Fast USEPA 8270 Semivolatiles Analysis Using the 6890/5973 inert GC/MSD with Performance Electronics

Application

Environmental Analysis

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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 6890/5973 *inert* GC/MSD system with Performance Electronics 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 mixture of acids, bases, and neutrals. Most laboratories analyze for 70–100 compounds with a chromatographic run time of 25–40 min. Laboratories want to reduce this run time for productivity increases. The calibration range required for the analysis varies depending on a particular laboratory's statement of work (SOW). Historically, a range of 20–160 ng has been used. With the increased sensitivity of newer gas chromatograph/mass spectrometer (GC/MS) systems, laboratories are moving toward lower minimum detection limits (MDLs) and pushing the calibration range down to 1 ng.

The Agilent 6890/5973 *inert* GC/MSD (Gas Chromatograph/Mass Selective Detector) system with Performance Electronics 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 diameter columns, such as 0.18-mm id, 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, therefore, can be matched to the 0.18-mm column. Performance comparisons using the inert source were published previously [1, 2].

This application note will demonstrate the use of the Agilent 6890/5973 *inert* with Performance Electronics for USEPA Method 8270. Smaller id columns with faster scan rates yield run times of 15 min while meeting Method 8270 criteria.

Experimental

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

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC	Agilent Technologies 6890
Inlet	EPC Split/Splitless
Mode	Pulsed splitless, 0.5 µL injection
Inlet temp	250 °C
Pressure	21.48 psi
Pulse pres	40.0 psi
Pulse time	0.20 min
Purge flow	50.0 mL/min
Purge time	1.00 min
Total flow	54.0 mL/min
Gas saver	Off
Gas type	Helium
Inlet Liner	Agilent splitless, single taper, 4-mm id, p/n 5181-3316
Oven	240 V

Oven ramp	**°C/min**	**Next °C**	**Hold min**
Initial		55	1.00
Ramp 1	25	100	0.00
Ramp 2	30	280	0.00
Ramp 3	25	320	4.60

Total run time	15 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
MSD	Agilent Technologies 5973 *inert* with Performance Electronics
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 = 1012 V
Low mass	35 amu
High mass	500 amu
Threshold	10
Sampling	1
Scans/s	5.92
Quad temp	150 °C
Source temp	230 °C
Transfer line temp	280 °C
Emission current	DFTPP tune @ 25 µA

Calibration Standards were obtained from Accustandard, New Haven, CT, (p/n M-8270-IS-WL-0.25x to 10x). They contain 74 target compounds at nine concentration levels with six ISTDs at 40 ppm.

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 (p/n 5181-3316) is the most commonly used liner for Method 8270 analysis. 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 Agilent 6890 240 V oven was necessary for the 25 °C/min Ramp 3 used.

A 120 V oven will achieve 20 °C/min at 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 vs 40 °C. This higher temperature shortens cool-down time by more

than 5 min, resulting in productivity increases for the laboratory. Benzo[b]fluoranthene and benzo[k]flouranthene met Method 8270 resolution requirements at the 80-ppm calibration level and lower, using the operating parameters in Table 1.

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

The 5973 *inert* was tuned using the automatic DFTPP target tune. The following steps were taken before executing DFTPP tune to insure that Method 8270 DFTPP criteria were met on injection.

1. Using the Tune Wizard, set the Mass 50 Target Abundance to 1.3% and the Emission Current to 25, as shown in Figures 1a–1f.
2. Edit the tuning macro as follows:
   a Copy atune73.mac from the MSDChem\msexe folder.
   b Paste the copy of atune73.mac into the MSDChem\msexe folder. The file name should be Copy of atune73.mac. This preserves an original copy of the file.
   c Open atune73.mac in Notepad. Refer to Figures 2a–2h.
   d Click Edit>Find and type samples in the Find What box.
   e Click Find Next.
   f Change the samples value from 3 to 1.
   g Change the averages value from 3 to 6.
   h Save the file and Close Notepad.

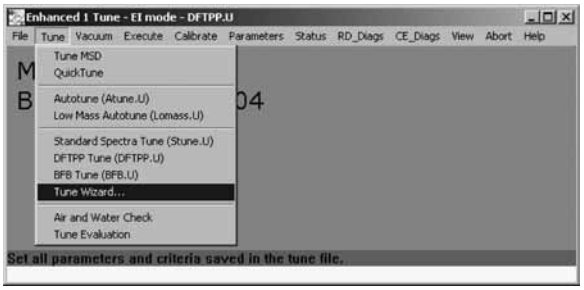

Figure 1a. Starting the Tune Wizard.

