Techniques for Optimizing the Analysis of Volatile Organic Compounds in Water Using Purge-and-Trap/GC/MS

Application

Environmental

Author

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Abstract

The analysis of volatile organic compounds in water is normally accomplished by purge-and-trap/gas chromatography/mass spectrometry. U.S. EPA Method 8260B with purge and trap sample introduction is widely used for the analysis of aqueous samples other than drinking water. This application note discusses problems that can arise and some easy solutions for them. These techniques have resulted in robust calibrations that meet Method 8260B calibration requirements over the range of 1–200 µg/L.

Introduction

U.S. EPA Method 8260B [1] is a general purpose method for the analysis of volatile organic compounds (VOCs) in matrices such as ground and surface water, sludges, soils and sediments, filter cakes, spent carbons, and spent catalysts. This method is only used for the analyses of target VOCs by gas chromatography with mass spectral detection (GC/MS). It refers analysts to other U.S. EPA sample introduction methods that are appropriate for the matrix to be analyzed. This paper focuses on the analysis of VOCs in water using purge and trap (P&T) sample introduction according to U.S. EPA Method 5030C [2] coupled to GC/MS for separation and analysis (P&T/GC/MS). For simplicity, the combination of Methods 5030C with 8260B is referred to as just Method 8260B.

This P&T/GC/MS procedure is widely used in environmental laboratories for the analysis of VOCs in surface, ground, and wastewater samples. A similar method for the analysis of drinking water is described in EPA Method 524.2 [3]. Though well established, P&T/GC/MS methods can be a challenge to run successfully. There are numerous P&T, GC, and MS variables to optimize in order to obtain good recoveries for the target VOCs without undo disturbance from water and methanol that are inevitably transferred to the GC during trap desorption.

This application note describes techniques for optimizing Method 8260B using the Agilent 6890N GC and new 5973 inert mass selective detector (MSD) coupled to the new Teledyne Tekmar Velocity XPT P&T system. Included, in the paper, are suggestions for MSD tuning, sample preparation, instrument setpoints, and maintenance techniques that lead to a robust method for the analysis of VOCs in water. The discussion is applicable to most other P&T/GC/MS methods.

Experimental

Chemical Standards, Reagents, and Vials

High purity B&J brand methanol was obtained from Honeywell Burdick & Jackson Co. (Muskegon, MI). Standard mixtures used for the preparation of calibration samples, spiking solutions, tune evaluation, and stability test samples were purchased from AccuStandard (New Haven, CT). These include the following: Part no. M-502-10X-Pak containing 60 VOC target analytes (54 liquids and 6 gases) at 2000 µg/mL each in methanol; Part no. M-8260A/B-IS/SS-10X-PAK containing p-bromofluorobenzene (BFB), chlorobenzene-d_5, dibromofluoromethane, 1,4-dichlorobenzene-d_4 (DCB-d_4) , 1,2-dichloroethane-d_4, fluorobenzene (FBz), and toluene-d_8 at 2000 µg/mL each in methanol; and part no. M-524-FS-PAK containing BFB, 1,2-dichlorobenzene-d_4, and fluorobenzene (FBz) at 2000 µg/mL each in methanol.

VOC-free water was used for the preparation of standards and test samples. TraceClean 40-mL (nominal volume, actual volume is 43 mL) VOA vials (part no. 15900-022) were purchased from VWR Scientific (West Chester, PA).

Preparation of Calibration and Spiking Solutions

Secondary spiking solutions were prepared in methanol for each calibration level so that each 43-mL water sample could be spiked with 10 µL of the calibration solution (containing 60 VOCs) and 10 µL of the internal standard/surrogate mixture. Table 1 provides details on how the eight calibration standards were prepared.

Table 1. Procedure for Preparing Calibration Samples

A	B	C	D	E
Calibration level (µg/L)	Volume of 2000 µg/mL VOC Standard (µL)	Diluted to this volume in methanol (mL)	Results in this secondary standard concentration (µg/mL)	Amount to spike into 43-mL vial (µL)
1	53.75	25.00	4.3	10.00
2	43.00	10.00	8.6	10.00
5	53.75	5.00	21.5	10.00
20	43.00	1.00	86	10.00
50	43.00	0.40	215	10.00
100	43.00	0.20	430	10.00
200	43.00	0.10	860	10.00
300	*	*	2000*	6.45**

Column A. Concentration of each analyte in the final aqueous calibration solution.

Column B. Volume of the 2000 µg/mL 60-component VOC standard solution which was diluted to the volume shown in column C.

Column C. Final volume of VOC solution after dilution in methanol.

Column D. Concentration of the calibration spiking solution prepared by diluting the amount of 2000 µg/mL standard in column B to the volume shown in column C.

Column E. Amount of the secondary standard solution (column D) added to 43 mL of water to prepare the calibration standard at the level shown in column A.

*The undiluted VOC standard (2000 µg/mL) was used for spiking.

**The 300 µg/L aqueous calibration standard was prepared by adding 6.45 µL of the 2000 µg/mL AccuStandard VOC solution and 3.55 µL of methanol to 43 mL of water in a VOA vial.

As discussed below, containers for storing the secondary standards (column C, Table 1) were chosen to minimize the headspace. Larger volumes were transferred to 2-mL screw top vials, while smaller volumes were transferred to crimp cap microvials of the appropriate size.

A solution of the internal standards (ISTDs) and surrogates was prepared at 215 ppm in methanol by diluting 43 µL of the 2000-µg/mL AccuStandard solution to a volume of 400 µL. Each 43-mL water sample was spiked with 10 µL of this solution so that all samples and standards contained 50 µg/L of each compound.

Preparation of Solutions for Repeatability Studies

Two kinds of spiked water samples were prepared for use in repeatability studies.

