Application Note: 10038

Analysis of Volatile Organics in Solid Wastes, Soils, and Water Using a Split Injection and the PolarisQ Ion Trap GC/MS

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Key Words

- PolarisQ Ion Trap
- EPA Method 8260
- GC/MS
- Volatile Organic Compounds
- Waste Water

Introduction

The analysis of waste water and soils for volatile organics is performed by purging the volatiles from the sample matrix into the gas phase and then concentrating them onto a sorbent trap.1 The trap is thermally desorbed into the gas chromatography (GC) capillary column for detection on a mass spectrometer (MS). Since the analyte concentrations are usually very high in these waste samples, covering concentration ranges from 20 to 200 µg/L (ppb), a split injection is used. The Thermo Scientific PolarisQ external ionization ion trap GC/MS system is a very sensitive MS. The split injection lowers the time spent on maintenance for the mass spec and GC in this routine analysis.

Method: Split Injection

The PolarisQ ion trap MS, TRACE GC Ultra™, Tekmar 3100 Concentrator, and AquaTek 70™ Autosampler (Figure 1) were used to evaluate the quality control criteria as specified in EPA Method 8260.[1]

The split injection provides a simpler, less expensive alternative to the traditional jet separator, post-column technique. A purge and trap interface kit was developed for modification of a standard GC split/splitless injector, providing the interface to the concentrator and TRACE GC Ultra™ (Figure 1), along with a typical Total Ion Chromatogram of a 200 µg/L standard is shown in Figure 2. Compounds evaluated are included in Table 1.

Figure 1: The PolarisQ ion trap GC/MS/MS

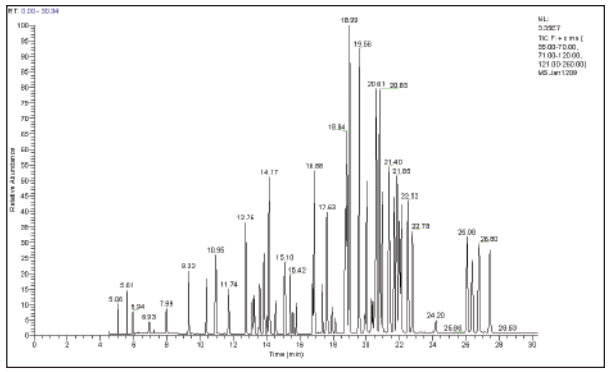

Figure 2: TIC of 200 ppb Standard

Configuration of the GC

In order to configure a GC for sample introduction from the Tekmar 3100, the carrier gas is diverted from the GC to the heated switching valve in the concentrator. This valve rotates, diverting the flow of the carrier gas across the trap to the inlet, for sample introduction.

Installing the Silcosteel Insert

For this evaluation the Silcosteel® Insert was installed into the Split/splitless inlet (Figure 3). The heated transfer line from the Tekmar 3100 was connected to the top of the GC inlet just below the septum nut (Figure 4).

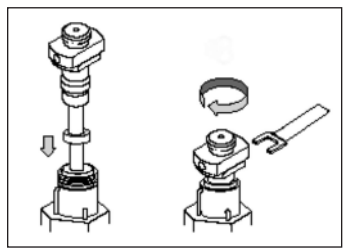

Figure 3: Replacement of glass liner with Silcosteel Insert

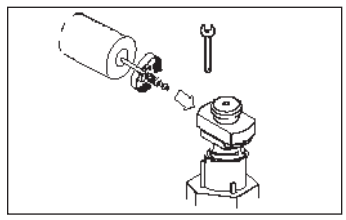

Figure 4: Connecting heated transfer line to inlet

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The Evaluation

A 60 m x 0.32 mm i.d. x 1.8 µm analytical column with a phase designed for volatile organics was installed in the inlet and the split flow was set to 50 mL/min of helium at 10 psi. The internal standard was automatically added by the autosampler and a 5 mL water sample was used.

In order to evaluate the performance of the instrument, the following areas were studied: the tune, linearity, SPCCs, CCCs and stability of response.

The Tune

The EPA has specific criteria for tuning, in order to bring some commonality to the spectra, and quality control to the data produced by the various GC/MS products on the market. The tuning protocol is given for 4-Bromofluorobenzene (BFB) in the method.[1]

Segmented Scanning

In order to meet the tune ratios the ion trap was operated in a scanning mode called segmented scan. By using segmented scans, the mass range is split into continuous segments and different injection times are applied to adjust the ion ratios.

The scanning method is used for all of the analysis runs. All of the tuning requirements were met and shown in the Target tune report in Figure 5.

