Application Note

Soils, Sludges, and Sediments

Determination of Volatile Organic Compounds in Soil and Sediment by Purge and Trap GC/MS

Method HJ 605-2011

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Abstract

Method HJ 605-2011 was used to determine the concentration of volatile organic compounds (VOCs) in soil and sediment. This Application Note presents a method for their analysis using an Agilent 7890B GC, an Agilent 5977B GC/MSD, and a Teledyne Tekmar Atomx XYZ purge and trap (P&T) sampler.

Introduction

With the acceleration of urbanization and industrialization, the pollution of VOCs in soil is becoming more and more serious. Volatile organic pollutants in soil affect the growth of plants and animals, thus harming human health. Soil organic pollutants easily enter the atmosphere and water through wind and water power, resulting in air and water pollution. Currently, most countries have corresponding detection standards for VOCs in soil, such as EPA 8260C in the United States. China has also issued corresponding detection standards, such as HJ 605-2011 (Determination of Volatile Organic Compounds in Soil and Sediment by Purge and Trap Gas Chromatography/Mass Spectrometry)[1] and HJ642-2013 (Determination of Volatile Organic Compounds in Soil and Sediment by Headspace Gas Chromatography/Mass Spectrometry).

This Application Note demonstrates that an 7890B GC combined with a 5977 GC/MSD with a purge and trap (P&T) sampler can easily achieve the performance specification for 65 VOCs in method HJ 605-2011. The calibration curves determined for those target compounds were found to be within method requirements. The correlation coefficients were also well above 0.993. A concentration RSD of 0.9 to 12.2 % was determined for each compound. Limits of detection (LODs) were 0.2 to 1.6 µg/L.

Experimental

Tables 1 and 2 describe the P&T/GC/MSD systems used for these experiments.

Sample preparation

The stock solution of 65 VOCs at a concentration of 10 µg/mL was prepared in methanol. An internal standard (IS) mixture of fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 was diluted with methanol at 25 µg/mL. A surrogate mixture of dibromofluoromethane, toluene-d_8, and 4-bromofluorobenzene at 10 µg/mL was prepared in methanol.

The 10 µg/mL stock solution and 10 µg/mL surrogate solution were diluted to create 5, 20, 50, 100, and 200 µg/L standard solutions. Five 40-mL vials were prepared at each calibration level by filling each vial with 5 mL of standard solutions and 10 µL of internal standard, corresponding to an internal standard concentration of 50 µg/L. Finally, 15 mL of ultrapure water was added to each vial.

Table 1. Teledyne Tekmar Atomx XYZ P&T Sampler conditions. Method type: soil. Teklink method for the Atomx with a 5-mL purge vessel using trap number 9.

Parameter	Value
Standby	
Valve oven temperature	140 °C
Transfer line temperature	140 °C
Sample mount temperature	90 °C
Water heater temperature	90 °C
Sample cup temperature	20 °C
Soil valve temperature	100 °C
Standby flow	10 mL/min
Purge ready temperature	40 °C
Purge	
Water volume	0 mL
Purge mix speed	Medium
Purge time	11 minutes
Purge flow	40 mL/min
Purge temperature	20 °C
MCS purge temperature	20 °C
Dry purge time	2 minutes
Dry purge flow	100 mL/min
Desorb	
Water needle rinse volume	7 mL
Sweep needle time	0.25 minutes
Desorb preheat temperature	245 °C
GC start signal	Begin desorb
Desorb time	2 min
Drain flow	300 mL/min
Desorb temperature	250 °C
Bake	
Bake time	2 minutes
Bake flow	200 mL/min
Bake temperature	280 °C
MCS bake temperature	180 °C

Results and discussion

The MSD data were collected in scan mode and analyzed by Agilent MassHunter software. Figure 1 shows a typical chromatogram of 65 target compounds at a concentration of 50 µg/L. Peak shape is very important for integration, quantitation, and reproducibility. The early eluting compounds should receive particular attention. These compounds are extremely volatile, and coelute with water and methanol. Note that the amount of methanol in the working solution may affect the peak shape and response of bromomethane and chloroethane. To obtain a stable and reliable response, the volume of methanol in each working solution was suggested to be fixed.

