O·I·Analytical

Low-Level Volatiles in Soil and Water by USEPA Method 5035 Using the Model 4552 Water/Soil Autosampler

Application Note 14120305

Keywords
BTEX
Model 4552
Purge and Trap
Soil
USEPA Method 5035
USEPA Method 8021B
VOC
Water

Introduction

One of the most difficult technical challenges associated with the analysis of volatile organic compounds (VOCs) in soil and water is preventing the loss of volatile target analytes during sampling, shipping, and handling in the laboratory. The observed loss of VOCs is usually attributed to two principal causes, volatilization and biodegradation. In water samples, loss of VOCs through volatilization is addressed fairly easily by eliminating or minimizing the headspace above the water in the sampling vial; losses accredited to biodegradation are prevented by adding a preservative.

Initially, methods for collecting soils in the field attempted to adapt the techniques used for water samples by tightly packing the soil into collection vials in a way that would minimize headspace. However, once in the lab, the vial had to be reopened for subsampling, disturbing the sample matrix and causing a loss of the volatile compounds. Even though surrogate and matrix spike recoveries were often excellent, analyte losses were occurring before the addition of analytical standards, and sample results could be biased low by as much as one or two orders of magnitude.[1] Methanol preservation in the field is a widely accepted alternative that will minimize VOC losses in midlevel soil samples, but the procedure is not always appropriate for low concentrations and introduces additional safety issues related to the handling and shipping of a flammable solvent.

In 1997, the United States Environmental Protection Agency (USEPA) released Update III of SW-846, which introduced USEPA Method 5035 for the collection, transport, storage, and analysis of low-level volatile compounds in solid matrices. Method 5035 addresses the loss of VOCs from soil matrices through a “closed-system purge-and-trap” approach. Once an appropriate sample aliquot has been added to a preservative in the sampling container, the seal is not broken again until analysis, thus minimizing analyte losses through volatilization. Sodium bisulfate is used as a chemical preservative to control the loss of VOCs through biodegradation. This updated SW-846 method is expected to improve the accuracy of VOC analytical results obtained from solid sample matrices.[1]

Method Summary

Method 5035 is a closed-system purge-and-trap process for the analysis of low concentration VOCs in soil, sediment, and other solid waste matrices. It is used in conjunction with determinative gas chromatography methods such as Method 8015 (GC/FID), Method 8021B (GC/PID/ELCD), Method 8260 (GC/MS), or BTEX (GC/PID) and specifies an anticipated concentration range of 0.5 to 200 mg/kg (ppb). The

OI Analytical Model 4552 Water/Soil Autosampler has been developed specifically for processing soil samples using the closed-system purge-and-trap process.

Soils

Approximately 5 g of the soil sample matrix is collected in the field and placed in a preweighed sample vial (usually a 40-mL VOA vial) that already contains the sodium bisulfate preservative solution and a magnetic stir bar. The vial is sealed with a cap and a Teflon®-lined, low-bleed silicon septum, weighed, and shipped cold to the laboratory for analysis. (Note: A low-bleed septum is critical to avoid "septum bleed" peaks in the GC analysis.) The entire vial is placed, unopened, into the Model 4552 Autosampler and the "Soil" method type is selected on the keypad. The vial is raised onto the patented soil probe, where organic-free reagent water, surrogates, and internal standards are added automatically. The sample is heated and stirred inside the sealed VOA vial via the magnetic stir bar. The volatilized compounds are purged from the sample and travel through the soil probe to an inert, heated transfer line and onto a cool sorbent trap (in the purge-and-trap sample concentrator) that is specific to the application. The trap is then rapidly heated and, with a valve change, the analytes are desorbed as a "plug" under reversed flow of carrier gas onto the GC column. Low bias due to volatilization is minimized because the seal of the sample vial is never broken from the time of sampling until the time of analysis.[2]

Waters

If the sample has been identified as a "Water" in the autosampler method, the Model 4552's robotic arm moves the vial to a separate water sampling location. The vial is then lifted onto the water sampling probe and a programmed volume of water is transferred from the VOA vial to the purge and trap's sparge vessel. During the transfer, one or two analytical standards can be added to the sample. Once in the sparge vessel, the volatile components are stripped from the sample, trapped, and desorbed in the usual manner. The Model 4552 will also clean the needle, sparge tube, and all transfer lines using hot rinse water to minimize any carryover within the system.

