

Advances in Organic Analyses OF WASTEWATER USING GC/MS

**WATER/
Wastewater**

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ABSTRACT

The analysis of wastewater for organic contaminants is important in maintaining the quality of water for natural ecosystems and for recreational use. The possibility of damage from endocrine disrupting compounds at low concentrations will emphasize the importance of efficient analyses at increasingly lower concentrations in the future.

Gas chromatography with specific detectors has become well established over the years in the environmental analysis of wastewater. The sensitivity was good and the specificity of the detector could be chosen to match the analysis requirements. More recently GC/MS has gained prominence because confirmation can be achieved in the same step as the analysis with a second dimension of information. This provides increased confidence in the result in conjunction with increased productivity. US EPA methods using GC/MS routinely specify 40-100 compounds that may be measured in a single run.

Advances in GC/MS technology have improved detection limits in complex samples. The ability to adjust the sensitivity requirements to match the analysis requirements makes the system useful for a wider range of applications. Full scan ion monitoring is by far the most prevalent mode of operation for semivolatile organic compound detection. It covers the necessary mass range and provides classical spectra that can be library searched for positive identification. Selected Ion Recording (SIR or SIM) is a GC/MS mode of operation where only the ions of interest are monitored, independent from surrounding interferences and coelutions, providing dramatic increases in sensitivity. SIR has not been widely accepted in environmental testing because it requires prior knowledge of the sample matrix. The combination of simultaneous Selected Ion and Full Ion (SIFI) scanning is a new approach providing the advantages of both techniques in a single chromatographic run.

Large volume injection can increase the sensitivity of an analysis or decrease the sample preparation constraints. Coupled with solvent purging, chromatographic integrity is maintained.

The advantages of these advances will be discussed for wastewater analysis. Compliance with EPA method requirements for semivolatiles will be shown. An extension of the method to measure more complicated matrices such as multicomponent analytes in solid waste will be presented.

INTRODUCTION

The analysis of wastewater presents a unique set of challenges. The suite of compounds to be measured varies by industrial category and may consist of a few or many compounds. The matrix components and complexity may be as simple as drinking water or as complicated as a hazardous waste extract. The concentrations to be measured will also vary, so developing a method for wastewater analysis that can be used for more than one source discharge must be able to cover a wide range of requirements. One way to evaluate the potential for meeting these requirements is to examine the two possible extremes. Drinking water requirements for low detection limits reflect the levels that might be measured in ambient water for evaluating background levels or modeling a watershed. The ability of a GC/MS to achieve low detection limits and meet quality control criteria specified in US EPA methods will be evaluated. A large suite of compounds are included in drinking water methods, demonstrating the breadth of analytes that might be examined. The ability to handle a more complicated matrix is routinely required in solid and hazardous waste analysis programs. The techniques used to accommodate a more complicated matrix will be described. The overall suitability of GC/MS for wastewater analysis will be summarized.

EXPERIMENTAL

The US EPA method for semivolatile organic chemicals in drinking water was developed a number of years ago using older technology than is available today. The concentration range specified for measurement in the method ranges from 0.1-10.0 ng/ μ L. Previous work has demonstrated compliance with the requirements of method 525.2 for drinking water.¹ The following conditions (Table 1) show the GC conditions for the measurement of drinking water at enhanced sensitivity (AutoSystem XL GC, PerkinElmer). The system is optimized for the lowest detection limits and calibrated from 0.02-1.0 ng/ μ L.

Table 1: Gas Chromatograph Conditions for Drinking Water Analyses

Instrument	AutoSystem XL
Column	PE-5MS 30 m x 0.25 mm; 0.25 μ m film thickness
Oven Temperature Program	40°C for 1min., 45°C/min. to 160°C for 3min; 6°C/min to 320°C for 2min
Programmable Pneumatic Control (PPC)	Helium @ 1.0 mL/min.
Injector	250°C
Injection Volume	1 μ L

The conditions for the mass spectrometer (TurboMass, PerkinElmer) are shown in Table 2.

Table 2: Mass Spectrometer Conditions for Drinking Water Analyses

Instrument	TurboMass MS
Mass Scan Range	45-450 m/z
Scan Speed	2.0 scans/sec
Filament Delay	3.0 min.
Ion Source Temperature	150°C
Transfer Line Temperature	250°C
Ionization Mode	EI

The US EPA has developed the solid waste methods for more complicated matrices that might be encountered during clean up or monitoring of hazardous waste sites. Method 8270, an EPA method for measurement of semivolatiles in hazardous waste was evaluated.² Identical standards were analyzed using two sets of experimental conditions. A 50- μ L large volume injection was used in both cases. One set of standards was analyzed using the GC/MS Full Scan mode (FS-50) and the second using the Selected Ion Recording mode (SIR-50). Table 3 lists the chromatographic conditions used for both experiments, while Table 4 lists the mass spectrometer conditions used for each set.

