Environmental Semivolatiles Using an Agilent Multimode Inlet for Maximum Sensitivity

Application Note

Environmental

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Abstract

The analysis of semivolatiles at very low levels presents challenges due to analyte activity, background contamination and instrument sensitivity. Method requirements vary worldwide, typically specifying 1-µL injections and full scan data acquisition. The lowest detection limits can be achieved using Agilent's Multimode Inlet, with either cold splitless or large volume injections.

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Introduction

Low level semivolatiles analysis is used to concurrently measure a mixture of acids, bases, neutrals and pesticides in drinking water or source water. Most laboratories analyze for >100 compounds with a chromatographic run time of 25 – 40 minutes. Sample extraction is accomplished using liquid-solid extraction (LSE) with C18 disks or catridges. Liquid-liquid extraction with a solvent such as dichloromethane is an alternative technique. Extract injection is typically 1-µL hot splitless with the mass selective detector (MSD) operating in full scan mode, as specified in some commonly used methods such as USEPA Method 525.2 [1].

Sensitivity is an area where laboratories are seeking improved performance. It can be affected by sample preparation, extract volume injected, instrument tuning, signal acquisition and overall system activity. Previous publications have focused on activity, linearity, speed, productivity and large volume injection [2–6 respectively]. Sensitivity is a factor in all of these, and many times is a trade-off.

The maximum sensitivity, described as the best signal to noise ratio (S/N), is often inlet and injection technique related. Agilent's Multimode Inlet (MMI) is designed for hot splitless (HSL), cold splitless (CSL) or large volume (LVI) injections [7]. This Application Note demonstrates the use of MMI with semivolatile compounds.

Instrument Operating Parameters

The recommended instrument operating parameters are listed in Table 1. These are starting conditions and may have to be optimized. Parameters should be chosen that transfer the maximum amount of analyte onto the column to achieve the best sensitivity. Additionally, the entire system must be inert because sensitivity is almost always lost on active analytes first.

Table1. Gas Chromatograph and Mass Spectrometer Conditions

GC:	Agilent Technologies 7890A		
Inlet:	Electronic pneumatic control (EPC) MMI		
Hot Splitless Mode Inlet Parameters			
Temp ramp:	°C/min	Next °C	Hold min
Initial		280	0.00
Purge time:	0.75 min		
Cold Splitless Mode Inlet Parameters			
Temp ramp	°C/min	Next °C	Hold min
Initial		20	0.05
Ramp 1	300	280	0.00
Purge time:	1.75 min		
Solvent Vent Mode Inlet Parameters			
Temp ramp:	°C/min	Next °C	Hold min
Initial:		–10	0.60
Ramp 1:	300	280	0.00
Purge time:	2.4 min		
Vent flow:	200 mL/min		
Vent pressure:	0.0 psi until 0.6 min		
Common Inlet Parameters			
Cryo:	On		
Cryo use temp:	100 °C		
Cryo timeout:	5.00 min (On)		
Cryo fault:	On		
Pressure:	17.292 psi (On)		
Purge flow:	50.0 mL/min		
Total flow:	53.9 mL/min		
Gas saver:	Off		
Gas type:	Helium		
MMI Liner	Agilent Helix, single taper, p/n 5188-5397		
Oven:	**240V**		
Oven ramp:	°C/min	Next °C	Hold min
Initial:		40	2.50
Ramp 1:	25	320	4.80
Total run time:	18.5 min		
Equilibration time:	0.5 min		
Oven max temp:	325 °C		
Column:	Agilent Technologies DB 5 MS UI, p/n 121-5523 UI		
Length:	20.0 m		
Diameter:	0.18 mm		
Film thickness:	0.36 µm		
Mode:	Constant flow		
Pressure:	17.292 psi		
Nominal initial flow:	0.864 mL/min		
Inlet:	Front		
Outlet:	MSD		
Outlet pressure:	Vacuum		
RTL:	System Retention Time Locked to Phenanthrene-d10 at 11.000 min		
Front Injector:	Agilent Technologies 7693A		
Injector Parameters for Hot and Cold Splitless Modes			
Injection volume:	1.0 µL		
Syringe size:	10 µL		
Plunger speed:	Fast		
Wash volume:	3 µL		
Injector Parameters for Solvent Vent Mode			
Injection volume:	25 µL		
Syringe size:	50 µL		
Wash volume:	15 µL		
Solvent wash draw speed:	1500 µL/min		
Solvent wash dispense speed:	30000 µL/min		
Sample wash draw speed:	1500 µL/min		
Sample wash dispense speed:	30000 µL/min		
Injection dispense speed:	50 µL/min		
Common Injector Parameters			
Sample washes:	1		
Sample pumps:	2		