Because the "Water" and "Soil" methods are configured separately, both types of samples can be run in one analytical sequence. Instrument configuration and operating conditions for both the "Water" and "Soil" methods used here are listed in Table 1.

Results and Discussion

Calibration

Six-point calibration curves were run for BTEX in both soil and water matrices over the calibration range of 0.5–200 ppb. The water calibration curve was created by selecting a "Water" method type. A 5-mL aliquot of each calibration standard was transferred from the Model 4552 directly to the purge-and-trap sample concentrator. The internal standard, fluorobenzene, was added automatically during the transfer, and the analysis proceeded in the usual manner. The soil calibration curve was acquired by selecting a "Soil" method type and purging a 5-mL aliquot of each calibration standard directly from the VOA vial using the Model 4552 soil probe. The calibration solutions for the "Soil" method contained sodium bisulfate preservative, precleaned white quartz sand, and a stir bar. They were heated and stirred during the purge step. Calibration response factors (RF), percent relative standard deviation (%RSD), and r^2 values for both types of calibration curves are listed in Table 2. Figure 1 and Figure 2 show graphical representations of the two types of calibration and typical BTEX calibration chromatograms from the Model 4552 Water/Soil Autosampler. The soil chromatogram shows the septum bleed peaks that appear when low-bleed septa are not used. The %RSD for all five peaks in both calibration curves fell significantly below the 20% criteria specified in USEPA Method 8000.[3]

Table 1. Instrument configuration and operating conditions

OI Analytical Model 4552 Water/Soil Autosampler	**Water Method**	**Soil Method**
Sample type	Water	Soil
Sample volume	5 mL	~5 g + 3 mL dilution water
Rinse volume (sparge vessel)	5 mL (rinsed twice)	(NA)
Standard 1 (Internal standard)	Yes	Yes
Standard 2	No	No
Stir	(NA)	YES
Preheat	(NA)	YES, 40°C
Purge time	(NA)	11 min
Transfer line temperature	(NA)	120°C
OI Analytical Model 4560 Purge and Trap	**Water Method**	**Soil Method**
Trap	#10 (Tenax®, silica gel, carbon molecular sieve)	
Purge time and temperature	11 min, 15 °C	11 min, 15 °C
Desorb time and temperature	4 min, 180 °C	4 min, 180 °C
Bake time and temperature	10 min, 190 °C	10 min, 190 °C
Infra-Sparge temperature	40 °C	(NA)
Sample inlet temperature	40 °C	(NA)
Water management	ON	ON
Valve temperature	100 °C	100 °C
Transfer line temperature	100 °C	100 °C
Total cycle time	25 min	25 min
Agilent 6890 Plus GC with EPC	**Setting**	
Column	Restek 502.2, 105 m, 0.53 I.D., 3-mm film thickness	
Carrier gas	Helium	
Injection port	OI Analytical Low-Dead Volume Injector, 180 °C	
Column flow	10 mL/min	
Oven program	*BTEX*	*8021B*
	30 °C for 1 min	35 °C for 5 min
	8 °C/min to 220 °C	4 °C/min to 200 °C
	Hold for 2.25 min	Hold for 2 min
	15 °C/min to 220 °C	Hold for 5 min
OI Analytical Model 4430 PID	**Setting**	
Temperature	220 °C	
Sweep gas	Hydrogen, 65 mL/min	
Make-up gas	Helium, 20 mL/min	
Total flow	100 mL/min	

Table 2. Calibration statistics for BTEX in water and soil with the Model 4552 Water/Soil Autosampler (calibration range 0.5–200 ppb)

Compound	**Water Calibration**			**Soil Calibration**		
	RF	**%RSD**	**r^2**	**RF**	**%RSD**	**r^2**
Benzene	1.32	1.1%	0.9997	1.09	3.7%	0.9997
Toluene	1.22	3.5%	0.9997	1.08	6.3%	0.9996
Ethyl Benzene	0.92	1.5%	0.9996	0.92	5.9%	0.9996
m/p-Xylene	2.35	3.6%	0.9993	2.17	5.2%	0.9994
o-Xylene	1.00	3.7%	1.0000	1.15	4.9%	0.9991