- System blanks consisted of clean water spiked with fluorobenzene, BFB, and 1,2-dichlorobenzene-d_4 at 10 µg/L each.
- VOC spikes consisted of clean water with fluorobenzene, BFB, and 1,2-dichlorobenzene-d_4 at 10 µg/L and the 60 VOC target compounds at 20 µg/L each.

Replicate samples were prepared as follows.

- Secondary dilution standards containing fluorobenzene, BFB, and 1,2-dichlorobenzene-d_4 at 50.0 µg/mL were prepared in 2-mL autosampler vials by diluting 25 µL of the 2000-µg/mL AccuStandard solution with 975 µL of methanol.
- Secondary dilution standards of the 60-component VOC solution were prepared at 100 µg/mL in 2-mL autosampler vials by diluting 50 µL of the 2000 µg/mL AccuStandard solution with 950 µL of methanol.

System blanks were prepared by adding 100 µL of the 50.0 µg/mL three component solution and 100-µL methanol to 500 mL of water in a 1.0-L screw-cap bottle. After inverting to mix thoroughly, this bottle was attached to the apparatus shown in Figure 1 and 11 VOA vials were filled by transferring the spiked water solution under nitrogen pressure.

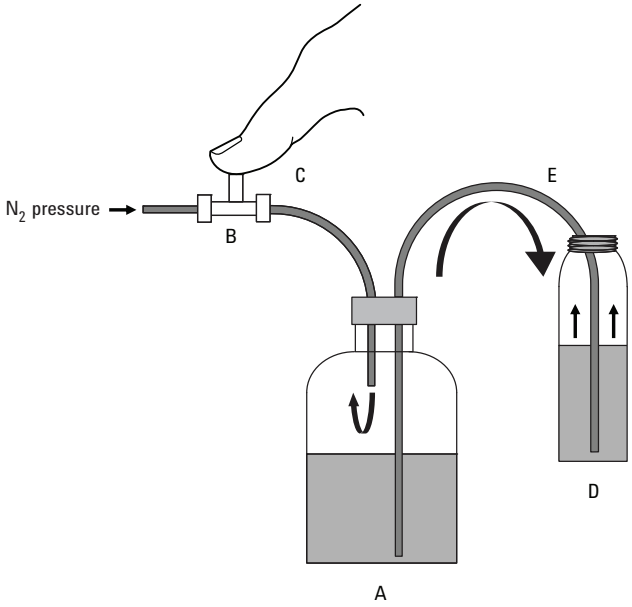

Figure 1. Apparatus used to fill multiple VOA vials with the same spiked water solution.
A) 1-L liquid chromatography solvent bottle
B) Swagelok Tee with nothing connected to one fitting
C) Finger used to cap fitting in order to pressurize the reservoir bottle
D) VOA vial
E) 1/8-inch PTFE tubing

VOA spiked samples were prepared by adding 100 µL of the 50.0-µg/mL three component solution and 100 µL of the 100-µg/mL 60-component VOC standard to 500 mL of water in a 1.0-L screw cap bottle. After inverting to mix thoroughly, this bottle was attached to the apparatus shown in Figure 1 and 11 VOA vials were filled by transferring the spiked water solution under nitrogen pressure.

Instrumentation and Analytical Conditions

The P&T instrumentation and setpoints are listed in Table 2. The following P&T options were not used: DryFlow trap, automatic ISTD addition, sample heating, dry purging, and sample cryofocusing. The method shown in Table 2 was derived using the wizard that is provided in the TekLink 2.2 P&T control software.

Table 2. Purge and Trap Instrumentation and Setpoints

P&T Instrument	**Teledyne Tekmar Velocity XPT**
Automatic sampler	**Teledyne Tekmar Aquatek 70**
Software control	Teledyne Tekmar VOC Teklink version 2.2
Trap	Vocarb 3000
P&T-GC interface	P&T transfer line spliced into the GC split/splitless inlet carrier gas line and GC carrier gas plumbed to the Velocity XPT
Sample size	5 mL
Valve oven temperature	150 °C
Transfer line temperature	150 °C
Sample mount temp	90 °C
Purge ready temp	45 °C
DryFlow standby temperature	175 °C
Standby flow	10 mL/min
Pressurize time	0.25 min
Fill I.S. time	0.00 (ISTDs added by hand)
Sample transfer time	0.25 min
Pre-purge time	0.00 min
Pre-purge flow	40 mL/min
Sample heater	Off (Samples not heated)
Sample preheat time	1.00 min
Preheat temperature	40 °C
Purge time	11.00 min
Purge temperature	0 °C (That is, less than the purge ready temp of 45 °C)
Purge flow	40 mL/min
Purge rinse time	0.25 min
Purge line time	0.25 min
Dry purge time	0.00 min (Dry purge not used)
Dry purge temp	40 °C
Dry purge flow	200 mL/min
GC start	Start of desorb
Desorb preheat temperature	245 °C
Desorb drain	On
Desorb time	1.00 min
Desorb temperature	250 °C
Desorb flow	200 mL/min
Bake rinse	On
Number of bake rinses	3
Bake drain time	0.50 min
Bake drain flow	400 mL/min
Bake time	3.00 min
Bake temperature	270 °C
Dry flow bake temperature	300 °C
Bake flow	400 mL/min
Focus temperature	Not used
Inject time	1.00 min
Inject temperature	180 °C
Standby temperature	100 °C

Table 3. GC/MS Instrumentation and Setpoints

Gas Chromatograph	**Agilent 6890N**
Inlet	Split/Splitless
Inlet liner	Single taper, deactivated (Agilent part no. 5181-3316)
Inlet temperature	250 °C
Split ratio	50:1
Column	20 m × 0.18 mm × 1.0 µm DB-VRX (Agilent part no. 121-1524)
Carrier gas	Helium at 1.0 mL/min constant flow
Oven temperature program	40 °C (3 min), 10 °C/min to 100 °C (0 min), 25 °C/min to 225 °C (3 min)
Mass Spectrometer	**Agilent 5973 Inert MSD**
Transfer line temperature	260 °C
Quad temperature	150 °C
Source temperature	230 °C
EM voltage	2035 volts
Scan range	35–260 *m/z*
Threshold	0
Samples	3
Solvent delay	0 min
Software	MSD Productivity ChemStation Software (Part no. G1701DA version D.01.00)

