Validation of Wisconsin Gasoline Range Organics

Application Note **By: Tyler Trent**

Abstract

The Wisconsin DNR Modified Gasoline Range Organics (Wisconsin GRO) Method is used to determine gasoline and gasoline components in water and soil. The water samples are analyzed by purge and trap, while the soil samples undergo an additional methanol extraction. For this application note, a working linear calibration curve and quality control checks were evaluted by using a Teledyne Tekmar's Atomx Automated VOC Sample Prep System. The Atomx utilizes an automated methanol extraction and purge and trap concentrator in conjunction with a gas chromatograph mass spectrometer (GC/MS) to determine the concentration of gasoline and gasoline components in water and soil samples.

Introduction

The Wisconsin DNR Modified GRO Method is used to determine gasoline and gasoline components in water and soil. The optimal hydrocarbon range is from C_6-C_{10} with a boiling point range from 60˚C-220˚C. This method utilizes purge and trap in conjunction with a gas chromatograph (GC) with a flame ionization detector (FID).[1]

The analysis of Wisconsin GRO (e.g. methyl-tert-butyl-ether, toluene, benzene, ethylbenzene, xylenes, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and naphthalene) is vital in determining the "composition and the origin of such products including weathered fuels leaking from underground storage tanks (LUST), spills in pipe lines and run-off from surface transportation."[2]

This study utilizes the Atomx, a VOC sample prep system that integrates a Purge and Trap (P&T) Concentrator with a Multi-Matrix Autosampler. This "all-in-one" set up allows for increased throughput by incorporating an 80-position autosampler capable of processing water, soil and automated methanol extractions with a P&T concentrator.

Since high level soil samples need to be methanol extracted this step adds time to the analysis. By using the Atomx, the instrument performs the methanol extraction by adding the methanol and surrogates to the soil samples, and then a dilution (1:100 or 1:50) is taken of the methanol extract. The methanol extract is then placed into 5mL of blank water in the sparge vessel. Once in the sparge vessel the sample is analyzed just like a water sample.

This integrated platform of the Atomx allows for running water, soil and methanol extractions in the same sequence. The Atomx brings advances in communication allowing faster analysis time by preparing one sample while another is being analyzed. In addition the ability to program internal standard and surrogate volumes automatically and new clean up techniques further improve sample capacity which is critical to today's environmental testing laboratories.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Since some labs run this analysis by GC/MS an FID was not used in this study. The GC/MS utilized in this application note is an Agilent 7890/5975 GC/MS. A linear calibration curve, lower limit of detection (LOD), lower limit quantitation (LOQ), and replicate laboratory control spikes (RLCS) and duplicate laboratory control spike (DLCS) were performed for water and high level soil matrices. Water samples were analyzed using a 5mL sample volume, while the soil analysis uses 7g of soil, 7mL of methanol and a 1:100 dilution for the automated methanol extraction process.

Experimental-Instrument Conditions

The Atomx, equipped with a #9 adsorbent trap, and an Agilent 7890A GC with a 5975C inert XL MSD were utilized for this study. **Tables 1-4** show the CG/MS and purge and trap conditions for both water and methanol extraction applications.

GC Parameters	
GC:	Agilent 7890A
Column	Restek RTX-VMS 20m x 0.18mmID x 1um
Oven Program:	40°C for 4 min; 16°C/min to 100°C for 0 min; 30°C /min to 200°C for 4 min, 15.083 min runtime
Inlet:	220°C
Column Flow	0.9mL/min
Gas:	Helium
Split:	80:1
Pressure:	21.542 psi
Inlet:	Split/Split less

MSD Parameters	
MSD:	5975C inert XL
Source:	230°C
Quad:	150°C
Solvent Delay:	0.5 min
Scan Range:	m/z 35-270
Scans:	5.76 scans/sec
Threshold:	150
MS Transfer Line Temp:	230°C

