O·I·Analytical

Reduction of Purge-and-Trap (P&T) Cycle Times in Volatile Organic Compounds (VOCs) Analysis

Application Note 30121207

Keywords
Purge-and-Trap (P&T)
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Infra-Sparge Infrared Sample Heater
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Appendix B to Part 136 in the Federal Register

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Introduction

The purge-and-trap (P&T) technique for gas chromatographic analysis of volatile organic compounds (VOCs) was pioneered in the 1970s at the United States Environmental Protection Agency (USEPA) research laboratory in Cincinnati (1). Many of the operational parameters developed during this time period are still included in USEPA methods for P&T analysis of VOCs. While these parameters still produce good analytical results, they do not take full advantage of advances in P&T instrumentation that enable analysis of emerging contaminants such as fuel oxygenates, and increased sample throughput.

The USEPA Office of Ground Water and Drinking Water Technical Support Center has recently reported on its' efforts to update and revise Method 524.2 for the Determination of Volatile Organic Compounds in Drinking Water (2,3). Some of the stated goals of this work include developing criteria to permit laboratories flexibility to modify prescriptive parameters in the method while maintaining data quality and improving throughput.

The P&T technique consists of multiple sample processing steps, each of which directly affect analytical performance and cycle time. The typical P&T analysis cycle can take as long as 25-30 minutes including autosampler and P&T operation, and gas chromatography-mass spectrometry (GC-MS) analysis. The longest sample processing step prescribed in USEPA methods is the 11-minute purge step. Reducing the time required to perform this one step can improve sample throughput.

This application note presents data demonstrating that maintaining sample temperatures at 40 °C during the purge step allows a reduction in purge time from 11 to 7 minutes without compromising analytical performance. This finding is consistent with results reported by the USEPA indicating a 7-minute purge time is sufficient for VOC methods(3).

Experimental

Instrumentation used for this study included an OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator equipped with a patented$^{(4)}$ Infra-Sparge™ sample heater (Figure 1), a 4551A Vial autosampler, and an Agilent 6890/5975 GC/MS.

Figure 1. Eclipse with 4551A Autosampler, SAM
(Standards Addition Module), and pH Detect Module

Methodology

Four 5-mL aliquots of a 25-ppb standard containing 86 compounds from the USEPA Method 524.2 list were analyzed using variable purge times from 1 to 11 minutes while maintaining sample temperature at either 40 °C or at ambient laboratory temperature. After purging, the compounds were desorbed onto the GC column, and the analytical trap was reconditioned in preparation for the next sample.

Percent recovery of the individual compounds at each purge time (1 to 11 minutes) was calculated relative to the response of compounds using an 11-minute purge and sample temperature of 40 °C. All instrument operating conditions are listed in Table 1, and a sample description is provided in Table 2.

Table 1. Equipment Configuration and Instrument Operating Conditions

Purge and Trap	Eclipse 4660 Sample Concentrator
Autosampler	OI Analytical 4551A Vial Autosampler
Trap	OI Analytical #10 Trap (Tenax®/silica/cms)
Purge Time	Variable (1 to 11 minutes)
Sample Temperature During Purge	40 °C and Ambient
Desorb Preheat	On, 180 °C
Desorb Time	1 minute
Desorb Temperature	190 °C
Bake Time	6 minutes
Bake Temperature	240 °C
Water Management	110 °C at Purge/0 °C at Desorb/240 °C at Bake
Gas Chromatograph	**Agilent 6890**
Column (Restek)	Rtx-624, 30 m × 0.250 mm × 1.40 μm
Carrier Gas	He
Inlet Temperature	220 °C
Column Flow	0.8 mL/minute
Split Ratio	35:1
Split Flow	27.8 mL/minutes
Total Flow	35.1 mL/minutes
Gas Saver	ON
Saver Time	2.0 minutes
Oven Program	45 °C for 4.50 minutes 12 °C/minute to 100 °C (0 minutes) 25 °C/minute to 240 °C (1.32 minutes) Total GC Time = 19.5 minutes
Mass Spectrometer	**Agilent 5975**
Mode	Scan 35 to 260
Scans/Second	3.25
Solvent Delay	1.40 minutes
Transfer Line Temperature	240 °C
Source Temperature	230 °C
Quad Temperature	150 °C

Table 2. Sample Description

Target Compound List	USEPA Method 524.2 Rev. 4 (all 86 compounds)
Sample Size	5 mL
Internal Standard	Fluorobenzene
Surrogate Standards	4-Bromofluorobenzene and 1, 2-dichlorobenzene-d_4
Sample Concentration	25 ppb, four replicates at each purge time

Results and Discussion

The average peak response (n = 4) of each compound was calculated for each purge time, and the percent recovery of each compound was determined relative to the response obtained for the compounds using an 11-minute purge. Figures 2 – 5 show the comparison of purge efficiencies of selected representative compounds using different purge times and a sample temperature of 40 °C.