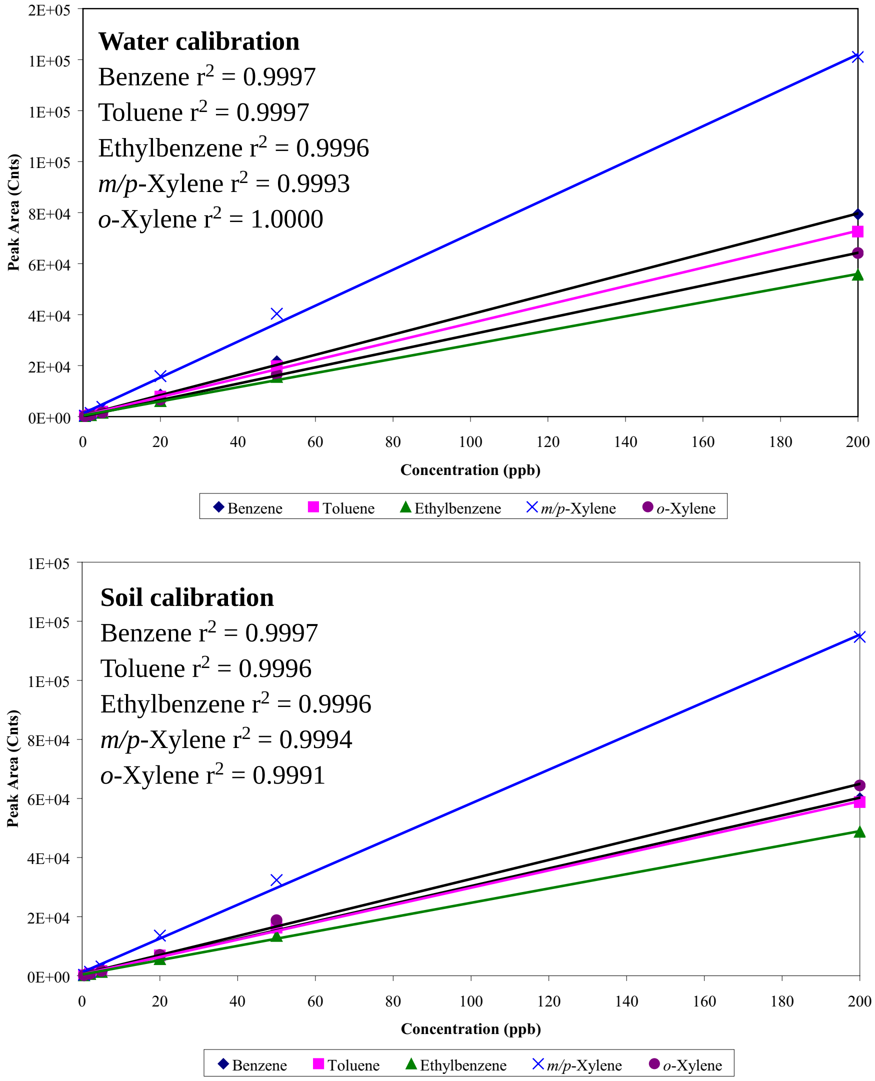

Figure 1. Water and soil calibration curves

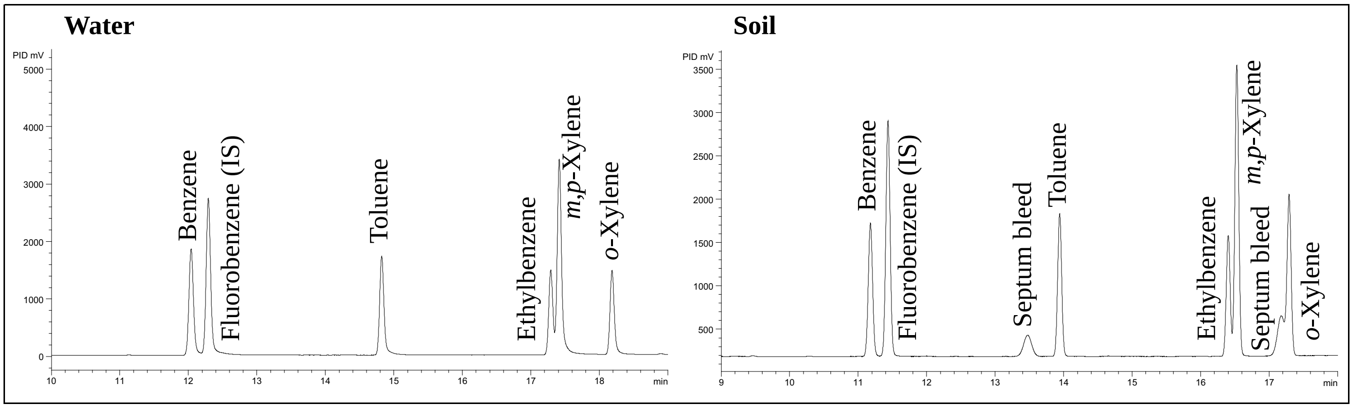

Figure 2. Typical PID chromatograms from calibration curves of BTEX in water and soil (The soil chromatogram shows "septum bleed" when low-bleed septa are not used.)

The ratio of raw area counts (soil/water) was calculated for all five peaks at each of the six calibration levels. For each compound, the ratio of raw area counts across the concentration range of 0.5–200 ppb remained consistent. In the calibration curve, there was a slightly better recovery of the lighter compounds using the "Water" method. For example, based on raw area counts, recovery of benzene using the "Soil" method averaged 77% recovery relative to the "Water" method. Relative recoveries for the other five compounds ranged from 82% to 107% (Table 3).

Table 3. Ratio of raw area counts (soil/water) for each compound in the six-point calibration curve

Concentration (ppb)	**Benzene**	**Toluene**	**Ethyl Benzene**	***m/p*-Xylene**	***o*-Xylene**
0.5	0.77	0.73	0.97	0.92	1.11
2.0	0.76	0.84	1.00	0.91	1.09
5.0	0.74	0.84	0.87	0.83	1.03
20.0	0.80	0.87	0.93	0.85	1.06
50.0	0.76	0.82	0.87	0.80	1.13
200.0	0.76	0.81	0.88	0.81	1.00
Average Ratio	*0.77*	*0.82*	*0.92*	*0.85*	*1.07*

The soil matrices' lower recovery can likely be attributed to two factors. In soil samples, analytes have a tendency to bind or adhere to the solid matrix, making them more difficult to strip during the purge cycle. Also, needle sparging, the purge method used for soils, is not as efficient as frit sparging. With