A Cleaner, More Sensitive Approach to EPA Method 8260 Using Large Volume Static Headspace and Active SPME Preconcentration Prior to GCMS Analysis

Application Note:

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Abstract

An improved approach for performing EPA method 8260 is presented. Large Volume Static Headspace (LVSH) sample introduction is used which improves method sensitivity relative to standard Purge & Trap technology while maintaining a cleaner system, resulting in longer operation without servicing. A 20mL sample volume is prepared in 40mL VOA vials along with 10g NaCl to help transfer VOCs to the headspace. After automated heating and mixing, 10cc of headspace is introduced into a 3-stage preconcentrator that extracts the SVOCs, water vapor, and VOCs in three different traps, followed by backushing of the Tenax® trap to the first trap for dynamic focusing prior to injection. Refocusing of the sample allows a splitless injection to be made into the GCMS, greatly improving sensitivity. Elimination of sample purging reduces foam and/or aerosol formation, keeping transfer lines clean for an extended period of time. Dean's Switch technology is used to control ows throughout the system, eliminating problematic rotary valves that increase system carryover and are often the points where leaks occur most frequently. A unique volume measurement technique provides a very consistent approach for volume measurement, insuring excellent overall analytical reproducibility. Data is presented showing 8260 method compliance in regards to calibration linearity, method detection limits, and reproducibility.

Figure 1 40mL Sample Vials with Silonite™ Micro-QT™ Valve.

Introduction

EPA 8260 is the required method for determining Volatile Organic Compound (VOC) concentrations in hazardous waste and groundwater samples. It has traditionally been performed with EPA methods 5030 and 5035 using purge and trap to extract the VOC's from the sample and concentrate them prior to introduction into a gas chromatograph/mass spectrometer (GC/MS). An alternative technique for VOC extraction is using headspace by EPA method 5020 followed by analysis using EPA method 8260. Headspace offers some advantages to purge & trap:

1. Headspace is a cleaner technique. Purge and trap can allow samples with surfactants to foam up and contaminate the system.
2. Hydrochloric acid used as a preservative in water samples can corrode tubing inside the system since purging carries acidic vapors through the sample flow path.
3. Rotary valves can score and cause cross purging or cross contamination from one sample to the next.
4. Strong multi-bed adsorbent traps can cause losses of multiple target compounds, and require frequent replacement.

Until now, headspace analysis has been less sensitive than purge & trap, but new technology enables the headspace to be concentrated by a technique which utilizes Active SPME. The headspace vapor is pulled through a 3-stage trapping system, which contains the active SPME trap, a water management trap, and a Tenax® trap cooled without liquid nitrogen. By actively pulling the vapor over the SPME lm, heavier compounds are quantitatively trapped, while a secondary cold Tenax® trap retains the lighter VOCs. Water is removed by a direct gas to solid phase transition that allows good recovery of water soluble compounds. The analytical system employs robotic automation that provides very consistent and reliable results.

7150 3-Stage Preconcentrator shown on Agilent 7890 GC. Distance to GC column after preconcentration is minimized, providing enhanced recovery of semi-volatiles.
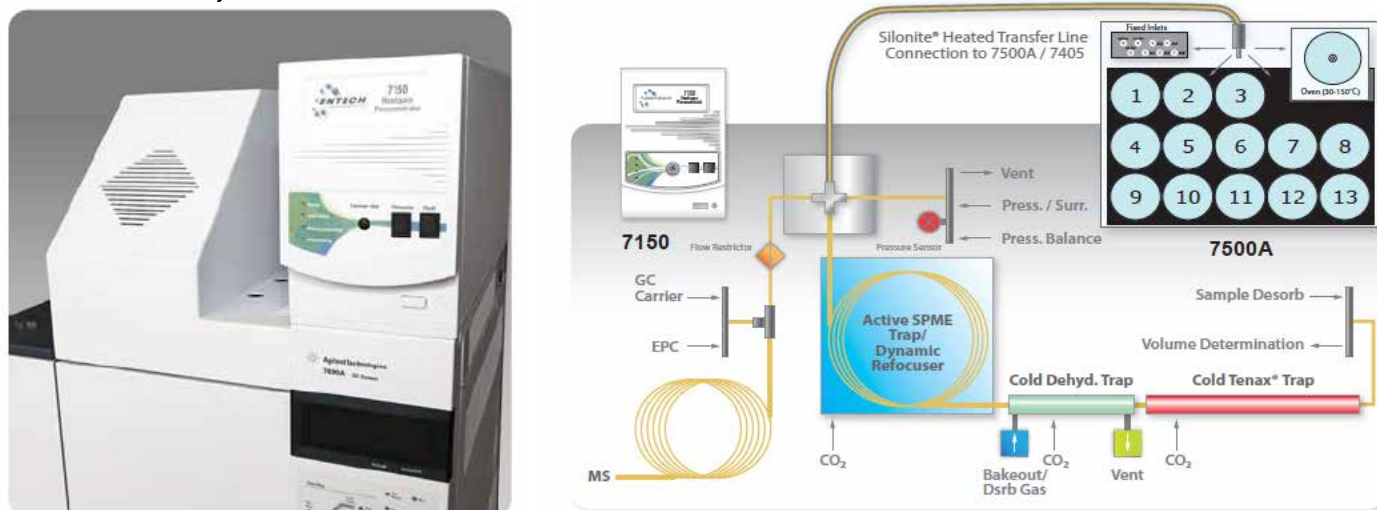

