APPLICATION NOTE

Gas Chromatography

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Measuring Environmental Volatile Organic Compounds by U.S. EPA Method 8260B with Headspace Trap GC/MS

Introduction

U.S. Environmental Protection Agency (EPA) Method 8260B1 is an environmental method for analysis, identification and quantification of volatile organic compounds (VOCs) that have boiling points below 200 °C. The method specifies gas chromatography/mass spectrometry (GC/MS) analysis and is widely used in the U.S. and internationally for a variety of sample matrices. These matrices are covered in the U.S. by the Resource Conservation and Recovery Act (RCRA) program and may include ground and surface water, sludge, waste solvents, oily wastes, soils and sediments. It is a challenging method with rigorous quality control requirements. It also covers a wide concentration range and accommodates both clean and complex matrices.

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This application note demonstrates the use of a new sample-introduction technology (incorporated in the PerkinElmer® TurboMatrix™ HS-110 Trap) for U.S. EPA Method 8260B. The TurboMatrix HS-110 Trap is an enhanced static headspace system with a built-in trap that pre-concentrates and focuses VOCs prior to injection into the GC.

The TurboMatrix headspace trap system was used in conjunction with a PerkinElmer Clarus® GC/MS. Results demonstrating compliance with U.S. EPA Method 8260B (henceforth referred to as '8260B') are presented here.

A summary of the method is available on Page 11.

Experimental

System setup and conditioning

Method 8260B requires GC/MS for data acquisition, so all sample analyses were performed using the PerkinElmer Clarus GC/MS system. The most common sample preparation technique for 8260B is provided by U.S. EPA Method 5030, which recommends purge and trap. The TurboMatrix HS-110 Trap was used here as an alternative sample preparation technique to purge and trap. All instrument parameters and method conditions for the integrated system are presented in Table 1.

Before beginning 8260B analysis, the GC/MS system should be conditioned and prepared for use. The GC column should be baked out (with helium flow) overnight at 250 °C. During bakeout, the column should not be connected to the MS, to avoid unnecessary contamination of the MS ion source. Similarly, the MS should be conditioned by residing at high vacuum for several hours (preferably overnight) to remove residual water from the system.

After conditioning, the MS system should be vented with dry nitrogen, in order to accept the newly conditioned column. While the MS is vented, the GC should also be connected to the headspace trap. The heated headspace transfer line is connected to the GC injector port with an injector adapter. The headspace-trap fused-silica transfer line should be fed completely through the injector port so approximately 20 cm resides in the oven and should then be connected to the GC column by using a universal capillary-column connector. Table 7 (Page 10) provides a list of PerkinElmer parts required for connecting the headspace trap to the GC/MS.

Table 1. **Instrument Parameters.**

Sample Introduction	**PerkinElmer TurboMatrix HS-110 Trap**
Needle Temperature	90 °C
Transfer Line Temperature	120 °C
Oven Temperature	80 °C
Trap Low Temperature	40 °C
Trap High Temperature	280 °C
Dry Purge (Helium)	5 min
Trap Hold Time	6 min
Desorb Time	0.5 min
Thermostatting Time	10 min
Pressurization Time	1 min
Decay Time	2 min
Outlet Split	20 mL/min
Column Pressure	25 psi
Vial Pressure	35 psi
Desorb Pressure	10 psi
Transfer Line	Deactivated Fused Silica 20 m x 320 µm
Gas Chromatograph	**PerkinElmer Clarus GC**
Headspace Connector	Universal Connector
Oven Program Initial Temperature	40 °C
Hold Time 1	2 min
Ramp 1	10 °C/min to 100 °C
Hold Time 2	0 min
Ramp 2	30 °C/min to 240 °C
Hold Time 3	5 min
Equilibration Time	0.5 min
Vacuum Compensation	On
Headspace Control	On
Column	Elite Volatiles – 30 m x 250 µm x 1.4 µ film
CarrierGas	Helium
Mass Spectrometer	**PerkinElmer Clarus MS**
Mass Range	35-300 u
Solvent Delay Time	0 min
Scan Time	0.10 sec
InterScan Delay Time	0.10 sec
Transfer Line Temperature	200 °C
Source Temperature	200 °C
Multiplier	350 V
Trap Emission	75 µA
Threshold	0
Software	TurboMass 5.0 with Reporting

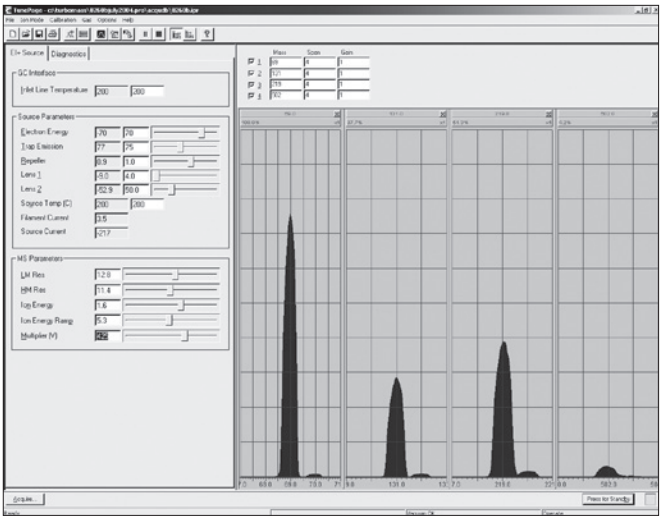

Figure 1. Instrument tuning parameters after full AutoTune.