The results show that both the gas-phase compounds and the heaviest compounds (except naphthalene) could be recovered at levels of 95% or better even when the purge time was reduced to 7 minutes (Figures 2 and 3). Most of the mid-range compounds were also recovered at 95% or better (Figure 4). Finally, the polar compounds, which are soluble in water, were recovered at 70% or better using the 7-minute purge (Figure 5). The average recovery for all 86 compounds was 89.4% with a 7-minute purge and a sample temperature of 40 °C.

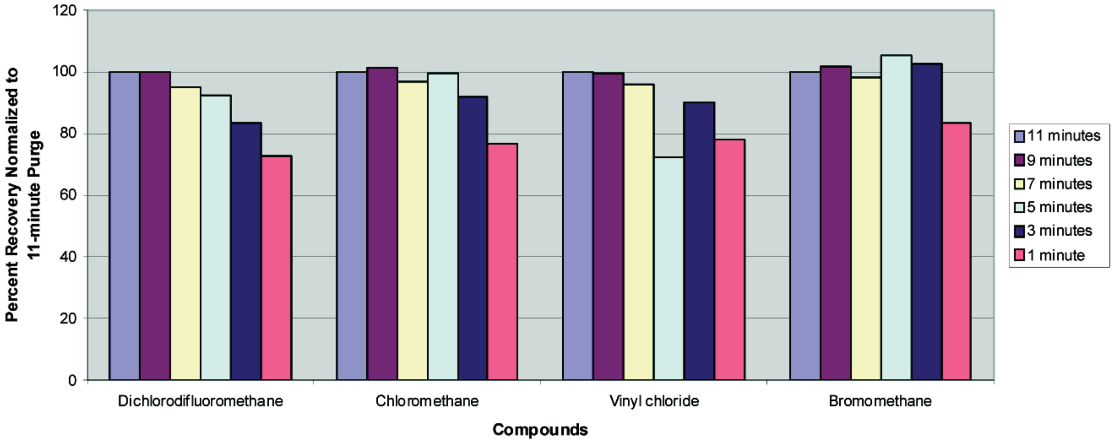


Figure 2. Relative purge efficiency of selected gas-phase compounds using variable purge times and sample temperature of 40 ºC. This chart illustrates that the gas-phase compounds can be recovered at levels of 95% or better, when purge time is reduced to 7 minutes.

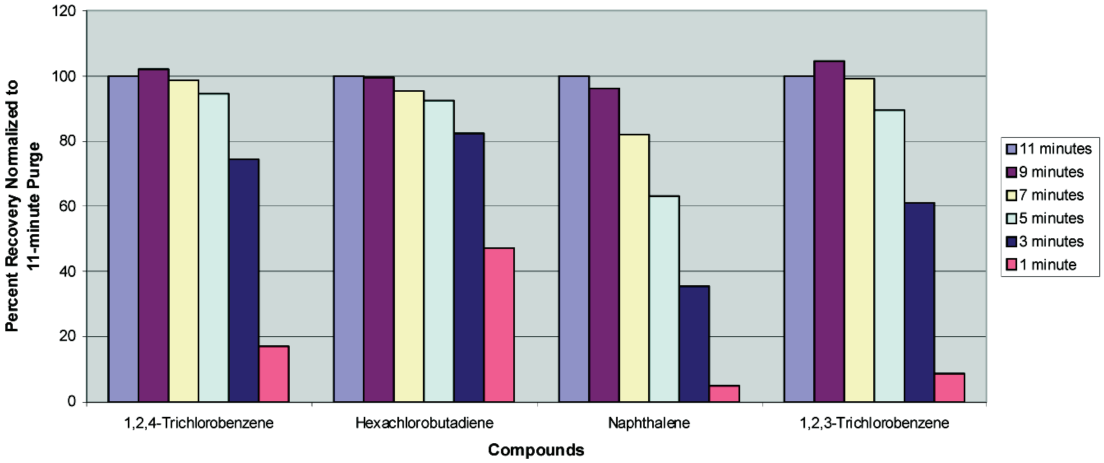


Figure 3. Relative purge efficiency of selected heavy compounds using variable purge times and sample temperature of 40 ºC. This chart illustrates that most of the heavy compounds can be recovered at levels of 95% or better when purge time is reduced to 7 minutes.