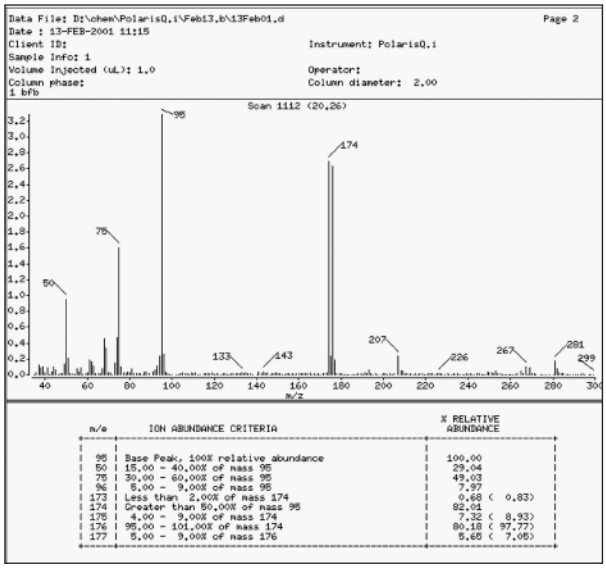

Figure 5: Target Tune Report for BFB

Linearity

The linearity of the method was evaluated by running a 5-point curve (20, 50, 100, 150, 200 µg/L) and determining the relative percent standard deviation (%RSD) across the points. Table 1 shows the results of the linearity study.

System Performance Check Compounds

Before running a calibration curve, the method requires determination of the response factor (RF) for each of the System Performance Check Compounds (SPCCs) listed in Table 2. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.[1]
The minimum RF is specific to each compound.
The SPCCs were determined and shown in Table 2 for the PolarisQ.

Calibration Check Compounds

The Calibration Check Compounds (CCCs) are used to evaluate the integrity of the instrument system. High variability may be indicative of leaks or active sites in the flow path.[1] The determined values shown in Table 3 were all within the EPA method criterion of <15 % Relative Standard Deviation (% RSD).

COMPOUND	% RSD
1,1-Dichloroethene	6.82
Chloroform	8.29
1,2-Dichloropropane	7.91
Toluene	10.5
Ethylbenzene	6.77
Vinyl chloride	8.89

Table 3: Calibration Check Compounds

COMPOUND	CHARACTERISTIC	DETERMINED RF	MINIMUM RF
Chloromethane	Lost if purge flow is too high	0.245	0.100
Bromoform	Low purging efficiencyCold spots and/or active sitesResponse of the quantitation ion 173 m/z is directly affected by the tuning of BFB	0.249	0.100
1,1,2,2-Tetrachloroethane	Contaminated transfer lineActive sites in trapping material	0.300	0.300
1,1-Dichloroethane	Contaminated transfer lineActive sites in trapping material	0.58	0.100
Chlorobenzene	Control	0.759	0.300