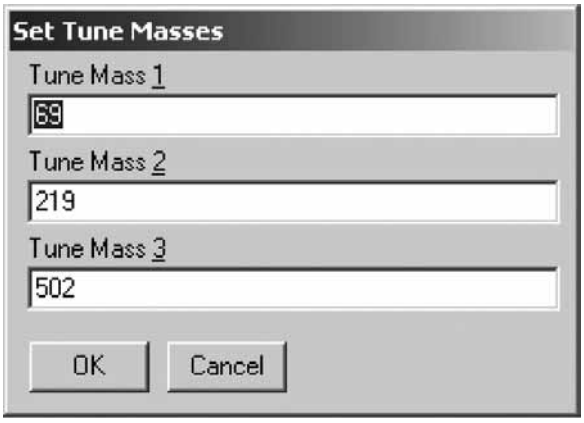

Figure 1b. Accept these masses.

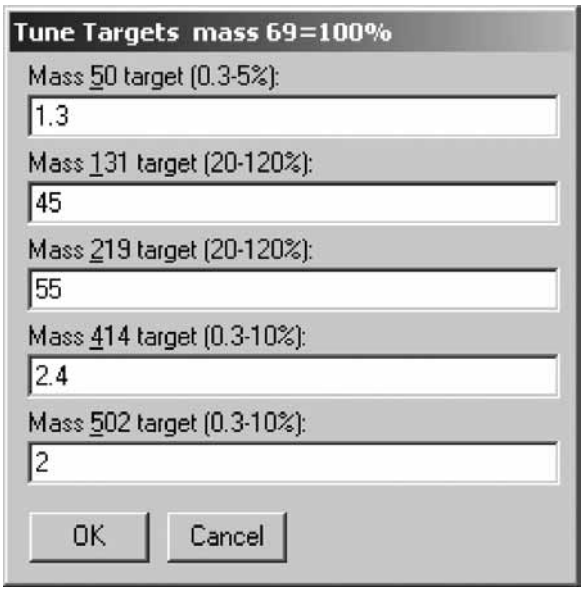

Figure 1c. Set Mass 50 target to 1.3.

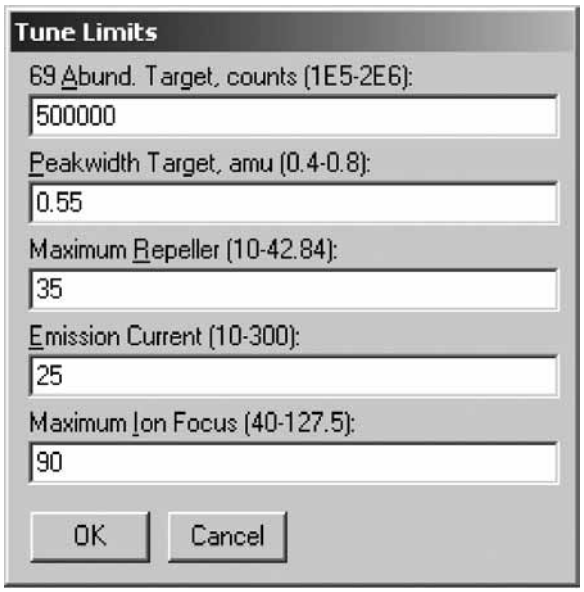

Figure 1d. Set Emission Current to 25.

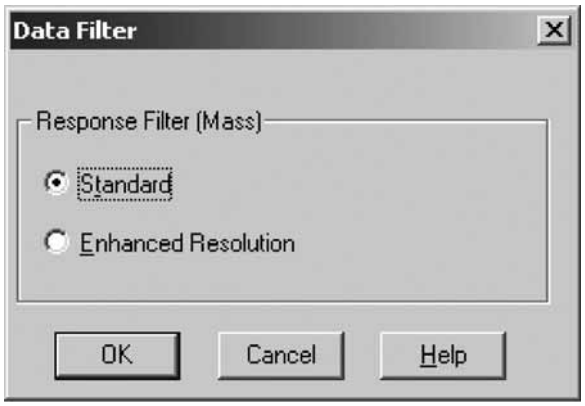

Figure 1e. Accept Standard.