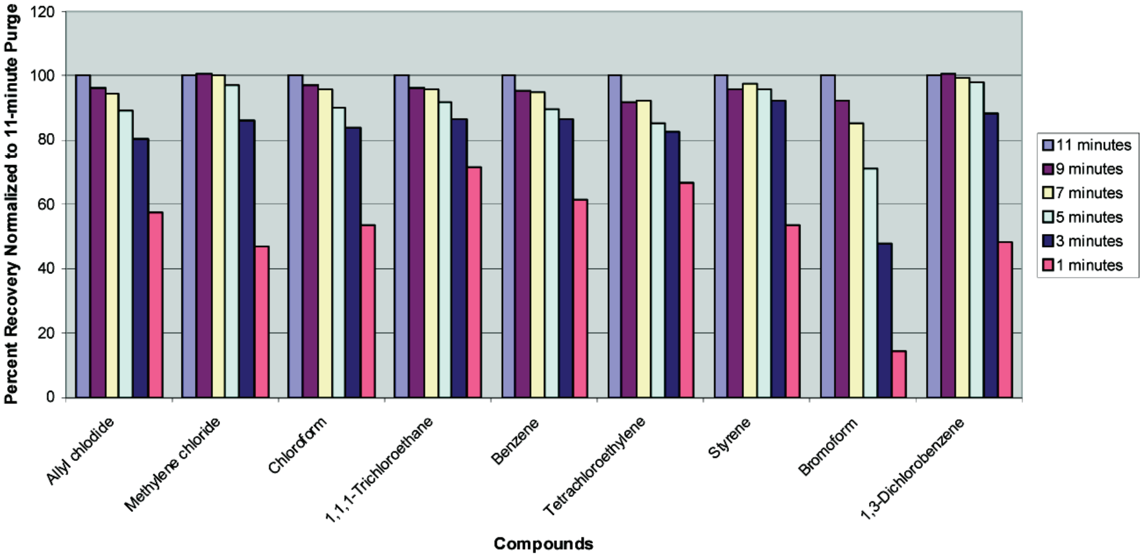


Figure 4. Relative purge efficiency of selected mid-range compounds using variable purge times and sample temperature of 40 ºC. This chart illustrates that most mid-range compounds can be recovered at levels of 95% or better when purge time is reduced to 7 minutes.

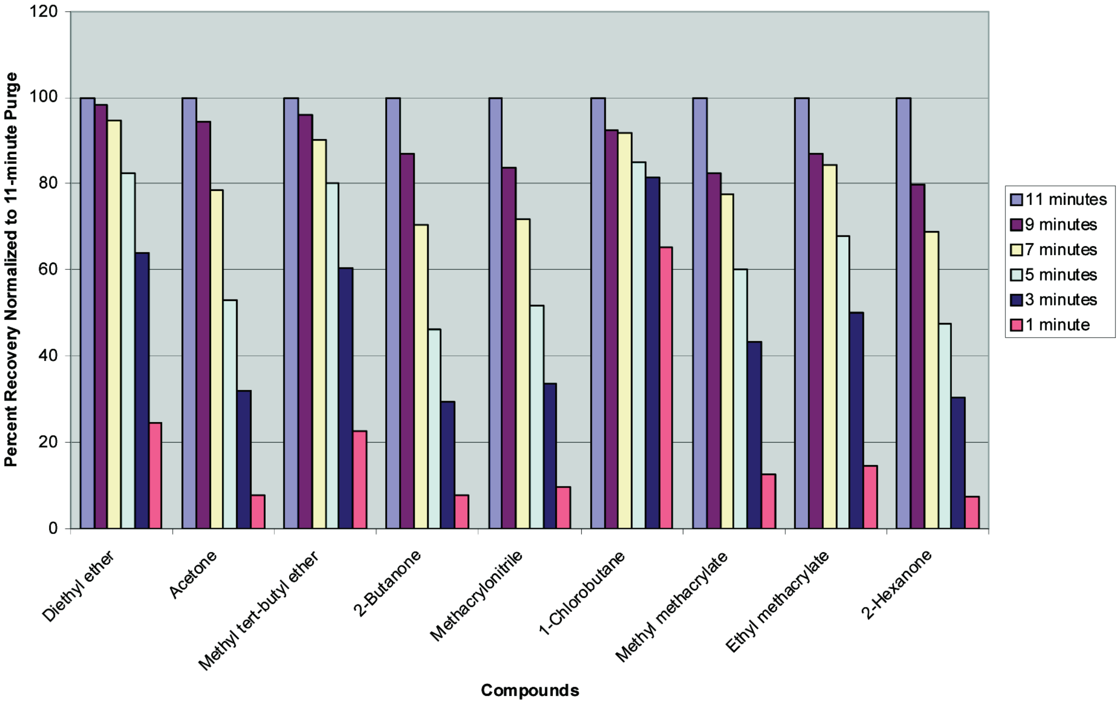


Figure 5. Relative purge efficiency of selected polar compounds using variable purge times and sample temperature of 40 ºC. This chart illustrates that the polar compounds can be recovered at levels of 70% or better when purge time is reduced to 7 minutes and sample temperature is controlled at 40 ºC, in spite of their high affinity for water.