PreInj solv A washes:	0
PreInj solv B washes:	1
PostInj solv A washes:	3
PostInj solv B washes:	2
Viscosity delay:	1 seconds
PreInjection dwell:	0 minutes
PostInjection dwell:	0 minutes
MSD:	Agilent Technologies 5975C, triple-axis detector
Drawout lens:	3 mm standard aperture drawout lens
Solvent delay:	3.5 min
Low mass:	35 amu
High mass:	550 amu
Threshold:	5
Sampling:	1
Quad temp:	180 °C
Source temp:	300 °C
Transfer line temp:	280 °C
Tune type:	Autotune
EMV mode:	Gain factor = 1

Calibration Standards

Ultra Scientific, North Kingstown, RI. Custom mix containing 18 analytes. All dilutions and internal/surrogate standard (IS/SS) additions done in dichloromethane using an automated standalone dual-tower 7693A-7890A system. Resulting concentration levels were 10, 5, 2, 1, 0.5, 0.2 and 0.1 ppm (ng/µl). Each level spiked with 7 IS/SS at 5 ppm each. Each level then diluted 1:100 in dichloromethane, resulting in 7 concentration levels, 100, 50, 20, 10, 5, 2, and 1 ppb (pg/uL) with IS/SS at 50 ppb.

Many analysts associate the use of a programmable temperature vaporizing inlet (PTV) only with LVI in solvent vent (SV) mode [4]. LVI will allow lower levels of calibration but method development is necessary to optimize recovery of compounds while eliminating the solvent. LVI also injects more matrix and may not improve S/N due to chemical noise. The Agilent MMI is a PTV and has other operating modes such as "cold" splitless that was used here. Splitless injection into a cold inlet instead of a typical hot splitless inlet offers the following advantages:

- Solvent expansion is minimized and analytes do not travel outside the liner and contact metal surfaces, minimizing degradation.
- Analytes vaporize at the lowest temperature, also minimizing degradation.
- Volatile solvent is transferred onto the column first. Analyte peak shape is improved for injections of 2–5 µL without solvent venting.

Figure 1 shows the MMI temperature and flow programs together with the oven program. The MMI is held at 20 °C, which is a temperature below the boiling point of the solvent dichloromethane (39.8 °C) during the fast injection period of 0.05 min. At the end of the injection period, the MMI is rapidly heated to 280 °C, transferring analytes onto the column. At the end of the splitless time, 1.75 min, the inlet is purged at 50 mL/min. The MMI program ramp can be adjusted and multiple ramps are possible.