Table 2. Instrument conditions. Method type: soil.

7890B GC	
Inlet	200 °C, split 30:1
Liner	Ultra Inert inlet liner, straight, 2 mm id (p/n 5190-6168)
Column	Agilent DB-624 Ultra Inert, 30 m × 0.25 mm, 1.4 µm (p/n 122-1334UI)
Carrier	Helium, 1.5 mL/min, constant flow
Oven	38 °C (1.8 minutes), then 10 °C/min to 120 °C, then 15 °C/min to 240 °C (2 minutes)
Transfer line temperature	280 °C
5977B GC/MSD	
Parameter	Value
Ionization type	EI
Source temperature	230 °C
Quad temperature	150 °C
Drawout plate	6 mm
Tune file	Atune.u
Acquisition type	Scan
Solvent delay	0 minutes
Gain factor	1

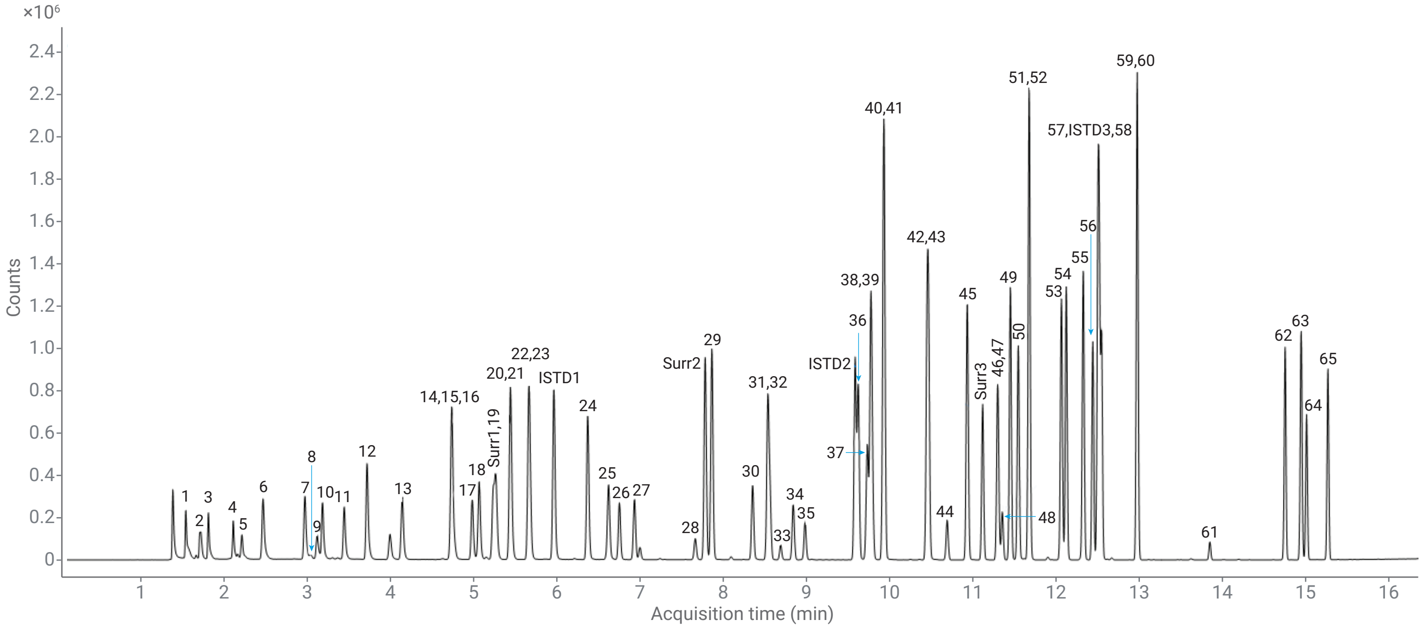

Figure 1. Total ion chromatogram of the 65 target compounds (50 µg/L). See Table 3 for peak identifications.