The same sets of experiments were performed with samples at ambient temperature during the purge step. When the two sets of results were compared (sample at 40 °C and at ambient), a significant difference was noticed. Figures 6 – 9 compare purge efficiencies of the compounds using 11- and 7-minute purge with sample at 40 °C, to purge efficiencies using the traditional 11-minute purge and ambient sample temperature. For most compounds, a 7-minute purge with the sample temperature held at 40 °C produced recoveries that were equivalent to or better than the traditional 11-minute purge at ambient temperature. These results indicate that heating the sample during the purge step is essential if purge time is to be reduced.

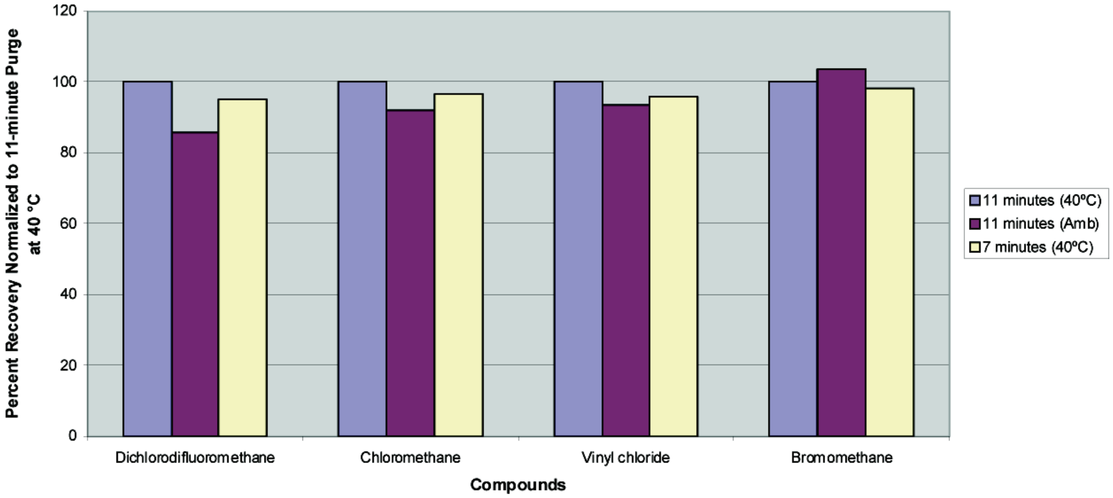


Figure 6. Relative purge efficiency of selected gas-phase compounds using variable purge times and sample temperature during purge. This chart illustrates that compound recoveries using a 7-minutes purge and a sample temperature of 40 ºC are equivalent to or better than recoveries using the traditional 11-minute purge and ambient temperature.

