

Drinking Water Semivolatiles Analysis using the 6890N/5975B inert GC/MSD

Application

Author

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

Abstract

The analysis of semivolatiles in drinking water presents challenges due to the required detection limits, desired calibration range, and analyte activity. In the United States (U.S.), method requirements are typically those found in USEPA 525.2 (525), but can vary widely outside the U.S. This application is based on 525 with differences described for laboratories that do not require 525. The 6890N/5975B inert GC/MSD system is designed to meet the criteria for semivolatiles analysis in drinking water through excellent sensitivity, minimal activity, and extended linearity.

Introduction

USEPA Method 525.2 for semivolatiles analysis is used to concurrently measure a mixture of acids, bases, neutrals, and pesticides in drinking water or source water [1]. Most laboratories analyze for >100 compounds with a chromatographic run time of 25 to 40 minutes. Sample extraction is accomplished using liquid-solid extraction (LSE) with C₁₈ disks or cartridges. A 1- μ L hot splitless injection is specified with the MSD operating in full scan mode.

Sensitivity and linearity are two areas where laboratories are seeking improved performance. Sensitivity can be affected by sample preparation, extract volume injected, instrument tuning, signal processing, and overall system activity. Linearity can be affected by source design, tuning, activity, data acquisition mode, and system reproducibility.

This application will demonstrate the use of the 6890N/5975B inert for USEPA Method 525.2. Performance has been improved through the use of inert columns, high-temperature inert source, and manual tuning. Additional specific areas for improved performance will be discussed for laboratories that are not required to follow 525 mandates.

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 700- μ L liner volume.

The inlet liner, 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. This liner



Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC	Agilent Technologies 6890N			RTL	System retention time locked to phenanthrene-d10 at 11.400 min
Inlet	EPC split/splitless			MSD	Agilent Technologies 5975B inert
Mode	Pulsed splitless, 1.0 μ L injected			Drawout lens	6 mm large-aperture drawout lens, part number G2589-20045
Inlet temperature	250 $^{\circ}$ C			Solvent delay	4.00 min
Pressure	11.56 psi			EM voltage	Run at Autotune voltage = 1294 V
Pulse pressure	40.0 psi			Low mass	45 amu
Pulse time	0.10 min			High mass	450 amu
Purge flow	30.0 mL/min			Threshold	25
Purge time	1.00 min			Sampling	2
Total flow	34.6 mL/min			Scans/second	3.54
Gas saver	Off			Quad temperature	180 $^{\circ}$ C
Gas type	Helium			Source temperature	300 $^{\circ}$ C
Inlet liner	Agilent direct connect, dual taper, 4 mm i.d., part number G1544-80700			Transfer line temperature	280 $^{\circ}$ C
Oven	240V			Emission current	Autotune @ 35 μ amp
Oven ramp	$^{\circ}$ C/min	Next $^{\circ}$ C	Hold min	MSD-SIM	AutoSIM was used to pick ions, groups, and switching times
Initial		40	1.00	Number of groups	26
Ramp 1	50	110	0.00	Compounds/group	Varied 1 to 22
Ramp 2	10	320	0.60	Ions/group	Varied 2 to 55
Total run time	24.0 min			Dwell times	Varied 5 to 10 ms
Equilibration time	0.5 min			Cycles/peak	Minimum 10
Oven max temperature	325 $^{\circ}$ C			Calibration standards	Ultra Scientific, North Kingstown, RI. Part number DWK-5252.
Column	Agilent Technologies HP 5 MSi, part number 19091S-433i			Four mixtures codiluted, resulting in 108 compounds at 10 concentration levels, spiked with 3 Internal Standards at 5 ppm and 4 Surrogate Standards at 5 ppm.	
Length	30.0 m				
Diameter	0.25 mm				
Film thickness	0.25 μ m				
Mode	Constant flow = 1.5 mL/min				
Inlet	Front				
Outlet	MSD				
Outlet pressure	Vacuum				

connects directly to the column and has a tapered top, minimizing contact with metal in the inlet. Other liners can be used; a detailed discussion of these can be found in Reference 2.

The 6890N 240V oven was used but a 120V oven can also achieve the ramp rates found in Table 1.

The HP-5MSi column is designed for inertness and is well suited to this method. This is the latest version of the most popular column in environmental laboratories, the HP-5MS. The column was run in constant flow mode at 1.5 mL/min to maintain peak shape and sensitivity.

