Fast USEPA 8270 Semivolatiles Analysis Using the 6890N/5975 inert GC/MSD

Application

Environmental

Author

Mike Szelewski
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808

Abstract

The analysis of semivolatiles using EPA Method 8270 presents challenges due to the simultaneous measurement of acids, bases, and neutrals over a wide concentration range. Due to productivity demands, laboratories want to run faster while maintaining linearity and sensitivity for even the most active compounds. The 6890N/5975 inert GC/MSD system is designed to meet the criteria for fast analysis, while minimizing activity and maintaining linearity.

Introduction

USEPA Method 8270 for semivolatiles analysis is used to concurrently measure a mix of acids, bases and neutrals. Most laboratories analyze for 70–100 compounds with a chromatographic run time of 25–40 minutes. Laboratories want to reduce this run time for productivity increases. The calibration range required for the analysis varies dependent on a particular laboratory's statement of work. Historically, a range of 20–160 ppm (parts-per-million) has been used. With the increased sensitivity of newer GC/MS systems, laboratories are moving toward lower minimum detection limits (MDLs) and pushing the calibration range down to 1 ppm.

The 6890N/5975 inert GC/MSD (gas chromatograph/mass selective detector) system was designed to meet the demand for faster runs and lower MDLs. Faster scan rates without loss of signal are now possible. This allows the use of smaller id columns, such as 0.18 mm, resulting in shorter runs, while maintaining sufficient data points across narrower chromatographic peaks.

The inert source allows for less material injected onto the column while maintaining mass spectrometer performance. Injection volume can therefore be matched to the 0.18-mm column. Performance comparisons using the inert source were previously published [1, 2, and 3].

This application note will demonstrate the use of the 6890N/5975 inert for USEPA Method 8270. Smaller id columns with faster scan rates yield run times of 15 minutes while meeting 8270 method criteria.

Instrument Operating Parameters

The recommended instrument operating parameters are listed in Table 1. These are starting conditions and may have to be optimized.

Pulsed splitless injection was used to minimize residence times of analytes in the liner, thereby reducing loss of active compounds. The column flow rate alone, without using a pulsed injection, would take too long to sweep the 900-µL liner volume.

The inlet liner, Agilent p/n G1544-80700, has shown the best performance for active compounds at low levels. It does not contain glass wool, which would contribute to active compound degradation. Other liners can be used and a detailed discussion of these can be found in Reference 1.

The 6890N 240 V oven was necessary for the 25 °C/min ramp used up to the final temperature of 320 °C/min. A 120 V oven will achieve 20 °C/min at these higher temperatures and could be used resulting in slightly longer run times.

The DB-5.625 column was recently introduced in the dimensions listed. A 0.5-µL injection volume is well suited to this column. The excellent resolution from this column allows a higher than normal initial temperature (55 °C versus 40 °C). This higher temperature shortens cool-down time by more than 5 minutes, resulting in productivity increases for the laboratory. Benzo[b]fluoranthene and benzo[k]fluoranthene met 8270 resolution requirements at the 80-ppm calibration level and lower, using the operating parameters in Table 1.

The system was Retention Time Locked to Phenanthrene-d10 at 8.700 minutes. The fundamentals of Retention Time Locking (RTL) for GC/MSD systems can be found in Reference 4. The primary benefit of RTL for the environmental laboratory is the ability to maintain retention times after clipping or changing the column. Quantitative database and integration events times do not have to be changed. For laboratories performing SIM analyses, switching group times remain constant. Additional RTL application notes detailing the numerous benefits of RTL are available at www.agilent.com/chem.

Previous work [1] showed improved linearity across a wide calibration range using a 6-mm drawout lens instead of the standard 3-mm lens. Although not shown here, that comparison was repeated on this 5975 inert system and is still valid. The 6-mm lens is also included in Agilent Kit p/n G2860A.

The 5975 inert was tuned using the automatic DFTPP target tune. A previous publication [3] detailed steps to match sampling rates to those used in data acquisition. This process is no longer necessary. The automatic tuning was significantly improved in the 5975 inert. Valid tune parameters are stored for all data acquisition sampling rates. These parameters are automatically called and used based on the method sampling rate.

Previous work showed improved linearity across a wide calibration range using a 25-µamp emission current, instead of the default 35 µamp. The emission current can be set by the user in the Tune Wizard. A mass 50 target = 0.7% was also set in the Tune Wizard.

