

# Determination of Volatile Organic Compounds in Soil and Sediments

Using an Agilent 7697A Headspace Sampler, 8890 GC, and 5977B GC/MSD combined platform

## Author

Zhang Jie  
Agilent Technologies Co. Ltd  
Shanghai

## Abstract

The accurate detection of volatile organic compounds (VOCs) in contaminated soil and sediment is of particular importance. The Chinese Ministry of Environmental Protection has produced a headspace GC/MS method, HJ642-2013, for the analysis of VOCs in soil and sediments. This Application Note has followed China method HJ642-2013 and demonstrated the excellent instrument performance of Agilent 7697A headspace, 8890 GC, and 5977B MSD combined platform for the targeted analysis.

## Introduction

VOCs are defined as having boiling points between 50 and 260 °C under normal atmospheric pressure. They are used in many industries as solvents or chemical intermediates. VOCs such as trichloroethene and toluene are often of principle concern in hazardous waste sites containing contaminated soil and sediments. Since site remediation is costly, decisions regarding the significance of contamination and cleanup must be based on accurate VOC measurement.

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

US EPA method 5021<sup>1</sup> gives guidelines for preparation of VOCs in soil and sediments using a headspace method. Gas chromatography/mass spectrometry (GC/MS) can be used to analyze the prepared sample, as mentioned in EPA method 8260. HJ642-2013<sup>2</sup> is a standard used by the Chinese Ministry of Environmental Protection for determination of 36 VOCs in soil and sediments by headspace GC/MS. HJ 741-2015<sup>3</sup> also specified headspace technique as the sample preparation method. Both EPA and Chinese methods require effective sample preparation and a reliable instrument platform to address targeted analysis.

The HES is a revolutionary design in ion generation, which produces a higher ion current yield and a lower detection limit<sup>4</sup>. In this Application Note, VOCs in clean quartz sand and in spiked soil samples were analyzed on a new combined platform, a 7697A headspace sampler with an 8890 GC and a 5977B GC/MSD with HES, by following method HJ642-2013. Linearity, repeatability, limits of detection (LODs), limits of quantitation (LOQs) for the targeted 36 VOCs, and method accuracy were tested to show what can be achieved on this new system.

## Experimental

### Chemicals and standards

**Stock solution:** A stock solution of a 36 VOCs mixture at 1,000 mg/L in methanol was prepared. An internal calibration standard stock solution was produced at a concentration of 2,000 mg/L in methanol. Internal calibration standards were fluorobenzene, chlorobenzene-d<sub>5</sub>, and 1,2-dichlorobenzene-d<sub>4</sub>. Surrogate standards were prepared at a concentration of 2,000 mg/L in methanol; toluene-d<sub>8</sub> and 4-bromofluorobenzene are used as surrogates.

**Matrix modifier:** Five hundred milliliters of organic free water was adjusted to pH ≤2 by drops of phosphoric acid, and saturated with analytical level sodium chloride.

**Working solution:** The 36 VOCs stock solution and surrogate stock solution were mixed to 10 and 1 mg/L working solution by methanol. The internal calibration standards stock solution was diluted to 100 and 10 mg/L by methanol.

### Calibration standards preparation:

Ten milliliters of matrix modifier and 2 g of quartz sand were added to a 20 mL headspace vial. Aliquots of working solutions of the 36 VOCs/surrogates mixture (10 mg/L) and internal calibration standards were spiked into the modifier solution quickly. The vials were sealed immediately after the spiking. The final calibration standards were prepared at 2, 5, 10, 20, 50, and 100 µg/L, and the internal standards were at 50 µg/L for all concentration levels.

For a low concentration sample test, the calibration standards in 10 mL of modifier were prepared at 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 µg/L, with internal standards at 5 µg/L.

### Instrumentation and analytical conditions

The 8890 GC was equipped with a split/splitless inlet. The 111-vial 7697A headspace sampler was used for gas injection from the headspace of the incubated vial to the GC. A flow-through connection through an inlet septum was used for gas introduction into the inlet. The 5977B GC/MSD configured with an HES was used for ion generation, scan, and detection.