The system was retention time locked to phenanthrene-d10 at 11.400 min. The fundamentals of retention time locking (RTL) for GC/MSD systems can be found in Reference 3. The primary benefit of RTL for the environmental laboratory is the ability to maintain retention times after clipping or changing the column. Quantitation 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 has shown improved linearity across a wide calibration range using a 6-mm drawout lens instead of the standard 3-mm lens [1]. Although 525 uses a lower calibration range, the linearity improvement is still valid. The signal/noise loss using the 6-mm lens, even at low levels, was minimal compared to the linearity gain. The 6-mm lens is also included in Agilent Kit part number G2860A.

EPA method 525 requires that the system meet DFTPP tune criteria, but in this case the 5975B inert was tuned using Autotune. A new entrance lens (EL) value was then manually input at half the tune value (16 versus 32). DFTPP was injected and tune criteria were checked. If the injection passed DFTPP criteria, the EL value was raised 4 volts and DFTPP was reinjected. This process continued until the highest EL value that allowed DFTPP to pass criteria was determined.

A sampling rate of 2, combined with the lower noise characteristics of the 5975B inert, was used to optimize signal/noise. This sampling rate resulted in 3.54 scans/sec, with a 45 to 450 scan range, typically yielding 10 data points across the peaks.

A previous publication [4] detailed steps to match sampling rates in tune with those used in data acquisition. This process is no longer necessary. The automatic tuning has been significantly improved in the 5975B 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.

AutoSIM setup was used in combination with the quantitation database to pick ions, groups, and switching times. Details of AutoSIM can be found in Reference 5. The SIM acquisition table from AutoSIM was used directly with only two modifications. Tebuthiuron (ion 156) and tricyclazole (ion 189) are known for poor peak shape. Their ions were manually added to the groups across which the peaks eluted.

A source temperature of 300 °C was used instead of the typical 230 °C to 250 °C range. This higher temperature has been used to minimize peak tailing, and therefore increase sensitivity, for PAHs [6]. Lower source temperatures have historically been used to maintain performance of the active pesticides. At 300 °C, the inert source shows equivalent or better performance for all but 14 compounds, compared to 230 °C. Of the 14 compounds, 10 still had single-digit percent relative standard deviations (%RSDs). More importantly, the average %RSD for all 115 analytes was reduced almost 2× using a source temperature of 300 °C versus 230 °C.

Calibration standards in dichloromethane were prepared only for the single component analytes. Standards were not prepared for toxaphene or the Aroclors. Disulfoton sulfoxide and disulfoton sulfone were not included in the commercially available mixture.

Alternatives to EPA Method 525

There are many laboratories both within the U.S. and in other geographies that are not required to follow 525 mandates. Many of these laboratories use 525 as a framework or starting point for drinking water analyses. This section will discuss areas in 525 that can be modified for improved performance. None of these have been approved as alternatives to Method 525 by the USEPA.

LSE is required by 525 for sample preparation, with ethyl acetate and dichloromethane (DCM) as

the final extract solvents. An alternative is a liquid-liquid extraction (LLE) using only DCM. Specific analyte recoveries should be determined just as they are with LSE and 525. The initial sample and final extract volumes are sized to meet the laboratory's detection limits. Traditionally, a liter or more of water is extracted with 3×100 mL aliquots of DCM. The aliquots are combined and concentrated. Some laboratories use 40-mL screw-cap vials, extracting 30 mL of water with 3 mL of DCM, with extract concentration as needed. Other laboratories, for screening purposes, use a tapered bottom 2-mL sample vial. A 1.25-mL water sample is extracted with 0.25 mL of DCM. The DCM layer is injected directly from the bottom taper of the vial. LLE of small volumes of water increases laboratory productivity compared to LSE.

A 1- μ L hot splitless injection is specified by 525. A cool-on-column inlet is allowed, with the same 1- μ L injection volume. Lower detection limits can be achieved using a programmable temperature vaporizing (PTV) inlet and large-volume injection (LVI) inlet [7]. A single 25- μ L injection of a DCM extract can easily be made using the PTV in solvent evaporation mode. Additionally, thermally labile compounds are less likely to degrade. The PTV is held near the solvent's boiling point during injection. As the inlet is programmed, analytes are transferred onto the column at the lowest possible temperature. This can result in better performance for active compounds.

Full scan data acquisition is mandated by 525. As an alternative, selected ion monitoring (SIM) could be used. With a defined compound list, quantitation (target) ions and qualifier ions/ratios are known or can be easily determined. Using SIM typically results in a sensitivity increase of 10 to 100× compared to scan [7]. Using either PTV or SIM increases laboratory throughput by allowing a wider calibration range on the GC/MSD system. Sample and extract volumes need less manipulation and fewer reruns are required to have results fall within the calibration range. Using SIM and PTV together can lower the detection limit up to 2,500× compared to a 1- μ L injection in scan mode [7].