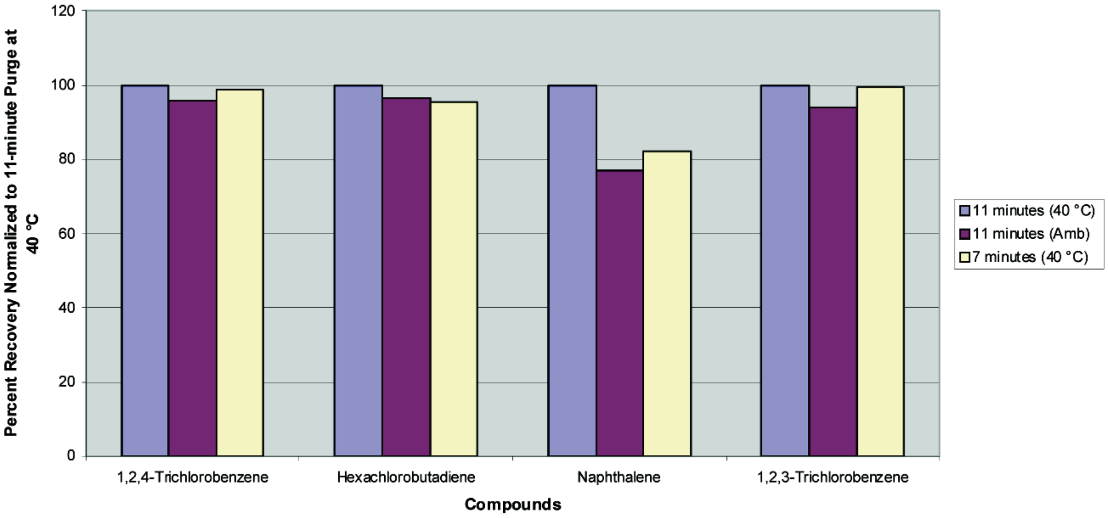


Figure 7. Relative purge efficiency of selected heavy compounds using variable purge times and sample temperature during purge. This chart illustrates that compound recoveries using a 7-minute purge and sample temperature of 40 °C are equivalent to or better than recoveries using the traditional 11-minute purge and ambient sample temperature.

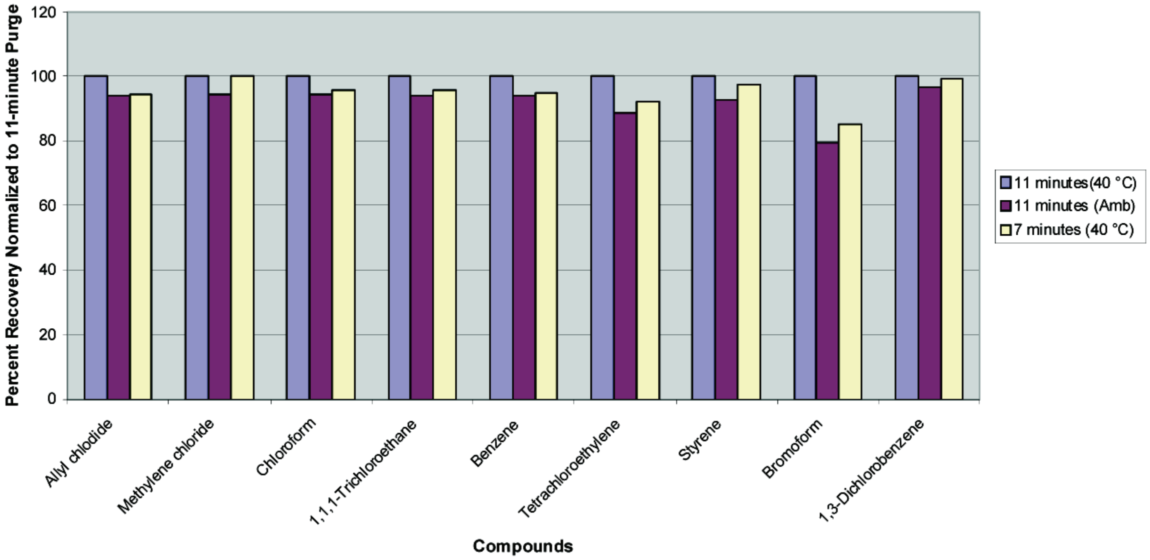


Figure 8. Relative purge efficiency of selected mid-range compounds using variable purge times and sample temperature during purge. This chart illustrates that compound recoveries using a 7-minute purge and sample temperature of 40 °C are equivalent to or better than recoveries using the traditional 11-minute purge and ambient sample temperature.

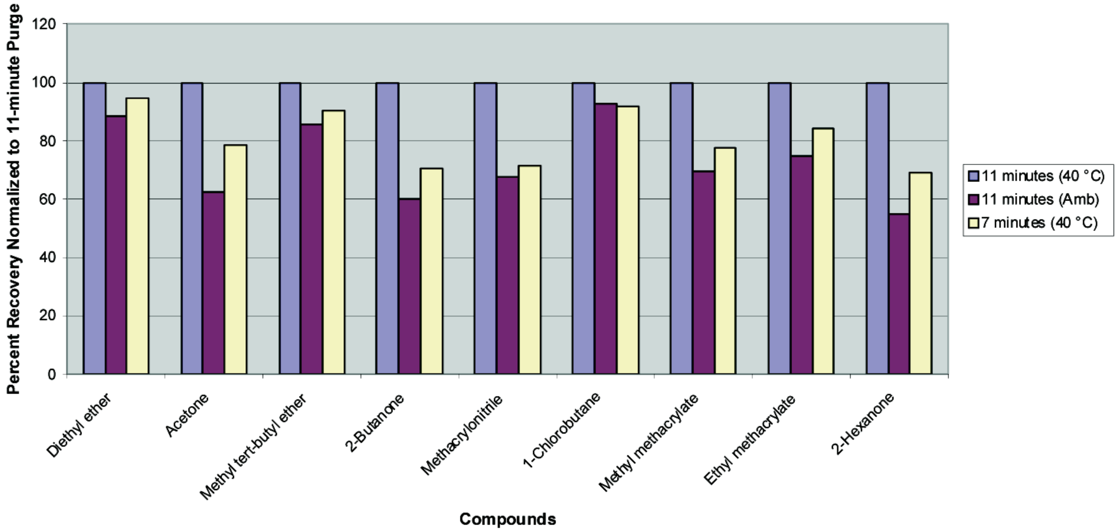


Figure 9. Relative purge efficiency of selected polar compounds using variable purge times and sample temperature during purge. This chart illustrates that compound recoveries using a 7-minute purge and sample temperature of 40 °C are equivalent to or better than recoveries using the traditional 11-minute purge and ambient sample temperature.