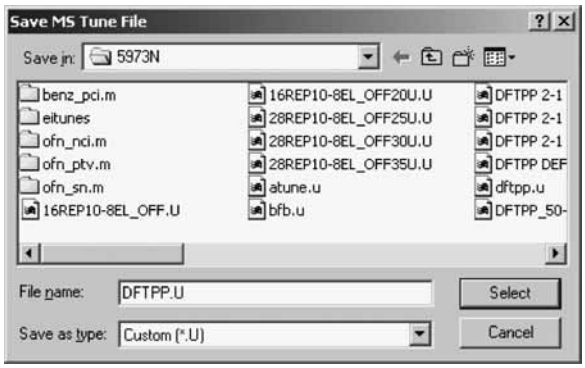

Figure 1f. Type in DFTPP.U if not present and click Select to save.

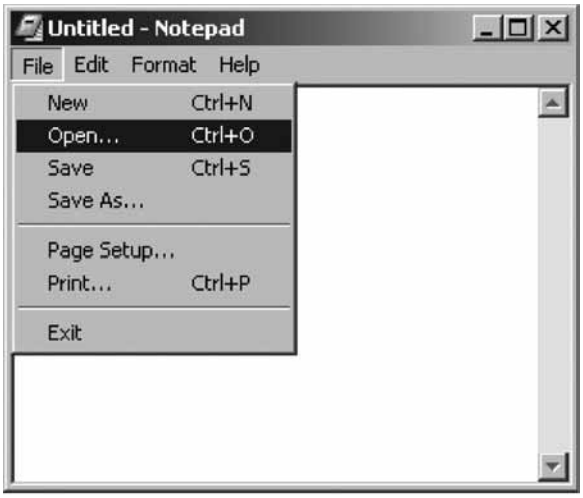

Figure 2a. Select File>Open in Notepad.

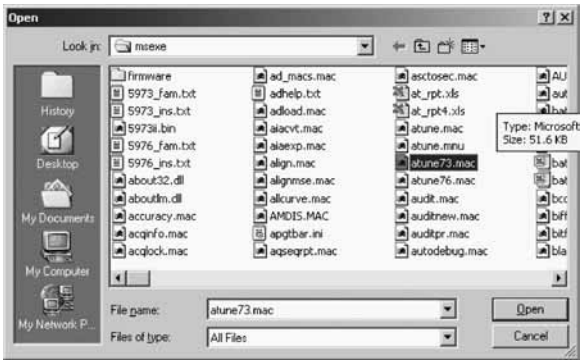

Figure 2b. Select atune.73.mac and click Open.

Figure 2c. Select Edit>Find.

Figure 2d. Type samples into the Find What box, then click Find Next.

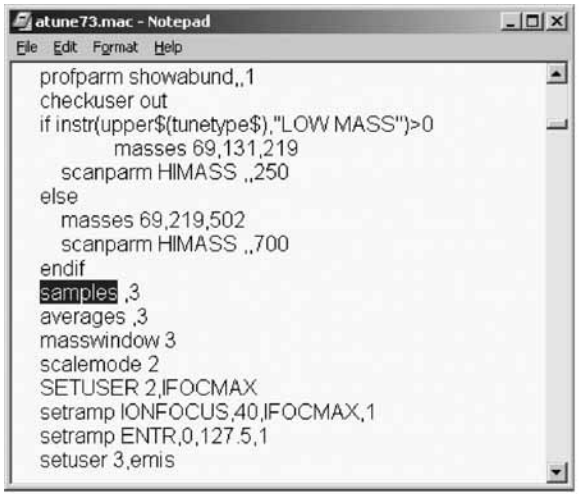

Figure 2e. Results of Find samples.

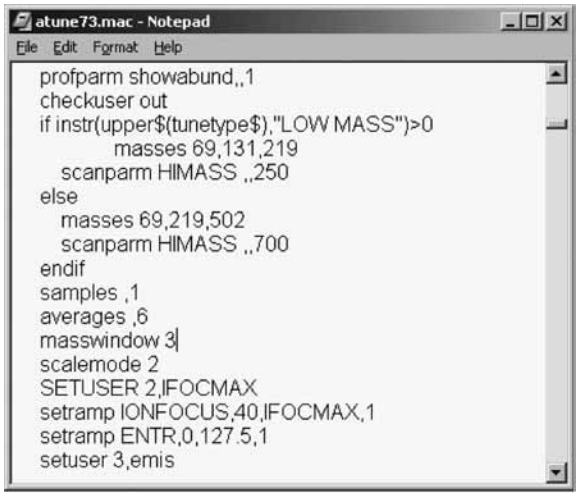

Figure 2f. Change samples from 3 to 1 and averages from 3 to 6.