Tables 1 & 2: GC and MSD Parameters

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Atomx Water Parameters			
Variable	**Value**	**Variable**	**Value**
Valve oven Temp	140°C	Dry Purge Flow	100mL/min
Transfer Line Temp	140°C	Dry Purge Temp	20°C
Sample Mount Temp	90°C	Methanol Needle Rinse	Off
Water Heater Temp	90°C	Methanol Needle Rinse Volume	3.0mL
Sample Vial Temp	20°C	Water Needle Rinse Volume	7.0mL
Sample Equilibrate Time	0.00 min	Sweep Needle Time	0.50min
Soil Valve Temp	50°C	Desorb Preheat Time	245°C
Standby Flow	10mL/min	GC Start Signal	Start of Desorb
Purge Ready Temp	40°C	Desorb Time	2.00 min
Condensate Ready Temp	45°C	Drain Flow	300mL/min
Presweep Time	0.25 min	Desorb Temp	250°C
Prime Sample Fill Volume	3.0mL	Methanol Glass Rinse	Off
Sample Volume	5.0mL	Number of Methanol Glass Rinses	1
Sweep Sample Time	0.25 min	Methanol Glass Rinse Volume	3.0mL
Sweep Sample Flow	100mL/min	Number of Bake Rinses	1
Sparge Vessel Heater	On	Water Bake Rinse Volume	7.0mL
Sparge Vessel Temp	40°C	Bake Rinse Sweep Time	0.25 min
Prepurge Time	0.00 min	Bake Rinse Sweep Flow	100mL/min
Prepurge Flow	0mL/min	Bake Rinse Drain Time	0.40 min
Purge Time	11.00 min	Bake Time	2.00 min
Purge Flow	40mL/min	Bake Flow	200mL/min
Purge Temp	20°C	Bake Temp	280°C
Condensate Purge Temp	20°C	Condensate Bake Temp	200°C
Dry Purge Time	2.00 min		

Table 3: Atomx Water Parameters (Parameters highlighted in yellow were not used.)

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Atomx Methanol Extraction Parameters			
Variable	**Value**	**Variable**	**Value**
Valve Oven Temp	140˚C	Dry Purge Flow	100mL/min
Transfer Line Temp	140˚C	Dry Purge Temp	20˚C
Sample Mount Temp	90˚C	Methanol Needle Rinse	On
Soil Valve Temp	100˚C	Methanol Needle Rinse Volume	2.0mL
Standby Flow	10mL/min	Water Needle Rinse Volume	7.0mL
Purge Ready Temp	40˚C	Sweep Needle Time	0.25min
Condensate Ready Temp	45˚C	Desorb Preheat Temp	245˚C
Presweep Time	0.25min	GC Start Signal	Star of Desorb
Methanol Volume	7mL	Desorb Time	2.00min
Sparge Vessel Heater	On	Drain Flow	300mL/min
Sparge Vessel Temp	40˚C	Desorb Temp	250˚C
Prepurge Time	0.00min	Methanol Glass Rinse	On
Prepurge Flow	0mL/min	Number of Methanol Glass Rinses	1
Sample Mix Speed	Fast	Methanol Glass Rinse Volume	3.0mL
Sample Mix Time	4.00min	Number of Water Bake Rinses	1
Sample Settle Time	2.00min	Water Bake Rinse Volume	7.0mL
Sample Sweep Time	0.25min	Bake Rinse Sweep Time	0.25min
Sample Sweep Flow	100mL/min	Bake Rinse Sweep Flow	100mL/min
Purge Time	11.00min	Bake Rinse Drain Time	0.40min
Purge Flow	40mL/min	Bake Time	2.00min
Purge Temp	20˚C	Bake Flow	200mL/min
Condensate Purge Temp	20˚C	Bake Temp	280˚C
Dry Purge Time	2.00min	Condensate Bake Temp	200˚C

Table 4: Atomx Methanol Extraction Parameters

Calibration / Results

A 50ppm working calibration standard was prepared in methanol using a 1000ppm Wisconsin GRO/PRVO standard from Restek. Calibration standards were then serially diluted with de-ionized water ranging from 10-200ppb. A 25ppm surrogate of fluorobenzene was prepared in methanol and transferred to one of the three standard addition vessels on the Atomx. The Atomx delivered the surrogate in 5µL aliquots to the sample.

Using Agilent Chemstation software, the summation of each standard from methyl-tert-butyl-ether to naphthalene were used to generate the calibration curve seen in **Figure 1**. The area of the surrogate fluorobenzene was subtracted from the total summed area to give the correct area needed for the Wisconsin GRO calibration.The calibration pass method criteria with a correlation coefficient (r^2) of 0.9992. Based upon the calibration results the average response factore (RF) was calculated to be $6.89X10^{-07}$.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