The 6890N/5975B inert GC/MSD can acquire both SIM and scan data in the same run [6]. This is an attractive alternative for laboratories that want a wider calibration range (SIM) but also want full scan spectra for confirmation. A SIM acquisition table is easily constructed using AutoSIM setup. A

check box is selected in data acquisition and both signals are collected. If SIM/scan is used, typically the scan sampling rate should be halved – in this case from 2 to 1.

Tuning to meet DFTPP criteria is required by 525. This enhances the response at lower m/z values but decreases the response at higher m/z values. With enhanced responses for higher m/z values as a result of Autotune, more unique ions can be used for identification. Most laboratories have found that DFTPP tuning also decreases the overall instrument sensitivity 3 to 6× compared to Autotune. To maintain maximum instrument sensitivity, Autotune should be used. Qualifier ion ratios are established for each system as a routine laboratory practice and will stay consistent using Autotune. Library matches against NIST are excellent using Autotune, as most NIST spectra were not obtained under DFTPP tune conditions.

Results

The 5975B inert passed DFTPP tune criteria for 525 with a 1- μ L splitless injection of 5 ppm. This was accomplished using the procedure discussed in the Instrument Operating Parameters section instead of using the DFTPP menu item. The sensitivity loss of 3 to 6× usually seen with DFTPP tuning was less than 2× with this manual procedure. Sensitivity loss is usually a result of DFTPP tuning with a low repeller in combination with the entrance lens offset (ELO) values. In the manual procedure, the repeller stays at its Autotune value, which is best above 20. The EL value is lowered only enough to allow passing.

The system was calibrated at seven levels, 0.1, 0.2, 0.5, 1, 2, 5, and 10 ppm in scan mode, with the 0.2 ppm level not required by 525. The total ion chromatogram (TIC) for the 0.5 ppm level in scan mode is shown in Figure 1. Each calibration level contained 108 compounds plus 3 internal standards (ISTDs) and 4 surrogate standards (SSs) at 5 ppm. Not all compounds showed a response at all levels as is stated in 525 and therefore expected. A listing of problem compounds and reasons can be found in Method 525.2, Section 13.2.

Full method-detection limits must be established in each laboratory using the sample preparation procedure as described in 525.2, Section 9.

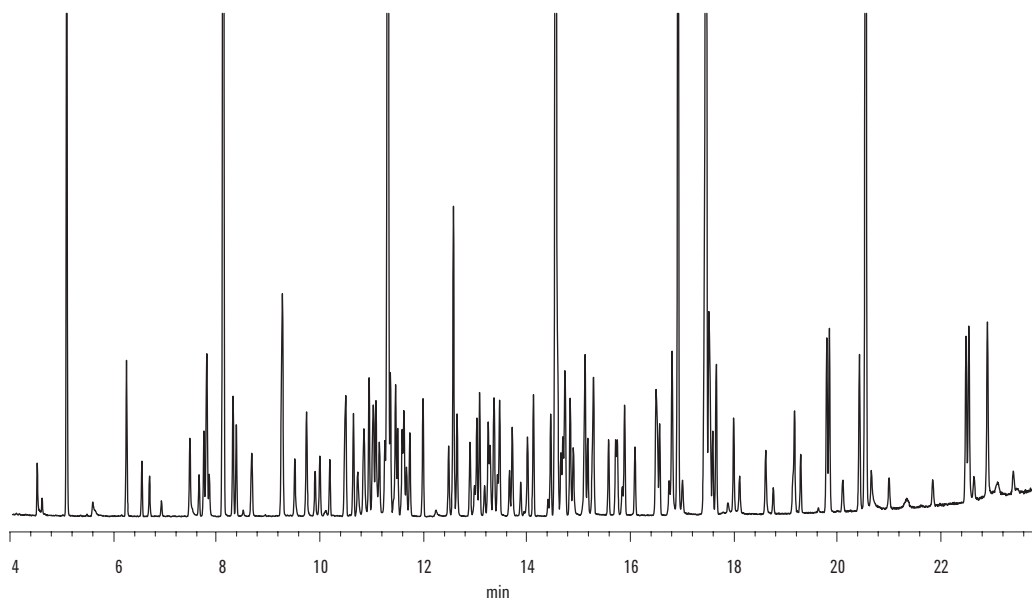


Figure 1. TIC for 0.5 ppm 525 semivolatiles – scan 45 to 450 m/z for 115 compounds

For SIM acquisition, three additional calibration levels were run: 0.01, 0.02, and 0.05 ppm. The TIC for the 0.05 ppm level in SIM mode is shown in Figure 2.