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 data analysis. Table 1 lists the analytical conditions.

## Results and discussion

According to HJ 642-2013, MSD performance should be checked daily to ensure MS data validity and reliability. The MSD was autonomously tuned by selecting **HES tune** mode. One microliter of 25 µg/mL BFB sample was injected to verify the conformity of the tune result to the requirement of HJ642-2013. Table 2 shows the tune evaluation result.

**Table 1.** Analytical conditions of 7697A headspace sampler, 8890A GC, and 5977B GC/MSD.

Parameter	Setpoint
Inlet temperature	250 °C
Liner	1 mm id Ultra Inert (p/n 5190-4047)
Column flow	Constant flow, 1.2 mL/min
Split ratio	10:1
Oven program	40 °C (2 minutes), 8 °C/min to 90 °C (4 minutes), then 6 °C /min to 200 °C (10 minutes)
Column	DB-624, 60 m × 0.25 mm, 1.4 µm (p/n 122-1364)
MSD transfer line	200 °C
MS source	230 °C/300 °C (300 °C is for low concentration sample)
MS quadrupole	150 °C
Mass scan range	m/z 35 to 300
Threshold	0
A/D samples	4
Gain factor	0.1/1 (GF 1.0 is for low concentration sample)
7697A 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	35 minutes
Vials size	20 mL, PTFE/silicone septa
Vial shaking	Level 7, 136 shakes/min with acceleration of 530 cm/S <sup>2</sup>
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 minutes
Carrier control mode	GC carrier control
Vent after extraction	On

**Table 2.** MSD HES tune result conformity assessment.

Target mass	Rel to mass	Lower limit %	Upper limit %	Relative abundance (%)	Raw abundance	Pass/Fail
95	95	100	100	100	677,753	Pass
96	95	5	9	7.2	48,518	Pass
173	174	--	2	0	0	Pass
174	95	50	--	84.6	573,269	Pass
175	174	5	9	7.9	45,371	Pass
176	174	95	105	98	561,620	Pass
177	176	5	10	6.9	38,635	Pass

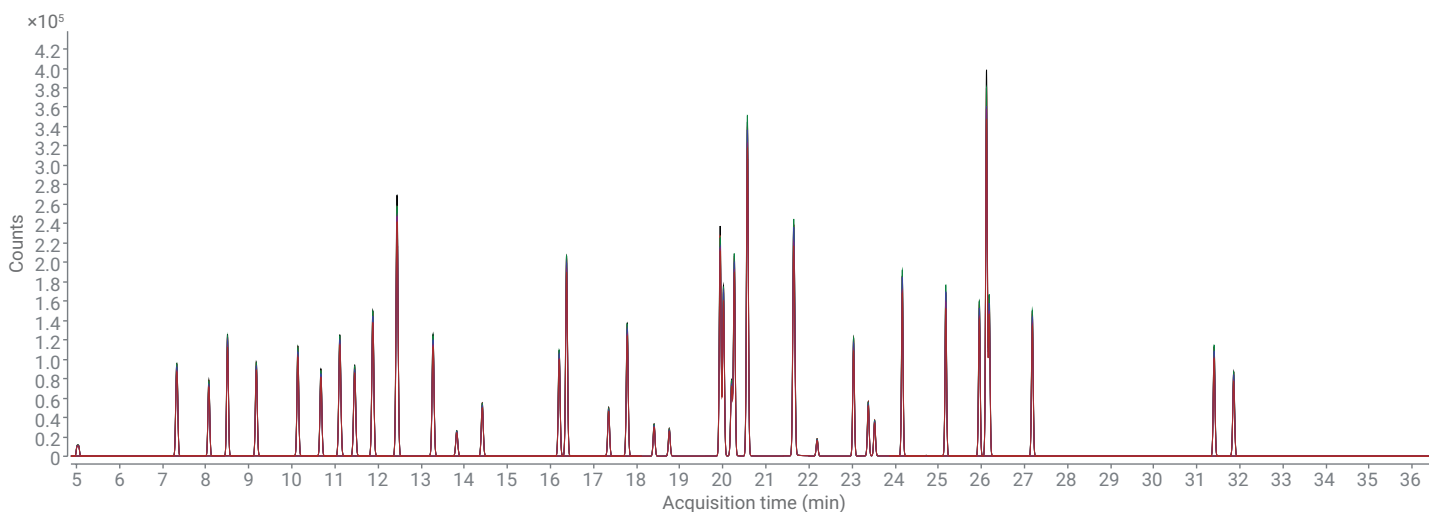
The MSD data were acquired in SIM mode; the quantifier ion and qualifier ion are listed in Table 3. Figure 1 shows the TIC SIM traces for 20 µg/L standards in 10 mL of matrix modifier and 2 g of quartz sand.