frit sparging, the purge gas passes through a fine mesh frit, creating very finely divided purge gas streams that pass through the water and efficiently purges all analytes. With needle sparging, the gas stream is not quite so finely divided and does not pass completely through the entire sample aliquot, making its less efficient.

Method Detection Limits and Reproducibility

A 0.1 ppb standard solution was used to determine Method Detection Limits (MDLs) for BTEX in both soil and water matrices. Seven aliquots were run using each method, and statistical MDLs were calculated using the USEPA's *Definition and Procedure for the Determination of the Method Detection Limit*.[4] The calculated, statistical MDLs for all compounds in both matrices fell significantly below the lowest point on the calibration curve (0.5 ppb) and were comparable to the MDLs listed in USEPA Method 8021B.[5] Results of the MDL calculations are tabulated in Table 4. Relative recovery trends for the individual compounds at low concentrations were similar to those observed in the calibration curve. Reproducibility statistics and ratio of raw peak areas (soil/water) are listed in Table 5.

Table 4. Statistical MDLs for BTEX in water and soil compared to MDLs from USEPA Method 8021B[4,5]

Compound	**Water**	**Soil**	**Method 8021B**
	MDL (ppb)	**MDL (ppb)**	**MDL (ppb)**
Benzene	0.007	0.011	0.009
Toluene	0.009	0.010	0.01
Ethyl benzene	0.009	0.005	0.005
m/*p*-Xylene	0.012	0.014	0.02*
o-Xylene	0.017	0.017	0.02

*USEPA Method 8021B lists the MDLs for *m*-xylene and *p*-xylene as 10 ppb for each compound.