The calibration curve was developed based on the ISTD method for five concentration levels from 5 to 200 µg/L. The 6-mm drawout lens was used for best linearity for all compounds.

Table 3 shows the R^2 values for the five-level calibration. Excellent linearity is shown for all compounds, with an R^2 range of 0.993 to 0.9999.

Repeatability (n = 6) was tested at 5 and 20 µg/L levels. The concentration %RSD was 0.9 to 12.2 %. For most compounds, the %RSD was well below 5 %.

Table 3. R^2 values for 65 VOCs in the calibration standard over the 5 to 200 µg/L range of this study.

Number	Name	RT	*m/z*	CF R^2
Istd1	Fluorobenzene	6.017	96	
1	Dichlorodifluoromethane	1.464	85	0.9998
2	Chloromethane	1.638	50	0.9998
3	Chloroethene	1.754	62	0.9998
4	Bromomethane	2.065	94	0.9999
5	Chloroethane	2.162	64	0.9989
6	Trichloromonofluoromethane	2.429	101	0.9999
7	1,1-Dichloroethene	2.962	96	0.9999
8	Acetone	3.069	58	0.9930
9	Iodomethane	3.107	142	0.9961
10	Carbon disulfide	3.165	76	0.9999
11	Methylene chloride	3.451	84	0.9999
12	*trans*-1,2-Dichloroethene	3.741	96	0.9999
13	1,1-Dichloroethane	4.165	63	0.9998
14	*cis*-1,2-Dichloroethene	4.776	95.9	0.9995
15	2,2-Dichloropropane	4.776	77	0.9997
16	2-Butanone	4.834	72	0.9971
17	Bromochloromethane	5.024	130	0.9995
18	Chloroform	5.117	83	0.9999
Surr1	Dibromofluoromethane	5.281	111	0.9995
19	1,1,1-Trichloroethane	5.316	99	0.9998
20	1,1-Dichloropropene	5.496	75	0.9997
21	Carbon tetrachloride	5.499	119	0.9996
22	Benzene	5.718	78	0.9999
23	1,2-Dichloroethane	5.724	62	0.9997
24	Trichloroethylene	6.441	132	0.9998
25	1,2-Dichloropropane	6.683	63	0.9999
26	Dibromomethane	6.808	174	0.9993
27	Bromodichloromethane	6.998	83	0.9996
28	4-Methyl-2-pentanone	7.756	85	0.9965
Istd2	Chlorobenzene-d_5	9.685	117	
Surr2	Toluene-d_8	7.869	98	0.9995
29	Toluene	7.949	92	0.9993
30	1,1,2-Trichloroethane	8.438	83	0.9991
31	Tetrachloroethylene	8.634	166	0.9985
32	1,3-Dichloropropane	8.644	76	0.9987
33	2-Hexanone	8.789	58	0.9974
34	Dibromochloromethane	8.924	129	0.9983
35	1,2-Dibromoethane	9.065	109	0.9985
36	Chlorobenzene	9.724	112	0.9992
37	1,1,1,2-Tetrachloroethane	9.837	133	0.9990
38	1,1,2-Trichloropropane	9.888	63	0.9993
39	Ethylbenzene	9.892	91	0.9997
40,41	*m,p*-Xylene	10.049	106	0.9993
42	*o*-Xylene	10.567	91.1	0.9991
43	Styrene	10.58	104	0.9989
44	Bromoform	10.782	173	0.9959
Istd3	1,4-Dichlorobenzene-d_4	12.608	152	
45	Isopropylbenzene	11.046	105	0.9996
Surr3	4-Bromofluorobenzene	11.22	174	0.9989
46	Bromobenzene	11.39	156	0.9988
47	1,1,2,2-Tetrachloroethane	11.396	83	0.9965
48	1,2,3-Trichloropropane	11.438	75	0.9986
49	*n*-Propylbenzene	11.56	91	0.9998
50	2-Chlorotoluene	11.644	91	0.9996
51	4-Chlorotoluene	11.779	91.1	0.9994
52	1,3,5-Trimethylbenzene	11.782	105	0.9995
53	*tert*-Butylbenzene	12.168	119	0.9994
54	1,2,4-Trimethylbenzene	12.226	105	0.9998
55	*sec*-Butylbenzene	12.432	105	0.9999
56	1,3-Dichlorobenzene	12.535	146	0.9995
57	*p*-Isopropyltoluene	12.609	119	0.9998
58	1,4-Dichlorobenzene	12.641	146	0.9996
59	1,2-Dichlorobenzene	13.062	146	0.9991
60	n-Butylbenzene	13.081	91	0.9998
61	1,2-Dibromo-3-chloropropane	13.93	157	0.9954
62	1,2,4-Trichlorobenzene	14.856	182	0.9984
63	Hexachlorobutadiene	15.065	224.8	0.9982
64	Naphthalene	15.113	128	0.9989
65	1,2,3-Trichlorobenzene	15.374	182	0.9987