Table 3: Gas Chromatographic Conditions for Solid Waste Matrices

Instrument	AutoSystem XL
Column	PE-5MS 30 m x 0.25 mm; 0.25 μ m film thickness
Pre-Column	1 m x 0.32 mm deactivated fused silica
Oven Temperature Program	55°C for 5 min., 45°C/min. to 160°C; 6°C/min to 320 °C
Programmable Pneumatic Control (PPC)	Helium @ 1.0 mL/min.
Programmable Split/Splitless (PSS) Injector	55°C for 4 min.; ballistic to 250°C; Solvent Purge Mode
Injection Volume:	50 μ L

Table 4: Mass Spectrometer Conditions for Solid Waste Matrices

Mode:	Full Scan	Selected Ion Recording
Selected Scan Masses	50 - 350 m/z	159, 231, & 233 m/z
Scan Speed	2.0 scans/sec	2.0 scans/sec
Filament Delay	5.0 min	5.0 min
Ion Source Temperature	150°C	150°C
Transfer Line Temperature	250°C	250°C
Ionization Mode:	EI	EI

RESULTS AND DISCUSSION

Enhanced sensitivity using the semivolatle drinking water method is shown in Figure 1. The practical quantitation limits are compared to the US maximum contaminant levels (MCL) in drinking water in Table 5. The quantitation limits are well below the level where a decision would be required. In fact, the levels are low enough that for the majority of compounds a 10-fold reduction in the MCL could be reliably reported.

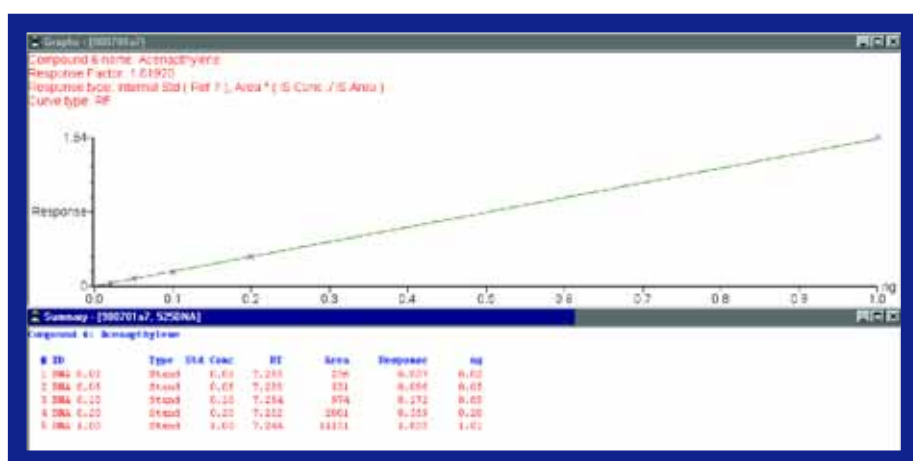


Figure 1: Acenaphthylene Calibration Curve.

Table 5: Comparison of Practical Quantitation Level and the US Maximum Contaminant Level for Selected Compounds

Compound	PQL (µg/L)	US MCL (µg/L)
Alachlor	0.01	2.
Atrazine	0.01	3.
Endrin	0.01	2.
Lindane	0.01	0.2
Methoxychlor	0.01	40
Simazine	0.01	4.

Calculation based on a 1 Liter separatory funnel extraction.

The challenge with a more complicated matrix is to maintain detection limits with the introduction of additional potential interfering components. Newer mass spectrometer technology has improved to better address these considerations. For example, the TurboMass incorporates a prefilter before the quadrupole to remove much of the unwanted material before it proceeds to the analytical quadrupole. In addition, the detector is sealed to prevent contamination, making the system more rugged for dirty samples, less often requiring clean up or maintenance.

Large volume injections can increase sensitivity, but the increased solvent can degrade chromatography and hamper clean out of the system. Solvent purging before the analytes of interest are introduced into the column can provide an efficient analysis of a larger volume sample, allowing less preconcentration or enhanced sensitivity. Figure 2 shows how solvent purging works.