Table 5. Reproducibility statistics for BTEX in water and soil with the Model 4552 Water/Soil Autosampler

Compound	**Water (0.1 ppb)**		**Soil (0.1 ppb)**		**Ratio**
	Avg Peak Area	**%RSD (n = 7)**	**Avg Peak Area**	**%RSD (n = 7)**	**Soil/Water**
Benzene	51.64	2.3%	43.08	1.5%	0.83
Toluene	50.62	2.2%	39.93	1.2%	0.79
Ethyl benzene	39.18	2.3%	30.75	0.6%	0.78
m/*p*-Xylene	81.73	2.1%	81.32	1.5%	0.99
o-Xylene	38.05	5.0%	42.19	1.6%	1.10
Fluorobenzene (IS) (n=23)	12779.39	1.9%	11917.98	1.2%	—

Extended Analyte List and Real World Samples

USEPA Method 8021B is a determinative method for detection of aromatic and halogenated volatiles by gas chromatography using PID and/or ELCD. The Method 8021B analyte list includes 60 volatile compounds, including the six gases and BTEX, that can be determined by the method. The stated applicable concentration range for the method is 0.1–200 µg/L (ppb), and several different preparative methods are cited, including Method 5035. The full Method 8021B volatiles analyte list can be sampled, purged, and desorbed using the closed-system purge-and-trap process described here without any significant configuration or method changes. A chromatogram of the full Method 8021B analyte list, acquired using the Model 4552 Water/Soil Autosampler, is shown in Figure 3. The GC program used is listed in Table 1. Chromatograms of several real-world soil samples are shown in Figures 4, 5, and 6.

