

Optimizing GC/MS Hardware and Software Parameters for Peak Performance in Environmental Analyses

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Introduction

A general gas chromatography mass spectrometry (GC/MS) system and method to fit multiple analyses is convenient to have in a laboratory; however, different environmental analyses can greatly benefit from optimizing the method to best fit the analysis. Optimizing the hardware, consumables and method parameters can provide better peak responses and calibration curve results with lower % RSD values.

Additionally changes in technology – hardware, software or consumables – provide opportunities to improve analyses, increase operation time between maintenance cycles, decrease MS source maintenance, and better data quality with greater peak response and fewer linear fits.

This work focuses on optimizing GC/MS parameters for EPA 525.2 and 525.3 calibration ranges along with an extended calibration range (0.02 – 15 ng/μL) to include state regulations that test beyond the limits of EPA 525, such as Arizona^{1,2,3}. Mass spectrometer drawout plate sizes, MS temperatures and injection parameters were tested to determine the effect on peak responses and calibration curve results.

Experimental

GC/MS system

An Agilent 8890 GC and Agilent 5977A Inert Single Quad MSD were utilized of the EPA 525 method with a DB-8270D Ultra Inert column. The selected method parameters and hardware components for the optimization testing are shown in Table 1. Method parameters, shared across all analyses, can be found in Table 2. Experiments were completed with the 6mm drawout plate first to optimize source and quadrupole temperatures. The better temperature set was then utilized for the 9mm drawout plate testing.

Table 1. Selected GC/MS method parameters and hardware components for optimization experiments.

Tested Parameters	Standard purge	Switched Purge
6mm drawout plate (p/n G2589-20045)	X	
9mm drawout plate (G3440-20022)	X	X
Source 300°C/ Quad 180°C	X	
Source 320°C/ Quad 200°C	X	X

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Experimental (continued)

Method Parameters

Table 2. Method parameters and consumables utilized in all EPA 525 analyses.

Parameter	Value
Injection volume	1 μL
Syringe	ALS syringe, Blue Line, 10 μL, PTFE-tip plunger (p/n G4513-80203)
Inlet septum	Agilent Advanced Green, non-stick 11mm septum (p/n 5183-4759)
Inlet	Split/Splitless 250°C; Pulsed Splitless 50 psi until 1 min; Purge 50 mL/min at 1 min
Inlet Liner	Agilent Ultra Inert single taper with wool splitless liner (p/n 5190-2293)
Column temperature program	40°C (hold for 1 minute), 25°C/min to 160°C (hold 3 minutes), 6°C/min to 312°C
Column	Agilent DB-UI 8270D, 30m x 0.25 mm x 0.25μm (p/n 122-9732)
Carrier gas and flow rate	Helium at 1.2 mL/min, constant flow
MS parameters	
Transfer line temperature	280°C
Solvent Delay	3 min
A/D samples	4

Standard preparation

Three multicomponent standards of semi volatiles (SVM-525), organochlorine pesticides (PPM-525E), and nitrogen/phosphorus pesticides (NPM-525C) were procured from Agilent at 100 ng/μL concentrations and combined to form a stock solution. Aliquots of stock solution were diluted with ethyl acetate to prepare calibration standards at 0.02, 0.05, 0.10, 0.20, 0.50, 1.0, 2.53, 5.0, 10, and 15.3 ng/μL for most compounds. The *cis* and *trans* permethrin isomers were present at a combined concentration of 200 ng/μL in PPM-525E and assumed to be equimolar. Pentachlorophenol was present at a four-fold higher concentration in SVM-525. MGK-264 was present as a mixture of isomers with a total concentration of 100 ng/μL in NPM-525C; two predominant isomers were identified and quantified separately with an assumed concentration of half of the above concentration. Alachlor and atrazine exist in two mixtures, resulting in two-fold greater concentrations at each calibration level. Internal standards (ISTDs) and surrogates (ISM-510) were added to each calibration standard to provide a concentration of 5 ng/μL at each level.