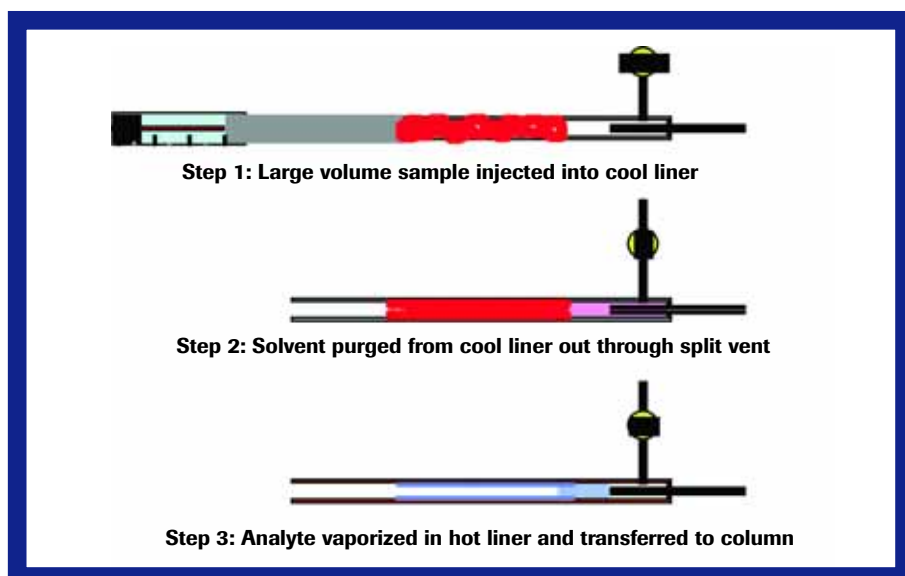


Figure 2: Solvent Purge process

The solvent purging mode was used with the solid waste extracts, while injecting 50 µL of sample. Figure 3 shows the pattern recognition possible and selected ions for Toxaphene.

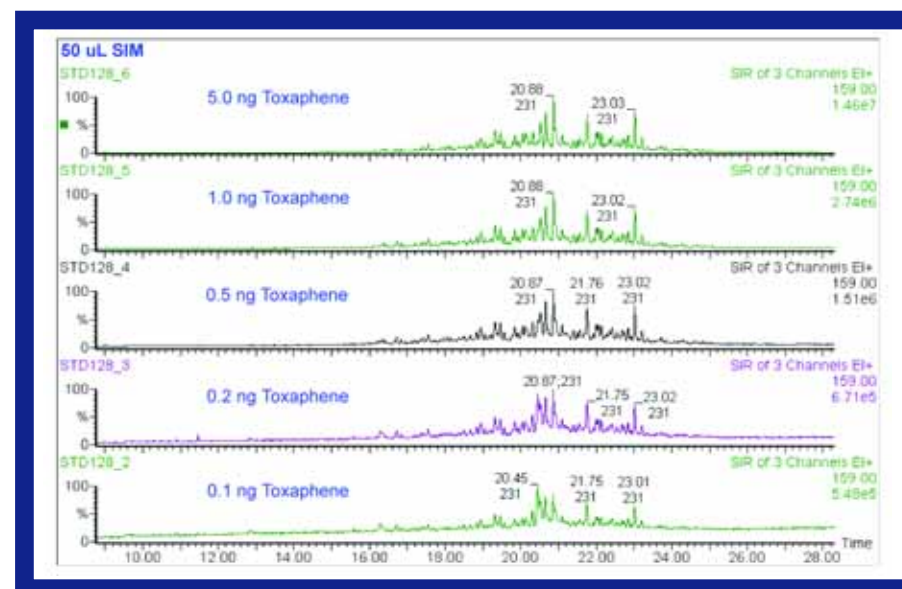


Figure 3: Toxaphene Calibration

Selected Ion Recording (SIR) is a demonstrated technique for increasing sensitivity, while a full scan is useful for pattern recognition to confirm analyte identification. The use of both techniques simultaneously provides primary and supporting information for an accurate identification at lower concentrations. The detection limits obtained in each mode are compared in Table 6.

Table 6: Detection Limit Comparison

Calibration Peaks	Calculated Analytical Detection Limits	
	FS-50 (ng/µL)	SIR-50 (ng/µL)
Peak #1	0.073	0.065
Peak #2	0.089	0.009
Peak #3	0.105	0.021
Peak #4	0.035	0.014
Toxaphene (Average)	0.076	0.027

Toxaphene MCL = 3 µg/L

DLs equivalent to ppb (µg/L) for 1L sample concentrated to 1 mL

CONCLUSIONS

Gas chromatography coupled with mass spectrometry has become indispensable in the analysis of environmental matrices. Wastewater provides a particular challenge because of the variety of matrix components that might be encountered. The suite of analytes can vary in number and content and the detection limit requirements can be difficult to achieve. We have demonstrated ways to enhance the sensitivity of a method using large volume injection and enhanced spectrometer performance. Coupled with modern techniques to handle complex matrices in the spectrometer, wastewater analysis becomes more productive with the application of GC/MS capability and flexibility.

REFERENCES

1. LeMoine, E.A., Semi-volatile Organics in Drinking Water using EPA Method 525.2 Optimized for Greater Sensitivity, PerkinElmer Application Note D-5886, Norwalk, CT (1998).
2. LeMoine, E.A. and Hoberecht, H., U.S. EPA Method 8270 for Multicomponent Analyte Determination, PerkinElmer Application Note D-6346, Norwalk, CT (2000).



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