Results and Discussion

Section 1.3 of Method 8260B can be used to quantitate most VOCs that have boiling points below 200 °C. It lists 123 compounds that can be determined by the method using various sample prep and sample introduction methods. Of these, seven are ISTDs or surrogates, nine are not recommended for P&T sample introduction, and three must be purged at 80 °C for efficient recovery. The remaining analytes vary considerably in their water solubility and volatility making this a challenging method to optimize. The intent of this application note is to share several techniques that one can use to optimize Method 8260B or any other P&T/GC/MSD method employed for water analysis.

For this study, the 60 VOCs listed in EPA Method 502.2 were analyzed along with three ISTDs and four surrogates (Table 4).

Table 4. Compound List with Average Response Factors (RF) and the RF %RSDs for Two Calibration Ranges: 1–300 and 1–200 µg/L

Type*	Compound	Retention time (min)	Minimum average response factor**	Maximum %RSD of calibration response factors***	Average RF 1–300 µg/L	RF %RSD 1–300 µg/L	Average RF 1–200 µg/L	RF %RSD 1–200 µg/L
T	Dichlorodifluoromethane	1.25		15	0.283	8.21	0.289	5.44
T,SPCC	Chloromethane	1.34	0.1	15	0.324	9.62	0.328	9.38
T,CCC	Vinyl chloride	1.42		30	0.220	2.47	0.220	2.66
T	Bromomethane	1.60		15	0.099	14.11	0.096	12.30
T	Ethyl chloride	1.67		15	0.152	5.57	0.154	4.27
T	Trichloromonofluoromethane	1.97		15	0.372	11.38	0.386	3.49
T,CCC	1,1-Dichloroethene	2.29		30	0.330	5.31	0.336	1.45
T	Methylene chloride	2.40		15	0.299	5.02	0.301	4.95
T	*trans*-1,2-Dichloro-ethene (E)	2.92		15	0.323	2.54	0.325	1.36
T,SPCC	1,1-Dichloroethane	3.14	0.1	15	0.444	4.93	0.446	5.22
T	*cis*-1,2-Dichloroethene (Z)	3.68		15	0.360	1.28	0.361	1.17
T	Bromochloromethane,	3.83		15	0.234	1.82	0.234	1.84
T,CCC	Chloroform	3.89		30	0.442	0.92	0.443	0.60
T	2,2-Dichloropropane	3.96		15	0.202	9.87	0.209	4.19
Sur	Dibromofluoromethane	4.01		15	0.248	0.83	0.248	0.89
Sur	1,2-Dichloroethane-d_4	4.47		15	0.298	1.76	0.299	1.79
T	1,2-Dichloroethane	4.55		15	0.359	1.57	0.359	1.66
T	1,1,1-Trichloroethane	4.64		15	0.388	7.99	0.398	1.43
T	1,1-Dichloropropene	4.86		15	0.336	12.44	0.351	3.16
T	Carbon tetrachloride	5.01		15	0.309	13.88	0.322	7.66
T	Benzene	5.08		15	1.063	7.10	1.077	6.52
ISTD	Fluorobenzene	5.34		15		1.34		1.41
T	Dibromomethane	5.68		15	0.198	1.86	0.198	2.01
T,CCC	1,2-Dichloropropane	5.75		30	0.266	1.58	0.268	0.77
T	Trichloroethylene	5.81		15	0.288	6.79	0.295	2.14
T	Bromodichloromethane	5.85		15	0.334	5.47	0.331	5.60
T	1,3-Dichloropropene (Z)	6.64		15	0.383	5.49	0.381	5.74
T	1,3-Dichloropropene (E)	7.18		15	0.322	8.76	0.318	8.93
T	1,1,2-Trichloroethane	7.32		15	0.236	1.57	0.237	1.67
Sur	Toluene-d_8	7.47		15	0.945	0.50	0.945	0.51
T,CCC	Toluene	7.55		30	1.098	7.47	1.126	2.07
T	1,3-Dichloropropane	7.62		15	0.428	1.28	0.428	1.20
T	Dibromochloromethane	7.86		15	0.254	12.10	0.249	11.88
T	1,2-Dibromoethane	8.15		15	0.244	1.88	0.244	2.03
T	Tetrachloroethylene	8.40		15	0.307	18.72	0.327	5.07
T	1,1,1,2-Tetrachloroethane	9.15		15	0.254	8.79	0.254	9.49
ISTD	Chlorobenzene-d_5	9.19		15		0.98		0.81
T,SPCC	Chlorobenzene	9.22	0.3	15	0.981	5.00	0.997	2.14
T,CCC	Ethylbenzene	9.51		30	1.559	11.66	1.623	1.90
T,SPCC	Bromoform	9.72	0.1	15	0.246	14.57	0.242	15.08
T	m- & p-Xylene	9.73		15	2.510	11.97	2.614	2.75
T	Styrene	10.03		15	1.008	5.68	1.022	4.25
T,SPCC	1,1,2,2-Tetrachloroethane	10.08	0.3	15	0.395	3.41	0.394	3.46
T	o-Xylene	10.10		15	1.289	9.27	1.330	1.89
T	1,2,3-Trichloropropane	10.21		15	0.347	2.90	0.346	2.94
Sur	BFB	10.44		15	0.381	0.93	0.382	0.82
T	Isopropylbenzene	10.44		15	1.474	17.44	1.562	4.13
T	Bromobenzene	10.58		15	0.643	5.20	0.653	3.12
T	n-propylbenzene	10.82		15	1.840	17.38	1.950	3.60
T	2-Chlorotoluene	10.85		15	1.124	10.66	1.166	1.93
T	4-Chlorotoluene	10.92		15	1.184	10.23	1.224	3.75