Table 4 shows that all compounds met the HJ 605 method criteria of less than 20 % RSD.

Table 4 also shows the LOD and limit of quantitation (LOQ) study for 65 compounds. The LOD and LOQ values were calculated from the standard deviation of six replicate runs of the lowest calibration standard. All LODs were below 1 µg/L except for three compounds, which had LODs below 2 µg/L.

Method recoveries were measured by analyzing unspiked and spiked soil samples. Standards containing 65 target compounds were spiked into the real soil sample at 50 µg/L. Table 4 shows the results, illustrating that the recovery of 50 µg/L ranged from 76.1 to 135.6 %.

Table 4. RSD, MDL, and recovery percentages for VOCs.

	RSD (n = 6)				
Name	**5 µg/L**	**20 µg/L**	**LOD**	**LOQ**	**Recovery %**
Dichlorodifluoromethane	3.3	2.7	0.5	1.6	88.9
Chloromethane	3.8	3	0.6	1.8	86.7
Chloroethene	2.3	3	0.3	1.1	98.7
Bromomethane	5	7.1	0.7	2.5	108.7
Chloroethane	12.2	4.2	1.6	5.4	83.3
Trichloromonofluoromethane	2.5	2.4	0.4	1.2	98.0
1,1-Dichloroethene	3.9	2.3	0.6	1.9	98.0
Acetone	6.8	6.8	1.0	3.5	135.6
Iodomethane	1	1.5	0.2	0.5	76.1
Carbon disulfide	2.7	2.5	0.4	1.3	94.0
Methylene chloride	1.7	2.5	0.2	0.8	105.0
trans-1,2-Dichloroethene	2.7	2.6	0.4	1.3	95.9
1,1-Dichloroethane	2.5	2.3	0.4	1.3	98.9
2,2-Dichloropropane	2.3	2	0.3	1.1	97.9
cis-1,2-Dichloroethene	3.1	4	0.4	1.5	126.9
2-Butanone	5.9	5.6	0.9	3.1	119.6
Bromochloromethane	2.1	1.7	0.3	1.0	100.3
Chloroform	2.7	4.2	0.4	1.4	101.2
Dibromofluoromethane	2.4	2.5	0.3	1.2	99.2
1,1,1-Trichloroethane	2.6	2.4	0.4	1.3	97.1
1,1-Dichloropropene	1.9	1.7	0.3	1.0	95.5
Carbon tetrachloride	3.3	2.1	0.5	1.6	92.1
Benzene	2.3	2.6	0.3	1.1	98.7
1,2-Dichloroethane	1	2	0.2	0.5	98.0
Trichloroethylene	2	2.5	0.3	1.0	99.5
1,2-Dichloropropane	2.4	2.6	0.4	1.2	102.1
Dibromomethane	2.1	0.9	0.3	1.0	97.0
Bromodichloromethane	2.1	2.2	0.3	1.0	98.6
4-Methyl-2-pentanone	3.3	2.4	0.5	1.6	96.4
Toluene-d_8	1.9	2	0.3	0.9	99.1
Toluene	2.7	2.2	0.4	1.3	101.3
1,1,2-Trichloroethane	3.1	1.5	0.5	1.6	99.5
