

Gas Chromatography/ Mass Spectrometry

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Determination of Volatile Organic Compounds in Soils By HS-GC/MS

Introduction

Volatile organic compounds (VOCs) are a series of compounds with boiling points from 50 to 250 degrees centigrade and are widely used as industrial chemicals/

solvents. Low concentrations of VOCs can have a significant impact on human health, as many are regarded as highly toxic, refractory and carcinogenic. The detection and determination of VOCs in the environment is of the utmost importance for both human and environmental health.

The US EPA method 5021 is a general purpose method for the preparation of VOCs in soil samples using a headspace procedure for determination by gas chromatography/mass spectrometry (GC/MS) as mentioned in method 8260.¹ China environmental protection standard HJ642-2013 is also established for determination of VOCs in soil and sediment by HS-GC/MS which is applicable to thirty-six VOCs.²

The EPA methods and China standard mentioned above requires not only the demonstration of laboratory sample preparation and handling competence but instrument performance as well. The study presented here demonstrates the determination of volatile organic compounds in soils using a PerkinElmer TurboMatrix™ HS40 and the PerkinElmer Clarus® SQ8 GC/MS. In this study, thirty-six VOCs are investigated in soil. Detailed instrument method parameters are presented with precision, recovery, linearity and detection limit results. This application note demonstrates that the TurboMatrix HS40 and Clarus SQ 8 GC/MS meets or exceeds the performance criteria set out in HJ642-2013 and EPA method 5021/8260.

Experimental

The PerkinElmer Clarus SQ 8 GC/MS operating in electron ionization mode with TurboMatrix HS40 were used to perform these experiments with the method conditions presented in Table 1. The transfer line of the headspace device was connected directly to the injector port of the Clarus 680 GC. A PerkinElmer Elite 624 column (60 m × 0.32 mm × 1.8 μm) was used as this column efficiently focuses and separates the volatiles.

Thirty-six compounds were investigated using standards that were purchased from ANPEL Laboratory Technologies (Shanghai) Inc.

- Calibration standards: thirty-six VOCs.
- Internal standards: fluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4.
- Surrogate compounds: 4-bromofluorobenzene and toluene-d8.

The method for preparing the matrix modifying solution was carried out according to the following steps: Using a pH meter, added concentrated phosphoric acid (H₃PO₄) drop wise to 500 mL of organic-free reagent water until the pH was 2. Add 180 g of NaCl and mix well until all components were dissolved. Stock standards, internal and surrogate standards were diluted with methanol to the required concentration then added to the 22 mL glass headspace vials containing 2.0 g of quartz sand and 5.0 mL of matrix modifying solution. The vials were sealed immediately with the PTFE side of the septum facing toward the sample. The calibration levels in this study are presented in Table 2.

Results and Discussion

Figure 1 shows the total ion chromatogram (TIC) of a high-level (500 μg/kg) standard. A low initial oven temperature (35 °C) was used to achieve good peak resolution especially for the low boiling point VOCs.

In comparison with the 10 mL of modifier reported in HJ642-2013 and EPA method 5021, 5 mL of modifier was added to the vial in this study. We evaluated two different volumes of modifier solution and determined that the peak area with 5 mL of modifier is larger than that with 10 mL of modifier especially for polar compounds which have a larger partition coefficient (K) in the soil matrix. Therefore 5 mL of modifier was used in this study. The use of a smaller volume of modifier meets the performance criteria set out in regulatory requirements and reduces sample preparation costs and produces less waste.

Table 3 presents the results for linearity, precision (%RSD), method detection limits (MDLs), method quantitation limits (MQLs) and percent recovery. Method detection limits were determined by analyzing seven replicate samples at a concentration of 2.5 μg/kg. Precision and recovery were measured by analyzing ten replicates at a concentration of 100 μg/kg and 250 μg/kg as per HJ642-2013. All of the analytes meet or exceed the minimum method requirements with excellent detection limits, stability and recovery.

Table 1. Analytical parameters.