Table 4. Compound List with Average Response Factors (RF) and the RF %RSDs for Two Calibration Ranges: 1–300 and 1–200 µg/L (Continued)

Type*	Compound	Retention time (min)	Minimum average response factor**	Maximum %RSD of calibration response factors***	Average RF 1–300 µg/L	RF %RSD 1–300 µg/L	Average RF 1–200 µg/L	RF %RSD 1–200 µg/L
T	1,3,5-Trimethylbenzene	11.08		15	1.275	14.63	1.340	3.02
T	Tertbutylbenzene	11.26		15	1.196	18.98	1.274	4.24
T	1,2,4-Trimethylbenzene	11.36		15	1.353	12.22	1.411	2.35
T	sec-Butylbenzene	11.43		15	1.729	21.91	1.858	5.67
T	1,3-Dichlorobenzene	11.44		15	1.529	10.75	1.579	5.61
T	1,4-Dichlorobenzene	11.49		15	1.597	9.97	1.643	5.99
ISTD	1,4-Dichlorobenzene-d_4	11.47		15		1.09		1.17
T	p-Isopropyltoluene	11.58		15	2.587	19.00	2.757	3.52
T	1,2-Dichlorobenzene	11.73		15	1.485	6.33	1.516	2.74
T	Butylbenzene	11.87		15	2.355	20.68	2.522	4.81
T	1,2-Dibromo-3-chloropropane	12.06		15	0.186	13.90	0.180	11.56
T	1,2,4-Trichlorobenzene	12.95		15	1.211	12.42	1.250	8.76
T	Naphthalene	13.10		15	2.879	5.54	2.852	5.32
T	Hexachlorobutadiene	13.16		15	0.750	24.53	0.809	10.56
T	1,2,3-Trichlorobenzene	13.22		15	1.196	11.09	1.226	9.06
	Average %RSD of targets				9.07		4.60	
	Average %RSD of all compounds					8.22		4.23

*Compound designations as follows: T (target); SPCC (system performance check compound); CCC (calibration check compound); Surr (surrogate); ISTD (internal standard). Target compounds may also be designated as SPCCs or CCCs.

**The minimum average RF that must be met for the SPCCs.

***The maximum %RSD of the RFs. If any one or more of the CCC RF RSDs exceeds 30%, instrument maintenance is required. If the RF %RSD for any target compound exceeds 15%, other curve fits must be substituted for the average RF.

Method 8260B Requirements

Below is a summary of the most significant requirements of Method 8260B. If you are already very familiar with this method, you may want to skip this section.

ISTDs and surrogates: The ISTDs and surrogates listed in Table 4 are the recommended compounds for this method, although other compounds may be used instead.

Tuning requirements: Prior to running samples, the MSD must be adjusted so as to pass Method 8260B's BFB tuning specifications [1]. However, the method allows users to substitute CLP [4], Method 524.2 [3] or manufacturers' instructions for the specified BFB ion ratios. Table 5 lists the BFB tuning specifications for all three EPA methods. A scan range of 35–260 m/z is recommended.

Table 5. Criteria for BFB Tuning for Three Capillary GC/MS Volatiles Methods

Mass (*m/z*)	Relative abundance criteria Method 524.2	Method 8260B*	CLP-SOW
50	15%–40% of 95	Same**	8%–40% of 95
75	30%–80% of 95	30%–60% of 95	30%–66 % of 95
95	Base Peak, 100%	Same	Same**
96	5%–9% of 95	Same	Same
173	<2% of 174	Same	Same
174	>50% of 95	Same	50%–120% of 95
175	5%–9% of 174	Same	4%–9% of 174
176	>95% but <101% of 174	Same	93%–101% of 174
177	5%–9% of 176	Same	Same

*Alternative tuning criteria may be used (for example, CLP or Method 524.2) including manufacturer's instructions provided that method performance is not adversely affected.

**"Same" implies that this requirement is the same as that shown for Method 524.2. Note, however, that alternative tuning criteria may be used for Method 8260B (see previous footnote).

System Performance Check Compounds (SPCCs): The SPCCs are used to check the performance of the system after calibration and before analysis of samples. These compounds are known to be sensitive to active sites and instrument contamination. They must meet a minimum RF that is specified in Table 4.

Calibration Requirements: As a minimum, Method 8260B requires a five-point calibration curve. In order to assume linearity of the calibration curve, the RF RSD of all target compounds must be less than or equal to 15%. Six analytes are designated as Calibration Check Compounds (CCCs) (Table 4). If the RF RSDs for any of these compounds exceeds 30%, it is indicative of instrument problems and repairs must be made. Compounds that exceed 15% RSD for their RFs can use alternative curve fitting methods as specified in EPA Method 8000B [5].

GC/MS Calibration Verification for Each 12-hour Shift: The P&T/GC/MSD performance must be re-evaluated every 12 hours. The most significant requirements are:

- The BFB tune must be rechecked and pass the original tuning requirements.
- A sample near the midpoint of the calibration curve must be analyzed using P&T sample introduction, demonstrating that:
  - Each SPCC meets its minimum RF.
  - The percent difference (between current and original response) must be less than 20% for each CCC.
  - The retention time of each ISTD must not drift by more than 30 s.
  - The ISTD areas must not change by more than a factor of 2 from the original mid-point calibration level (50% to 200%).
  - A method blank must be run to show that there is no carryover or contamination of the system.