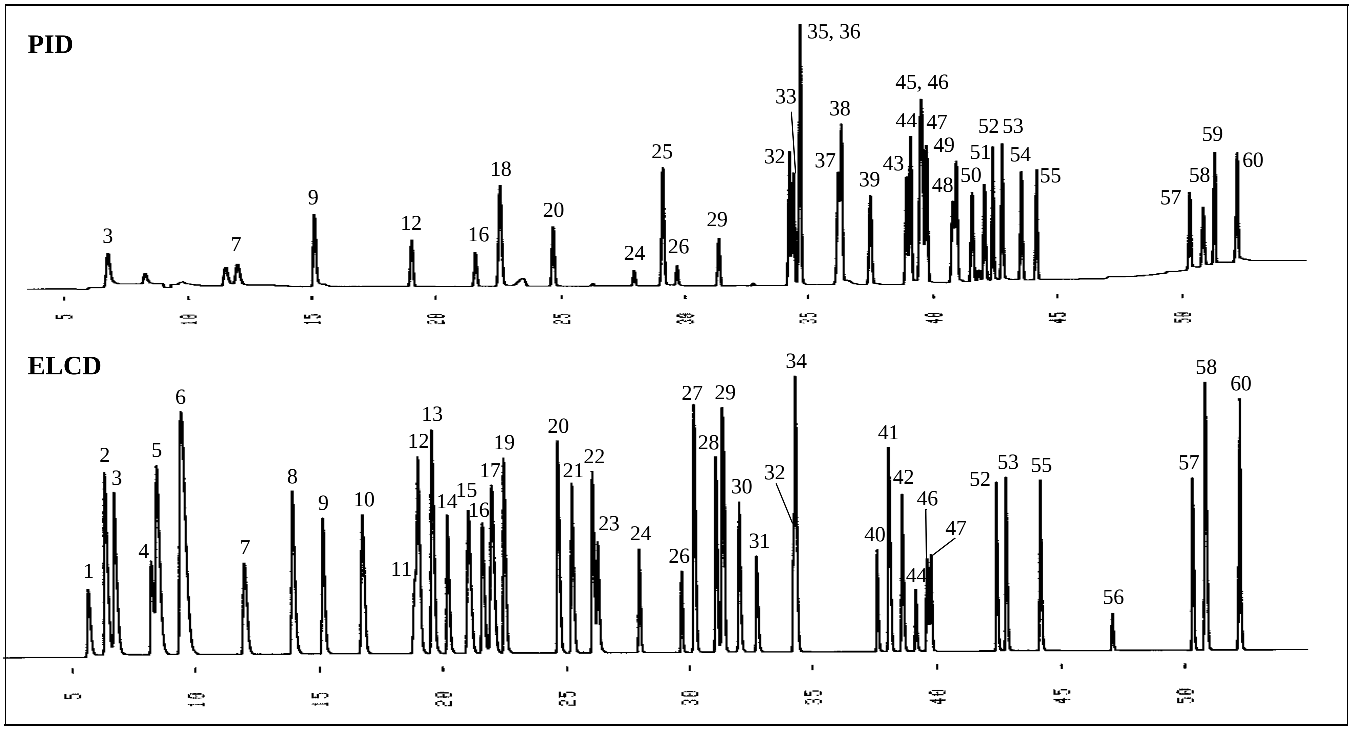

Figure 3. PID/ELCD chromatogram of a USEPA Method 8021B standard mixture (20 ppb), acquired using the Model 4552 W/S Autosampler (soil method)