Table 2: System Performance Check Compounds

EPA METHOD 8260	20 µg/L	50 µg/L	100 µg/L	150 µg/L	200 µg/L	AVERAGE	STD. DEV.	% RSD
Dichlorodifluoromethane	0.2743	0.2901	0.2631	0.2324	0.2479	0.2616	0.020	7.68%
Chloromethane	0.2584	0.2875	0.2319	0.2118	0.2365	0.2452	0.026	10.54%
Vinyl chloride	0.2884	0.2692	0.2368	0.2276	0.2732	0.2590	0.023	8.89%
Bromomethane	0.0951	0.0898	0.0872	0.0803	0.0928	0.0890	0.005	5.75%
Chloroethane	0.0326	0.0297	0.0292	0.0285	0.0315	0.0303	0.002	5.00%
Trichlorofluoromethane	0.3529	0.3484	0.3099	0.2938	0.3417	0.3293	0.023	7.07%
1,1-Dichloroethylene	0.1785	0.1947	0.1772	0.1649	0.1992	0.1829	0.012	6.82%
Methylene chloride	0.0832	0.0807	0.0693	0.0655	0.0768	0.0751	0.007	8.96%
trans-1,2-Dichloroethylene	0.2105	0.2248	0.1971	0.1867	0.2223	0.2083	0.015	7.00%
1,1-Dichloroethane	0.5963	0.6355	0.5566	0.5117	0.6181	0.5837	0.045	7.64%
2,2-Dichloropropane	0.2485	0.2434	0.2232	0.2082	0.2516	0.2350	0.017	7.09%
cis-1,2-Dichloroethylene	0.2113	0.2250	0.1934	0.1850	0.2128	0.2055	0.014	7.00%
Bromochloromethane	0.0429	0.0469	0.0397	0.0370	0.0449	0.0423	0.004	8.44%
Chloroform	0.3845	0.4067	0.3456	0.3252	0.3942	0.3712	0.031	8.29%
Dibromofluoromethane	0.1930	0.1961	0.1942	0.1926	0.1901	0.1932	0.002	1.03%
1,1,1-Trichloroethane	0.3487	0.3625	0.3095	0.2927	0.3512	0.3329	0.027	8.09%
1,1-Dichloropropylene	0.2316	0.2519	0.2258	0.2112	0.2540	0.2349	0.016	6.89%
Carbon tetrachloride	0.2807	0.2907	0.2519	0.2355	0.2927	0.2703	0.023	8.40%
1,2-Dichloroethane-d4	0.6211	0.6685	0.6738	0.6537	0.6803	0.6595	0.021	3.20%
1,2-Dichloroethane	0.5923	0.6467	0.5400	0.5101	0.6080	0.5794	0.049	8.41%
Benzene	0.9511	0.9657	0.8413	0.7881	0.9343	0.8961	0.069	7.73%
Fluorobenzene	2172140	2168263	2450336	2545007	2243925	2315934	153758	6.64%
Trichloroethylene	0.2892	0.3119	0.2619	0.2390	0.2870	0.2778	0.025	9.02%
1,2-Dichloropropane	0.2378	0.2539	0.2184	0.2010	0.2364	0.2295	0.018	7.91%
Dibromomethane	0.1438	0.1525	0.1314	0.1170	0.1483	0.1386	0.013	9.30%
Bromodichloromethane	0.2594	0.2866	0.2460	0.2339	0.2738	0.2599	0.019	7.25%
Toluene	0.8643	0.7756	0.6902	0.6371	0.7741	0.7483	0.078	10.46%
Toluene-d8	1.4335	1.3950	1.4338	1.4226	1.3861	1.4142	0.020	1.41%
1,1,2-Trichloroethane	0.1505	0.1648	0.1369	0.1230	0.1536	0.1458	0.014	9.91%
1,3-Dichloropropane	0.1090	0.1159	0.0958	0.0861	0.1071	0.1028	0.011	10.27%
Tetrachloroethylene	0.4630	0.4488	0.3715	0.3513	0.4489	0.4167	0.046	11.01%
Dibromochloromethane	0.2752	0.2772	0.2322	0.2134	0.2711	0.2538	0.026	10.27%
1,2-Dibromoethane	0.1818	0.2001	0.1716	0.1541	0.1929	0.1801	0.016	9.01%
Chlorobenzene	0.7865	0.8144	0.7388	0.6686	0.7847	0.7586	0.051	6.74%
Chlorobenzene-d5	1662209	1717691	1904707	1802962	1764315	1770377	81999	4.63%
1,1,1,2-Tetrachloroethane	0.3149	0.3146	0.2758	0.2839	0.3072	0.2993	0.016	5.45%
Ethylbenzene	2.0009	2.0428	1.7156	1.8030	2.0034	1.9131	0.129	6.77%
m&p-Xylene	1.9918	1.9281	1.6419	1.7174	1.8375	1.8233	0.129	7.10%
o-Xylene	0.9231	0.9352	0.8437	0.7872	0.8851	0.8749	0.054	6.20%
Styrene	1.1693	1.1902	1.0688	1.0379	1.1369	1.1206	0.058	5.20%
Bromoform	0.2490	0.2589	0.2295	0.2357	0.2703	0.2487	0.015	5.98%
Isopropylbenzene	2.3383	2.3667	1.9434	1.9737	2.2296	2.1703	0.179	8.25%
1-Bromo-4-fluorobenzene	0.8591	0.8465	0.9144	0.9504	0.8381	0.8817	0.043	4.93%
1,1,2,2-Tetrachloroethane	0.3100	0.2962	0.2702	0.2717	0.3100	0.2916	0.018	6.05%
1,2,3-Trichloropropane	0.4217	0.4841	0.3486	0.4035	0.4523	0.4220	0.046	10.86%
Bromobenzene	0.6065	0.5962	0.5176	0.5174	0.5558	0.5587	0.038	6.74%
n-Propylbenzene	2.8169	2.8412	2.2348	2.3055	2.7145	2.5826	0.260	10.05%
1,3,5-Trimethylbenzene	2.2394	2.3274	1.8223	2.0067	2.2819	2.1355	0.192	8.98%
2-Chlorotoluene	2.0774	2.0573	1.6865	1.7766	1.9863	1.9168	0.157	8.18%
4-Chlorotoluene	1.9697	1.9203	1.6277	1.6897	1.9266	1.8268	0.140	7.65%
tert-Butylbenzene	2.0721	2.1447	1.5860	1.7247	1.9970	1.9049	0.214	11.21%
1,2,4-Trimethylbenzene	2.3030	2.3474	1.8259	1.9685	2.3981	2.1686	0.228	10.52%
sec-Butylbenzene	2.9476	2.9115	2.1016	2.2972	2.7713	2.6058	0.343	13.15%
p-Isopropyltoluene	2.5776	2.6265	1.9106	2.1494	2.4913	2.3511	0.276	11.75%
1,3-Dichlorobenzene	1.4569	1.4194	1.1728	1.2246	1.4122	1.3372	0.115	8.62%
1,4-Dichlorobenzene-d4	1511070	1534225	1672700	1659707	1517318	1579004	71718	4.54%
1,4-Dichlorobenzene	1.6126	1.6879	1.3934	1.3676	1.6507	1.5424	0.135	8.73%
n-Butylbenzene	2.8399	3.0441	2.0719	2.3131	2.9531	2.6444	0.382	14.46%
1,2-Dichlorobenzene	1.4967	1.4946	1.2432	1.2362	1.4910	1.3923	0.125	8.95%
1,2-Dibromo-3-chloropropane	0.1486	0.1543	0.1363	0.1356	0.1782	0.1506	0.016	10.32%
1,2,4-Trichlorobenzene	1.8500	1.8988	1.4312	1.4822	1.9486	1.7221	0.220	12.75%
Hexachlorobutadiene	1.3572	1.3458	0.8040	0.9729	1.2224	1.1405	0.218	19.10%
Naphthalene	3.1212	3.4763	2.7836	2.8387	3.4934	3.1427	0.302	9.61%
1,2,3-Trichlorobenzene	1.7516	1.8158	1.3610	1.4342	1.8163	1.6358	0.197	12.06%