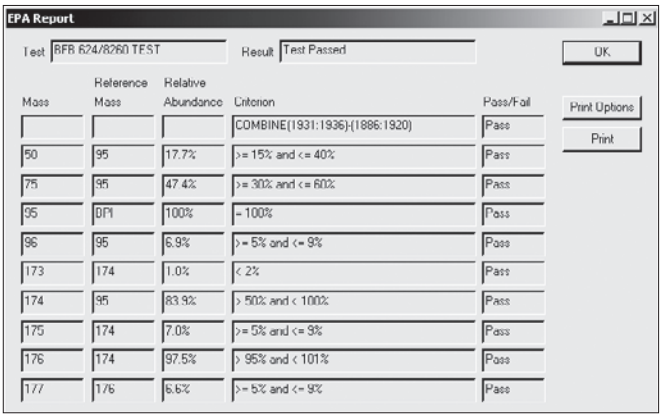

Figure 2. BFB tuning criteria for U.S. EPA 8260B.

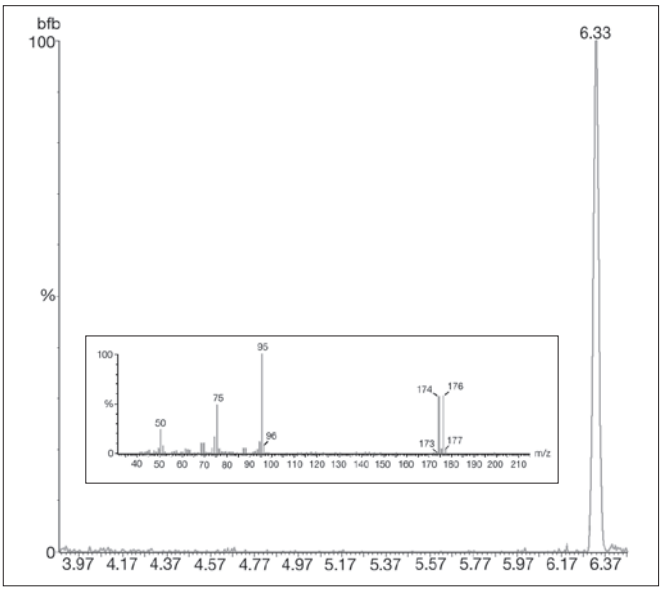

Figure 3. 4-Bromofluorobenzene (BFB) injection – 25 µg/L, with spectral results.

A 20:1 split ratio was chosen and provided by the outlet split of the headspace-trap system. Alternative gas-flow options are to close the outlet split on the headspace trap and to run in splitless mode or to connect the headspace transfer line inside of the injector port and use the GC injector split.

Initial MS tuning and optimization

The MS was set up for electron impact (EI) ionization at the 8260B specified 70 eV and a full AutoTune was performed and saved. See Figure 1 for the AutoTune generated parameters. After AutoTune, the multiplier was decreased to 350 V and the emission current decreased to 75 µA because the headspace trap provided so much sensitivity that the MS sensitivity could be reduced to prolong filament life, increase stability and extend linearity for higher concentrations.

Using the standard AutoTune parameters without modification should produce acceptable results, as long as the multiplier voltage is not set too high. The correct multiplier voltage can by determined by checking the linearity of a calibration curve. If the calibration curve begins to exhibit non-linear behavior at the highest concentration standard(s), then the detector may be saturating. If this occurs, the multiplier voltage should be lowered in 50 V increments and the calibration standards re-run.

Instrument EPA tuning

Method 8260B requires the analysis of a 5 to 50 ng 4-bromofluorobenzene (BFB) standard in methanol to check for specified ion ratios (Figure 2). This EPA tuning spectrum is calculated using, at a minimum, an average of the three-peak-apex spectra and then subtracting out the background (Figure 3). This EPA instrumenttuning check must be done once every 12 hours. After a BFB tune is successfully completed, instrument parameters must remain unchanged for all subsequent analyses until the next BFB tune is performed. Consequently, any change to the integrated system requires this BFB test to be passed before data acquisition can resume.

Figure 3 shows a BFB injection at a 25-µg/L concentration acquired under identical conditions as those used for the 8260B analyses. The BFB standard was prepared by spiking 5 µL of a 2500-µg/L BFB standard into 10 mL of organic-free water (in a standard 22-mL headspace vial) and injected using the headspace trap. Figure 2 demonstrates the ability of the integrated system to pass the BFB test.