Results and Discussion

6mm Drawout Lens Testing: MS Temperatures

Two sets of temperatures (300°C source / 180°C quad temperatures and 320°C source / 200°C quad temperatures) were evaluated with a 6mm drawout lens installed in the source. Calibration curves were generated for each set of temperatures. The average response factors (RFs) were calculated for each compound at the three calibration ranges; if the average RF was higher than 20%, a linear fit was used to pass calibration. The results for both temperature sets on the 6mm drawout plate are summarized for each calibration range in table 3. For the 300 °C \ 180 °C temperatures, 23 target analytes required linear regression for the extended range, 8 targets for EPA 525.2 range and 7 targets required regression for EPA 525.3 range. The average RSD values for the RFs across 102 compounds, was below 16% for the three calibration ranges. Figure 1 provides a visual representation of all % RSDs for each analyte and calibration range. The later eluting compounds require more linear regressions than early eluting analytes, which may be attributed to the “colder” MS temperatures causing incomplete transmission.

Increasing the source and quad temperatures (320°C and 200°C, respectively) precipitously decreased the number of target analytes requiring linear regression across the calibration ranges.

Table 3. Statistical characteristics for three calibration ranges of target analytes, using the 6mm drawout plate, comparing the 300°C source / 180°C quad temperatures (left) and 320°C source / 200°C quad temperatures (right).

Calibration Range (ng/μL)	300 °C source / 180 °C quad			320 °C source / 200 °C quad		
	Average RSD in RFs	Standard Deviations in Average RSD RFs	Number of Targets Requiring Linear Regression	Average RSD in RFs	Standard Deviations in Average RSD RFs	Targets Requiring Linear Regression
0.02 to 15	15.59	8.14	23	15.18	7.51	Methyl paraoxon, Fluridone
0.1 to 10	13.23	7.18	8	12.07	6.67	Methyl paraoxon, Fluridone
0.1 to 5	13.51	6.84	7	11.82	6.31	Fluridone

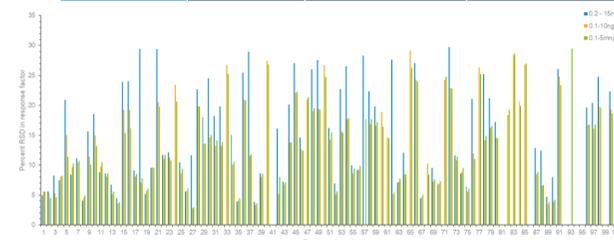


Figure 1. Comparison of percent RSDs for calibration from 0.02 to 15 ng/μL (blue), 0.1 to 10 ng/μL (orange), and 0.1 to 5 ng/μL (green) at 300 °C source and 180 °C quad temperatures.

Linear regression was required for only two analytes in the extended and EPA 525.2 ranges, and only fluridone needed a linear fit for EPA 525.3 range (Table 3). The average RSD values also are lower with higher source and quad temperatures for the EPA ranges. Figure 2 shows an overlay of TICs (16 to 29 min) for the different MS temperatures; the higher MSD temperature (red trace) has increased peak responses across the time range (and entire TIC). The increased peak responses at low concentrations with higher MSD temperatures may account for the decrease in number of linear fits.

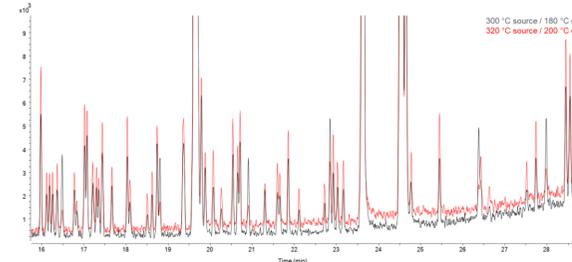


Figure 2. Comparison of TIC region from 16 – 29 min for source and quad temperatures (300 °C/180 °C, black trace; 320 °C/200 °C, red trace) of EPA 525 target analytes (0.05 ng/μL), ISTDs and surrogates (5 ng/μL).

