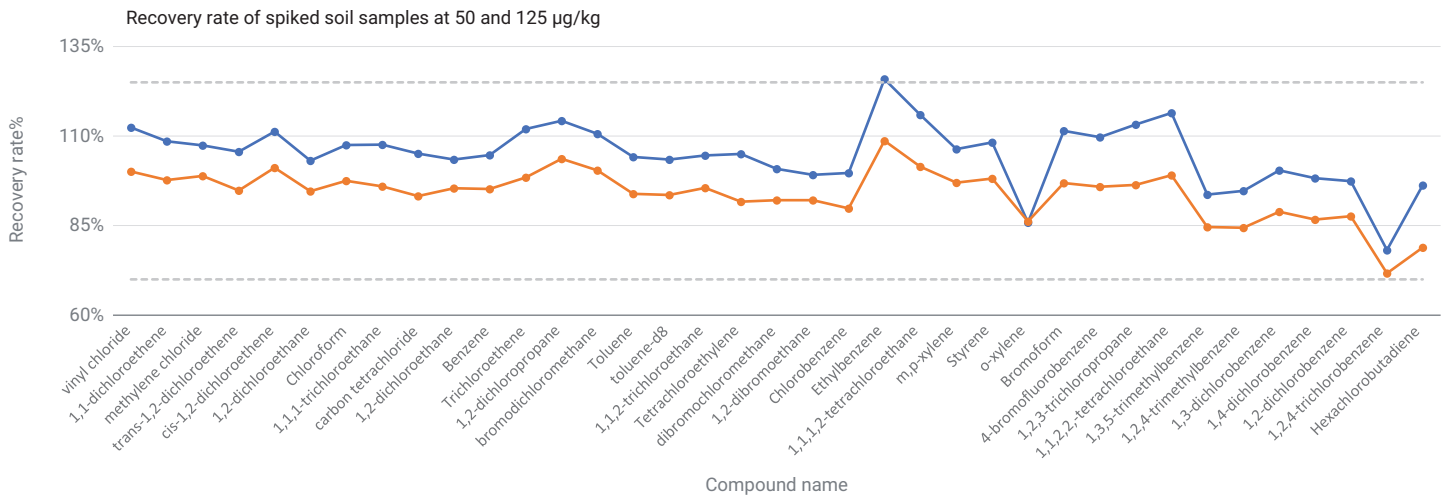**Figure 4.** TICs of soil blank and spiked soil samples.

Figure 5. Recovery rate of spiked soil samples.

Conclusion

This application note demonstrated that the 8697 headspace sampler is an excellent means of introducing VOCs trapped in soils and sediments to GC for identification and quantitation. The combination of the 8697 headspace sampler with the 8860 GC and 5977B GC/MSD system delivered good repeatability, which was demonstrated in response precision from 1.0 to 4.3% for 38 VOCs. The calibration curves of targeted compounds in the tested concentration range (4 to 100 µg/L) showed satisfactory linearity, with all correlation coefficient better than 0.996. The LOD and LOQ achieved on the described system showed equivalent performance as demonstrated in the HJ 642-2013 standard. The recovery rate of spiked soil samples at 50 and 125 µg/kg was 78.2 to 125.9% and 71.7 to 108.7%, demonstrating that the 8697 headspace sampler coupled with the 8860 smart GC can provide reliable and accurate VOCs analysis in real-world soil and sediments samples.

Reference

1. Chinese Environmental Protection Industry Standard HJ 642-2013: Soil and Sediment–Determination of Volatile Organic Compounds– Headspace-Gas Chromatography/ Mass Method. Chinese Ministry of Environmental Protection (published on 21 January 2013).

Appendix

Table 3. Instrument linearity, LOD, area precision, and recovery rate at applied operation conditions.