Calibration standards preparation

Good laboratory practice must be followed at all times

All glassware and syringes must be properly cleaned for trace analysis. All methanol used must be of pesticide quality or equivalent and must be kept away from all other solvents. All water used must be organicfree reagent water. This is described in detail in Chapter One of the EPA SW-846 methods.

Quantification according to 8260B is accomplished by processing a five-concentration-level calibration curve that encompasses the predicted typical sample concentration. Each level of this curve compares the target ion of each compound with its corresponding internal standard target ion. Typical environmental laboratories run a 5-200 µg/L curve and this is demonstrated here.

Preparation of secondary standard-stock solution

A standard-stock solution containing all target analytes was prepared from two primary certified calibration mixes. 125 µL of a 2000-µg/mL VOC standard (Restek® Corporation, Bellefonte, PA) was added to slightly less than 10 mL of methanol in a 10-mL volumetric flask. An additional 125 µL of a 'gas' calibration mix (Restek®) was added to the flask and then the flask was filled to the 10-mL line with methanol. This standard-stock mix was kept in a freezer until the final water standards were prepared. Standards were prepared fresh on a weekly basis (especially important if they include the gas calibration mix). If the standards are to be prepared individually (not purchased from a certified standard company), refer to 8260B for instructions. Table 7 (Page 10) provides a list of standards available from Restek that were used in this experiment.

Table 2. **Calibration Amount to be Added to 100-mL Volumetric Flasks.**

Calibration Standard	Water-standard Conc. Level	Secondary Standard-stock Solution Added
1	5 µg/L	20 µL
2	20 µg/L	80 µL
3	50 µg/L	200 µL
4	100 µg/L	400 µL
5	200 µg/L	800 µL

Preparation of internal standard and surrogate solution

All samples and calibration standards were spiked with both internal standards and surrogates. Both the internal standard solution and the surrogates (Restek®) were prepared by adding 200 µL of each 2500-µg/mL mix to 9 mL of methanol in a 10-mL volumetric flask. Then the balance was filled with methanol. This yielded a final concentration of 50 µg/mL.

Preparation of working concentrations of water standards

Five 100-mL volumetric flasks were filled with approximately 95 mL of water. Each flask was labeled with its concentration level and then spiked with the correct amount of secondary stock standard, then the balance filled with water to 100 mL. See Table 2 for the stock solution required for each water-standard calibration level.

Preparation of headspace-vial calibration standards

10 mL of each prepared water-standard calibration level was transferred to a separate headspace-trap vial. Each vial was spiked with 10 µL of the internal standard/surrogate mix, resulting in a final concentration of 50 µg/L for each internal standard and surrogate in the water solution. All vials were sealed immediately after adding the internal standard and surrogate mix.

All five levels of working water standards vials were labeled and transferred to the headspace-trap analyzer in preparation for analysis. In addition, a water-blank sample was added both before and after the water-standards sample queue to check for potential carryover.

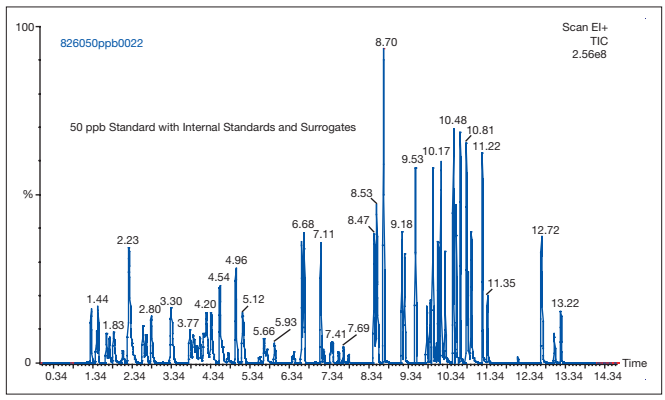

Figure 4. Mid-point level calibration standard chromatogram – 50 µg/L per target analyte.

Table 3. **Example Response Factor Table from Initial Calibration.**

Compound	RRF Level 1	RRF Level 2	RRF Level 3	RRF Level 4	RRF Level 5	Avg. RRF	% RSD
Bromochloromethane	0.082	0.063	0.067	0.063	0.066	0.068	11.71
Chloroform	0.253	0.252	0.252	0.235	0.269	0.252	4.70
Carbon Tetrachloride	0.223	0.233	0.242	0.230	0.261	0.238	6.10
Methyl Acrylate	0.070	0.066	0.069	0.066	0.079	0.070	7.61
Tetrahydrofuran	0.059	0.052	0.050	0.051	0.062	0.055	9.39
Dibromofluoromethane	0.172	0.174	0.162	0.148	0.137	0.159	10.09

Results

A minimum of five calibration levels is required for 8260B. All calibration samples must be above the minimum detection limits, yet bracket the expected concentrations of the real samples. All standards must contain the analytes of interest.

Method 8260B requires that each sample be processed using an internal standard method. This calculation is a response factor (RF) based on the target ion in the compound of interest and the internal standard target ion (Equation 1). Each compound at each level will have an RF that is dependent on its respective internal standard. There are three internal standards analyzed in this application (fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4). The internal standard closest in retention time to the target analyte is used in the RF calculation for each compound.