Headspace Sampler Parameters			
Oven Temperature	70 °C		
Needle Temperature	95 °C		
Transfer Line Temperature	110 °C		
Thermostat Time	50 min		
Vial Pressurization Time	1.5 min		
Withdraw Time	0.2 min		
Injection Time	0.05 min		
Column Pressure	22 psi		
Vial Pressure	30 psi		
GC Parameters			
Analytical Column	Perkinelmer Elite-624 (60 m x 0.32 mm x 1.8 μm)		
Injector Type	Capillary injector with capillary split liner		
Injector Temp	120 °C		
Carrier Gas Flow	1 mL/min		
Split Flow	20 mL/min		
Oven Program	Temperature	Hold Time	Rate
	35 °C	3 min	4 °C/min
	120 °C	0 min	8 °C/min
	180 °C	0 min	15 °C/min
	220 °C	10 min	END
MS Parameters			
GC Inlet Line Temp	250 °C		
Ion Source Temp	230 °C		
Solvent Delay	3 min		
Function Type	SIFI		

Table 2. Calibration points employed in this study.

Calibration Level	1	2	3	4	5
Calibration Standards Concentration (μg/kg)	25.0	50.0	100.0	250.0	500.0
Surrogate Concentration (μg/kg)	25.0	50.0	100.0	250.0	500.0
Internal Standards Concentration (μg/kg)	250.0	250.0	250.0	250.0	250.0

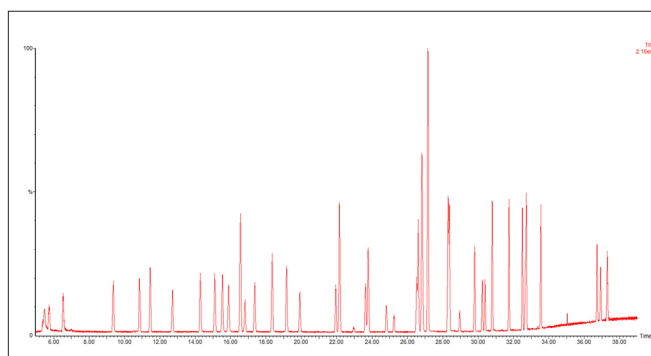


Figure 1. TIC of volatile organic standard mix at 500 μg/kg. Targets are listed in Table 3.

Table 3. Summarized results of the analyzed VOCs.