Name	RT/min	CF Formula	CF R²	Response RSD%	LOD (µg/kg)	LOQ (µg/kg)	Recovery Rate 50 µg/kg	Recovery Rate 125 µg/kg
Vinyl chloride	4.997	y = 0.213223 * x + 7.451340E-004	0.9995	1.6	1.22	4.05	112.4%	100.1%
1,1-Dichloroethene	7.271	y = 0.280056 * x + 0.002079	0.9994	1.9	0.62	2.06	108.5%	97.7%
Methylene chloride	8.004	y = 0.251349 * x + 0.002364	0.9992	1.1	0.73	2.43	107.4%	98.9%
trans-1,2-Dichloroethene	8.435	y = 0.287348 * x + 0.002651	0.9991	1.8	0.83	2.77	105.6%	94.8%
cis-1,2-Dichloroethene	9.093	y = 0.397743 * x + 0.003192	0.9994	1	0.62	2.05	111.3%	101.2%
1,2-Dichloroethane	10.040	y = 0.297696 * x + 0.002091	0.9994	1.8	0.75	2.48	103.1%	94.6%
Chloroform	10.566	y = 0.369739 * x + 0.005035	0.9992	1.2	0.60	1.99	107.5%	97.5%
1,1,1-Trichloroethane	10.999	y = 0.329690 * x + 0.002463	0.9995	1.5	0.62	2.06	107.6%	96.0%
Carbon tetrachloride	11.336	y = 0.318289 * x + 0.002059	0.9996	1.7	0.57	1.89	105.1%	93.3%
1,2-Dichloroethane	11.746	y = 0.193792 * x + 0.001507	0.9993	1.2	0.74	2.45	103.4%	95.4%
Benzene	11.750	y = 1.051625 * x + 0.006656	0.9996	1.8	0.72	2.41	104.7%	95.2%
Trichloroethene	13.141	y = 0.360773 * x + 0.002391	0.9996	2	0.65	2.15	112.0%	98.5%
1,2-Dichloropropane	13.689	y = 0.291754 * x + 8.914385E-004	0.9998	1.4	0.65	2.16	114.3%	103.7%
Bromodichloromethane	14.281	y = 0.338244 * x + 0.001356	0.9997	1.8	0.65	2.15	110.6%	100.4%
Toluene	16.069	y = 1.164353 * x + 0.001734	0.9997	3.7	0.85	2.85	104.2%	93.9%
Toluene-d8	16.243	y = 0.883187 * x - 1.193050E-004	0.9995	3	0.83	2.76	103.5%	93.6%
1,1,2-Trichloroethane	17.217	y = 0.218556 * x + 6.038936E-004	0.9996	1.6	0.67	2.24	104.6%	95.5%
Tetrachloroethylene	17.652	y = 0.384694 * x + 0.002042	0.9997	2.5	0.68	2.26	105.0%	91.7%
Dibromochloromethane	18.272	y = 0.287628 * x + 6.739824E-004	0.9992	2.4	0.71	2.38	100.8%	92.1%
1,2-Dibromoethane	18.622	y = 0.236576 * x + 2.992586E-004	0.9991	2.3	0.82	2.74	99.2%	92.1%
Chlorobenzene	19.884	y = 1.062315 * x + 0.003659	0.9997	2.4	0.68	2.28	99.7%	89.8%
Ethylbenzene	20.071	y = 0.587171 * x + 0.002820	0.9995	2	0.61	2.04	125.9%	108.7%
1,1,1,2-Tetrachloroethane	20.135	y = 2.915519 * x – 0.001669	0.9997	3	0.62	2.06	115.9%	101.5%
m,p-Xylene	20.442	y = 2.580795 * x – 0.023563	0.9983	3.5	0.70	2.34	106.4%	97.0%
Styrene	21.510	y = 1.204945 * x – 0.009297	0.9989	3.6	0.69	2.29	108.2%	98.1%
o-Xylene	21.537	y = 1.637392 * x – 0.019908	0.9974	3.5	0.79	2.64	85.9%	86.2%
Bromoform	22.055	y = 0.350684 * x + 1.159518E-005	0.9990	2.4	0.78	2.61	111.5%	96.9%
4-Bromofluorobenzene	22.902	y = 0.892720 * x + 0.002945	0.9998	3.2	0.75	2.49	109.7%	95.9%
1,2,3-Trichloropropane	23.249	y = 0.801680 * x + 0.002143	0.9994	1.8	0.75	2.48	113.2%	96.4%
1,1,2,2,-Tetrachloroethane	23.397	y = 0.617940 * x + 0.001429	0.9995	1.7	0.74	2.48	116.5%	99.1%
1,3,5-Trimethylbenzene	24.037	y = 2.308429 * x – 0.030655	0.9966	4	0.72	2.41	93.7%	84.6%
1,2,4-Trimethylbenzene	25.046	y = 2.284967 * x – 0.033058	0.9963	4.3	0.82	2.74	94.7%	84.4%
1,3-Dichlorobenzene	25.823	y = 1.737283 * x + 0.007524	0.9997	3.1	0.68	2.26	100.4%	88.9%
1,4-Dichlorobenzene	26.054	y = 1.710684 * x + 0.009649	0.9997	3.1	0.73	2.45	98.2%	86.7%
1,2-Dichlorobenzene	27.052	y = 1.626089 * x + 0.010158	0.9995	2.7	0.64	2.12	97.4%	87.6%
1,2,4-Trichlorobenzene	31.265	y = 1.080196 * x + 0.006445	0.9996	4.1	0.95	3.17	78.2%	71.7%
Hexachlorobutadiene	31.715	y = 0.610358 * x + 0.008732	0.9995	2.5	0.51	1.69	96.3%	78.9%

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