Equation 1. **Calculation of Response Factor.**

$$\mathbf{RF} = \frac{(\text{Area of analyte x Concentration of internal standard})}{(\text{Area of internal standard x Concentration of standard})}$$

Once all RFs are generated, the percent relative standard deviation (%RSD) is calculated for all five levels. An example of this calculation is presented in Table 3. Each compound must be below a 15% RSD threshold to continue with the method. If the compound does not pass the 15% limit, then it should be processed using alternate curve methods that are outlined in U.S. EPA Method 8000B2, or the initial calibration must be re-run.

This application note provides data for 77 volatile compounds listed in Table 4. These 77 compounds are typical of a full 8260B analysis. Figure 4 is an example chromatogram of a 50-µg/L standard injection, including all compounds of interest, three internal standards and three surrogates. In addition, six of the compounds of interest are calibration check compounds (CCCs) and five are system performance check compounds (SPCCs). The SPCCs are monitored because they are known to degrade if there are any active sites in the sample path or other instrument contamination. The CCCs are monitored for stability of the calibration curve during sample analysis. See Table 4 to identify which compounds are SPCCs and CCCs.

MDL results

The method detection limits (MDLs) for this method were calculated (Equation 2) using the procedure outlined in Chapter One of SW-846 analytical methods. Water blanks were analyzed to determine the baseline and nine samples were prepared at 0.5 µg/L. This concentration was determined to be approximately 2.5 to 5 times the potential detection limit.

Each individual analyte's MDL was obtained by multiplying the standard deviation by the appropriate onesided 99% t-statistic. The standard deviation of the determined concentration was calculated from the nine sample analyses and then, using the t-statistic, the MDL was calculated. This gives a 99% confidence level using a standard-deviation estimate with n-1 degrees of freedom. In addition, each compound was manually verified for correct response. See Table 4 for the complete list of MDLs.

Equation 2. **Method Detection Limit (MDL) calculation.**

$$\mathbf{MDL} = \mathbf{t}_{(n-1,\ a\ =\ .99)}(\mathbf{s})$$

The MDLs calculated for these analyses were very low and the precision was excellent. They were well within the requirements of 8260B.

It is possible to achieve even lower MDLs by modifying or optimizing instrument parameters. For example, modifying MS instrument settings (i.e., higher multiplier voltage or emission current) or using a lower split ratio can result in improved MDL numbers than those presented here.

Surrogate recovery results

Surrogates are measured periodically during 8260B analyses to monitor the % recovery of samples (Equation 3). When a known quantity is injected and an area response is obtained, a similar response is expected for a repeat injection at a later time. Three of the standard surrogates listed in 8260B are listed in Table 5, along with their actual % recoveries. In all cases, throughout the course of the analyses, the surrogates were well within the limits of 8260B requirements.

Stability

There are multiple ways to check for system stability and reproducibility, while performing 8260B analyses. During this experiment, two different checks were performed. The first check was for stability of the internal standards. This is vital to the response factor calculations. If the internal standard's signal fluctuates, the continuing calibration sample %RSDs will exceed 20%.

Equation 3. **Surrogate recovery calculation.**

$$\mathbf{Recovery(\%)} = (\text{Concentration found} / \text{Concentration added}) \times 100$$

If this occurs, the system will need to be re-tuned and the full calibration re-run. Therefore, the longer the internal standard area counts remain stable, the longer samples can be injected and pass the method requirements for reporting purposes.