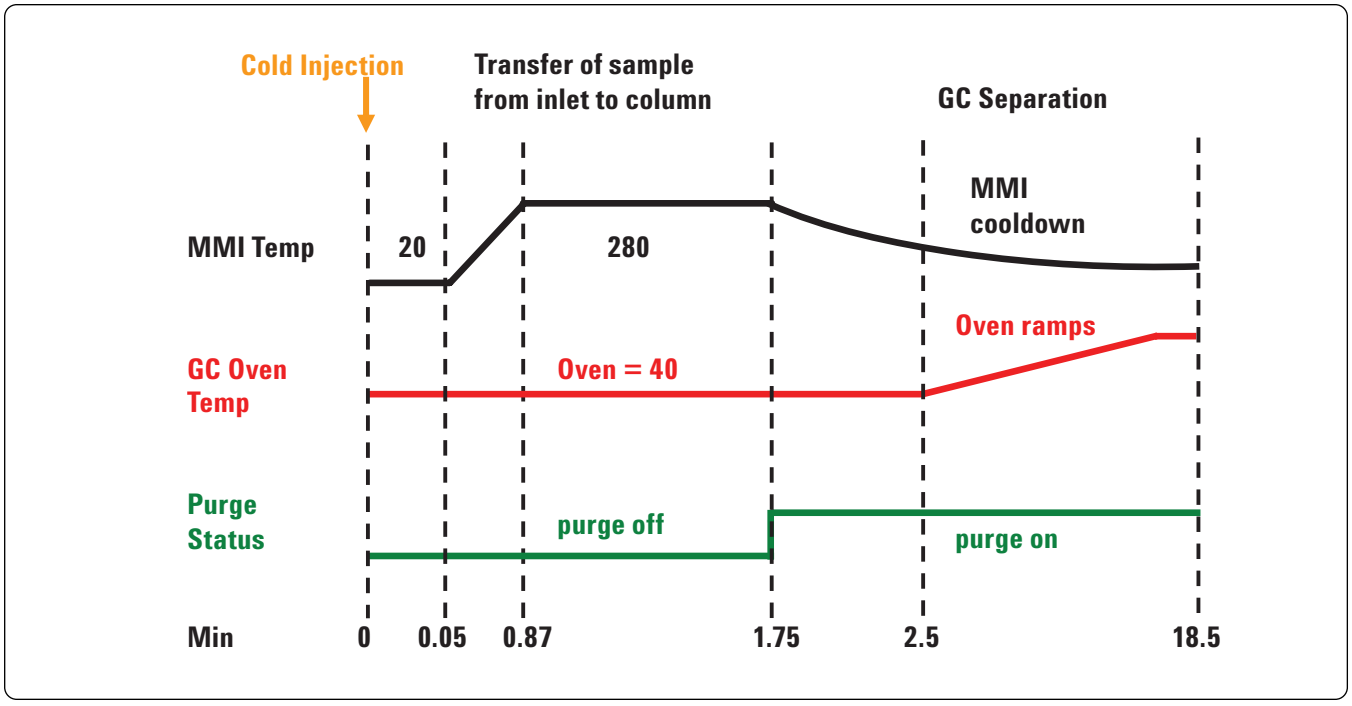

Figure 1. MMI cold splitless and SV – temperature and flow programs.

A key advantage of the MMI is the ability to use the same liner for HSL, CSL and LVI-SV modes. This significantly reduces method development time. The column does not have to be moved to a second inlet, which previously used a liner of much smaller volume. Changes in inlet parameters are made without hardware changes. Maximum sensitivity is achieved in the shortest possible development time.

The helix inlet liner, 5188-5397, prevents line of sight from the needle tip to the inlet base and is deactivated. This is important for both HSL and CSL modes. Liquid will not reach the inlet base and analyte decomposition is minimized when the inlet is heated. It does not contain glass wool which could contribute to active compound degradation. This liner has sufficient capacity to accommodate a 2–5 µL cold injection volume at fast speed.

LVI-SV mode is just an extension of cold splitless injection. The injection speed is slower to allow vaporization and venting of the solvent. The inlet is held at a lower temperature to prevent loss of the earliest eluting analytes. The boiling point difference of the most volatile compounds and the solvent should be at least 100 °C, preferably 150 °C.

Each of the inlet modes require a different purge time (splitless time), due to heating of the inlet and injection time. The inlet is held at the final temperature for at least 0.75 minutes in each mode.

The oven program relationship to the MMI parameters is shown in Figure 1. The oven starts at 40 °C, and is held there during the injection cycle and splitless transfer of analytes onto the column. The oven then programs to 320 °C. The system is Retention Time Locked (RTL) which requires an initial 2.5-min hold for LVI-SV mode. This maintains fixed retention times regardless of the inlet/injection mode used.