Calibration Results

Many laboratories employing Method 8260B generate five-point calibration curves between 5 and 200 µg/L. Knowing that laboratories often try to extend this range at both ends, an eight-point calibration was run at 1, 2, 5, 20, 50, 100, 200, and 300 µg/L. The signals for all analytes at 1 µg/L were sufficient to allow calibration at even lower levels. However, the lowest calibration level run for this work was 1 µg/L. Figure 2 shows a chromatogram of the targets, surrogates, and ISTDs at 50 µg/L each.

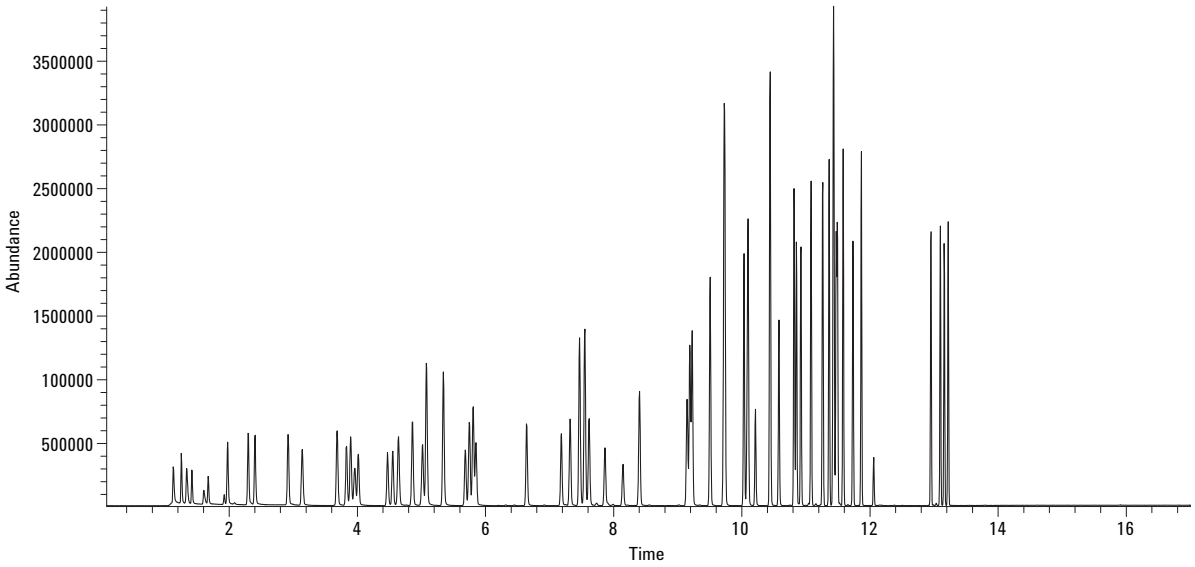

Figure 2. P&T/GC/MS analysis of a standard containing all of the compounds listed in Table 4, each at 50 µg/L in VOC-free water.

The average RF and %RSD of the RFs were calculated for each compound over the 1–300 µg/L and 1–200 µg/L ranges. As seen in Table 4, all five of the SPCCs exceeded their minimum RFs by a comfortable margin for both calibration ranges.

As mentioned above, the CCC RF RSDs must not exceed 30%. Table 4 shows that all six CCCs were significantly less than this for both calibration ranges. In fact, the average %RSD of the CCCs was only 4.90% for the 1–300 µg/L calibration and a remarkably small 1.58% in the narrower 1–200 µg/L range.

Only eight compounds exceeded the 15% RSD requirement in the 1–300 µg/L calibration range. In all cases, the RF fell off significantly for the 300 µg/L standard, suggesting that the strong target ion response overloaded the MSD at that very high concentration.

In the 1–200 µg/L calibration range, the average RF could be used for all targets except, perhaps, bromoform which exceeded the 15% limit by 0.08%. If one justifies only two significant figures, even bromoform could use an average RF for calibrations. The average of the %RSDs for all targets was 8.9% for the 1–300 µg/L calibration and only 4.5% for the 1–200 µg/L range (Table 4). Figure 3 shows a plot of the RFs for each target compound over the 1–200 µg/L calibration range.

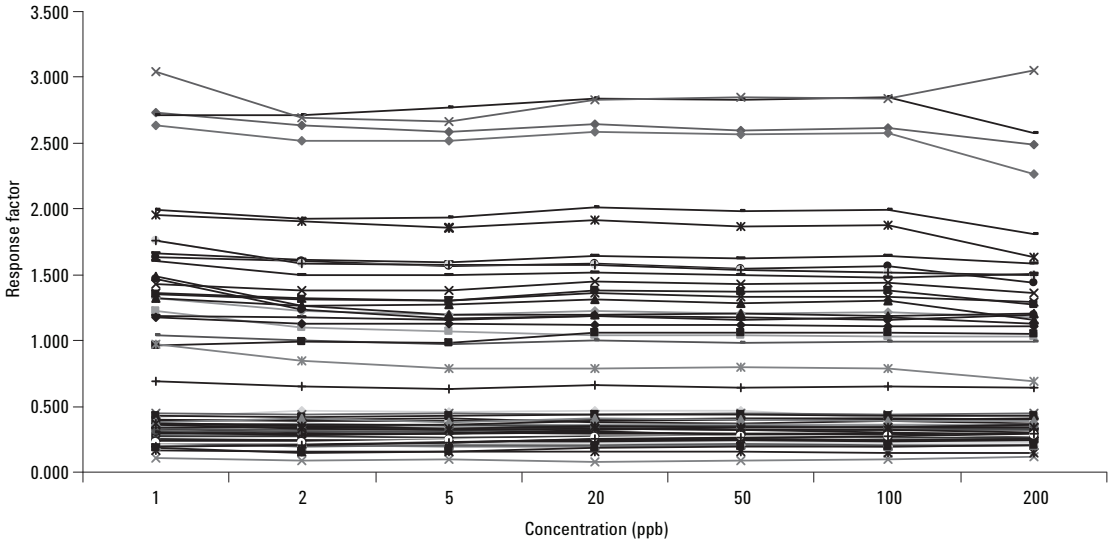

Figure 3. Plot of the RFs from a seven-level calibration for all of the target compounds listed in Table 4. Concentrations were at 1, 2, 5, 20, 50, 100, and 200 µg/L.