HJ642-2013 used an ISTD method for quantitation, so the instrument repeatability and linearity performance were verified based on concentration quantitation results instead of the absolute response of targeted analytes.

Six consecutive analyses of calibration standards at 20 µg/L were run. The RSD% of detected concentrations for 38 VOCs were in the range of 1.7 to 4.6 % with one exception, styrene, with RSD% of 7 %, which demonstrated excellent quantitation precision.

**Table 3.** Instrument linearity, LOD, precision, and recovery rate under normal HES-MSD operating conditions.

Name	RT/min	CF Formula	CF R <sup>2</sup>	Concentration RSD%	LOQ (µg/kg)	LOD (µg/kg)	Recovery rate	
							20 µg/L	40 µg/L
Vinyl chloride	5.034	y = 0.101690 * x + 6.290804E-004	0.996	2.2	4.8	1.4	112.5 %	107.1 %
1,1-Dichloroethene	7.327	y = 0.276991 * x - 3.581275E-004	0.998	2	4.0	1.2	111.5 %	106.8 %
Methylene chloride	8.07	y = 0.207358 * x + 0.002525	0.996	2.2	5.1	1.5	102.3 %	104.3 %
trans-1,2-Dichloroethene	8.503	y = 0.287113 * x + 0.001344	0.997	2.1	4.1	1.2	100.6 %	100.3 %
cis-1,2-Dichloroethene	10.136	y = 0.276668 * x - 1.884161E-004	0.999	2.2	3.8	1.1	99.4 %	101.0 %
1,1-Dichloroethane	9.175	y = 0.484499 * x + 0.002331	0.997	2.1	3.7	1.1	109.9 %	106.8 %
Chloroform	10.672	y = 0.445198 * x + 0.007469	0.996	2	4.2	1.3	110.0 %	105.7 %
1,1,1-Trichloroethane	11.109	y = 0.491543 * x + 0.001691	0.998	1.7	3.6	1.1	107.4 %	105.8 %
Carbon tetrachloride	11.454	y = 0.455046 * x + 0.001120	0.998	1.8	4.0	1.2	104.6 %	103.5 %
1,2-Dichloroethane	11.874	y = 0.255379 * x + 0.011468	0.996	2.1	4.9	1.5	110.4 %	105.5 %
Benzene	11.878	y = 1.042873 * x + 0.004004	0.998	2.2	3.5	1.0	106.0 %	104.6 %
Trichloroethene	13.272	y = 0.411061 * x - 0.001326	0.999	2	3.9	1.2	103.0 %	104.3 %
1,2-Dichloropropane	13.824	y = 0.306996 * x - 0.002118	0.999	2.2	3.3	1.0	107.5 %	107.9 %
Bromodichloromethane	14.416	y = 0.378155 * x - 0.002188	0.999	2.1	4.1	1.2	106.6 %	106.4 %
Toluene	16.37	y = 0.889250 * x - 0.010461	0.999	2.3	4.2	1.2	101.7 %	104.9 %
Toluene-d <sub>8</sub>	16.201	y = 1.206994 * x - 0.010969	0.998	2.3	4.1	1.2	101.0 %	105.1 %
1,1,2-Trichloroethane	17.348	y = 0.190979 * x - 6.646855E-004	0.999	1.9	4.6	1.4	107.4 %	105.8 %
Tetrachloroethylene	17.779	y = 0.389153 * x + 1.166931E-004	0.999	2	3.9	1.2	100.3 %	100.0 %
Dibromochloromethane	18.404	y = 0.216751 * x - 0.002372	0.999	2	4.9	1.5	100.3 %	101.7 %