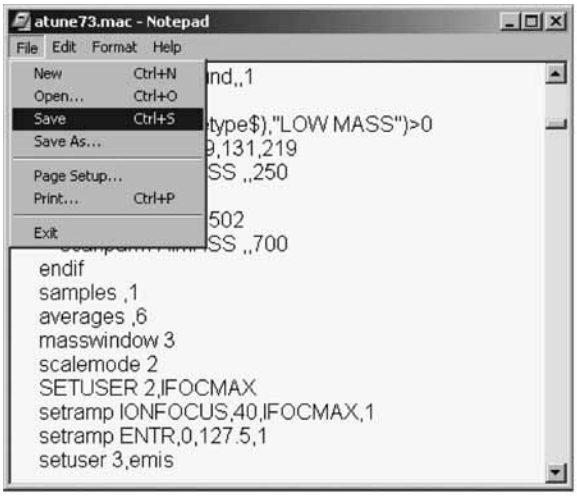

Figure 2g. Select File>Save (do not use Save as).

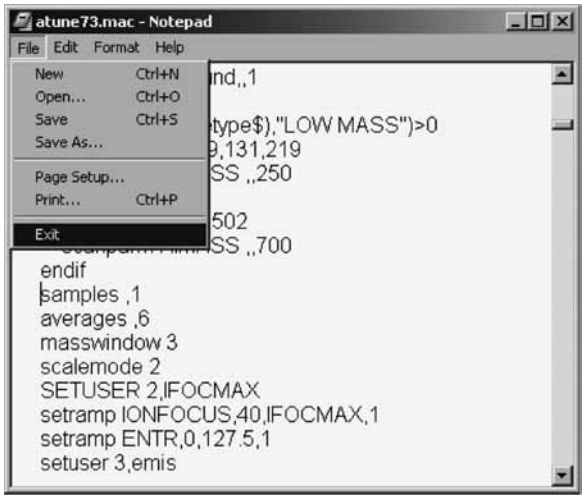

Figure 2h. Select File>Exit to close Notepad.

Previous work has shown improved linearity across a wide calibration range using a 25-µA emission current instead of the 35-µA default. The tuning macro was changed so that the sampling rate during tuning matched the sampling rate during data acquisition. The system was tuned at 2^1 and data were collected at 2^1. These changes resulted in reliably passing Method 8270 criteria on injection of DFTPP.

Remember that the tune macro changes are also reflected if an Autotune is done. The copy of atune73.mac contains the macro without the changes.

The sampling rate for data acqisition was changed-from the usual 2^2 to 2^1, while preserving sufficient sensitivity. The resultant 5.92 scans/s typically yield 10 data points across the peaks that have a width of 1.8 s.

Results

The system was calibrated at nine levels: 1, 2, 5, 20, 50, 80, 120, 160, and 200-ppm. The TIC (Total Ion Chromatogram) for the 5-ppm level is shown in Figure 3. The peak shape is excellent and the run time is less than 15 min. The benzo[b]fluoranthene and benzo[k]flouranthene resolution can be seen at about 11.4 min. Each calibration level contained 74 compounds together with 6 ISTDs at 40 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 the performance of the 5973 inert. The 5973 *inert* data easily exceeds the 8270D criteria, and are very good considering the low end of the calibration range. This performance margin allows more samples to be run before system maintenance is necessary.