The Agilent J&W DB-5ms Ultra Inert column is designed for inertness and well suited to this method. This shorter, smaller id column is gaining popularity in environmental laboratories for faster runs and good capacity with a thicker film. The column was run in constant flow mode at 0.86 mL/min to maintain peak shape and sensitivity.

The system was RTL to Phenanthrene-d10 at 11.000 min. RTL allows eaiser compound identification, especially with Deconvolution Reporting Software (DRS). After clipping the column, a rerun and analysis of the locking standard is all that is needed to restore shifted peak times. Times for quantitation database entries, integration events and selected ion monitoring (SIM) groups do not have to be changed. Additional RTL application notes are available at www.agilent.com/chem, detailing the numerous benefits of RTL.

The standard 3-mm drawout lens was used for best sensitivity. Previous work has shown improved linearity across a wide calibration range using the optional 6-mm lens [2]. Using the 6-mm lens will show a typical loss of 2-5 times in S/N.

A source temperature of 300 °C was used instead of the typical 230 – 250 °C range. This higher temperature has been used to minimize peak tailing, and therefore improve sensitivity, for polynuclear aromatic hydrocarbons (PAHs) [5].

The subset of compounds was taken from USEPA 525 and is typical of the analytes that laboratories worldwide are interested in analyzing at low levels. The USEPA 8270 list was not used because this list specifies waste samples that contain higher concentrations of target compounds in high level matrices and are not comparable here. The best way to improve sensitivity for solids and waste samples is through extract cleanup.

Standards were made from 0.01–10 ppm, containing 5 ppm of internal standards (ISTDs) and surrogate standards (SSs). A 1:100 dilution of each of these yields a range of 0.1–100 ppb, with ISTDs and SSs at 50 ppb, for a lower working range used for LVI-SV. All dilutions were done using an Agilent dual tower 7693 Autosampler system configured on a separate standalone Agilent 7890A GC system. Standards were prepared in 2-mL vials containing 300-uL inserts, using 10-µL and 500-µL syringes in the front and rear autoinjectors, respectively.

Results

Data comparing CSL and HSL for selected analytes at 1 ppm (1 ng/µL) are shown in Table 2. The S/N for each analyte was calculated using the extracted ion listed. The ratio of S/N values for CSL:HSL are shown in the last column. Inert compounds, such as Fluorene and Aldrin have an increase of >30% in S/N, or sensitivity. More of the analyte is reaching the column and MSD using CSL. Active compounds, Endrin and DDT, have a 50% increase in sensitivity. The most active compound, Pentachlorophenol, exhibits >100% better sensitivity. These increases demonstrate that CSL is a milder vaporization and that more analyte is transferred from the inlet.

Table 2. Signal-to-Noise Improvement Using Cold Spliltess vs Hot Splitless Injections

	RT	Mass	Ratio cold S/N : hot S/N
Fluorene	11.152	166	1.36
Aldrin	15.205	66 263	1.33 1.33
Mevinphos	9.338	127	1.33
Pentachlorophenol	12.989	266	2.19
Endrin	17.600	263	1.48
p,p'-DDT	18.600	235	1.51

The raw area comparisons of all 18 compounds run with HSL and CSL at 1 ppm are shown in Figure 2, in elution order. Internal standards and surrogate standards are not included. The first blue bar is the ratio of raw area of a 1-µL cold splitless injection to a 1-µL hot splitless injection. Non-active compounds such as Isophorone and Aldrin show more response. The second to fifth bars are the ratios of 2, 3, 4, and 5-µL cold splitless to a 1-µL hot splitless raw areas. These are normalized to 1 µL. For the inert compounds, such as Isophorone and Aldrin, the ratios are constant. This shows that with CSL you can inject more, achieve consistent performance and reduce detection limits.

For active compounds, Pentachlorophenol is the best example. The blue bar shows an increase of ~180% of the response, comparing CSL to HSL. A 2-µL injection gives over 250% response. Injecting 3, 4 or 5 µL yields a constant response. Active compounds benefit from additional amounts on column and reduced inlet activity.