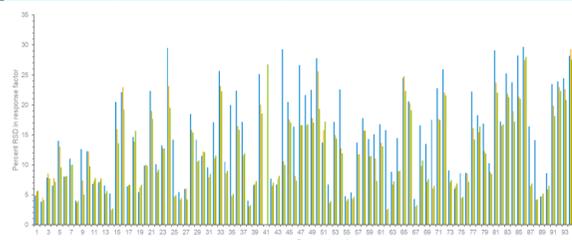


Figure 3. Comparison of percent RSDs for calibration from 0.02 to 15 ng/μL (blue), 0.1 to 10 ng/μL (orange), and 0.1 to 5 ng/μL (green) at 320 °C source and 200 °C quad temperatures.

Results and Discussion

6mm Drawout Lens Testing: MS Temperatures (Cont'd)

Figure 3 represents the % RSDs for every target at the higher MSD temperatures; comparison to Figure 1 shows the clear increase in analytes achieving calibration requirements with average RFs, across the tested ranges, especially in the later eluting analytes, along with decreases in some average %RSD values across the entire set of analytes.

9mm Drawout Lens Testing: MS Temperatures

The 9mm drawout lens was utilized at the higher MSD temperatures. There is a reduction in number of linear fits to one analyte in the extended range and none in the EPA 525 ranges and decreases in the average %RSD values by 2 - 3%. The 9mm lens allows for more ions to pass through the MS source across the concentration levels, which results in better calibration data.

Standard vs. Switched Septum Purge

Injection parameters, such as pulsed injections or switched septum purge, can affect the peak responses and ultimately calibration data, especially of early eluting compounds. Experiments with 6mm drawout lens used standard septum purge, as did the above 9mm work; switched septum purge was then tested on 9mm lens.

Table 4. Statistical characteristics for three calibration ranges of target analytes, using the 9mm drawout plate, comparing the standard septum purge (left) and switched septum purge (right) during pulsed splitless injections.

Calibration Range (ng/μL)	Standard Septum Purge			Switched Septum Purge		
	Average RSD in RFs	Standard Deviations in Average RSD RFs	Targets Requiring Linear Regression	Average RSD in RFs	Standard Deviations in Average RSD RFs	Targets Requiring Linear Regression
0.02 to 15	13.07	6.57	Chlorothalonil	12.71	6.60	Chlorothalonil, endosulfan I, endosulfan sulfate
0.1 to 10	9.52	4.64	--	8.97	4.46	--
0.1 to 5	9.47	4.60	--	8.96	4.45	--

Conclusions

Based on the components and parameters tested for EPA 525.2 (and EPA 525.3) and the extended calibration set, the optimal parameters for high quality data and calibration curve results were:

- Pulsed splitless injection, ideally with switched septum purge
- MS temperatures of 320 °C for source and 200 °C for quadrupole
- 9 mm drawout plate (or extraction lens)

Standard vs. Switched Septum Purge (Cont'd)

Switched septum purge experiments had similar results as the standard purge (Table 4), where average %RSDs were slightly lower, while the extended range needed three linear fits. In Figure 4, the switched purge TIC has higher peak responses, especially for early eluting compounds, compared to standard purge TIC. Switched purge can be even more beneficial in splitless injections.

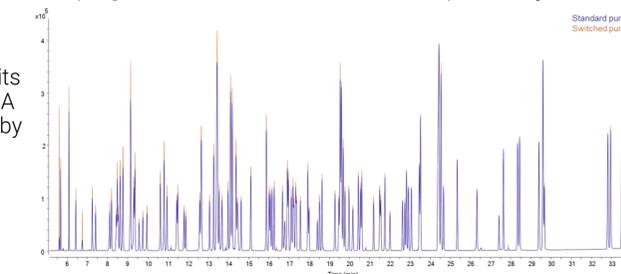


Figure 4. Comparison of TICs for standard (purple trace) and switched (orange trace) septum purge injections of EPA 525 target analytes (2.5 ng/μL), ISTDs and surrogates (5 ng/μL).

References

- 1 Munch, J. W. Method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry. United States Environmental Protection Agency, Department of Water, 1995.
- 2 Munch, J. W.; et al. Method 525.3: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column gas chromatography/mass spectrometry. United States Environmental Protection Agency, 2012.
- 3 Title 18. Environmental Quality, Chapter 11. Department of Environmental Quality – Water Quality Standard, Arizona Department of State, Phoenix, AZ, USA, 2016.

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