USEPA Method 525 does not specify minimum RRFs for system performance check compounds (SPCCs). USEPA Method 8270 for semivolatiles in wastewater does have criteria for SPCCs and should not be confused with 525.

Linearity can be determined by the %RSD of the relative response factor (RRF) for each compound across the calibration range. The %RSD and the RRF calculations are done automatically by the GC/MSD Chemstation software in conjunction with Microsoft Excel. Not all compounds meet the 525 criteria of <30%, which is allowed, with the most active compounds showing the highest %RSD. However, as an overall measure of system linearity, the average of all %RSDs was 8% for scan data. The %RSDs are summarized in Table 2.

Linear regression is allowed by 525 as an alternative to mean RRF and %RSD. When linear regression is used, a continuing calibration check (CCC) must report values of $\pm 30\%$ of the true value for each compound. A CCC was run and all but one of the 108 compounds were within the criteria. USEPA method 525 allows up to 10% of the compounds to miss the CCC criteria on a single day.

The SIM data were reduced two ways, using a seven-level calibration or a 10-level calibration,

including three lower concentrations. For the seven-level SIM, the average %RSD of all 108 compounds was 6%. The ISTDs were 4% and SS ranged from 1 to 3%. For the 10-level SIM, the average %RSD for all compounds was 11%; ISTDs at 4% and SS ranged from 1 to 5%.

Table 2. Summary of Linearity for Scan and SIM Calibrations

	Avg %RSD 108 Analytes	%RSD Range 3 ISTDs	%RSD Range 4 SS
Scan 7-level cal	8	6 to 8	1 to 3
SIM 7-level cal	6	4	1 to 3
SIM 10-level cal	11	4	1 to 5

Conclusions

The 6890N/5975B inert meets USEPA Method 525.2 criteria. Analysis of 108 analytes and 7 ISTDs/SSs is accomplished in 24 minutes. The 525 DFTPP tune criteria are routinely achieved, and sensitivity is increased through manual tuning. Linearity is met over the method calibration range in scan mode; CCC requirements of $\pm 30\%$ are also attained. Laboratories that are not required to follow 525 mandates can achieve productivity gains. Autotune can be used for better sensitivity compared to DFTPP tuning. PTV can reduce sample preparation and reduce detection limits. SIM further lowers detection limits, extends the calibration range, and improves

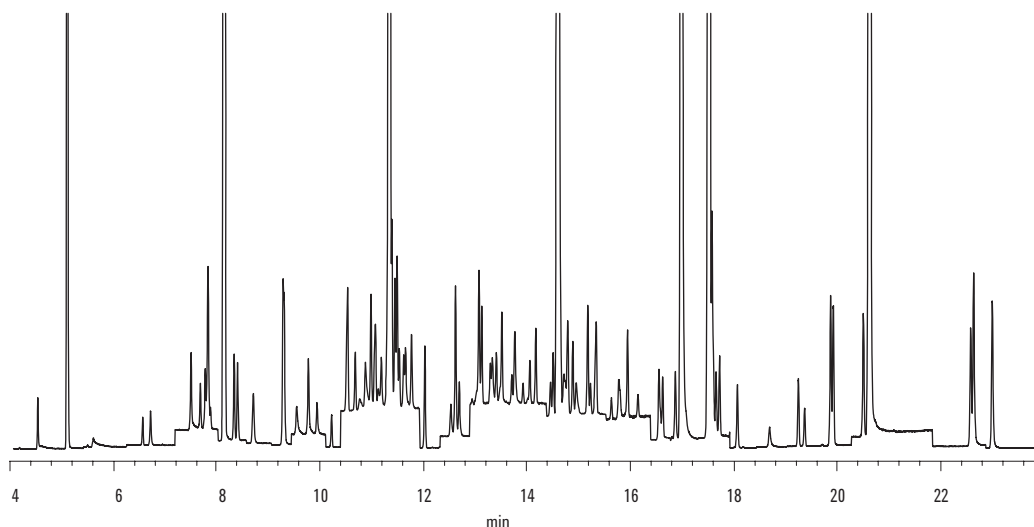


Figure 2. TIC for 0.05 ppm 525 semivolatiles — SIM 115 compounds in 26 groups

linearity. SIM/scan mode has all of the benefits of SIM with full scan spectra available for analyte confirmation.

References

1. USEPA Method 525.2 is available from different sources listed on this Web site: www.epa.gov/OGWDW/methods/where.html.
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