Application Note: 51900

Combining Hardware, Software, and Chromatography to Improve the GC/MS Analysis of Semi-Volatile Compounds

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Key Words

- ISQ Single Quadrupole GC-MS
- TRACE GC Ultra
- Semi-volatile Compounds
- US EPA Method 8270D

Introduction

Analysis of semi-volatile organic compounds by GC/MS according to well-established methodologies requires integration of a complete system of GC-MS instrumentation and software for data interpretation, analysis and reporting. While the overall process of analyzing these target compounds is a mature technique, there are continuous innovations that allow laboratories to meet lower detection limits and analyze new compounds to comply with changing regulations, with higher throughput and improved quality.

Experimental Conditions

For this experiment, a standard GC/MS method for the analysis was developed according to published quality control and method guidelines.[1] After establishing a baseline of performance according to these guidelines, improvements to the method were tested by combining changes to the chromatography, leveraging of the performance capabilities of the hardware, and applying a software package developed around routine GC/MS workflows. By combining these techniques, laboratories can increase the number of samples that can be analyzed at lower detection limits.

A Thermo Scientific ISQ GC-MS system was operated at a scan speed of 4,650 u/sec (0.1 s/scan) over a mass range of *m/z* 35 to 500 (Figure 1). The Thermo Scientific AS 3000 II autosampler was used to deliver 1 µL of sample for analysis. The Thermo Scientific TRACE GC Ultra gas chromatograph was operated in the split mode to eliminate a significant portion of the matrix. The sensitivity of the mass spectrometer was more than able to reach accepted detection limits.

Results and Discussion

Shortening Analysis Time

Many methodologies around the world accept the use of splitless injection with an analysis time of 30 minutes for a long list of active compounds. A split injection can be used if the sensitivity of the mass spectrometer is sufficient. A split injection offers several advantages, including lower detector and column maintenance, better peak shapes for volatile compounds, and increased working range with low film thicknesses which reduces column bleed rates. The method developed operates at a column flow rate of 3 mL/min and a split flow of 60 mL/min, resulting in the injection of only 5% of the sample. An example of the advantages of a split injection are shown in Figure 2.

This example shows the separation of two of the more volatile compounds – pyridine and N-nitrosodimethylamine (NDMA). Gaussian peak shapes were observed. This is due to the elimination of the adverse effects of polar solvents from the stock standard solutions. These solvent effects are more evident in a splitless injection due to the much larger amount of solvent on the column (Figure 3).

A shortened analysis time of 20 minutes was achieved using faster scan rates and a rapid oven temperature program (Figure 4). The combination of high scan speeds and fast temperature ramps results in better chromatographic separation. This is seen in Figure 5 showing separation of closely eluting analytes. Using decafluorotriphenylphosphine (DFTPP) we are able to demonstrate expected fragmentation and resolution at these fast rates, Figure 6. The transferline design of the mass spectrometer reduces band broadening of the late eluting polynuclear aromatics (PNAs), resulting in more Gaussian peak shapes (Figure 7).

Extending the Working Range

In the analysis of waste samples, extended working ranges mean fewer dilutions and lower detection limits. The goal is to generate results from a single injection of the sample. This can only happen with a mass spectrometer with sufficient analytical linearity. A study was performed to determine the working range for the method. The instrument parameters for the study are listed in Table 1. A calibration curve was generated across the following levels: 0.5, 1, 2, 5, 10, 20, 40, 80, 160 and 200 ng/µL in methylene chloride. This is equivalent to µg/L or ppb in a standard liter sample size.

Figure 1: ISQ™ mass spectrometer and TRACE GC Ultra™ with AS 3000 II liquid autosampler