Table 4. **Calibration Table for all 77 VOCs.**

Sample Type	Compound Name	Retention Time[1]	Primary Ion	Avg. RF	% RSD	% RSD Required to Pass	Corr. Coeff.[2]	SPCC Check (Minimum)[3]	MDL (ppb)
Target	Dichlorodifluoromethane	1.27	85	0.50	14.37	15%	0.99988	–	0.03
SPCC	Chloromethane	1.40	50	0.38	12.80	15%	0.99461	0.39 (0.10)	0.04
CCC	Vinyl Chloride	1.45	62	0.52	7.61	30%	0.99895	–	0.18
Target	Bromomethane	1.66	94	0.19	9.21	15%	0.99666	–	0.22
Target	Chloroethane	1.74	64	0.03	13.36	15%	0.97185	–	0.50
Target	Trichlorofluoromethane	1.83	101	0.44	11.59	15%	0.99260	–	0.05
Target	Diethylether	2.07	74	0.08	7.71	15%	0.99917	–	1.10
CCC	1,1-Dichloroethene	2.22	96	0.34	5.80	30%	0.99989	–	0.11
Target	Carbon Disulfide	2.59	76	0.11	10.13	15%	0.99980	–	0.14
Target	Allyl Chloride	2.59	76	0.34	10.94	15%	0.99959	–	0.07
Target	Methylene Chloride	2.68	84	0.18	5.22	15%	0.99989	–	0.15
Target	trans-1,2-Dichloroethene	2.81	96	0.30	6.50	15%	0.99979	–	0.13
SPCC	1,1-Dichloroethane	3.32	63	0.44	3.28	15%	1.00000	0.45 (0.10)	0.06
Target	Chloroprene	3.29	88	0.23	8.40	15%	0.99965	–	0.10
Target	Acrylonitrile	3.30	53	0.35	10.08	15%	0.99985	–	0.07
Target	cis-1,2-Dichloroethene	3.79	96	0.21	5.04	15%	0.99992	–	0.12
Target	2,2-Dichloropropane	3.88	77	0.28	10.34	15%	0.99933	–	0.42
Target	Bromochloromethane	3.96	128	0.06	3.87	15%	0.99986	–	0.81
CCC	Chloroform	4.04	83	0.28	3.34	30%	0.99999	–	0.07
Target	Carbon Tetrachloride	4.14	117	0.22	10.79	15%	0.99950	–	0.11
Target	Methyl Acrylate	4.17	55	0.07	9.92	15%	0.99977	–	0.21
Target	Tetrahydrofuran	4.18	42	0.04	11.87	15%	0.99929	–	0.70
Surrogate	Dibromofluoromethane	4.12	111	0.16	3.29	NA	NA	–	NA
Target	1,1,1-Trichloroethane	4.22	97	0.41	9.18	15%	0.99976	–	0.10
Target	1,1-Dichloropropene	4.34	75	0.40	9.05	15%	0.99922	–	0.40
Target	Benzene	4.56	78	0.96	6.32	15%	0.99988	–	0.07
Target	Propionitrile	4.61	54	0.01	7.54	15%	0.99968	–	0.58
Target	Methacrylonitrile	4.63	67	0.03	10.67	15%	0.99938	–	0.60
Target	1,2-Dichloroethane	4.76	62	0.11	3.56	15%	0.99995	–	0.18
Int.Std.	Fluorobenzene	4.97	96	NA	NA	NA	NA	–	NA
Target	Trichloroethylene	5.14	95	0.29	5.86	15%	0.99959	–	0.10
Target	Dibromomethane	5.56	93	0.04	10.10	15%	0.99960	–	1.00
CCC	1,2-Dichloropropane	5.68	63	0.16	2.74	30%	0.99999	–	0.40
Target	Bromodichloromethane	5.76	83	0.13	5.14	15%	0.99979	–	0.10
Target	MethylMethacrylate	5.95	69	0.08	14.69	15%	0.99885	–	0.78
Target	cis-1,3-Dichloropropene	6.44	75	0.10	8.34	15%	0.99623	–	0.22
Surrogate	Toluene-d8	6.64	98	0.99	2.82	NA	NA	–	NA
CCC	Toluene	6.70	91	1.08	5.05	30%	0.99988	–	0.06

[1] *Using Elite Volatiles Column – 30 m x 250 µm x 1.4 µ film.*
[2] *Linear regression using internal standard (5-200 µg/L).*
[3] *SPCC response factor (min. pass value).*

(cont. next page)

