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Prevent Damage to Your Purge and Trap by Pre-Screening with Static Headspace

Application Note

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Introduction

Much time and money is lost in environmental laboratories bringing Purge and Trap Gas Chromatography Mass Spectrometer systems back in operation from a sample containing dangerously high levels of volatile organic contaminants. Often soil and water samples contain concentration levels that are much higher than the normal operating range of Purge and Trap. EPA method 5021, a static headspace method is recommended for screening of volatile organic analytes prior to PT-GC/MS analysis because of its speed, simplicity and minimal carryover. This method can be used to quickly predetermine dilution levels or calibration ranges necessary for PT-GC/MS analysis, saving time and preventing costly damage to the volatiles system. An excellent tool for the pre-screening process is Teledyne Tekmar's new HT3 Static and Dynamic Headspace Auto sampler.

Experimental

This paper presents a method for rapid screening that can be used as a screening tool and also tests the new capability of the Dynamic Headspace option of the HT3, which dramatically improves sensitivity. The Dynamic option continually sweeps the headspace of the vial, depositing and concentrating the compounds onto an analytical trap. The compounds listed below were analyzed using a Teledyne Tekmar HT3 with a mass spectrometer. A 5-point calibration curve was analyzed using a range of 200ppb to 2ppm, and analyzing a curve of 5ppb to 100ppb tested the dynamic capabilities.

The parameters for the HT3 Headspace auto sampler and the GC conditions are listed in Tables 1, 2, and 3.

Table 1. HT3 Static Headspace Parameters (Loop Method)

Variable	Value
GC Cycle Time	20.00 min
Valve Oven Temp	100 degrees C
Transfer line Temp	100 degrees C
Standby Flow Rate	50 mL/min
Platen/Sample Temp	85 degrees C
Sample Equil. Time	30.00 min
Mixer	on
Mixing Time	20.00 min

Variable	Value
Mixing Level	Level 5
Mixer Stabilize Time	0.50 min
Pressurize	10 PSIG
Pressurize Time	1.50 min
Pressurize Equil. Time	0.50 min
Loop Fill Pressure	5 PSIG
Loop Fill Time	0.50 min
Loop Fill Equil. Time	0.50 min
Inject Time	1.00 min

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Table 2. HT3 Dynamic Headspace Parameters (Trap Method)

Variable	Value
GC Cycle Time	20.00 min
Valve Oven Temp	150 degrees C
Transfer Line Temp	150 degrees C
Standby Flow Rate	40 mL/min
Trap Standby Temp	30 degrees C
Platen/Sample Temp	65 degrees C
Sample Preheat Time	20.00 min
Preheat Mixer	On
Preheat Mixer Level	Level 5

Variable	Value
Preheat Mixing Time	2.00 min
Preheat Mixer Stabilize Time	0.50 min
Sweep Flow Rate	75 mL/min
Sweep Flow Time	6.00 min
Desorb Preheat	255 degrees C
Desorb Temp.	260 degrees C
Desorb Time	2.00 min
Trap Bake Temp.	300 degrees C
Trap Bake Time	5.00 min
Trap Bake Flow	450 mL/min

Table 3. GC/MS Parameters

Column	RTX-VMS 20m x 0.18, 1.0 micrometer film
Carrier	He at 0.8 mL/min
Injector	Split ratio: 50:1, total flow 43.3mL/min, temp 220 degrees C
Oven	Initial temp 35 degrees C, hold for 2.00 min, rate of 14.00
	to 85, hold for 0.00 min, rate of 40 to 210 and hold for 3.00 min
	(Total run time of 11.70 min)
MS	Interface at 280 degrees C, MS quad 150 degrees C,
	MS source at 230 degrees C