Compound	Linearity		RSD% (n=10)		MDL µg/kg	MQL µg/kg	Recovery%	
	Calibration Curve	r ²	100 µg/kg	250 µg/ kg			100 µg/kg	250 µg/kg
Vinyl Chloride	0.2675 X - 8.2806	0.9995	2.08	3.25	0.97	3.86	102.72	100.91
1,1-Dichloroethene	0.1948 X - 6.672	0.9994	3.18	3.27	0.85	3.4	107.3	102.32
Methylene Chloride	0.2182 X - 4.3497	0.9991	3.53	4.22	1.11	4.44	92.72	97.71
Trans-1,2-Dichloroethene	0.2143 X - 5.3891	0.9994	2.51	3.3	0.58	2.34	104.81	102.19
1,1-Dichloroethane	0.3642 X - 7.2780	0.9997	2.79	4.57	0.84	3.35	100.95	100.19
Cis-1,2-Dichloroethene	0.2226 X - 4.6008	0.9992	2.78	3.44	0.62	2.47	100.25	99.85
Chloroform	0.3611 X - 5.2598	0.9997	3.32	4.63	0.8	3.18	98.82	99.9
1,1,1-Trichloroethane	0.2911 X - 8.9176	0.9997	3.22	4.83	0.7	2.81	108.86	105.22
Carbon Tetrachloride	0.2570 X - 8.8008	0.9998	3.12	4.66	0.79	3.14	106.61	105.88
1,2-Dichloroethane	0.1959 X - 3.7388	0.9991	3.47	4.37	1.09	4.36	87.95	99.15
Benzene	1.0065 X - 4.5943	0.9998	2.06	3.03	0.54	2.17	100.6	101.81
Fluorobenzene	-	-	-	-	-	-	-	-
Trichloroethene	0.2162 X - 4.8155	0.9995	2.78	3.39	1.07	4.28	108.49	105.65
1,2-Dichloropropane	0.2357 X - 5.4219	0.9995	3.42	3.88	0.92	3.66	100.22	100.28
Bromodichloromethane	0.1956 X - 4.8842	0.9994	3.84	4.06	1	4.01	95.59	98.82
Toluene-d8	0.2786 X - 1.7432	0.999	8.76	7.87	-	-	93.23	105.18
Toluene	0.7943 X + 1.7986	0.9984	1.67	2.2	0.75	2.98	106.71	106.52
1,1,2-Trichloroethane	0.1253 X - 3.4926	0.9985	4.58	3.63	1.16	4.66	89.55	96.16
Tetrachloroethene	0.1895 X - 3.1960	0.9996	2.86	3.01	0.95	3.79	99.98	108.15
Dibromochloromethane	0.1171 X - 4.5257	0.9992	4.53	3.24	1.24	4.95	90.03	97.53
1,2-Dibromoethane	0.1074 X - 4.1482	0.9991	4.93	3.01	1.16	4.64	86.48	94.58
Chlorobenzene-d5	-	-	-	-	-	-	-	-
Chlorobenzene	0.7983 X - 5.7920	0.9999	2.9	2.15	0.77	3.07	101.08	99.14
Ethylbenzene	1.3471 X - 11.0651	0.9997	1.52	2.05	0.92	3.68	105.97	107.52
1,1,1,2-Tetrachloroethane	0.2892 X - 12.2255	0.9996	3.63	4.31	0.6	2.4	102.38	95.6
m-Xylene/p-Xylene	0.9678 X - 14.4938	0.9993	1.56	2.07	0.76	3.02	103.51	107.39
o-Xylene	0.4476 X - 9.6751	0.9996	1.59	1.83	0.82	3.28	110.14	109
Styrene	0.6339 X - 11.0403	0.9987	1.79	1.79	0.73	2.91	97.83	98.3
Bromoform	0.1132 X - 7.7739	0.9987	7.22	3.54	1.24	4.95	86.96	92.51
4-Bromofluorobenzene	0.2874 X - 5.2776	0.9992	4.98	6.14	-	-	97.7	102
1,1,1,2,2-Tetrachloroethane	0.3646 X - 7.1050	0.9999	3.08	2.58	1.08	4.3	75.69	91.49
1,2,3-Trichloropropane	0.3104 X - 8.1093	0.9998	3.17	2.67	1.02	4.06	74.92	89.56
1,3,5-Trimethylbenzene	3.0164 X - 26.6019	0.9987	1.55	3.34	0.79	3.18	108.75	103.7
1,2,4-Trimethylbenzene	2.5894 X - 19.6923	0.9995	1.48	2.89	0.84	3.36	109.87	102.42
1,3-Dichlorobenzene	1.4837 X - 14.1402	0.9996	2.06	2.88	0.71	2.85	100.52	93.09
1,4-Dichlorobenzene-d4	-	-	-	-	-	-	-	-
1,4-Dichlorobenzene	1.3404 X - 1.4877	0.9991	1.91	2.55	0.91	3.63	99.47	92.63
1,2-Dichlorobenzene	1.3460 X - 13.2789	0.9997	2.25	2.78	0.89	3.57	93.7	89.5
1,2,4-Trichlorobenzene	0.7417 X - 29.6262	0.9954	2.35	7.45	1.18	4.71	104.24	108.82
Hexachlorobutadiene	0.4066 X - 24.1479	0.995	3.4	8.94	1.17	4.69	117.51	106.41

Summary

The analysis of thirty-six VOCs in soil following HJ642-2013 and EPA method 5021-8260 is reproduced easily by the PerkinElmer TurboMatrix HS40 - Clarus SQ 8 GC/MS.

All of the analytes presented meet or exceed the minimum method requirements with excellent detection limits, stability and recovery.

References

1. Method 5021, Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis, USEPA.
2. HJ642-2013, Soil and sediment-Determination of volatile organic compounds-Headspace-gas chromatography/mass method, The China's Ministry of Environmental Protection.