Table 4. **Calibration Table for all 77 VOCs *(continued)*.**

Sample Type	Compound Name	Retention Time[1]	Primary Ion	Avg. RF	% RSD	% RSD Required to Pass	Corr. Coeff.[2]	SPCC Check (Minimum)[3]	MDL (ppb)
Target	Tetrachloroethylene	7.12	164	0.67	10.30	15%	0.99547	–	0.12
Target	trans-1,3-Dichloropropene	7.20	75	0.16	10.11	15%	0.99908	–	0.26
Target	1,1,2-Trichloroethane	7.38	97	0.17	9.05	15%	0.99989	–	0.26
Target	Ethyl Methacrylate	7.43	69	0.19	11.83	15%	0.99907	–	0.25
Target	Dibromochloromethane	7.58	129	0.16	10.38	15%	0.99952	–	0.14
Target	1,3-Dichloropropane	7.71	76	0.23	8.73	15%	0.99992	–	0.16
Target	1,2-Dibromoethane	7.84	107	0.12	13.50	15%	0.98877	–	1.00
Int. Std.	Chlorobenzene-d5	8.47	117	NA	NA	NA	NA	–	NA
CCC	Ethylbenzene	8.54	91	2.27	5.53	30%	0.99996	–	0.03
SPCC	1,1,1,2-Tetrachloroethane	8.57	131	0.32	2.29	15%	0.99979	0.32 (0.30)	0.16
SPCC	Chlorobenzene	8.49	112	0.99	1.25	15%	0.99998	1.00 (0.30)	0.08
Target	p,m-Xylene	8.54	106	0.76	7.60	15%	0.99990	–	0.09
Target	o-Xylene	8.72	106	1.74	9.45	15%	0.99998	–	0.07
SPCC	Bromoform	9.25	173	0.12	3.09	15%	0.99988	0.11 (0.10)	0.50
Target	Styrene	9.25	104	0.80	10.25	15%	0.99997	–	0.07
Target	Isopropylbenzene	9.53	105	2.42	12.11	15%	0.99989	–	0.06
Surrogate	Bromoflurorobenzene	9.81	95	0.90	0.67	NA	NA	–	NA
Target	Bromobenzene	9.90	156	0.73	3.45	15%	0.99981	–	0.38
Target	n-Propylbenzene	9.97	91	6.83	7.17	15%	0.99990	–	0.06
Target	1,1,2,2-Tetrachloroethane	10.05	83	0.46	7.56	15%	0.99694	–	0.24
Target	2-Chlorotoluene	10.11	91	2.62	4.71	15%	0.99998	–	0.12
Target	1,2,3-Trichloropropane	10.23	75	0.13	3.65	15%	0.99909	–	0.44
Target	1,3,5-Trimethylbenzene	10.18	105	4.34	8.71	15%	0.99995	–	0.06
Target	4-Chlorotoluene	10.28	91	2.62	2.93	15%	0.99998	–	0.09
Target	Pentachloroethane	10.50	167	0.38	13.63	15%	0.97725	–	0.50
Target	tert-Butylbenzene	10.49	119	4.50	11.28	15%	0.99996	–	0.05
Target	1,2,4-Trimethylbenzene	10.56	105	3.64	8.06	15%	0.99993	–	0.04
Target	sec-Butylbenzene	10.67	105	69.96	10.95	15%	0.99979	–	0.07
Target	p-Isopropyltoluene	10.82	119	5.40	11.36	15%	0.99982	–	0.07
Target	1,3-Dichlorobenzene	10.86	146	1.56	0.78	15%	0.99998	–	0.52
Int. Std.	1,4-Dichlorobenzene-d4	10.94	152	NA	NA	NA	NA	–	NA
Target	1,4-Dichlorobenzene	10.95	146	1.40	1.45	15%	0.99988	–	0.13
Target	n-Butylbenzene	11.23	91	5.31	8.82	15%	0.99945	–	0.07
Target	1,2-Dichlorobenzene	11.36	146	1.19	3.82	15%	0.99967	–	0.04
Target	1,2-Dibromo-3-chloropropane	12.13	75	0.06	10.56	15%	0.99940	–	0.91
Target	1,2,4-Trichlorobenzene	12.76	182	1.46	8.25	15%	0.99630	–	0.02
Target	Hexachlorobutadiene	12.73	225	1.46	7.26	15%	0.99812	–	0.08
Target	Naphthalene	13.06	128	1.31	7.01	15%	0.99897	–	0.01
Target	1,2,3-Trichlorobenzene	13.23	180	0.89	8.32	15%	0.99854	–	0.02

[1] *Using Elite Volatiles Column – 30 m x 250 µm x 1.4 µ film.*
[2] *Linear regression using internal standard (5-200 µg/L).*
[3] *SPCC response factor (min. pass value).*

Table 5. **Surrogate Recovery Data.**

Surrogate Compound	8260B Restriction Limits in water (%)	Surrogate Injection	Actual Recovery (%)
4-Bromofluorobenzene	86-115	1	104
		2	102
		3	100
		4	102
		5	97
Toluene-d8	88-110	1	98
		2	98
		3	99
		4	100
		5	100
Dibromofluoromethane	86-118	1	108
		2	101
		3	96
		4	92
		5	88

Table 6. **Minimum Response Factors for the SPCCs.**

System Performance Check Compounds (SPCCs)	Minimum Response Factor	Actual Response Factor
Chloromethane	0.10	0.39
1,1-Dichloroethane	0.10	0.45
Bromoform	0.10	0.11
Chlorobenzene	0.30	1.00
1,1,1,2-Tetrachloroethane	0.30	0.32

Table 7. **Parts and Standards Used for U.S. EPA Method 8260B.**

PerkinElmer Part No.	Description
B0505266	HS Injector Adapter
N9301357	Deactivated Fused Silica 5 m x 320 µm
N9316388	Elite Volatiles – 30 m x 250 µm x 1.4 µ film
N9302149	Universal Connector
Restek® Part No.	**Description**
30475	2000 µg/mL VOC standard
30042	Gas Standard (2000 µg/mL)
30241	Internal Standards (2500 µg/mL)
30240	Surrogates (2500 µg/mL)

Using the 77-compound mix, the internal standard areas were monitored for 24 hours. Chlorobenzene-d5 exhibited a standard deviation of 4.3, demonstrating very high stability for the integrated system (Figure 5). All other internal standards showed similar results.

The second stability check was performed on the surrogate compounds. The surrogates must fall within percentages outlined by the U.S. EPA (Table 5). The data in Figure 6 demonstrates that the system passed this test easily over a 24-hour period of time.

System performance check compounds (SPCCs)

During 8260B analysis, the SPCCs must be monitored with every calibration curve and every 12 hours. Six SPCCs are monitored and they must meet or exceed the required minimum response factors. If the SPCCs do not meet the response factor requirements, the system needs to be evaluated and corrective action taken. Possible problems might be injector contamination, column contamination or active sites in the sample path.[1]

Table 6 lists the minimum response factors for the SPCCs along with the actual values determined (Table 4). The TurboMatrix HS Trap system passed these checks easily, demonstrating no contamination or active sites in the sample path. At just over 0.1 RF, the closest compound to the limit was bromoform. However, over the 24-hour testing time, it still met 8260B requirements and remained stable.