Tetrachloroethylene	3.1	2.3	0.5	1.5	98.9
1,3-Dichloropropane	2.9	2.5	0.4	1.5	99.1
Dibromochloromethane	9.1	3.8	1.5	5.0	106.1
1,2-Dibromoethane	1.7	1.8	0.3	0.9	97.7
2-Hexanone	2.4	1.8	0.4	1.2	95.7
Chlorobenzene	1.7	2	0.3	0.9	100.2
1,1,1,2-Tetrachloroethane	2.4	2.3	0.4	1.2	101.6
1,1,2-Trichloropropane	1.9	2.2	0.3	1.0	100.8
Ethylbenzene	2.2	1.6	0.3	1.1	101.9
m,p-Xylene	2.1	2.3	0.3	1.0	98.7
o-Xylene	2.1	2.1	0.3	1.0	96.5
Styrene	2.4	2	0.4	1.2	89.7
Bromoform	2.7	2.5	0.4	1.4	90.8
Isopropylbenzene	4.3	4.5	0.6	2.2	102.6
4-Bromofluorobenzene	4.5	4	0.7	2.2	101.1
Bromobenzene	3.9	4.3	0.6	1.9	100.2
1,1,2,2-Tetrachloroethane	3.5	4.4	0.5	1.8	90.7
1,2,3-Trichloropropane	7.5	4.7	1.1	3.7	95.1
n-Propylbenzene	4.2	4.2	0.6	2.1	103.8
2-Chlorotoluene	3.6	4.3	0.5	1.8	103.1
4-Chlorotoluene	3.9	4	0.6	1.9	102.2
1,3,5-Trimethylbenzene	3.8	3.8	0.6	1.9	103.6
tert-Butylbenzene	3.7	4.5	0.5	1.8	98.9
1,2,4-Trimethylbenzene	4.2	3.9	0.6	2.1	104.6
sec-Butylbenzene	4.1	3.9	0.6	2.0	100.5
1,3-Dichlorobenzene	4.1	4	0.6	2.0	103.0
p-Isopropyltoluene	4.1	3.8	0.6	2.0	99.2
1,4-Dichlorobenzene	4.2	3.8	0.6	2.1	102.8
1,2-Dichlorobenzene	4.5	3.9	0.7	2.2	95.0
n-Butylbenzene	4.4	3.9	0.6	2.1	99.2
1,2-Dibromo-3-chloropropane	5.7	4.2	0.9	3.0	86.6
1,2,4-Trichlorobenzene	4.2	4.4	0.6	2.1	87.2
Hexachlorobutadiene	4.4	4	0.7	2.2	80.5
Naphthalene	5.4	5.7	0.8	2.8	78.3
1,2,3-Trichlorobenzene	4.1	4.8	0.6	2.0	83.7

Conclusion

This Application Note demonstrates the capability of the 7890B GC, 5977B GC/MSD, and the Atomx XYZ P&T sampler system to process VOCs in soil and sediment following the HJ 605-2011 method. Correlation coefficients were found to be 0.993 or better. The concentration RSD was 0.9 to 12.2 %. The LOD was 0.2 to 1.6 µg/L, and for most compounds, the LOD was less than 1 µg/L. The recovery was 76.1 to 135.6 %.

Reference

1. Soil and Sediment-Determination of Volatile Organic Compounds-Purge and Trap Gas Chromatography/ Mass Spectrometry Method. HJ 605-2011.

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