Figure 4 plots a distribution of the RF %RSD values for the 59 calibrated peaks (m- and p-Xylene were not resolved). It shows that most compounds have RFs over the 1–200 µg/L calibration range with less than six percent RSD. More than 91% of the compounds have RSD values of 10% or less.

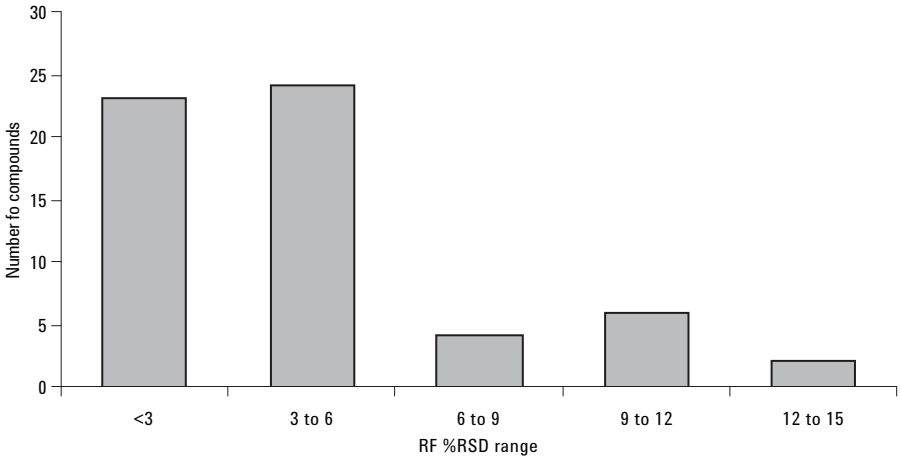

Figure 4. Distribution of the RF RSDs for the 59 calibrated peaks (m- and p-xylene were not resolved).

Response Stability

The longevity of any calibration depends upon having a consistent response for all compounds, even when running samples almost continuously over the course of several days, weeks, or even months. Some laboratories have observed a falloff in response over time that can jeopardize the calibration. Moreover, it has been observed that the recoveries for certain compounds may be dependent upon the presence or absence of other VOCs in the sample. A complete discussion of this problem and some simple solutions for it may be found in the "Optimization Techniques" section below.

In order to assess instrument stability over time, two types of samples were prepared. "System Blanks" contained only FBz, BFB, and 1,2-dichlorobenzene-d_4 (DCB-d_4) at 10 µg/L in water. The first compound was used as the ISTD while the latter two were chosen as surrogates. "Spiked" samples were the same as the system blanks but with the 60 target VOCs added at 20 µg/L each. These samples were analyzed alternately, typically for 22 runs, but sometimes many more runs over several days.

Figure 5 is a plot of the normalized recoveries for FBz, BFB, and DCB-d_4. It illustrates the two problems that can be observed when instrument parameters are not optimized. First, there is a gradual drop in response for all three compounds as illustrated by the sloping arrows. Superimposed upon this is a reduction in surrogate recovery in the absence of added VOCs. Because system blanks and spiked samples were alternated in the sequence, there was a "zigzag" appearance to the plot.

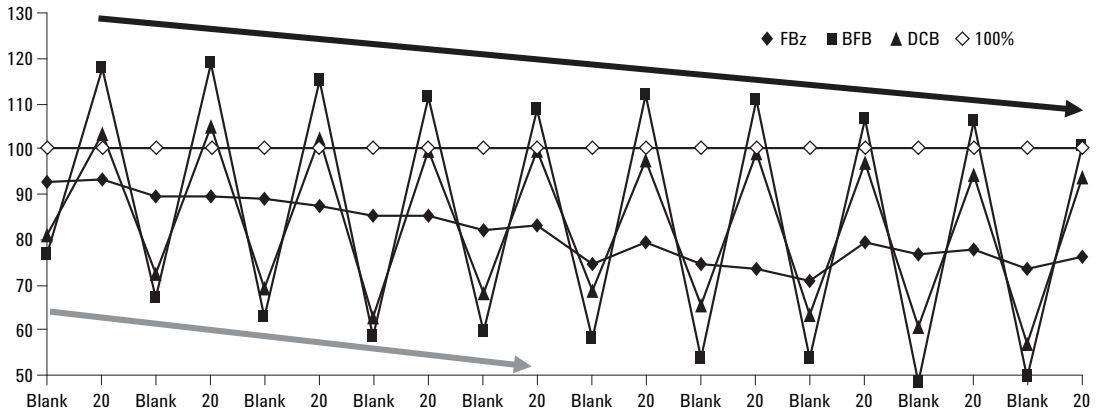

Figure 5. Normalized recoveries for FBz, BFB, and 1,2-DCB-d_4. System blanks (containing only FBz, BFB, and DCB-d_4 at 10 µg/L each) were analyzed alternately with system blanks spiked with an additional 60 VOCs at 20 µg/L each. Arrows show a gradual loss of response over the course of the sequence. The zigzag pattern arises because the recovery of BFB and DCB-d_4 is higher in the presence of other VOCs.

The problems illustrated in Figure 5 can be avoided rather easily by not overloading the MSD's electron multiplier (EM) and by ensuring that there are no active sites in the sample flow path. Figure 6 shows normalized recovery plots for BFB and DCB-d_4 that are typical when the instrument parameters are set correctly. Once again, system blanks and spiked samples were alternated, but this time there was no drop in response over time. Surrogate recovery was independent of sample spiking. Simple solutions for resolving these problems are discussed below.