Shortening the P&T cycle time for each sample by 4 minutes can make a significant difference in laboratory productivity. For example, if the total P&T cycle time for one sample is 20 minutes, reducing the purge time by 4 minutes allows the laboratory to analyze nine additional samples in each 12-hour tune period, directly impacting laboratory productivity and profitability. A comparison of Eclipse P&T cycle times using the traditional 11-minute purge and the proposed 7-minute purge is shown in Table 3.

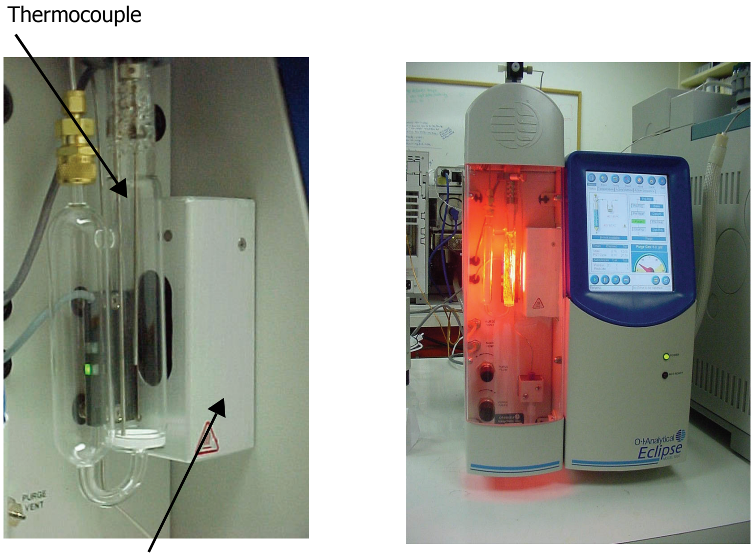
Table 3. Comparison of Purge Cycle Time

Steps	Before* (minutes)	After (minutes)
Purge	11.0	7.0
Desorb	1.0	1.0
Bake	6.0	6.0
Cooling	0.5	0.5
Total Time (minutes)	**18.5**	**14.5**
* *EPA Method 524.2*		

Sample Heating

The purge efficiency of each compound is directly related to sample temperature. At ambient temperature some compounds will have lower purge efficiency, but when the sample is heated to a moderate temperature, the purge efficiency of all compounds is improved and recoveries are higher. Thus, even a conservative sample temperature of 40 to 45 °C can result in significantly improved purge efficiencies and reduction in the time required to purge the compounds from the sample.

The equipment used in this study included the patented Infra-Sparge™ sample heater shown in Figure 10. The Infra-Sparge sample heater uses focused radiant infrared light to heat the sample during the purge step. The lamp is equipped with a reflector to concentrate infrared light for rapid and efficient heating. A thermocouple submerged in the sample ensures that each sample is heated to precisely the same temperature. This temperature control mechanism provides improved sample-to-sample repeatability and more stable calibration curves.



Heating a Sample

Figure 10. Infra-Sparge Sample Heater

Calibration, Repeatability, and Method Detection Limit (MDL)

To demonstrate the performance of the system using a shortened purge time, a seven-point calibration curve (0.5 to 200 ppb), a repeatability study, and an MDL study were run using the 7-minute purge, while holding sample temperature constant at 40 °C. All compounds were found to have a linear response over the full concentration range using the percent relative standard deviation (%RSD) of the average response factors (RF). Most compounds had an RSD of 9% or better, easily meeting all USEPA method requirements. A representative chromatogram of the mid-point calibration standard is shown in Figure 11.