Results

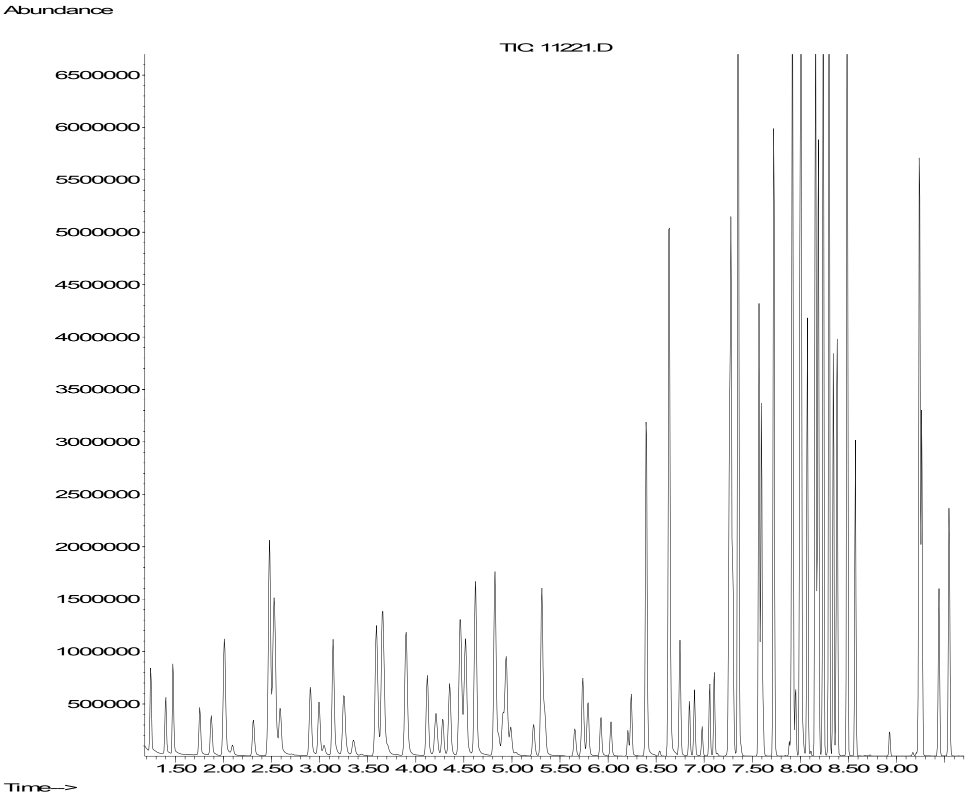
The results for this study are listed in table 4 for both the Static and Dynamic option. The curves were analyzed using internal standardization and calculating response factors (the internal standards used were Pentafluorobenzene, 1,4-difluorobenzene, and Chlorobenzene-d5). MDL's were calculated for both techniques and are included in the data. Most compounds were less than 15% for their calculated RSD and the fast GC time of 11.70 minutes still yielded excellent peak separation.

Table 4. Static and Dynamic curves along with the calculated MDL's

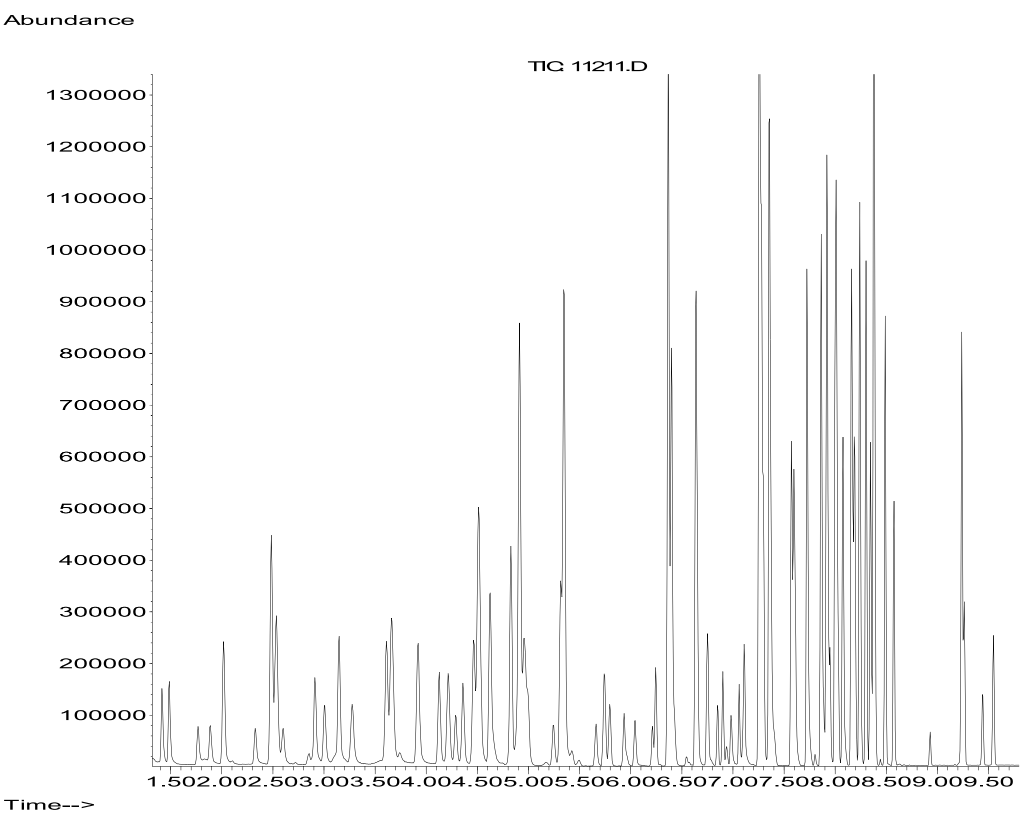
Compounds	Static (Loop Curve) 200ppb to 2ppm %RSD's	Static MDL's (ppb)	Dynamic (Trap Curve) 5ppb to 100ppb %RSD's	Dynamic MDL's (ppb)
Dichlorodifluoromethane	2.50	36.24	9.08	0.58
Chloromethane	1.64	30.11	10.02	0.67
Vinyl Chloride	3.37	22.87	6.81	0.60
Bromomethane	6.60	17.63	3.90	0.95
Chloroethane	2.92	20.83	6.97	0.44
Trichloromonofluoromethane	4.03	15.29	8.47	1.16
Methylene Chloride	3.18	23.75	10.15	0.94
trans-1,2-dichloroethene	5.18	12.35	7.06	0.73
Carbon disulfide	3.42	15.03	5.74	0.48
MTBE	6.43	20.97	7.44	1.05
1,1-dichloroethane	3.26	15.65	6.36	0.64
cis-1,2-dichloroethene	3.99	19.06	5.98	0.66
Bromochloromethane	3.75	25.40	6.79	0.94
Chloroform	2.59	19.45	5.25	0.60
Carbon tetrachloride	5.01	14.48	10.05	0.65
1,1,1-trichloroethane	2.12	15.16	8.53	0.69
2-Butanone	5.86	61.59	8.44	5.32
Benzene	2.76	19.22	6.44	0.62
1,2-dichloroethane	5.04	21.53	8.98	0.91
Trichloroethene	16.59	45.97	4.15	0.52
Dibromomethane	4.81	23.60	4.08	0.68
1,2-dichloropropane	3.74	12.10	5.44	0.46
Bromodichloromethane	6.01	16.31	6.58	0.35
cis-1,3-dichloropropene	10.66	27.26	8.50	0.78
Toluene	2.04	13.34	5.66	0.29
Tetrachloroethene	10.35	12.40	11.30	0.82
trans-1,3-dichloropropene	12.85	30.07	9.12	0.61
1,1,2-trichloroethane	5.80	20.83	5.27	0.92
Dibromochloromethane	9.55	19.31	9.00	1.13
1,3-dichloropropane	3.93	17.16	5.50	1.01
1,2-dibromoethane	6.11	17.10	4.12	1.05
2-hexanone	5.50	48.34	10.21	1.84
Chlorobenzene	1.01	9.55	4.31	0.25
Ethyl benzene	4.03	9.45	4.89	0.45
1,1,1,2-tetrachloroethane	3.61	9.80	7.77	0.51