Peak shapes are good for all compounds up to 3 µL, with some distortion at 4 µL and most at 5 µL. For ease of integration, a 3 µL injection volume can be routinely used. The total ion chromatograms for 1,3-dimethyl-2-nitrobenzene are shown in Figure 3 as an example. The worst response is 1-µL HSL, black trace. Some peak shape distortion can be seen starting at the 4-µL CSL level.

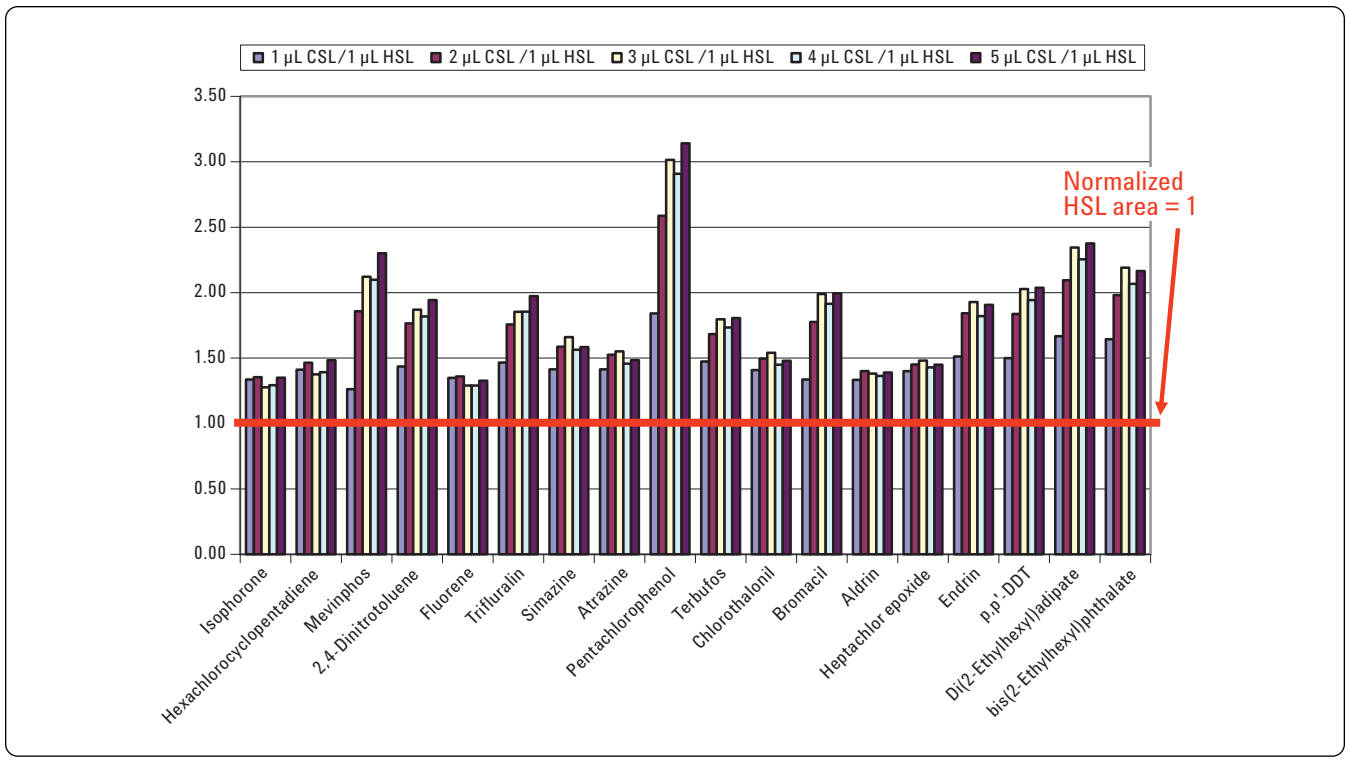

Figure 2. Raw Area Ratios of 1-5 µL CSL:1 µL Hot SL.