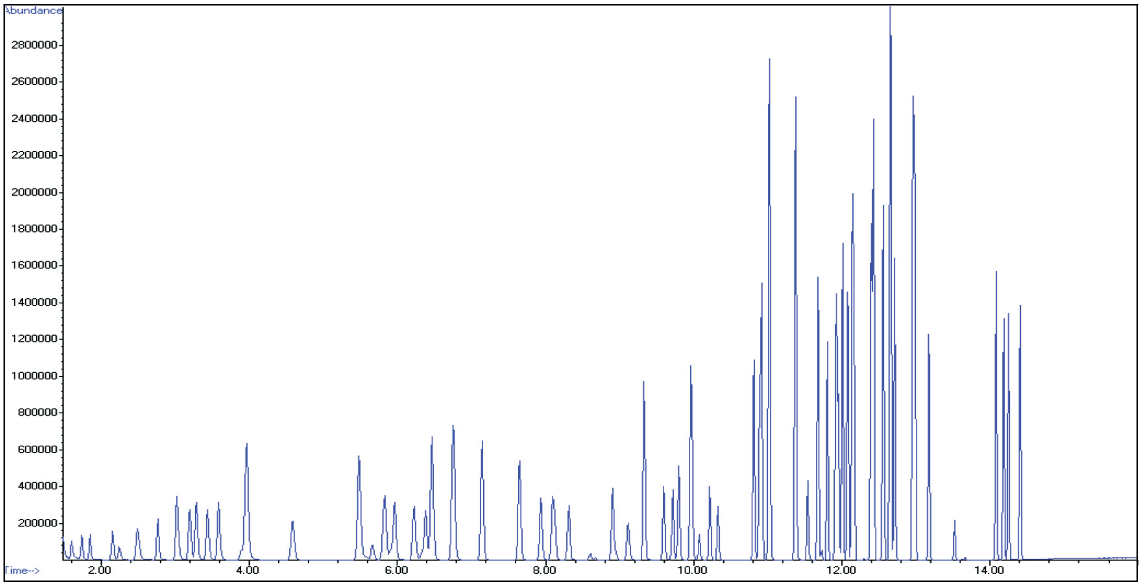


Figure 11. Representative chromatogram of 10-ppb standard using 7-minutes purge time and 40 ºC sample temperature (Rtx-624; 30 m × 0.250 mm × 1.40 μm column)

To measure repeatability, four 5-mL replicates of a 25-ppb standard were analyzed using the modified analytical conditions. The average %RSD for all compounds was less than 3% when the sample temperature was held constant at 40 °C. The required MDL study was performed using the method described in Appendix B to Part 136 in the Federal Register(5). All results for the calibration curve, repeatability study, and MDL study are shown in Table 4.

Table 4. Average calibration responses, %RSD of calibration curve; MDL and repeatability %RSD using 7-minutes purge and sample temperature of 40 ºC. All compounds met calibration criteria for USEPA Methods 524 and 8260.

Analytes	Average Calibration Response Factors (7 points)	Calibration %RSD	MDL µg/L	Repeatability %RSD (n=4)
Dichlorodifluoromethane	0.19	7.4	0.08	1.9
Chloromethane	0.17	9.4	0.09	2.6
Vinyl chloride	0.17	7.7	0.08	1.8
Bromomethane	0.14	7.7	0.06	4.3
Chloroethane	0.09	9.5	0.14	1.8
Trichlorofluoromethane	0.30	8.6	0.04	1.5
Diethyl ether	0.18	3.1	0.10	1.4
1, 1-Dichloroethene	0.23	6.9	0.05	1.6
Acetone	0.05	8.8	0.12	3.2
Iodomethane	0.47	6.3	0.05	1.4
Carbon disulfide	0.64	8.3	0.05	1.7
Allyl chloride	0.13	5.2	0.10	1.6
Methylene chloride	0.27	6.4	0.08	1.0
Acrylonitrile	0.06	10.0	0.10	1.4
Methyl *tert*-butyl ether	0.60	5.0	0.10	0.2
trans-1, 2-Dichloroethene	0.26	6.2	0.03	1.2
1, 1-Dichloroethane	0.38	6.1	0.06	1.4
2-Butanone	0.07	7.7	0.28	2.6
2, 2-Dichloropropane	0.25	7.9	0.16	2.0
cis-1, 2-dichloroethene	0.29	5.2	0.10	1.0
Propionitrile	0.03	7.3	0.30	3.2
Methyl acrylate	0.15	8.9	0.08	4.9
Methacrylonitrile	0.09	7.8	0.21	3.1
Bromochloromethane	0.16	3.5	0.08	1.0
Tetrahydrofuran	0.03	10.9	0.49	3.6
Chloroform	0.42	7.0	0.06	1.6
1, 1, 1-Trichloethane	0.33	6.8	0.08	1.3
1, 1-Dichloropropene	0.34	7.4	0.05	2.3
1-Chlorobutane	0.29	7.4	0.04	2.7
Carbon tetrachloride	0.31	9.1	0.05	1.6
Benzene	0.96	7.3	0.04	1.9
1, 2-Dichloroethane	0.25	4.4	0.06	1.8
Trichloroethylene	0.26	7.0	0.07	2.1
1, 2-Dichloropropane	0.20	5.2	0.04	2.2
Dibromomethane	0.15	3.5	0.08	2.0
Methylmethacrylate	0.12	15.0	0.09	5.0
Bromodichloromethane	0.27	9.8	0.04	2.3
Chloroacetonitrile	0.01	16.0	1.56	2.4
cis-1, 3-Dichloropropene	0.32	9.8	0.04	2.3
4-Methyl-2-Pentanone	0.22	9.2	0.09	2.8
1, 1-Dichloro-2-Propanone	0.22	9.2	0.09	2.7
Toluene	0.59	6.1	0.04	2.2
trans-1, 3-Dichloropropene	0.27	13.2	0.05	3.3
Ethyl methacrylate	0.23	16.7	0.10	4.0