The sampling rate was changed from the default of 2 to 1, while preserving sufficient sensitivity. The resultant 5.92 scans/s typically yield 10 data points across the peaks.

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC	Agilent Technologies 6890N		
Inlet	EPC Split/Splitless		
Mode	Pulsed splitless, 0.5-µL injected		
Inlet temp	250 °C		
Pressure	21.29 psi		
Pulse pressure	40.0 psi		
Pulse time	0.20 min		
Purge flow	30.0 mL/min		
Purge time	0.75 min		
Total flow	34.0 mL/min		
Gas saver	Off		
Gas type	Helium		
Inlet liner	Agilent direct connect, dual taper, 4-mm id, p/n G1544-80700		
Oven	240 V		
Oven ramp	°C/min	Next °C	Hold min
Initial		55	1.00
Ramp 1	25	320	3.80
Total run time	15.4 min		
Equilibration time	0.5 min		
Oven max temp	325 °C		
Column	Agilent Technologies DB-5.625, p/n 121-5622		
Length	20.0 m		
Diameter	0.18 mm		
Film thickness	0.36 µm		
Mode	Constant Flow = 1.0 mL/min		
Inlet	Front		
Outlet	MSD		
Outlet pressure	Vacuum		
RTL	System Retention Time Locked to Phenanthrene-d10 at 8.700 min		
MSD	Agilent Technologies 5975 inert		
Drawout lens	6-mm Large Aperture Drawout lens p/n G2589-20045		
Solvent delay	1.90 min		
EM voltage	Run at DFTPP tune voltage - 153 V = 1282 V		
Low mass	35 amu		
High mass	500 amu		
Threshold	0		
Sampling	1		
Scans/s	5.92		
Quad temp	180 °C		
Source temp	230 °C		
Transfer line temp	280 °C		
Emission current	DFTPP tune @ 25 µamp		
Calibration standards	Accustandard, New Haven, CT. p/n M-8270-IS-WL 0.25X to 10X, 77 compounds at 10 concentration levels with 6 Internal Standards at 40 ppm		

Results

The 5975 inert passed DFTPP tune criteria for Method 8270 at both 50 ppm and 5 ppm.

The system was calibrated at 10 levels: 1, 2, 5, 10, 20, 50, 80, 120, 160, and 200 ppm. The TIC (total ion chromatogram) for the 10-ppm level is shown in Figure 1. Each calibration level contained 77 compounds together with six ISTDs (internal standards) at 40 ppm.

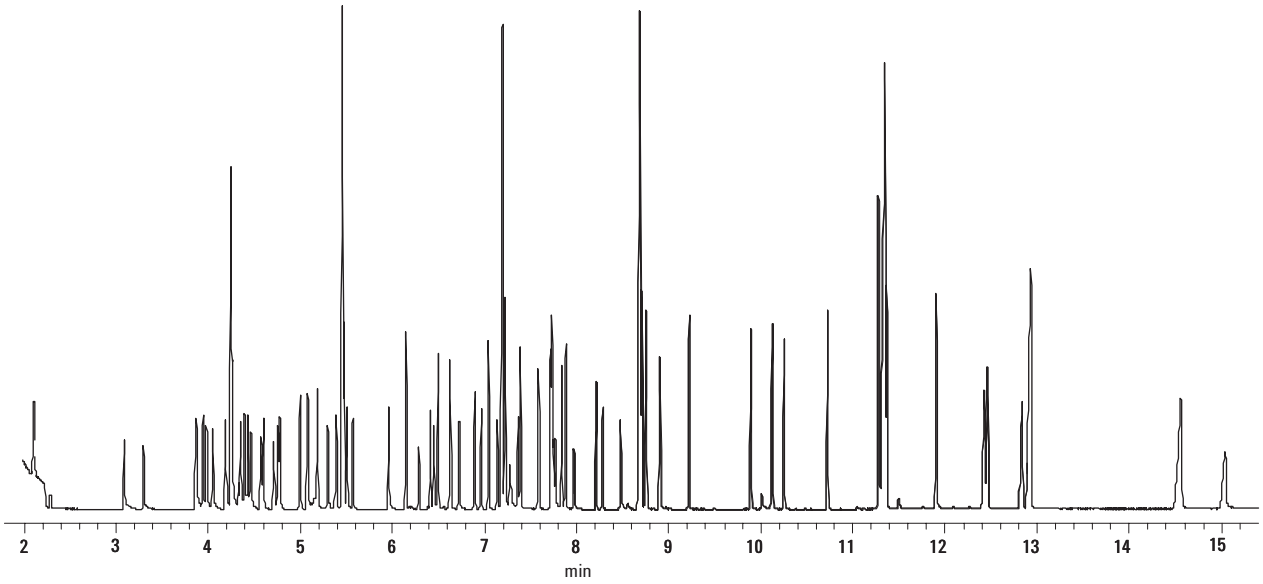

Figure 1. TIC for 8270 semivolatiles at 10 ppm.