Figure 2 7150 / 7500A Automated 8260 System utilizing Active SPME and cold trapping to improve 8260 consistency and sensitivity.

Experimental

8260 Calibration standards were prepared using an initial 200 ug/ml mix in methanol, (Accustandard 502-A-R/B). Aliquots of this mixture were diluted into water at 5 different concentrations ranging from 1 ug/L to 20 ug/L. Twenty milliliter sample volume was added to each vial which contained 10 g of NaCl2, used as a matrix modier to increase recovery. Sample handling was performed on an Entech 7500A Autosampler (Simi Valley, Ca) utilizing a new mixing oven capable of heating the 40mL vial from ambient to 150°C. Analyses were performed at 60°C with a 20 minute pre-heat. A 15mL aliquot of headspace was extracted from the vial through a heated, Silonite™ coated transfer line to an Entech 7150 (Active SPME) Preconcentrator. Sampling preparation was performed as follows:

	Trapping	Water Bakeout	T1 Refocus	Desorb	Bakeout
T1 Active SPME Trap	60°C	60°C	-52°C	230°C	220°C
T2 Dehydration Trap	-30°C	160°C	60°C	60°C	150°C
T3 Tenax® Trap	-50°C	-50°C	200°C	200°C	210°C

After preconcentration, a splitless injection was made into an Agilent 7890/5975 GCMS (Palo Alto, CA). The column (HP1, 60m, 0.32mmID, 1um film) temperature was held at 35°C for 5 minutes, then ramped at 10C/min to 210°C, with a final 5 minute hold. The mass spectrometer was operated in full scan mode, monitoring m/z 35 to 270 approximately 3 times per second.

Figure 3 7150 / 7500A Automated 8260 Analysis System shown with Agilent 7890 / 5975 GCMS.
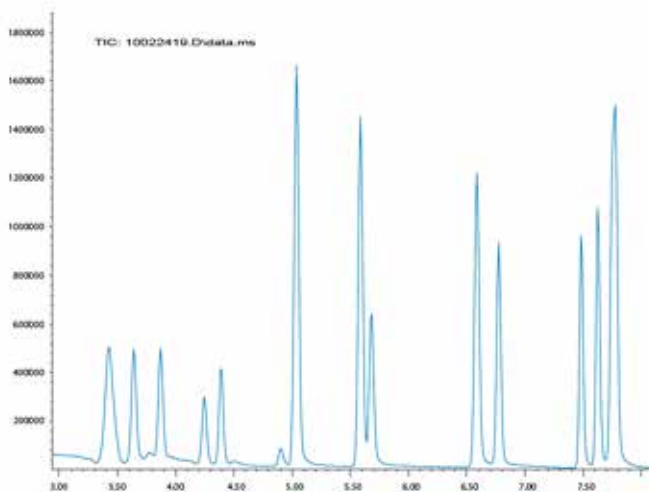