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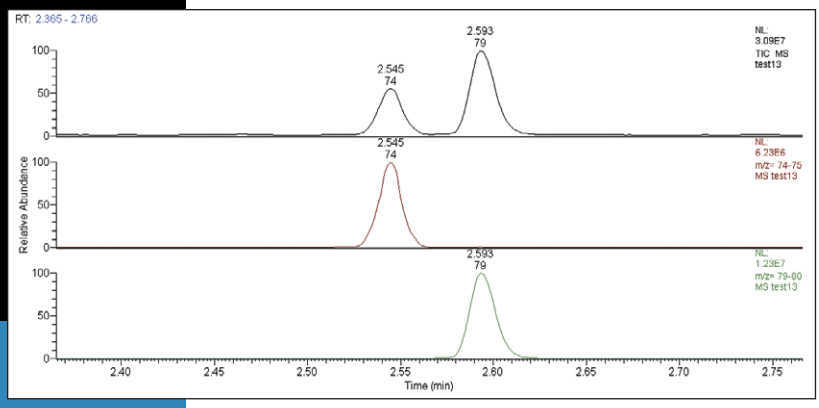

Figure 2: Gaussian peak shapes for pyridine and N-nitrosodimethylamine (NDMA) in the split mode of injection

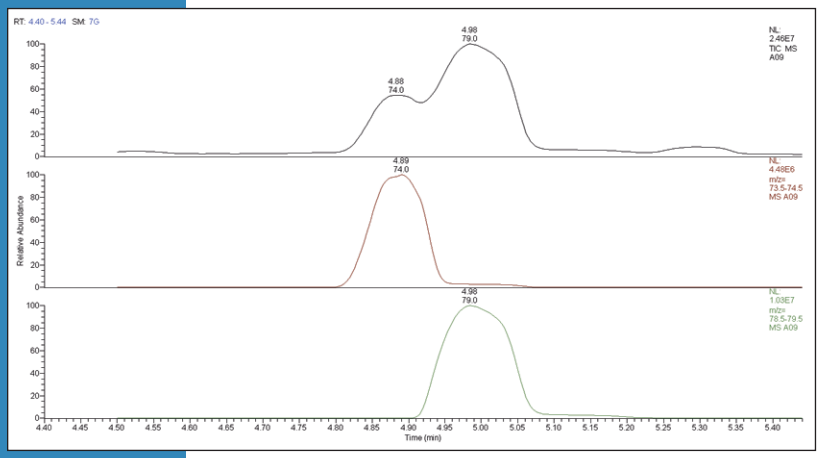

Figure 3: Distorted peaks shapes of pyridine and NDMA in the splitless mode of injection

Parameter	Conditions
Column	Trace GOLD TG-5 MS 0.25 mm × 30 meter, 0.5 µm
Inlet Liner	Siltek™ 5 mm splitless
Inlet Temperature	250 °C
Injection	Split, hot needle
Split Flow	60 mL/min
Oven Program	40 °C, 0.5 min., 14 °C/min.; 90 °C, 0 min., 22 °C/min.; 310 °C, 10 min.
Column Flow	3 mL/min
MS Transferline Temperature	310 °C
MS Source Temperature	275 °C
Multiplier Voltage	1220 V
Emmision Current	25 µA
Scan Rate	4,650 u/sec (0.1 s/scan)
Scan Range	Full Scan: *m/z* 35–500

Table 1: Instrument parameters

Once the calibration curve was acquired, the results were reviewed in Thermo Scientific EnviroLab Forms to check for any failures in the method quality control (QC) criteria. Data review is simplified in the Active View window, allowing access to all points in the calibration curve, confirming ions, and spectra for quick visual review of all compounds or only the ones that failed QC (Figure 8).

Lowering Method Detection Limits

When adequate precision is observed at lower concentrations, replicates can be made at this level that result in lower method detection limits (MDL) than are achieved with a calibration range at high levels. Eight replicate runs were made at 0.5 ng/µL in methylene chloride with the internal standards and surrogates spiked at 40 ng/µL for the determination of the instrument detection limit (IDL). The results are shown in Table 2 with an average IDL of 0.082 ng/µL.