1,2-Dibromoethane	18.756	y = 0.135619 * x - 8.135818E-004	0.999	1.9	4.8	1.5	102.0 %	101.8 %
Chlorobenzene	20.014	y = 0.990760 * x - 0.002667	0.999	2.2	3.8	1.1	99.1 %	99.3 %
Ethylbenzene	20.266	y = 3.093411 * x - 0.049524	0.998	2.7	3.7	1.1	109.0 %	114.1 %
1,1,1,2-Tetrachloroethane	20.199	y = 0.649519 * x - 0.006668	0.999	1.9	5.0	1.5	116.0 %	115.7 %
m,p-Xylene	20.569	y = 2.458761 * x - 0.043076	0.997	2.8	4.2	1.3	108.6 %	114.2 %
Styrene	21.663	y = 1.726545 * x - 0.067283	0.995	7	8.1	2.4	81.0 %	91.3 %
o-Xylene	21.637	y = 1.235302 * x - 0.031450	0.998	2.9	3.9	1.2	100.5 %	110.5 %
Bromoform	22.187	y = 0.239708 * x - 0.004527	0.998	2	6.8	2.0	104.5 %	106.4 %
4-Bromofluorobenzene	23.032	y = 0.952233 * x - 0.016871	0.999	2.4	3.9	1.2	94.6 %	101.4 %
1,2,3-Trichloropropane	23.523	y = 0.490147 * x - 0.002929	0.999	2.1	6.2	1.9	119.1 %	114.8 %
1,1,1,2-Tetrachloroethane	23.375	y = 0.606064 * x - 0.007174	0.999	2	6.1	1.8	113.4 %	111.8 %
1,3,5-Trimethylbenzene	24.162	y = 2.577696 * x - 0.080450	0.996	3.6	5.0	1.5	89.5 %	100.5 %
1,2,4-Trimethylbenzene	25.17	y = 2.492454 * x - 0.083100	0.996	4.6	4.0	1.2	86.8 %	99.1 %
1,3-Dichlorobenzene	25.951	y = 1.545224 * x - 0.011240	0.999	2.4	4.2	1.3	97.0 %	97.5 %
1,4-Dichlorobenzene	26.181	y = 1.547282 * x - 0.007234	0.998	2.3	4.7	1.4	96.4 %	96.3 %
1,2-Dichlorobenzene	27.18	y = 1.415233 * x - 0.010719	0.999	2.5	4.1	1.2	98.1 %	97.9 %
1,2,4-Trichlorobenzene	31.399	y = 1.102990 * x - 0.011530	0.998	2.9	4.7	1.4	82.1 %	80.1 %
Hexachlorobutadiene	31.854	y = 0.825483 * x - 3.454680E-004	0.998	2.9	4.0	1.2	84.2 %	73.6 %



**Figure 1.** Overlaid TIC SIM traces for six replicates of 20 µg/L samples.

Instrument linearity was evaluated in the concentration range of 2 to 100 µg/L in 10 mL of matrix modifier, corresponding to 10 to 500 µg/kg in real samples. All targeted components showed good linearity, with coefficients ( $R^2$ ) of the linear regression formula exceeding 0.995.

The method recovery was tested by spiking 20 and 50 µL of 10 mg/L calibration standards into 2 g real soil samples (corresponding to 100 and 250 µg/kg VOCs in the soil sample). The soil sample without spiking was tested, then the difference between the spiked sample and nonspiked sample was used for recovery rate calculation. The recovery rate for 20 µL spiking was between 81 and 119 %, and for 50 µL spiking between 74 and 115 %. The results were equivalent to the referenced recovery performance in the HJ642-2013 method.