Table 1: Compound List and Calibration Curve for EPA Method 8260

Stability of Tune

The calibration of the PolarisQ was very stable over the 4 week study period. The isotope ratios for 174/176 *m/z* for BFB showed no significant drift outside the minimum (pink bar) and maximum limits (yellow bar) of the tuning criteria during the study. (Figure 6).

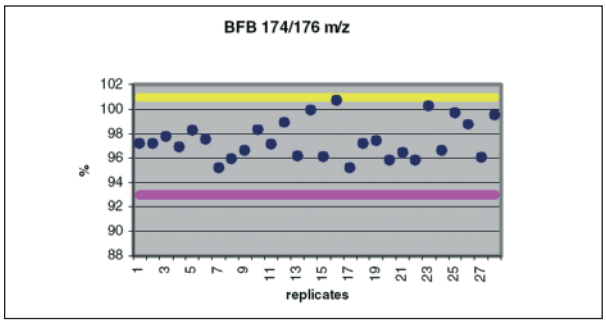

Figure 6: Isotope ratios for BFB over 4 weeks

POLARISQ MS		
Ion Source temperature: 200 °C		
Ionization Mode: +EI, 70 eV		
Multiple prescans at AGC: 25		
Microscans: 5		
Waveforms: ON at default of 15 volts		
Acquisition threshold: 0		
Target scale factor: disabled		
Scan Mode: segmented scans		
Segment 1: 35-70 *m/z*	Inj RF 25	Inj Scale 200 %
Segment 2: 71-120 *m/z*	Inj RF 25	Inj Scale 100 %
Segment 3: 121-300 *m/z*	Inj RF 29	Inj Scale 90 %

TRACE GC Ultra
Column: J & W DB 624 0.32 mm x 60 m, 1.8 micron film
Liner: Purge and Trap Interface Kit Silcosteel
Carrier Gas: helium
Constant pressure: 10 psi
Split/splitless Inlet: 150 °C
Mode: Split
Split flow: 50 mL/min
Transfer line: 210 °C
Oven Ramp: 35 °C, 4.0 min.; 5 °C/min, 55 °C, 0 min.; 15 °C/min, 210 °C, 12 min

TEKMAR 3100 CONCENTRATOR:
Trap: VOCARB 3000
Sample volume: 5 mL
Purge Ready: 30 °C
Purge flow: 40 mL/min
Purge time: 11 min.
Dry Purge time: 2 min.
Desorb preheat: 245 °C
Desorb time: 4 min.
Bake time: 6 min.
Bake temperature: 260 °C
MCS line temp: 40 °C
MCS Bake temp: 300 °C
Transfer line: 150 °C
Valve: 150 °C
Mount: 80 °C

Table 4: Instrument Parameters

Conclusion

The Thermo Scientific PolarisQ proved to be a quantitative tool for EPA Method 8260. The tuning criteria for BFB were easily met by using segmented scans. The pre-column split injection minimized the adverse effects of water and methanol.

The linearity was very good and the tune and response were stable over the test period of 4 weeks. In order to facilitate the start up of this environmental application, a detailed users guide with copies of the instrument method, tune file, and calibration curve data are included with the software, Xcalibur, which arrives with each PolarisQ.

References

1. Method 8260B Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry, Revision 2.0, 1996, SW 846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

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