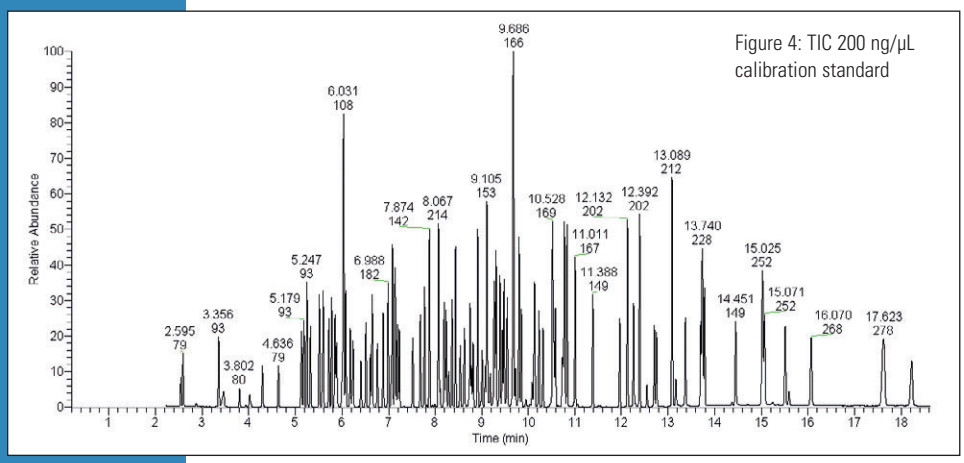

Figure 4: TIC 200 ng/µL calibration standard

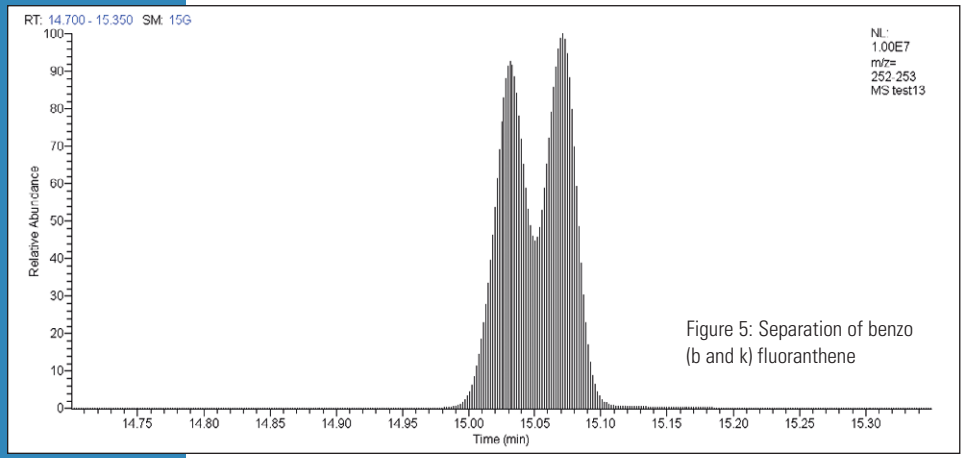

Figure 5: Separation of benzo (b and k) fluoranthene

Conclusions

After establishing a baseline of performance according to the guidelines in US EPA Method 8270D, improvements to the method were made in chromatography, taking advantage of the performance capabilities of the hardware, and applying a software package developed around routine GC-MS workflows. By combining these techniques, an average IDL of 0.082 ng/µL and an extended working range from 0.5 to 200 ng/µL was established. The improvements resulted in shorter run times and increases in overall throughput for sample analysis with less time spent in data review due to the introduction of an intelligent Active View feature in the EnviroLab Forms reporting software.