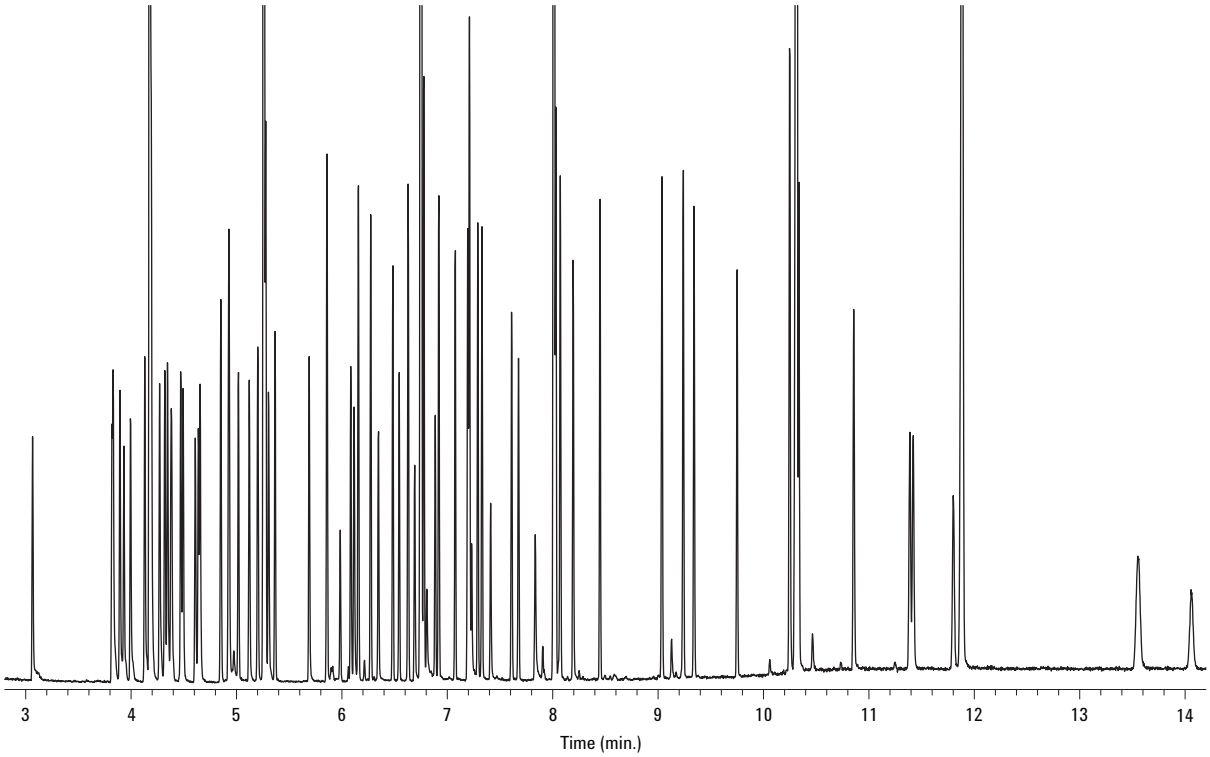

Figure 3. TIC for 5 ppm Method 8270 Semivolatiles.

Table 2. SPCCs and Comparison of Average RRF

	8270D Criteria	1–200 ng 5973 *inert*
N-Nitroso-di-n-propyl amine	0.050	0.963
Hexachlorocyclopentadiene	0.050	0.216
2,4-Dinitrophenol	0.050	0.133
4-Nitrophenol	0.050	0.139

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 a calibration range of 2–200 ppm. Across a 1–200 ppm range, pentachlorophenol does not pass due to its known activity.

Table 3. CCC %RSD of RRFs from 1–200 ppm and 2–200 ppm

	1–200	2–200
Phenol	6	6
1,4-Dichlorobenzene	7	6
2-Nitrophenol	6	6
2,4-Dichlorophenol	5	4
Hexachlorobutadiene	6	4
4-Chloro-3-methylphenol	5	5
2,4,6-Trichlorophenol	12	10
Acenaphthene	11	10
Diphenylamine	8	8
Pentachlorophenol	36	24
Fluoranthene	8	7
Benzo[a]pyrene	3	3

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

Conclusions

The Agilent 6890/5973 *inert* with Performance Electronics shows improved sensitivity at faster scan rates. The faster scan rates allow using 0.18 mm id columns for faster runs and shorter cool-down times. Analysis of 74 analytes and 6 ISTDs can be accomplished in less than 15 min. EPA Method 8270D tune criteria can be routinely achieved. SPCC performance and CCC linearity can be met over a wider calibration range than that historically used. Productivity increases are possible through shorter runs, faster cool-down, easier peak integration, and use of a wider 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 Technologies, publication 5989-0207EN, www.agilent.com/chem.

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