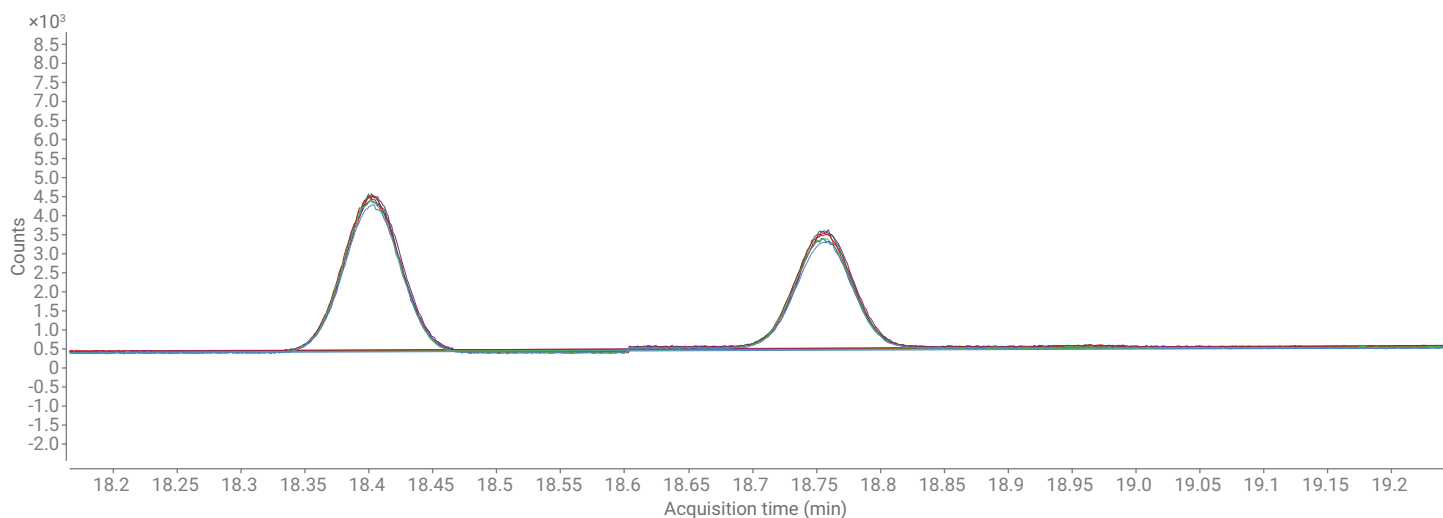
The minimum detection limits (MDLs) for 38 targeted VOCs, including two surrogates, were calculated based on quantitation precision at 2 µg/L, then translated into method LOD (µg/kg) and LOQ (µg/kg) according to method HJ642-2013 (Table 3). The LOD provided by the applied workflow was between 1.0 and 2.5 µg/kg (with MSD GF at 0.1). This was sufficient to detect the targeted VOC compounds at a single-digit µg/kg level, as required by HJ642-2013.

This Application Note used the HES for ion generation and transmission. We compared results with our previous work on VOCs analysis (based on an extractor ion source but with similar quadrupole and EMV gain factor settings). We found that, for the same sample, the S/N achieved by HES was approximately three to seven times higher than those achieved with the extractor ion source. To further test the impact of HES on MSD detection capability, the MSD gain factor was

set at 1.0. This is the same value as that generally used by the extractor ion source in similar applications, and the ion source temperature was optimized to 300 °C. A series of VOCs samples, from 50 ng/L to 5 µg/L (equivalent to 0.25 to 25 µg/kg in real matrix) were prepared in 10 mL of matrix modifier and 2 g of clean quartz sand for testing. The MDLs based on the new analytical conditions were calculated according to the quantitation precision of eight replicates of 50 ng/L standards. Table 4 presents MDLs and linearity. Figure 2 shows the overlaid TIC SIM traces of eight replicates of dibromochloromethane and 1,2-dibromoethane at 50 ng/L to show the instrument repeatability for low concentration sample analysis. The data demonstrated that the established system is an ideal choice for reliable and sensitive detection of VOCs in solid matrices even at the 100 ppt (ng/kg) level.