The RRF (relative response factor) was calculated automatically for each compound by the GC/MSD ChemStation software. Linearity was determined by calculating the %RSD (percent relative standard deviation) of the RRFs across the calibration range for each compound. This is also done automatically by the software in conjunction with Excel.

USEPA Method 8270D specifies criteria for suitable RRFs and %RSD. Minimum system performance is determined by four active compounds, the SPCCs (system performance check compounds), and is measured by the average RRF.

Table 2 lists the Method 8270D SPCC criteria, and performance of the 5975 inert. The 5975 inert data easily exceeds 8270D criteria and are very good considering the low end of the calibration range. The average RRF of 0.156 for 2,4-Dinitrophenol is difficult to achieve in other systems. This performance margin allows more samples to run before system maintenance is necessary.

Table 2. SPCCs, Comparison of Average RRF

	8270 D Criteria	1-200 ppm 5975 inert
N-Nitroso-di-n-propylamine	0.050	1.270
Hexachlorocyclopentadiene	0.050	0.243
2,4-Dinitrophenol	0.050	0.156
4-Nitrophenol	0.050	0.172

Linearity is shown in Table 3. Method 8270D specifies that this group of Calibration Check Compounds (CCCs) meet a 30% RSD criteria. The %RSD is calculated across the RRFs determined at each calibration level. All CCCs pass criteria using the full calibration range of 1–200 ppm. Pentachlorophenol is a very difficult compound on which to pass criteria. The average of all 77 compound %RSDs is 7%, significantly better than the method criteria of 15%.

Table 3. CCC %RSD of RRFs from 1–200 ppm

	%RSD
Phenol	6
1,4-Dichlorobenzene	3
2-Nitrophenol	5
2,4-Dichlorophenol	8
Hexachlorobutadiene	3
4-Chloro-3-methylphenol	9
2,4,6-Trichlorophenol	16
Acenaphthylene	6
Diphenylamine	5
Pentachlorophenol	25
Fluoranthene	5
Benzo[a]pyrene	3

The excellent system linearity shown here is due to many factors including tuning, the large aperture drawout, and the new electronics. The new electronics allow using a scan rate of 2^1, while maximizing sensitivty. This improved signal/noise together with more data points across a peak yields easier and more reproducible peak integration.

Conclusions

The 6890N/5975 inert meets USEPA Method 8270D criteria. Faster scan rates allow using 0.18-mm id columns for faster runs and shorter cool-down times. Analysis of 77 analytes and six ISTDs can be accomplished in 15 minutes. USEPA Method 8270D tune criteria are routinely achieved. SPCC performance and CCC linearity can be met over a wider calibration range than that historically used. Productivity increases are possible through faster runs, faster cool-down, easier peak integration, and use of a wide calibration range.

References

1. M. Szelewski, B. Wilson, and P. Perkins, "Improvements in the Agilent 6890/5973 GC/MSD System for Use with USEPA Method 8270", Agilent Technologies, publication 5988-3072EN, www.agilent.com/chem.
2. M. Szelewski, "Fast Semivolatiles Analysis using the Agilent Technologies 6890/5973 inert GC/MSD", Agilent Tecnologies, publication 5989-0207EN, www.agilent.com/chem.
3. M. Szelewski, "Fast USEPA 8270 Semivolatiles Analysis using the 6890/5973 inert GC/MSD with Performance Electronics ", Agilent Technologies, publication 5989-1510EN, www.agilent.com/chem.
4. K. Weiner, N. Mata and P. Wylie, "Retention Time Locking with the G1701BA MSD Productivity ChemStation" Agilent Technologies, publication 5968-3433E, www.agilent.com/chem.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
April 27, 2005
5989-2981EN

Agilent Technologies