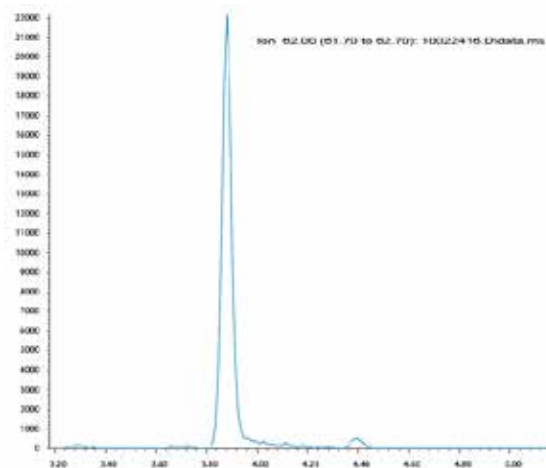**Figure 4** Excellent peak shape for the light gases allows for maximum signal to noise ratio.

Figure 5 m/z 62 for Vinyl Chloride at 0.5 PPB.

Discussion

Figure 2 displays operation of the 7150 sample concentrator which utilizes a 3 stage trapping system employing a new trap called Active SPME. The headspace is pulled through the trapping system which traps out the heavier compounds on the Active SPME lm, then passes through the water management cold trap and nally to the cooled tenax trap to trap out the lighter VOCs. This is combined with a 100 position robotic autosampler that creates superior automation.

In Figure 4 you can see the resolution of the light VOCs with sharp peaks which improves sensitivity which is displayed in Figure 5 with 0.5 ppb of vinyl chloride. Figure 7 shows the excellent peak shape of the entire total ion chromatogram. Sensitivity is really maximized by the splitless injection technique, other VOC concentration techniques utilize strong trap adsorbents which require high flow rates during desorption. To provide these higher flow rates a split injection is performed but that creates at least a 10 fold dilution factor. The 7150 injects 100 percent of the sample onto the analytical column, this is accomplished by refocusing the sample on the active SPME trap prior to injection to the GC. This refocusing brings all of the VOCs into a tight band so that a slower carrier gas injection can be performed without sacrificing resolution.

3

Discussion

As you can see in table 1 this concentration technique is very reproducible. Headspace is a well established technique and is a cleaner approach to VOC analysis than purge and trap since there is no chance of foaming samples. The only limitation headspace has had over purge and trap is lack of sensitivity. With the 7150 splitless injection, sensitivity is now greater with headspace than purge and trap.