References

1. EPA Method 8270D Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), SW-846 Rev 4, February 2007

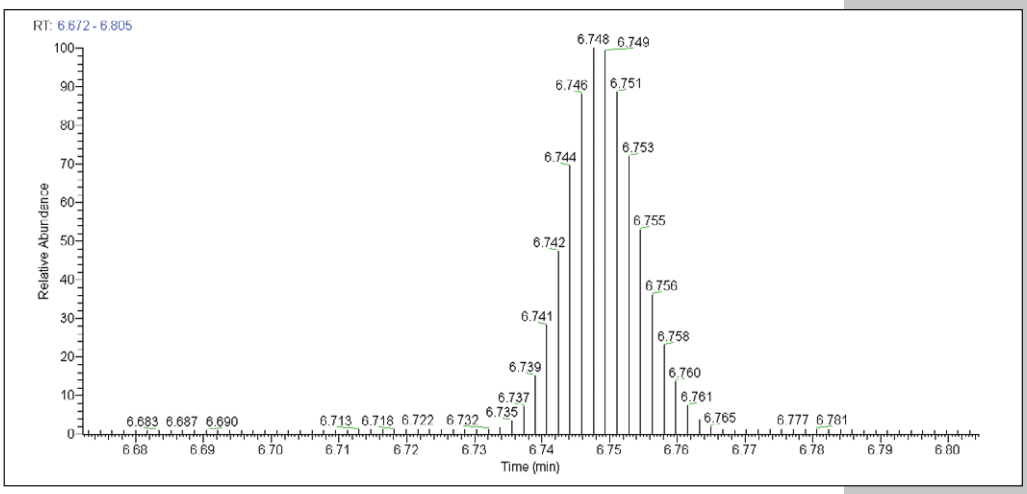

Figure 6: 20 scans across 1.8 second wide DFTPP peak, demonstrating good peak characterization

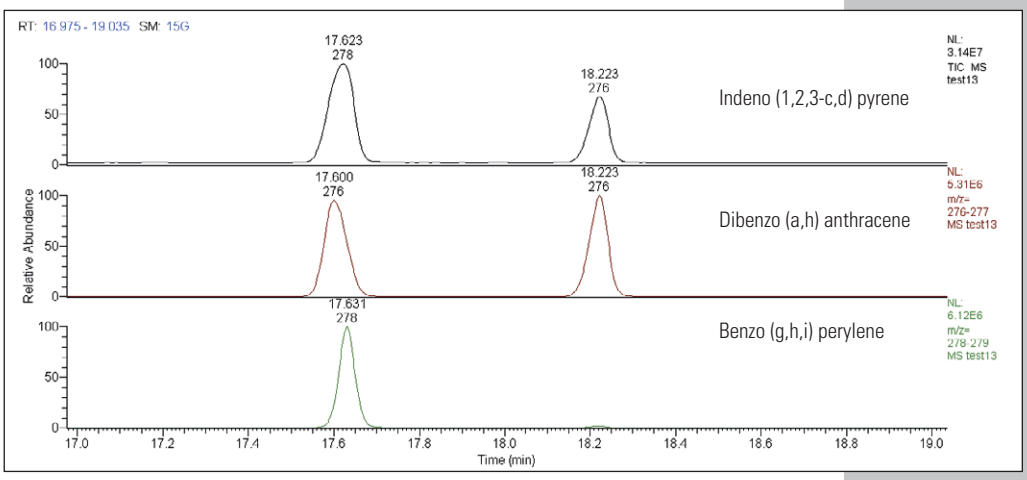

Figure 7: The transferline design of the mass spectrometer reduces band broadening of the late eluting polynuclear aromatics (PNAs): indeno (1,2,3-c,d) pyrene, dibenzo (a,h) anthracene, and benzo (g,h,i) perylene