**Table 4.** Method LOD, LOQ, and linearity (50 ng/L to 5 µg/L) under optimized HES-MSD conditions.

	Name	RT (min)	CF Formula	CF R <sup>2</sup>	LOQ (µg/kg)	LOD (µg/kg)	Quantifier ion (m/z)	Qualifier ions (m/z)
1	Vinyl chloride	5.047	$y = 0.658957 * x - 6.016395E-005$	0.9994	0.142	0.043	62	64
2	1,1-Dichloroethene	7.327	$y = 2.339186 * x - 2.969010E-004$	0.9992	0.078	0.024	96	61, 63
3	Methylene chloride (200 ppt to 5 ppb)	8.074	$y = 1.802609 * x + 0.031520$	0.9994	0.267	0.080	84	86, 49
4	<i>trans</i> -1,2-Dichloroethene	8.506	$y = 2.307819 * x - 1.849103E-004$	0.9995	0.096	0.029	96	61, 98
5	1,1-Dichloroethane	10.139	$y = 2.378814 * x - 1.544549E-004$	0.9996	0.094	0.028	63	65, 83
6	<i>cis</i> -1,2-Dichloroethene	9.174	$y = 4.499424 * x - 4.801002E-004$	0.9996	0.122	0.037	96	61, 98
7	Chloroform	10.671	$y = 3.927227 * x + 0.002925$	0.9996	0.109	0.033	83	85
8	1,1,1-Trichloroethane	11.114	$y = 4.064121 * x - 4.835625E-004$	0.9995	0.139	0.042	97	99, 61
9	Carbon tetrachloride	11.453	$y = 3.628096 * x - 4.676820E-004$	0.9995	0.139	0.042	117	119
10	1,2-Dichloroethane	11.875	$y = 2.527376 * x + 0.025430$	0.9995	0.115	0.035	62	98
11	Benzene	11.881	$y = 9.837078 * x + 0.026800$	0.9994	0.143	0.043	78	-
12	Trichloroethene	13.275	$y = 4.037059 * x - 1.428444E-004$	0.9996	0.081	0.025	95	97, 130, 132
13	1,2-Dichloropropane	13.827	$y = 3.372180 * x - 3.653243E-004$	0.9996	0.114	0.034	63	112
14	Bromodichloromethane	14.419	$y = 3.320849 * x + 1.474400E-004$	0.9996	0.119	0.036	83	85, 127
15	Toluene-d <sub>8</sub> (surrogate)	16.375	$y = 8.946947 * x + 0.004931$	0.9996	0.078	0.024	98	-
16	Toluene	16.204	$y = 14.159816 * x - 5.075302E-004$	0.9996	0.087	0.026	92	91
17	1,1,2-Trichloroethane	17.347	$y = 1.974437 * x - 1.028654E-004$	0.9997	0.133	0.040	83	97, 85
18	Tetrachloroethylene	17.783	$y = 3.351350 * x + 1.908451E-004$	0.9996	0.101	0.030	164	129, 131, 166
19	Dibromochloromethane	18.402	$y = 1.886300 * x - 1.633177E-004$	0.9996	0.117	0.035	129	127
20	1,2-Dibromoethane	18.758	$y = 1.485851 * x - 1.379536E-004$	0.9997	0.119	0.036	107	109, 188
21	Chlorobenzene	20.017	$y = 9.561805 * x + 0.014300$	0.9996	0.322	0.097	112	77, 114
22	1,1,1,2-Tetrachloroethane	20.266	$y = 36.572088 * x + 0.001083$	0.9997	0.101	0.031	131	133, 119
23	Ethylbenzene	20.205	$y = 5.817481 * x - 0.001149$	0.9995	0.171	0.052	91	106
24	<i>m,p</i> -Xylene	20.570	$y = 27.057635 * x + 0.003155$	0.9995	0.102	0.031	106	91
25	Styrene	21.666	$y = 12.418970 * x - 0.004286$	0.9931	0.241	0.072	106	91
26	<i>o</i> -Xylene	21.640	$y = 13.423336 * x + 0.001023$	0.9997	0.100	0.030	104	78
27	Bromoform	22.189	$y = 2.204780 * x - 3.367844E-004$	0.9997	0.172	0.052	173	175, 254
28	4-Bromofluorobenzene (surrogate)	23.036	$y = 11.487625 * x - 7.553560E-004$	0.9996	0.105	0.032	95	174, 176
29	1,1,2,2-Tetrachloroethane	23.523	$y = 5.835213 * x - 0.001140$	0.9998	0.134	0.040	83	131, 85
30	1,2,3-Trichloropropane	23.375	$y = 6.683218 * x - 2.225683E-004$	0.9998	0.206	0.062	75	77
31	1,3,5-Trimethylbenzene	24.162	$y = 29.367748 * x - 0.006584$	0.9990	0.192	0.058	105	120
32	1,2,4-Trimethylbenzene	25.173	$y = 26.561166 * x + 2.444729E-004$	0.9990	0.149	0.045	105	120
33	1,3-Dichlorobenzene	25.954	$y = 15.629264 * x - 0.001070$	0.9996	0.104	0.031	146	111, 148
34	1,4-Dichlorobenzene	26.181	$y = 14.892998 * x - 0.001860$	0.9994	0.091	0.028	146	111, 148
35	1,2-Dichlorobenzene	27.184	$y = 14.968164 * x - 8.822657E-004$	0.9997	0.108	0.033	146	111, 148
36	1,2,4-Trichlorobenzene	31.401	$y = 10.835935 * x - 5.724957E-004$	0.9994	0.158	0.048	180	182, 145
37	Hexachlorobutadiene	31.856	$y = 7.775980 * x - 7.142012E-004$	0.9997	0.139	0.042	225	223, 227