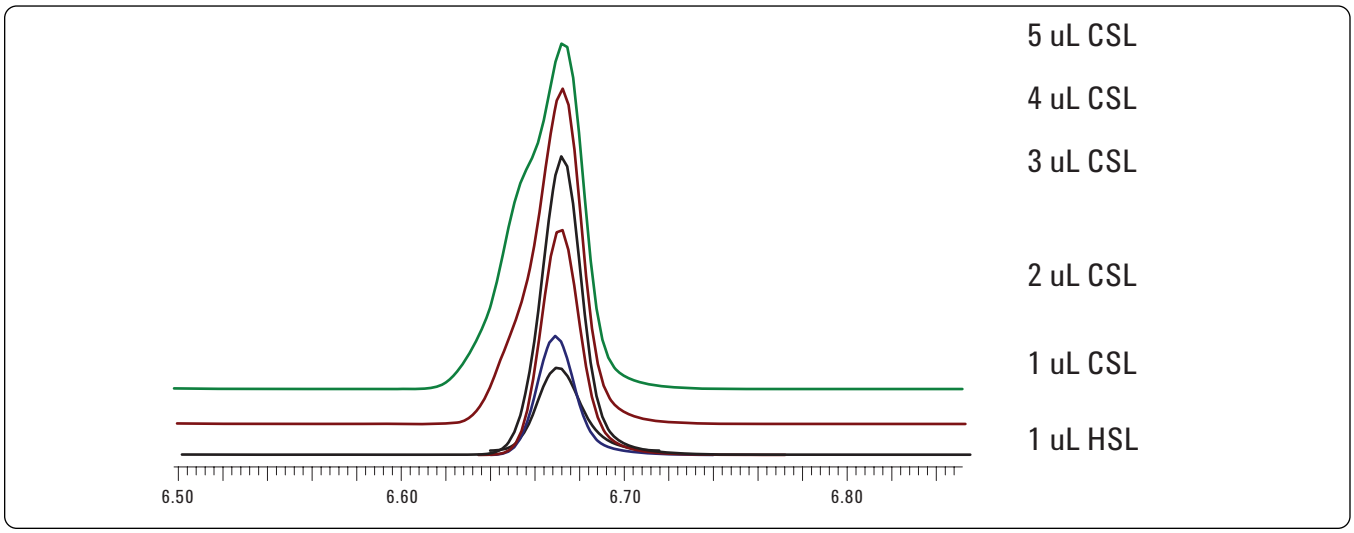

Figure 3. 1,3-dimethyl-2-nitro-benzene TICs. 4 and 5 uL traces offset for clarity.

A 7 level calibration set was prepared using the 7693A Autosampler together with a 100 times lower set of dilutions as described in Table 1. The 0.1–10 ppm standards were run with both HSL (1 µL) and CSL (3 µL). The relative response factors (RRFs) were calculated at each level using the area of the curves. The relative standard deviation (%RSD) of the RRFs was calculated and a normalized comparison is shown in Figure 4. The blue bar is HSL, the red bar is CSL and the yellow bar is 25-µL LVI-SV. The LVI-SV calibration range was 1–100 ppb. The ISTD %RSDs are based on raw area and are very consistent across the various injection techniques. The %RSDs for ISTDs and SS are all below 10%, demonstrating the accuracy and precision of the 7693A for sample preparation.