Discussion

The headspace trap utilizes an alternative sample-handling technology to that used in purge and trap systems. Purge and trap systems are constrained by their purging efficiencies. For example, chloromethane is likely to be lost if the purge flow is too fast, yet bromoform is a compound that has very poor purging efficiency. A typical %RSD for bromoform is usually very close to 15% and can be much higher. The headspace trap typically has a bromoform %RSD of less than 5% because of the good partition coefficient bromoform has at higher temperatures. A calibration curve for bromoform is shown in Figure 7.

The headspace trap uses heat to extract (partition) the compounds out of the water (into the headspace) instead of purging. For this application, the TurboMatrix HS Trap offers the following advantages:

- Easy and convenient sample preparation
- Reduced levels of water extracted from the sample
- Increased sample throughput by overlapping the thermostatting
- No need to clean delicate glassware between injections
- No need to purge the lines to remove residual contamination
- No risk of sample foam contaminating the purge and trap device
- No cross-contamination of samples from using the same purge vessel

Overlapped thermostatting of the headspace samples is achieved by heating multiple samples at a time.

By overlapping the thermostatting step with the headspace trap, the GC now becomes the rate-limiting step in the overall analysis, not the sampling device. When using a purge and trap sample introduction system, each sample must be thermostatted and purged separately, making this the rate-limiting step.

Headspace trap technology is based on two well established techniques: equilibrium headspace sampling and thermal desorption. These two techniques are combined in this instrument to provide the operational convenience of headspace, but achieve the detection limits observed using thermal desorption systems. The headspace technology performs the initial extraction of the analytes from the aqueous sample. The migration of each analyte into the headspace vapor from the aqueous sample is dictated by its partition coefficient.[3] Fortunately, in the case of many 8260B target

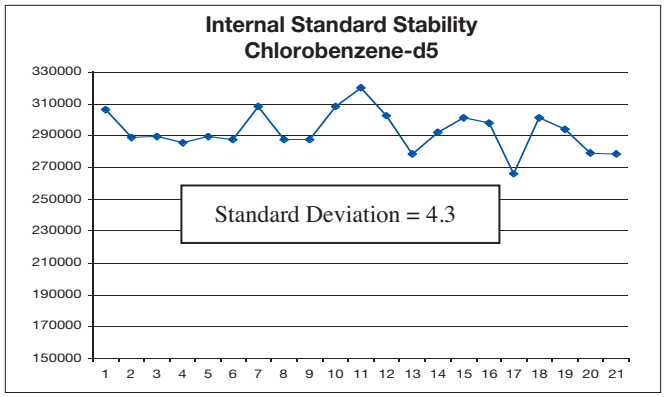

Figure 5. Internal standard stability for chlorobenzene-d5 (50-µg/L injection).

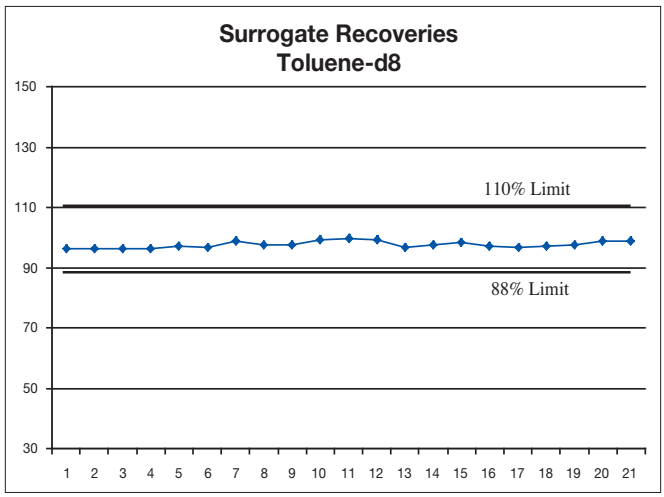

Figure 6. Surrogate recovery for toluene-d8 (50 µg/L injection).

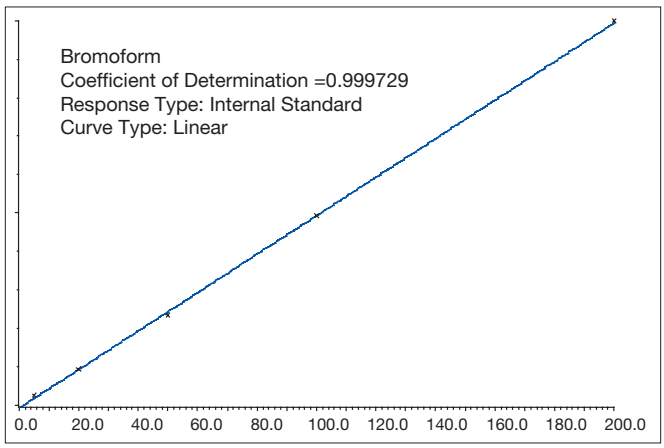

Figure 7. Calibration curve for bromoform (5-200 µg/L).

analytes, the partition coefficients are very favorable at the elevated temperatures used in headspace methods. The system is therefore able to sweep a significant and reproducible fraction of the analytes from the sample and into the thermal desorption trap, where they are retained and focused on an optimized adsorbent packing.