**Figure 2.** Overlaid TIC SIM traces of eight replicates of dibromochloromethane and 1,2-dibromoethane at 50 ng/L in 10 mL of matrix modifier.

In the concentration range (50 ng/L to 5 µg/L), 36 compounds had  $R^2 > 0.999$ . Two compounds were exceptions: methylene chloride and styrene. The  $R^2$  for styrene was 0.993, not as good as other compounds, but still within HJ642-2013 requirements for linear calibration. The methylene chloride concentration in the background was more than 100 ng/L, which interfered with the low end of the linearity range. With background subtraction, methylene chloride linearity improved, from 200 ng/L to 5 µg/L, as shown in Table 4.

## Conclusions

This Application Note demonstrates that an 8890 GC and 5977B GC/MSD coupled with a 7697A headspace sampler is an ideal platform for sensitive and reliable analysis of VOCs in soil and sediments. System quantitation precision (1–5 %), low LOD/LOQ (LOD was in the range of 1.0 to 2.5 µg/kg for real soil or sediment sample), excellent linearity for most compounds with regression coefficients  $> 0.995$ , and good method recovery rates (73–115 %) all met or exceeded the

requirement of Chinese Environmental Standard HJ642-2013. In addition, if users require more sensitive detection, the HES MSD operating parameters can be optimized to give a 100 ppt-level detection limit and good linearity in low concentration ranges.

## References

1. Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis. *US EPA Method 5021* **1996**, revision 0, US EPA, USA.
2. Soil and Sediment. Determination of Volatile Organic Compounds - Headspace-Gas Chromatography/Mass Method. HJ 642-2013, published by Ministry of Ecology and Environment of the People's Republic of China.
3. Soil and Sediment - Determination of Volatile Organic Compounds - Headspace-Gas Chromatography Method. HJ 741-2015 published by Ministry of Ecology and Environment of the People's Republic of China.
4. Improved Volatiles Analysis Using Static Headspace, the Agilent 5977B GC/MSD, and a High-efficiency Source. *Agilent Technologies Application Note*, publication number 5991-6539EN, **2016**.

[www.agilent.com/chem](http://www.agilent.com/chem)

This information is subject to change without notice.

© Agilent Technologies, Inc. 2019  
Printed in the USA, March 27, 2019  
5994-0662EN