Compounds	Static (Loop Curve) 200ppb to 2ppm %RSD's	Static MDL's (ppb)	Dynamic (Trap Curve) 5ppb to 100ppb %RSD's	Dynamic MDL's (ppb)
M&P Xylene	5.70	13.74	6.56	0.79
Ortho Xylene	2.60	10.86	6.23	0.40
Styrene	5.23	13.08	5.69	0.38
Bromoform	10.25	10.69	14.33	0.88
Isopropylbenzene	3.97	10.99	8.59	0.42
n-propylbenzene	4.77	13.04	9.93	0.47
Bromobenzene	3.88	10.27	2.12	0.43
1,3,5-TMB	4.19	8.81	10.07	0.34
2-chlorotoluene	2.16	11.33	3.90	0.31
1,2,3-trichloropropane	3.38	25.30	3.87	0.58
4-chlorotoluene	2.45	14.05	5.45	0.30
Tertbutylbenzene	2.61	11.42	15.51	0.34
1,2,4-TMB	3.81	11.95	13.89	0.30
Sec-butylbenzene	6.15	11.21	15.05	0.49
p-isopropyltoluene	5.31	11.51	18.47	0.29
1,3-dichlorobenzene	2.15	13.88	4.06	0.34
1,4-dichlorobenzene	2.21	12.70	3.51	0.26
n-butylbenzene	5.54	13.22	21.85	0.25
1,2-dichlorbenzene	1.41	11.80	3.12	0.42
1,2-dibromo-3-chloropropane	9.51	24.02	11.26	0.94
Hexachlorobutadiene	2.17	9.41	13.13	0.62
1,2,4-trichlorobenzene	4.26	10.26	12.24	0.59
Naphthalene	7.09	11.43	13.13	0.79
1,2,3-trichlorobenzene	3.76	13.61	9.41	0.58

Example chromatogram of a 2ppm standard run by the Static (Loop) Method



Example chromatogram of a 20ppb standard run by the Dynamic (Trap) Method



Conclusion

Static Headspace is a much-needed tool for the pre-screening of samples that contain volatile organic concentrations greater than 200ppb. At the minimum the sample is out of the calibration range and will need to be repeated. At higher concentration levels carryover may cause re-analysis of samples or contamination may require the whole system to be taken offline and cleaned. A rapid headspace screening method can be successful in preventing these problems, which is much more cost effective than trying to clean up a problem after it occurs.

The Dynamic capabilities were also tested in this study, and the data shows the versatility of the HT3 and its increased analytical range.