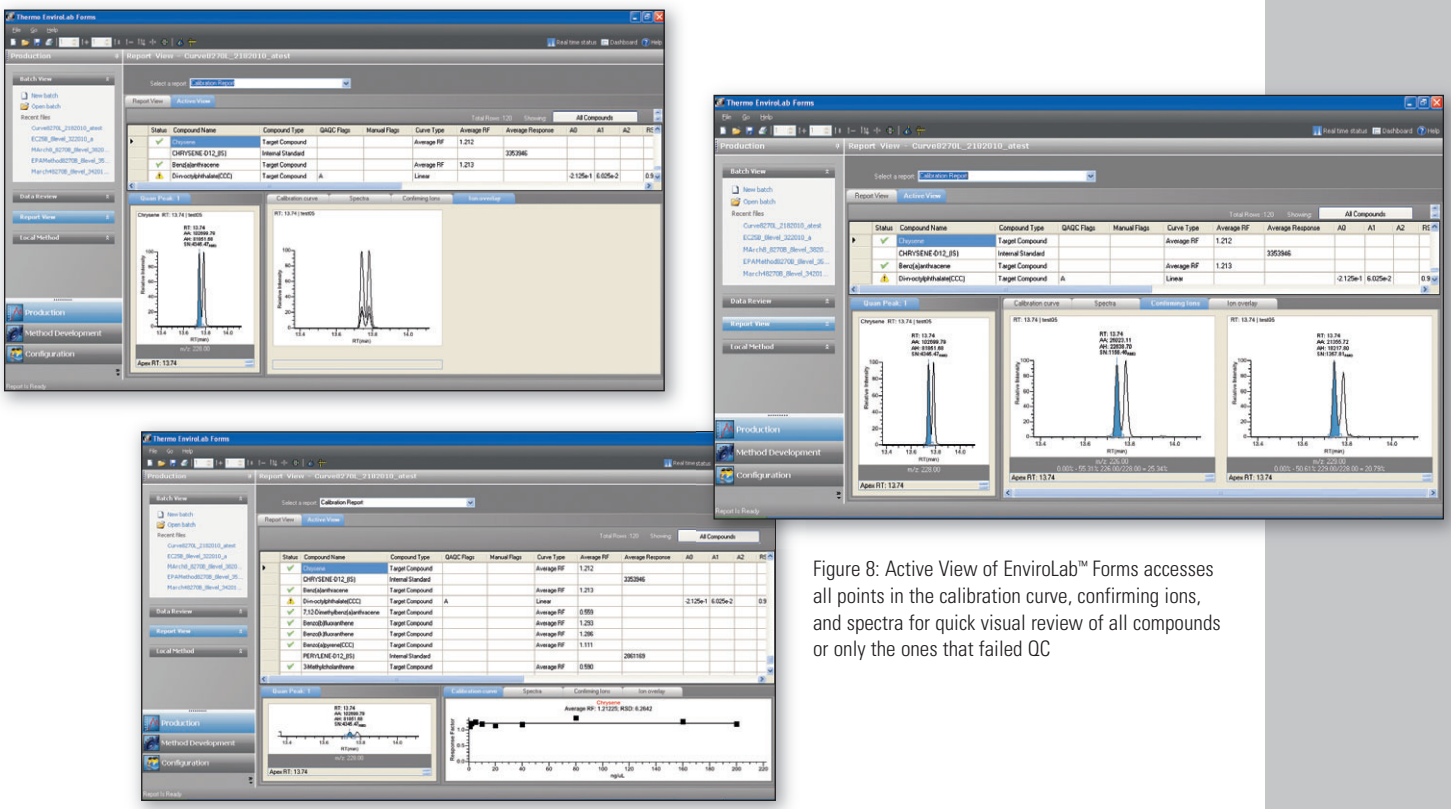

Figure 8: Active View of EnviroLab™ Forms accesses all points in the calibration curve, confirming ions, and spectra for quick visual review of all compounds or only the ones that failed QC