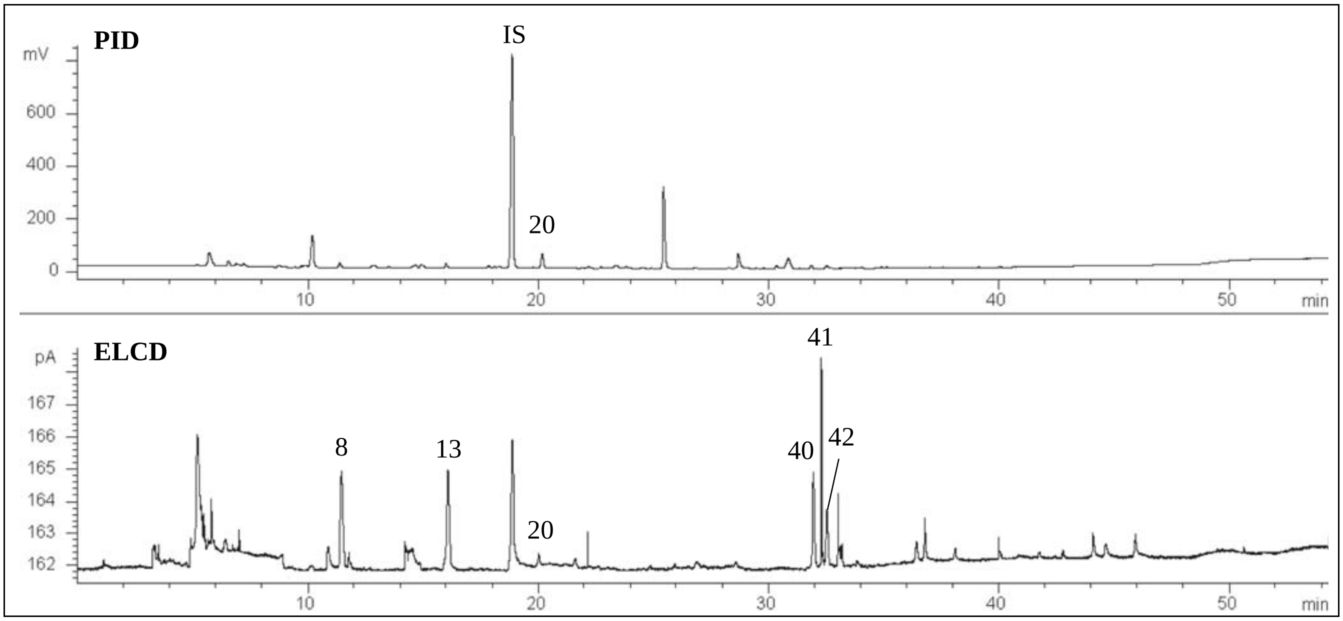

Figure 4. PID/ELCD chromatogram of soil near a construction site utility meter

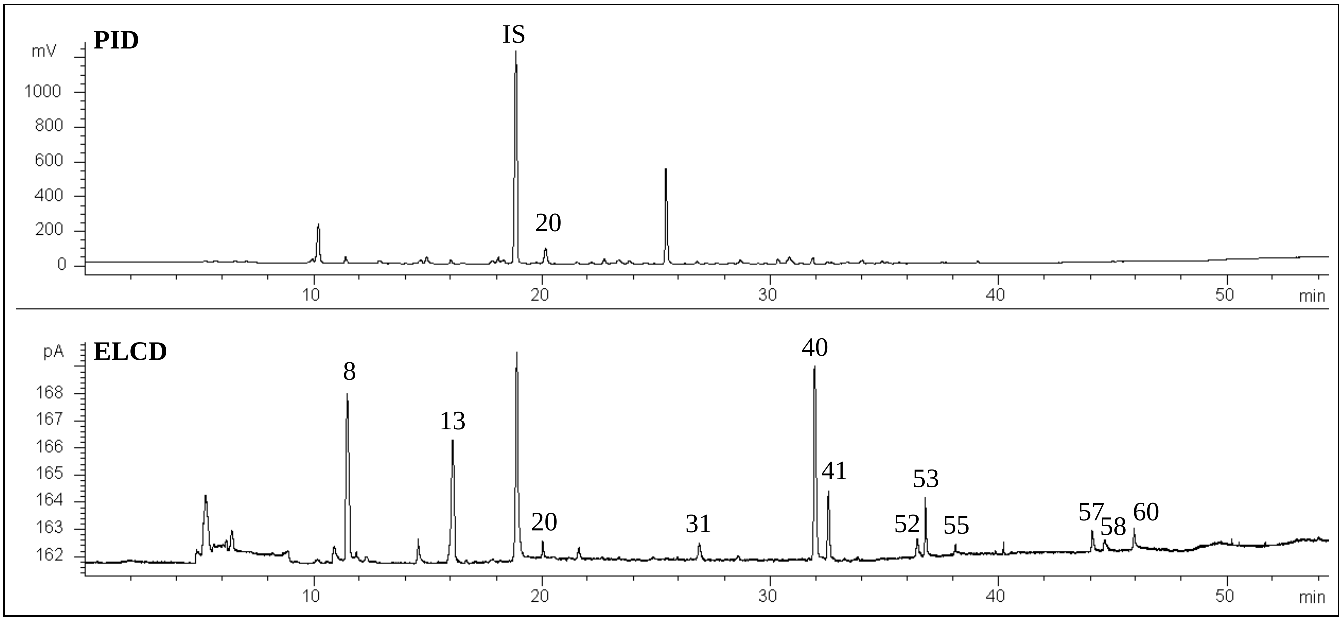

Figure 5. PID/ELCD chromatogram of soil near an industrial plant air conditioner

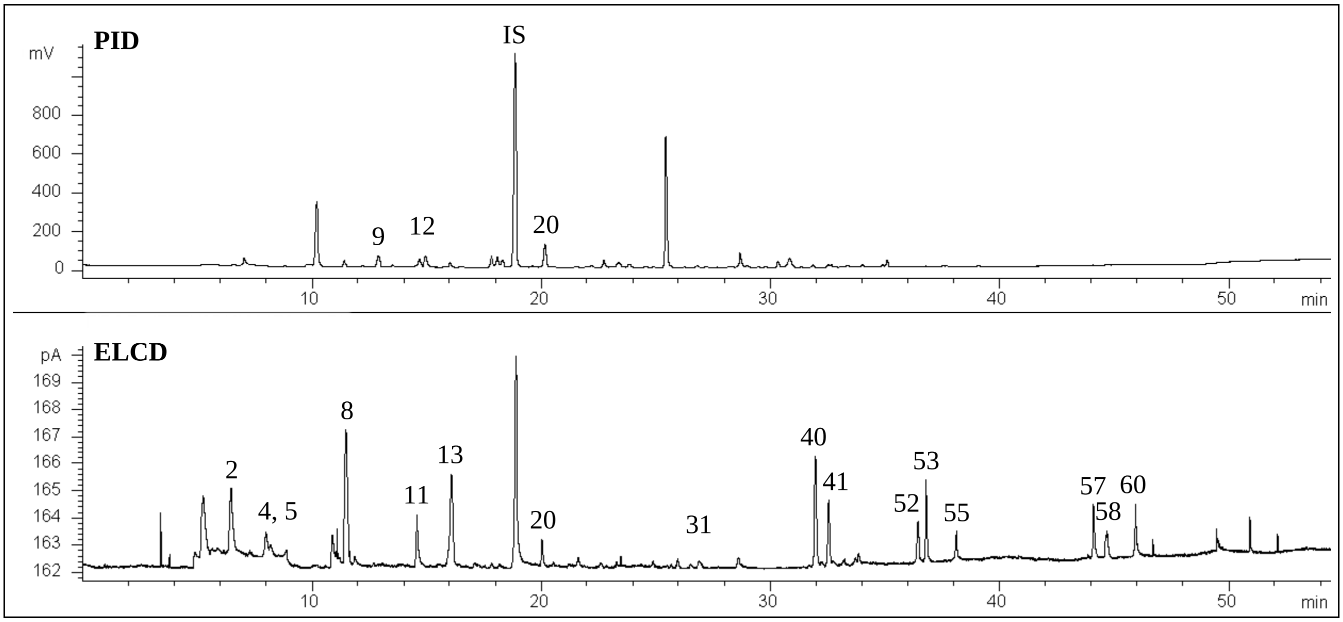

Figure 6. PID/ELCD chromatogram of soil near a residential barbeque pit

Table 6. Compound list for Figures 3, 4, 5, and 6

1	Dichlorodifluoromethane	31	1,2-Dibromomethane
2	Chloromethane	32	Chlorobenzene
3	Vinyl chloride	33	Ethyl benzene
4	Bromomethane	34	1,1,1,2-Tetrachloroethane
5	Chloroethane	35	*m*-Xylene
6	Trichlorofluoromethane	36	*p*-Xylene
7	1,1-Dichloroethene	37	*o*-Xylene
8	Methylene chloride	38	Styrene
9	*trans*-1,2-Dichloroethene	39	Isopropyl benzene
10	1,1-Dichloroethane	40	Bromoform
11	2,2-Dichloropropane	41	1,1,2,2-Tetrachloroethane
12	*cis*-1,2-Dichloroethene	42	1,2,3-Trichloropropane
13	Chloroform	43	*n*-Propyl benzene
14	Bromochloromethane	44	Bromobenzene
15	1,1,1-Trichloroethane	45	1,3,5-Trimethylbenzene
16	1,1-Dichloropropene	46	2-Chlorotoluene
17	Carbon tetrachloride	47	4-Chlorotoluene
18	Benzene	48	*tert*-Butyl benzene
19	1,2-Dichloroethane	49	1,2,4-Trimethylbenzene
20	Trichloroethene	50	*sec*-Butyl benzene
21	1,2-Dichloropropane	51	*p*-Isopropyl toluene
22	Bromodichloromethane	52	1,3-Dichlorobenzene
23	Dibromomethane	53	1,4-Dichlorobenzene
24	*cis*-1,3-Dichloropropene	54	*n*-Butyl benzene
25	Toluene	55	1,2-Dichlorobenzene
26	*trans*-1,3-Trichloropropene	56	1,2-Dibromo-3-chloropropane
27	1,1,2-Trichloroethane	57	1,2,4-Trichlorobenzene
28	1,3-Dichloropropane	58	Hexachlorobutadiene
29	Tetrachloroethene	59	Naphthalene
30	Dibromochloromethane	60	1,2,3-Trichlorobenzene

Conclusion

The instrument configuration and operating conditions described here for volatiles analysis produce outstanding method performance for BTEX in both soil and water matrices. Analysis of extended analyte lists, such as USEPA Method 8021B, are also easily accommodated without additional equipment modification. Calibration response factors, relative standard deviations, MDLs, and reproducibility for all target compounds are comparable for the two sample types and meet acceptance criteria specified in USEPA Methods. Analytes are purged from the solid matrices at about 80–100% efficiency compared to aqueous matrices. The system is easy to use and maintain, allows for unattended operation, and can analyze both soil and water samples in the same analytical sequence.

References

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