Table 4. Average calibration responses, %RSD of calibration curve; MDL and repeatability %RSD using 7-minutes purge and sample temperature of 40 ºC. All compounds met calibration criteria for USEPA Methods 524 and 8260.

Analytes	Average Calibration Response Factors (7 points)	Calibration %RSD	MDL µg/L	Repeatability %RSD (n=4)
1, 1, 2-trichloroethane	0.17	4.6	0.10	2.9
Tetrachloroethylene	0.36	5.8	0.78	3.2
1, 3-Dichloropropane	0.31	4.6	0.08	3.2
2-Hexanone	0.10	14.0	0.16	5.9
Dibromochloromethane	0.24	14.7	0.06	2.2
1, 2-Dibromoethane	0.22	5.9	0.07	3.2
Chlorobenzene	0.72	6.1	0.03	2.1
1, 1, 1, 2-Tetrachloroethane	0.27	8.2	0.05	1.2
Ethylbenzene	1.09	8.0	0.06	1.8
m-, *p*-Xylene	0.91	9.8	0.07	1.9
o-Xylene	0.47	9.4	0.07	1.1
Styrene	0.77	7.3	0.06	1.4
Bromoform	0.20	17.4	0.07	1.4
Isopropylbenze	1.03	8.4	0.07	0.8
1, 1, 2, 2-Tetrachloroethane	0.30	7.5	0.07	1.0
Bromobenzene	0.39	7.1	0.04	0.8
1, 2, 3-trichloropropane	0.35	6.7	0.04	1.1
trans-1, 4-Dichloro-2-b...	0.07	7.8	1.34	1.1
n-Propylbenzene	1.32	8.6	0.07	0.7
2-Chlorotoluene	0.84	8.0	0.04	0.8
1, 3, 5-Trimethylbenzene	0.99	8.9	0.06	0.6
4-Chlorotoluene	0.95	8.2	0.06	0.9
tert-Butylbenze	1.16	9.7	0.24	0.5
Pentachloroethane	0.22	9.5	0.64	1.0
1, 2, 4-Trimethylbenzene	1.03	9.5	0.07	0.5
sec-Butylbenzene	1.31	9.5	0.06	0.9
1, 3-Dichlorobenzene	0.73	4.3	0.07	0.6
p-Isopropyltoluene	1.31	9.5	0.06	0.9
1, 4-Dichlorobenzene	0.77	7.0	0.07	0.4
n-Butylbenzene	0.97	9.7	0.08	1.0
1, 2-Dichlorobenzene	0.71	8.5	0.03	0.4
Hexachloroethane	0.20	9.7	0.07	1.2
1, 2-Dibromo-3-Chloropr	0.04	9.0	0.08	1.4
Nitrobenzene	0.01	17.9	2.05	2.9
1, 2, 4-Trichlorobenzene	0.53	6.0	0.11	0.8
Hexachlorobutadiene	0.32	7.3	0.09	1.6
Naphthalene	1.02	8.3	0.16	1.2
1, 2, 3-Trichlorobenzene	0.51	4.4	0.06	1.1
Average		**8.2**		**2.2**

Conclusions

This study confirms that the purge time in a VOC analysis can be reduced from 11 to 7 minutes when the sample temperature is maintained at 40 °C. Keeping the sample temperature at 40 °C during purge also improves purge efficiency, increases compound recovery, lowers calibration and repeatability %RSDs, and enhances overall instrument performance. It has also been shown (3) that a slight increase in the purge flow rate can improve recoveries when using a reduced purge time. Reducing P&T cycle time by 4-minutes per sample significantly improves sample throughput and provides a means to increase laboratory productivity and profitability.

Acknowledgement

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