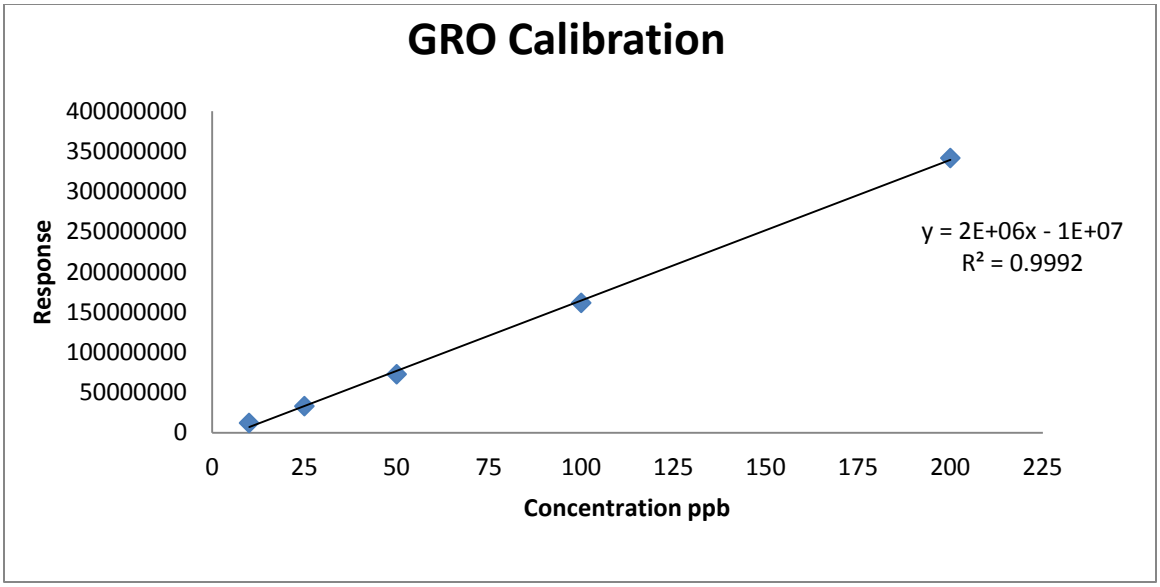

Figure 1: Wisconsin GRO Calibration from 10-200ppb

The Wisconsin GRO method requires for Quality Control (QC) checks to demonstrate the capabilty to generate acceptable accuracy and precision by running the following tests. For the water/soil, each matrix must run a Replicate Laboratory Control Spike (RLCS), Duplicate Laboratory Control Spike (DLCS), Lower Limit of Detection (LOD) and Limit of Quantitation (LOQ). Each of these test listed above must fall between required limits that are set forth in the Wisconsion GRO method. Results of these test can be seen in **Table 5-6**. **Table 5** demonstrates the capabilty of the Atomx to generate acceptable accuracy and precision for both water and soil matrices. All the experimental values fall with in the acceptable range set forth by the Wisconsin GRO Method.

Water Quality Control				
	Theoretical (ppb)	**Experimental (ppb)**	**%Recovery**	**Experimental %RSD**
RLCS	100 +/-20%	106.77*	106.77	2.70
DLCS	100+/-20%	103.45	103.45	
Soil Quality Control				
	Theoretical (ppm)	**Experimental (ppm)**	**%Recovery**	**Experimental %RSD**
RLCS	10+/-120-75%	8.97*	89.7	5.94
DLCS	10+/-120-75%	8.65	86.5	

Table 5: Replicate Laboratory Control Spike (RLCS) and Duplicate Laboratory Control Spike (DLCS) Results for water and soil. **Firgures 2-3** show the chromatograms for the RLCS for water and soil. *n= 5 replicates

The LOD was performed in accordance with 40 CFR, Part 136, Appendix B for both water and soil. For the soil, a GRO free sand or soil must be used and put through the same extraction method that is used as the soil samples. The LOQ is ten times the standard deviation determined from analysis of seven replicate blanks. As the method states the LOQ for soil should be less then 10ppm and for groundwater it should be 0.1ppm or less. **Table 6** shows that the LOQs for both matrices are below the required limits set by the method.

Water/Soil Quality Control		
Matrix	**LOD* (ppb)**	**LOQ*(ppb)**
Water	0.160	0.511
Soil	0.126	0.402

Table 6: Results for for the LOD and LOQ for both water and soils.*n=7 replicates

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Chromatograms.