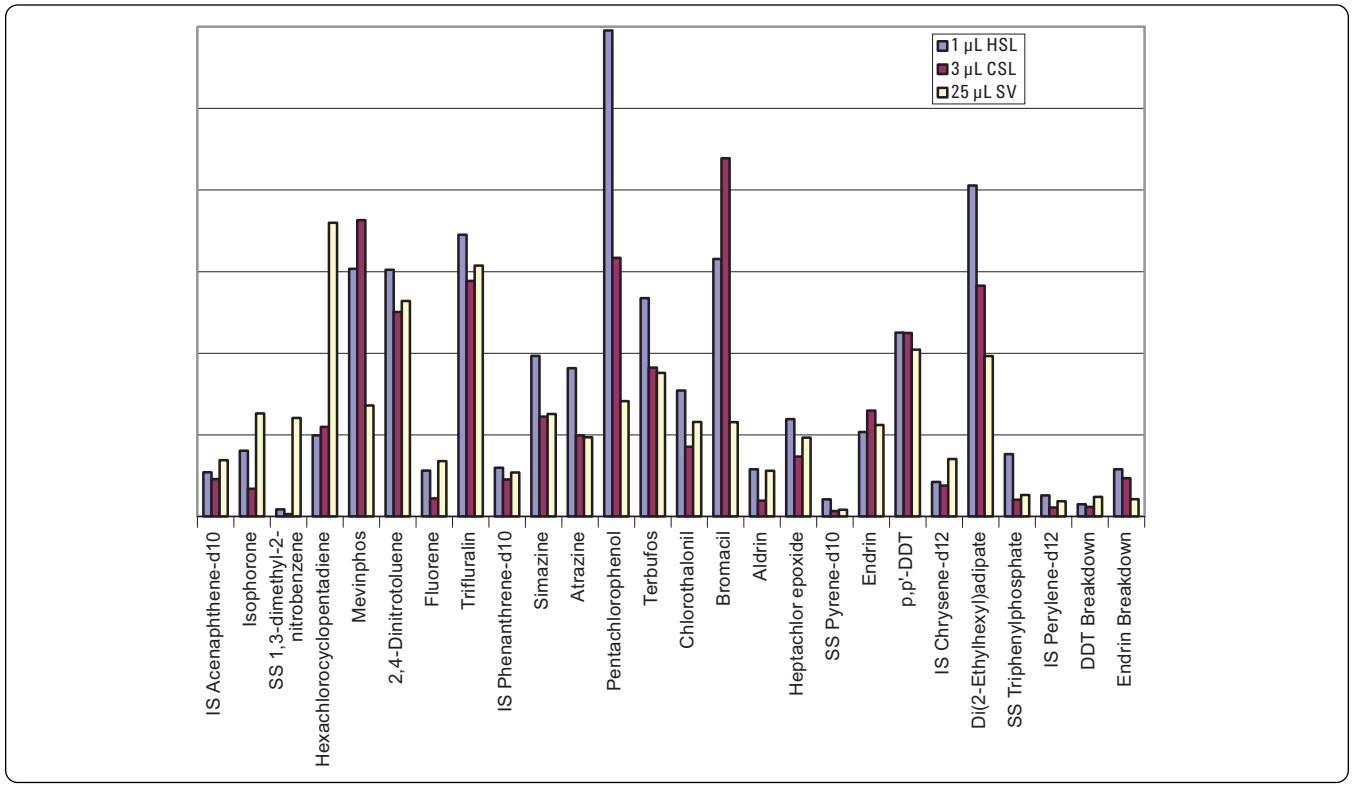

Figure 4. Comparison of HSL, CSL, and LVI-SV, normalized %RSDs of a 7 level calibration.

Active compounds such as Simazine, Atrazine, Pentachlorophenol and Terbufos show significant improvement in %RSD using CSL. Phthalates and adipates are known "sticky" compounds and also improved. Bromacil is a bad behaving compound, usually fronting on the column. Its peak shape in cold splitless was worse than in hot splitless. The exact cause of this is unkown but it may react with the helix liner used.

Breakdown of Endrin and DDT are shown in the last two sets of data. These are an average of the % breakdown across the 7 calibration levels. All injection techniques showed excellent results using the MMI and inert helix liner.

The %RSDs for LVI-SV were comparable to the CSL values for most compounds, with a few compounds higher. This could be caused by the lower calibration range and excess solvent on column affecting the earliest eluters. The linearity is still very good and the detection limits are at least 25 times lower compared to those with hot splitless.

Conclusions

Traditional semivolatiles methods can be altered to achieve better instrument detection limits. The Multimode Inlet provides for cold splitless injections with minimum method development time. More analyte reaches the column and active compound degradation is reduced resulting in lower detection limits compared to hot splitless. Large volume injection with solvent venting can further maximize sensitivity. The analyst can develop methods more rapidly, without moving the column, resulting in greater productivity.

References

1. USEPA Method 525.2 is availble from different sources listed on this website. www.epa.gov/OGWDW/methods/where.html
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