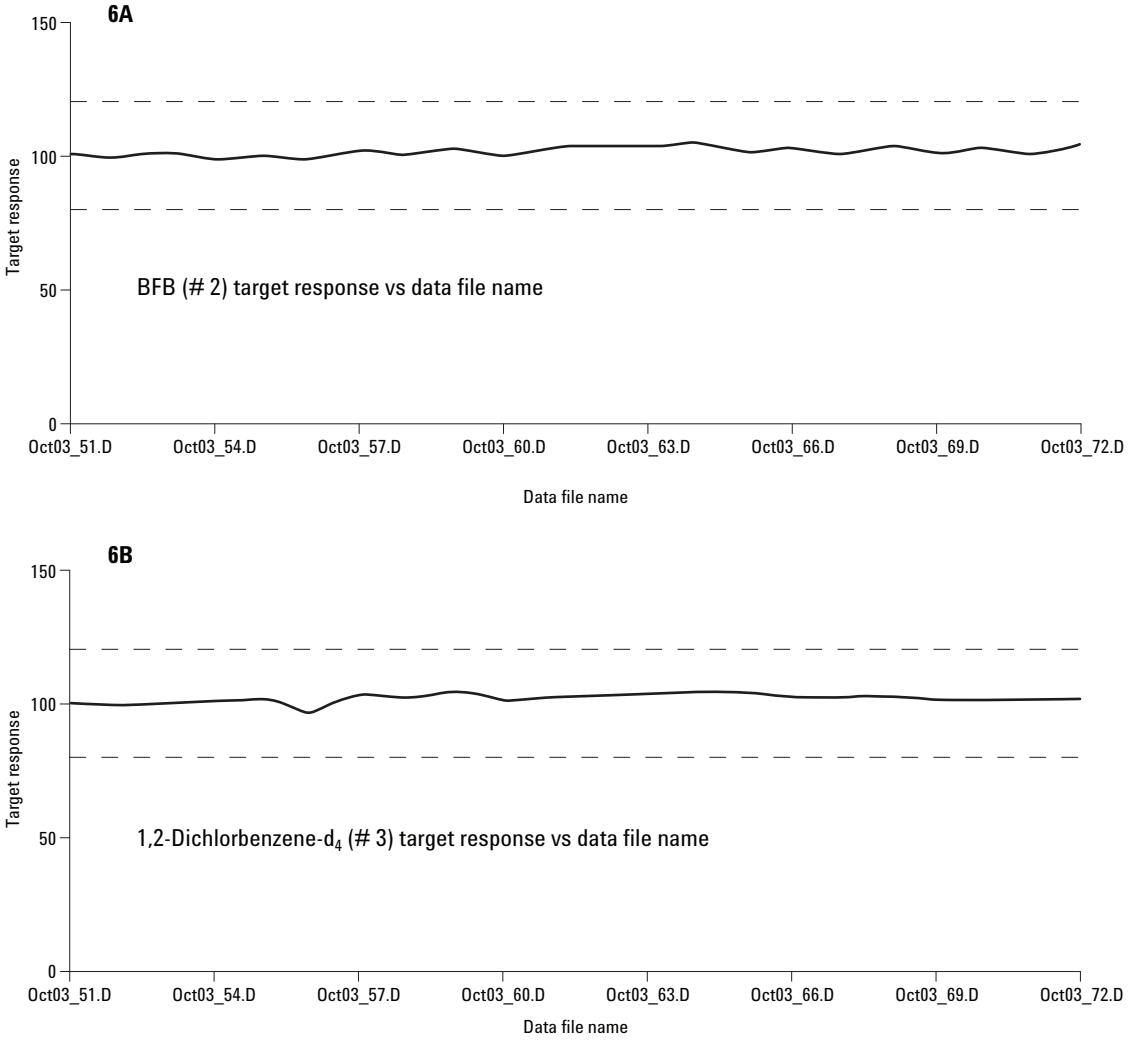

Figure 6. Normalized recovery for BFB (6A) and DCB-d_4 (6B) using the Agilent 6890N/5973 inert GC/MS coupled to the Velocity XPT P&T with optimized system parameters.

Optimization Techniques

MSD Tuning: Application Note 5988-4373EN [6] discusses three different ways to tune Agilent's 5973N MSD in order to meet BFB requirements. With the recent introduction of the 5973 inert MSD, these procedures still apply, though it is helpful to turn off the variable entrance lens setting when using the BFB autotune. The CLP Statement of Work specifications (Table 5) offers more latitude than the 8260B tuning requirements. Most importantly, ion 174 can be up to 120% of ion 95 (the reference ion). It is helpful to tune the MSD so as to produce a 174/95 ion ratio that is in the 90%–120% range because this improves the signal for bromoform (base peak = 173), which purges with poor efficiency. For this work, the "modified autotune" method was used and the 174/95 ratio was about 105%. It has been our experience that once the Agilent 5973 inert has been tuned to meet BFB requirements, the tune is stable for many weeks. It is impossible to say how long, because once tuned, it never failed to pass the BFB requirements.

MSD Parameter Optimization: When ISTD or surrogate responses fall off with repeated injections, overloading the Agilent 5973 MSD's high energy dynode (HED) EM may be the cause. The 5973 was designed to be significantly more sensitive than its predecessors and incorporates an HED in the EM. This reduces the noise and increases the signal, especially for ions of higher mass. However, this highly sensitive detector can be overloaded by continuous ion bombardment or by operating it at too high a voltage. The symptom is an unusually large loss of response over time.

Many GC/MS users erroneously believe that they can increase the sensitivity of their MSD by increasing the EM voltage. This can be done by raising the target value during tuning or by adding voltage to the tune value in the "MS SIM/Scan Parameters" window. However, in the electron impact mode, the noise increases at approximately the same rate as the signal. So, the true sensitivity (signal/noise) does not increase. The main consequence is to reduce the EM's lifetime. This can show up as a reduced response over time that might even be noticeable after several runs. (Note that these statements about signal/noise ratios do not necessarily apply to chemical ionization techniques.)