Figure 6 Entech Instruments, Inc. 7500A shown with mixing oven. Mixing oven facilitates rapid sample headspace equilibrium prior to the withdrawal of 10mL of headspace into the 7150 Preconcentrator.
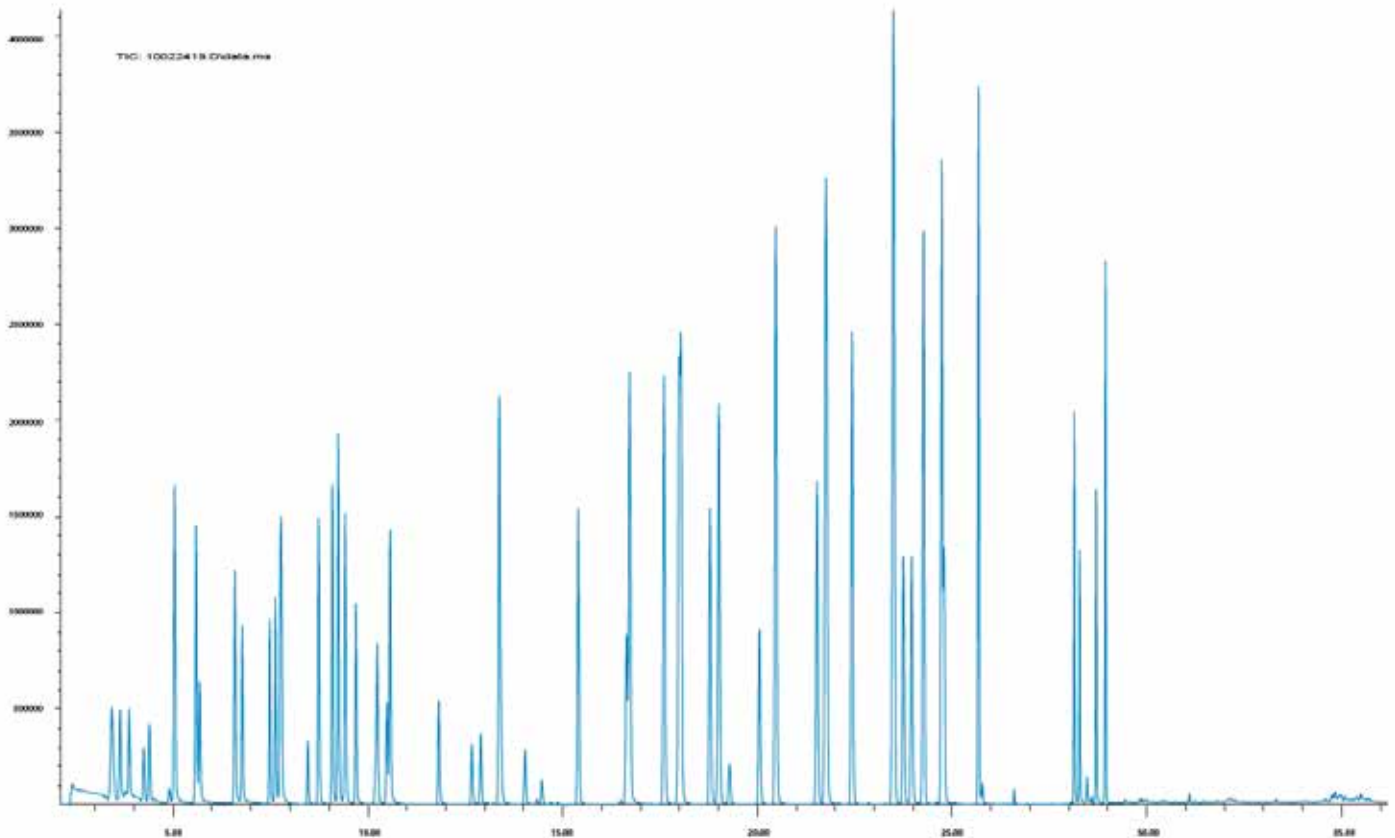

Figure 7 Total ion chromatogram of all 8260 components.