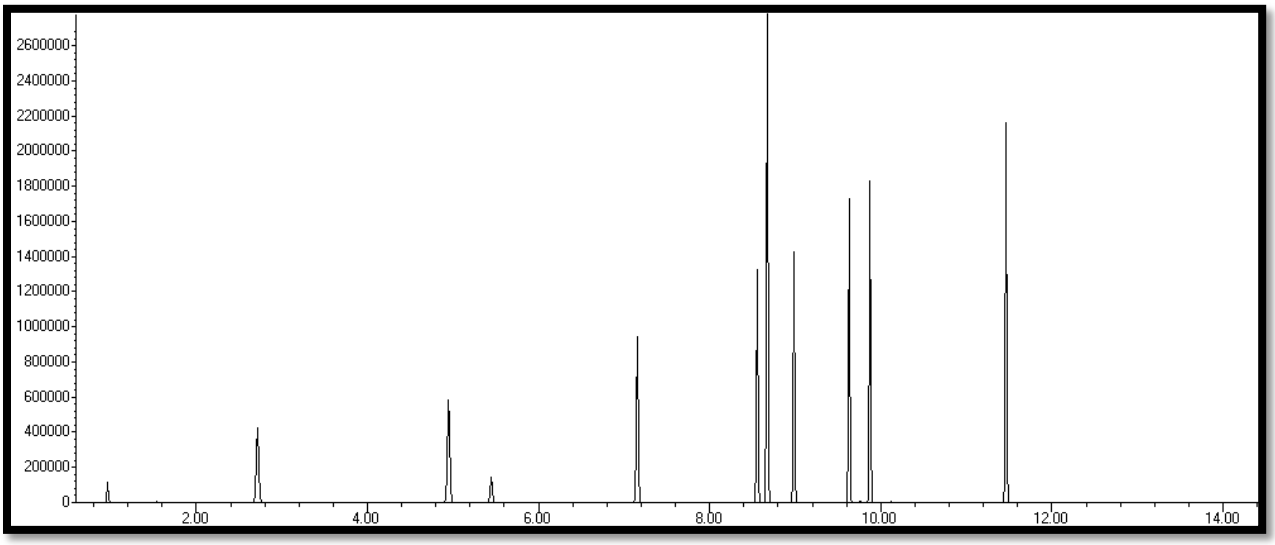

Figure 2: TIC of a 100ppb RLCS water chromatogram for Wisconsin GRO

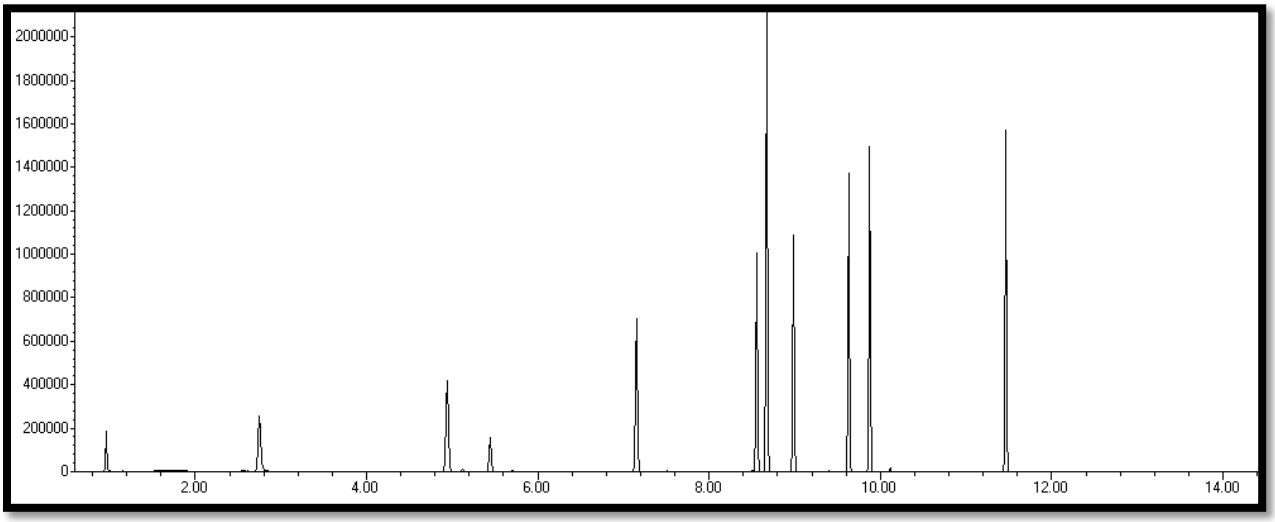

Figure 3: TIC of 10ppm RLCS methanol extraction chromatogram for Wisconsin GRO

Conclusion

This study validates the use of the Atomx automated sample prep system in conjunction with an Agilent 7890/5975 GC/MS for the Wisconsin DNR Modified GRO Method. Calibration and QC data met all performance criteria of the method. The Atomx system is so versatile that this “all-in-one” set up allows for increased throughput by incorporating an 80 position autosampler capable of processing water, soil and automated methanol extractions with a P&T concentrator. Utilizing the methanol extraction feature for high level soil samples can save time and labor by automating the sample extraction process. When dealing with high level samples the Atomx is able to use the methanol rinsing function to help control/eliminate carryover. The Atomx proved to be an excellent system to increase productivity in the lab.

In closing the methodology for the Wisconsin GRO analysis specifically states the use of a GC equipped with a PID/FID detection scheme. This note is not intended as replacement for the requirements of the Wisconsin method but rather as a validation of a Single Automated Sample Preparation System. Please consult with your state and local regulatory agencies to determine which detection scheme is preferred or allowed for the analysis of Gasoline Range Organics.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

References

1. Modified GRO Method for Determine Gasoline Range Organics Wisconsin DNR September 1995 PUBL-SW-140
2. C. Chang, Z Ji “Optimized Analysis of Gasoline (BTEX) in Water and Soil Using GC/FID with Purge and Trap”

Acknowledgments

Teledyne Tekmar wishes to thank Jessica Leck, Volatiles Supervisor from Pace Analytical Services, Inc., for the critical review of this application note.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com