For analytes with less favorable partition coefficients, the extraction efficiency can be improved with a technique called salting. The addition of inorganic salts into the aqueous sample favors the partition towards the headspace and significantly improves the extraction efficiency.

Once the analytes have been extracted and transferred, the trap is then dry-purged to eliminate most of the moisture, which would otherwise interfere with the chromatographic analysis. Finally, the trap is heated at 2400 °C/min with carrier gas passing through it to carry the desorbed analytes as a narrow band into the GC/MS system for analysis.

An example of a U.S. EPA-approved method utilizing headspace technology is Method 5021 (Volatile Organic Compounds in Soil and Other Solid Matrices Using Equilibrium Headspace Analysis).

Conclusions

U.S. EPA 8260B is a challenging method used in a majority of U.S. and many international environmental laboratories for the analysis of VOCs. It is a complex method that requires multiple quality criteria be passed throughout the analysis. As demonstrated here, the PerkinElmer Clarus GC/MS system configured with a TurboMatrix HS-110 Trap meets all the 8260B method requirements. This includes, but is not limited to: instrument tuning, minimum detection limits, initial calibration, surrogate recovery and system performance checks.

This application note demonstrates the successful use of headspace trap technology to perform the sample handling required for 8260B. All compounds determined passed the 8260B %RSD requirements, and all SPCCs met their minimum RF values (Table 6). Correlation coefficients (using linear regression) are also included in the calibration table to provide additional information on individual compound performance.

This application note provides details and suggestions on how to use a new sample handling technology to comply with U.S. EPA Method 8260B. In addition to method compliance, this technology provides significant advantages over purge and trap to recover compounds with poor purging efficiencies. System cleanup is easier because the headspace vials are disposable and not reused, reducing the chance of carryover and the need for cleaning. In addition to 8260B, other VOC methods may also be run using this configuration. For example, U.S. EPA Method 524.2 for VOCs in drinking water is a similar method with lower detection limits, that would benefit from this technology.

References

1. "Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)", U.S. Environmental Protection Agency, Office of Solid Waste, SW-846 Method 8260B, revision 2, December 1996.

2. "Determinative Chromatographic Separations", U.S. Environmental Protection Agency, Office of Solid Waste, SW-846 Method 8260B, revision 2, December 1996.

3. L.S. Ettre and B. Kolb "Static Headspace-Gas Chromatography", Wiley, New York, 1997.

Summary of method

1. Set up instruments (Headspace Trap and GC/MS), per PerkinElmer service specifications.
2. Attach instruments and set up methods as described in the instrument-parameters section of this application note.
3. Run a blank water sample to look for impurities in the water or contamination in the system.
4. Perform a bromofluorobenzene (BFB) test as outlined in the tuning section of this application note.
5. When the BFB test passes, run five levels of calibration standards that are in the range of expected sample-compound concentrations. The typical U.S. EPA 8260B calibration curve is from5 to 200 µg/L.
6. Calculate the response factor (RF) for all compounds at all levels and the %RSD for the complete five levels. If all %RSDs are lower than 15% (30% for some compounds), proceed; if not, check the instrument and re-run the initial calibration curve. Possible modifications include: lowering the detector voltage, checking for leaks or changing the split ratio.
7. Run a water blank to check for interferences.
8. Run a matrix spike, then a matrix-spike duplicate and verify results. See U.S. EPA Method 8260B for instructions.[1] These standards should be representative of the compounds being monitored. At a minimum, the spike is required to contain: 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene and benzene.
9. Check system stability through surrogate recovery (see the section on surrogate recovery; Table 5 and Figure 6) and internal standard retention times. See U.S. EPA Method 8260B for instructions.[1]
10. Run samples.
11. In each work group of samples (you can define this as you wish), or every 20 samples, or at least once per day, a laboratory control sample (LCS) must be run. This sample must consist of a clean matrix similar to the sample matrix and be of the same weight and volume. This LCS should then be spiked with the same analytes as the matrix spike. The LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.[1]
12. Every 12 hours, three instrument calibration checks must be performed:
    - A BFB injection must be repeated and the ion ratios checked. The BFB peak must pass the U.S. EPA parameters (see the section on tuning).
    - The system performance check compounds (SPCCs) should be monitored for a minimum RF (Table 6).
    - Calibration check compounds (CCCs) should be injected and checked against the initial calibration curve. The %RSD of the CCC should be within 20% drift of the initial calibration %RSD number. See Table 4 for the list of CCCs.

If any of these checks fail, the instrument may need to be cleaned or re-tuned and the initial calibration run again.

Establish method performance

- Check for method detection limits (MDLs) on the system as described in the MDL section of this application note.
- Check for precision by running standards and monitoring the percent recoveries, the standard deviation of these recoveries and the %RSD.

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