	% RSDs	IDL ng/µL
N-Nitrosodimethylamine	6	0.089
Pyridine RCRA	3	0.039
2-Picoline	4	0.052
N-Nitrosomethylethylamine APP9	16	0.289
Methyl methanesulfonate	9	0.171
2-fluorophenol (sur)	3	NA
N-Nitrosodiethylamine APP9	7	0.086
Ethyl methanesulfonate	8	0.092
phenol-d5 (sur)	2	NA
Phenol (CCC)	6	0.086
Aniline	5	0.072
Bis(2-chloroethyl)ether	5	0.068
Pentachloroethane	6	0.093
2-chlorophenol	5	0.068
1,3-Dichlorobenzene	4	0.054
1,4-DICHLOROBENZENE-D4 (IS)	2	NA
1,4-Dichlorobenzene (CCC)	1	0.022
Benzyl alcohol	8	0.075
1,2-Dichlorobenzene	4	0.068
2-methylphenol	10	0.126
Bis(2-chloroisopropyl)ether	4	0.055
N-Nitrosopyrrolidine APP9	6	0.075
3-Methylphenol&4-methylphenol	3	0.035
Acetophenone	6	0.084
N-Nitroso-di-N-propylamine (SPCC)	5	0.073
o-toluidine APP9	6	0.084
Hexachloroethane	7	0.101
nitrobenzene-d5 (sur)	5	NA
Nitrobenzene	5	0.084
N-Nitrosopiperidine	7	0.095
Isophorone	5	0.066
2-Nitrophenol (CCC)	7	0.072
2,4-Dimethylphenol	4	0.045
Bis(2-chloroethoxy)methane	2	0.032
2,4-Dichlorophenol (CCC)	7	0.082
1,2,4-Trichlorobenzene	5	0.074
NAPHTHALENE-D8 (IS)	4	NA
Naphthalene	4	0.056
p-Chloroaniline	7	0.078
2,6-Dichlorophenol	7	0.083
Hexachloropropene APP9	10	0.142
Hexachlorobutadiene (CCC)	6	0.099
N-Nitroso-di-N-butylamine	9	0.110
4-Chloro-3-methylphenol (CCC)	8	0.084
Safrole APP9	4	0.050
2-Methylnaphthalene	5	0.065
Hexachlorocyclopentadiene (SPCC)	4	0.045
1,2,4,5-Tetrachlorobenzene	6	0.104
2,4,5-Trichlorophenol	7	0.079
2,4,6-Trichlorophenol (CCC)	9	0.094
2-fluorobiphenyl (sur)	4	NA
Isosafrole APP9	7	0.097
2-Chloronaphthalene	5	0.077
2-Nitroaniline	9	0.096
1,4-Naphthoquinone APP9	9	0.087
Dimethyl phthalate	4	0.060
1,3-Dinitrobenzene app9	12	0.101
2,6-Dinitrotoluene	7	0.078
Acenaphthylene	3	0.044
3-Nitroaniline	15	0.115
ACENAPHTHENE-D10 (IS)	3	NA
Acenaphthene (CCC)	4	0.056
2,4-Dinitrophenol (SPCC)*	7	0.436
4-Nitrophenol (SPCC)*	6	0.545
2,4-Dinitrotoluene	7	0.073
Pentachlorobenzene	4	0.061
Dibenzofuran	4	0.061
1-Naphthylamine	5	0.068
2,3,4,6-Tetrachlorophenol	12	0.127
2-Naphthylamine	4	0.052
Diethyl Phthalate	4	0.060
4-Chlorophenyl phenyl ether	5	0.067
5-Nitro-o-toluidine APP9	9	0.080
4-Nitroaniline	18	0.105
Fluorene	3	0.039
2-Methyl-4,6-dinitrophenol*	3	0.305
Diphenylamine (CCC)	4	0.053
Azobenzene	4	0.051
2,4,6-tribromophenol (sur)	3	NA
1,3,5-Trinitrobenzene APP9	12	0.109
Diallate APP9	7	0.087
Phenacetin	15	0.080
4-Bromophenyl phenyl ether	6	0.088
Hexachlorobenzene	5	0.070
4-Aminobiphenyl	4	0.044
Pentachlorophenol (CCC)	11	0.084
Pentachloronitrobenzene	7	0.085
Pronamide	4	0.046
Dinoseb*	5	0.432
PHENANTHRENE D10 (IS)	2	NA
Phenanthrene	2	0.028
Anthracene	3	0.042
Carbazole app9	4	0.046
Di-N-butyl phthalate	5	0.058
Isodrin APP9	8	0.113
Fluoranthene (CCC)	3	0.037
Benzidine	10	0.087
Pyrene	3	0.042
p-terphenyl-d14 (sur)	2	NA
p-Dimethylaminoazobenzene	9	0.084
Chlorobenzilate APP9	7	0.073
3,3'-Dimethylbenzidine APP9	7	0.064
Butyl Benzyl Phthalate	3	0.031
Kepone APP9	23	0.196
2-Acetylaminofluorene APP9	15	0.083
3,3'-Dichlorobenzidine APP9	8	0.077
Bis(2-ethylhexyl)phthalate	8	0.071
Chrysene	3	0.050
CHRYSENE-D12 (IS)	2	NA
Benz(a)anthracene	4	0.064
Di-n-octylphthalate (CCC)	4	0.039
7,12-Dimethylbenz(a)anthracene	6	0.063
Benzo(b)fluoranthene	3	0.046
Benzo(k)fluoranthene	5	0.073
Benzo(a)pyrene (CCC)	4	0.046
PERYLENE-D12 (IS)	2	NA
3-Methylcholanthrene	7	0.071
Indeno(1,2,3-c,d)pyrene	3	0.036
Dibenzo(a,h)anthracene	4	0.055
Benzo(g,h,i)perylene	3	0.045
Average	6	0.082

**reps at 5 ng/µL*

Table 2: Instrument detection limits determined from 8 replicate injections of 0.5 ng/µL

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