The solution to this "problem" is relatively simple. The easiest way is to reduce the EM voltage, which reduces the signal and noise, but not the signal/noise ratio. It may also be necessary to reduce the threshold value in the "Edit Scan Parameters" window in order to see the smaller ions. The default EM voltage values from an Autotune or BFB tune are usually correct, but these can be decreased somewhat if the above-mentioned symptoms occur.

It is easier to overload the EM in the selected ion monitoring (SIM) mode, because only a few ion fragments are monitored. During peak elution in the scan mode, there are "blank" spaces in all spectra where the signal is small or zero. With SIM, the signal is almost continuous and the ions monitored are usually the most abundant ones. Here again, the solution is relatively simple. One can reduce the EM voltage, decrease the SIM dwell time, and/or reduce the peak width by choosing the "High Resolution" option. The latter two values are set in the "Edit SIM Parameters" window. In any case, it is important to remember that both signal and noise are roughly proportional to the EM voltage and nothing is sacrificed by making small reductions in its value. Just remember to lower the threshold value or set it to 0 at the same time.

Reducing System Activity: When surrogate recoveries are higher in the presence of other analytes, as illustrated in Figure 5, active sites in the sample flow path are a likely cause. Surrogates can adsorb on these active sites, reducing their recovery. Surrogate recoveries improve when other analytes are present that compete for the active sites. To prevent such problems, one must use a highly inert P&T/GC/MS system and maintain its cleanliness by avoiding contamination from foaming samples. The Agilent 6890N/5973 inert GC/MS coupled to the Velocity XPT P&T showed no signs of sample adsorption. As seen in Figure 6, surrogate recoveries were highly stable with this system. If target or surrogate recoveries vary depending upon the presence of other analytes, it may be helpful to increase the temperature of the MSD source or upgrade an older 5973A or N with the new "Inert" source.

The P&T Method and Water Management: The VOC Teklink software used to control the new Teledyne Tekmar Velocity XPT concentrator and Aquatek 70 autosampler offers a "wizard" tool to help the user choose parameters for the method. Only minor modifications were made to the wizard-generated method. ISTDs were added manually to each sample so the "Fill I.S. Time" was set to 0.00 min. The bake time was increased to 3 minutes and the number of bake rinses was increased to three. The wizard chose all other parameters after the user provided information about the system configuration.

One of the primary concerns of P&T/GC/MS methods is the management of water that is inevitably purged along with the analytes. Since calibration, surrogate, and ISTD solutions are prepared in methanol, some of this solvent is also purged and retained by the trap. By starting the scan at 40 µ, methanol and water ions were not detected by the MSD. Nevertheless, transferring large amounts of water or methanol from the P&T to the GC/MS can result in poor reproducibility for those compounds that co-elute with them. Using the Velocity XPT with the Agilent 6890N/5973 inert system there were no problems that could be attributed to water. Because the P&T was configured with a Vocarb 3000 trap, the DryFlow trap was not required. Various dry purge times and flow rates were tried, but the only affect this had was to distort the peak shape of one or more early eluting peaks. Therefore, the dry purge option was not used. It is likely that some problems attributed to an excess of water actually result from overloading the MSD EM.

Standard preparation: The careful preparation of standards for calibration cannot be overemphasized. As with most laboratories, the initial dilutions were purchased as 2000 µg/mL/component concentrates, which were stored without problem in a refrigerator. Experience in this laboratory showed that best results were obtained when observing the following guidelines:

- Prepare secondary dilutions used for sample spiking from freshly opened standards.
- Transfer secondary dilutions to appropriately sized glass containers so that there is little or no headspace in the vial. Store small quantities in microvials.
- Mininert vial closures were tried for sample storage but were prone to leakage and their use was discontinued. In addition, they were not available for microvials.
- It works well to prepare calibration standards by spiking methanolic solutions into pure water through the septum of the VOA vial. It works equally well to prepare standards in 50- or 100-mL volumetric flasks and pour the aqueous solutions into VOA vials.
- If several VOA vials of the same solution are being prepared at one time, do not prepare the solution in a single large volumetric flask. There will be some VOC loss by pouring repeatedly from the flask. Instead, spike vials individually or use the apparatus described in Figure 1 for sample transfer.
- When preparing calibration standards, transfer the same amount of methanolic solution to each VOC sample. This requires preparing secondary dilutions in methanol for each calibration level instead of spiking different amounts of a single standard.

Leaks: Leaks anywhere in the system can result in poor precision, loss of sample, and calibration failure. Leaks in the carrier gas flow path can easily be detected by the MSD as a high background of oxygen and nitrogen. To correct leaks, tighten or replace the offending fittings after finding the leaks using established techniques. A more difficult problem to detect results from leaks in the fittings that connect the purge vessel to the P&T instrument. Even the smallest leaks during the purge cycle can result in the loss of VOCs and cause poor precision. Leaks that a helium leak detector might miss, can still cause VOC loss. If all the RFs for a given calibration level seem to be low by a similar amount, or if the RF RSDs are all very similar (but too large), then P&T leaks are the likely cause. Tighten or replace the fittings associated with the purge vessel.

Conclusions

EPA Method 8260B with P&T sample introduction is one of the most widely used water analysis methods. There are numerous P&T, GC, and MS variables to optimize in order to obtain long-lasting linear calibration curves and good analytical results. This application note summarizes much of Agilent's experience in optimizing all facets of this VOC method. Most analysts know how to prepare calibration and check samples, tune the MSD, and set instrument parameters; and they find this method to be very rugged with infrequent need for retuning and recalibration. The suggestions in this paper are designed to help in case problems do arise or when an analyst runs this method for the first time. Though the focus was on Method 8260B, these techniques apply to almost any P&T/GC/MS method.

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Printed in the USA
April 6, 2011
5989-0603EN

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