7150 Calibration Curve (1.0 ppb to 20 ppb) Relative Response Factors (RRF)

Compound	1.0 ppb	2.0 ppb	5 ppb	10 ppb	20 ppb	Ave RRF	%RSD
Dichlorodifluororoethane	1.54	1.84	1.66	1.70	1.45	1.64	8.99
Chloromethane	0.87	1.00	0.84	0.82	0.81	0.87	8.93
Vinyl Chloride	8.20	9.68	8.35	7.72	6.31	8.05	15.0
Bromomethane	2.60	4.05	2.71	2.60	2.27	2.85	24.4
Chloroethane	4.13	5.20	4.55	4.42	4.03	4.47	10.3
Trichlorofluoromethane	2.37	1.37	2.44	1.35	2.06	1.92	27.5
1,1-Dichloroethene	1.72	1.58	1.98	1.35	1.62	1.65	13.9
Methylene Chloride	5.37	5.12	4.96	4.20	4.48	4.82	9.84
trans-1,2-Dichloroethene	1.42	1.36	1.54	1.36	1.31	1.40	6.12
1,1-Dichloroethane	1.36	1.77	1.51	1.33	1.28	1.45	13.5
cis-1,2-Dichloroethene	7.24	9.86	8.80	7.64	7.52	8.21	13.3
Chloroform	0.91	0.84	1.09	0.94	0.90	0.94	10.0
2-2-Dichloropropane	2.20	2.01	2.57	2.25	1.90	2.18	11.8
1,1,1-Trichloroethane	1.19	1.11	1.54	1.34	1.20	1.28	13.0
1,2-Dichloroethane	4.07	5.74	5.03	4.29	4.49	4.72	14.1
1,1-Dichloropropene	1.00	0.88	1.24	1.09	0.98	1.04	12.6
Benzene	2.42	2.25	2.73	2.39	2.28	2.41	7.90
Carbon Tetrachloride	1.15	1.09	1.53	1.34	1.20	1.27	13.8
Dibromomethane	1.47	1.98	1.60	1.39	1.51	1.59	14.2
Trichloroethene	7.09	6.45	8.38	7.39	6.89	7.24	9.97
1,2-Dichloropropane	4.81	5.16	5.34	4.62	4.67	4.92	6.43
Bromodichloromethane	5.36	6.70	6.52	5.69	5.81	6.01	9.48
cis-1,3-Dichloropropene	6.50	5.55	7.26	6.40	6.70	6.48	9.58
trans-1,3-Dichloropropene	4.90	5.55	5.34	4.75	5.12	5.13	6.29
Toluene	2.86	2.51	3.22	2.82	2.63	2.81	9.67
1,1,2-Trichloroethane	3.01	3.45	3.11	2.62	2.84	3.01	10.2
Dibromochloromethane	3.31	4.32	3.98	3.44	3.75	3.76	10.8
Tetrachloroethene	8.31	7.21	9.84	8.68	7.89	8.39	11.6
1,2-Dibromoethane	2.64	3.37	2.82	2.40	2.69	2.79	12.9
1,1,1,2-Tetrachloroethane	3.24	2.92	3.23	2.79	2.72	2.98	8.15
Chlorobenzene	9.76	7.98	9.58	8.43	8.14	8.78	9.48
Ethylbenzene	1.91	1.45	1.99	1.77	1.65	1.75	12.3
Styrene	1.00	0.82	1.01	0.91	0.91	0.93	8.29
o-Xylene	1.40	1.11	1.46	1.29	1.21	1.29	10.7
Bromoform	1.01	1.15	1.00	0.88	0.99	1.01	9.55
1,1,2,2-Tetrachloroethane	1.99	2.26	1.93	1.60	1.78	1.91	12.8
1,2,3-Trichlorobenzene	1.98	2.28	1.79	1.75	1.58	1.87	14.2
Isopropylbenzene	1.83	1.32	1.92	1.69	1.53	1.66	14.2
Bromobenzene	7.29	6.54	7.68	6.68	6.22	6.88	8.61
2-Chlorotoluene	1.15	0.94	1.25	1.10	1.05	1.10	10.3
4-Chlorotoluene	3.28	2.57	3.56	3.15	2.85	3.08	12.4
n-Propylbenzene	3.35	2.60	3.60	3.18	2.88	3.12	12.5
1,3,5-Trimethylbenzene	1.64	1.21	1.74	1.56	1.44	1.52	13.3
1,2,4-Trimethylbenzene	1.63	1.26	1.72	1.51	1.35	1.50	12.6
1,3-Dichlorobenzene	6.80	5.91	7.33	6.67	6.64	6.67	7.61
1,4-Dichlorobenzene	6.59	5.83	7.07	6.41	6.46	6.47	6.85
1,2-Dichlorobenzene	5.75	5.31	6.05	5.40	5.44	5.59	5.42
tert-Butylbenzene	1.05	0.81	1.15	1.00	0.88	0.98	13.7
sec-Butylbenzene	2.14	1.52	2.33	2.10	1.95	2.01	15.1
Isopropyltoluene	1.74	1.25	1.90	1.70	1.56	1.63	14.9
n-Butylbenzene	1.35	1.05	1.61	1.45	1.35	1.36	15.1
1,2-Dibromo-3-chloropropane	3.23	4.15	3.49	3.07	3.83	3.55	12.2
1,2,4-Trichlorobenzene	4.26	3.63	4.28	3.72	3.55	3.89	9.10
1,2,3-Trichlorobenzene	3.54	3.14	3.55	3.06	3.01	3.26	8.17
Naphthalene	1.01	0.99	0.97	0.83	0.87	0.94	8.49
Hexachlorobutadiene	2.55	1.87	2.75	2.42	2.11	2.34	15.0

Figure 6 Entech Instruments, Inc. 7500A shown with mixing oven. Mixing oven facilitates rapid sample headspace equilibrium prior to the withdrawal of 10mL of headspace into the 7150 Preconcentrator.

Conclusion

A classical technique has been reinvented and revolutionized. Headspace analysis has been optimized to provide the most sensitive technique to VOC analysis for water and solid matrices The 7150 3 stage concentrator has enabled headspace to gain the sensitivity needed to expand this sample preparation technique beyond conventional expectations and even beyond purge and trap, previously thought to be the only solution to VOC analysis of water samples.

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