# Wisconsin Gasoline Range Organics (GRO) with the Atomx XYZ and Agilent 7890B GC/5977B MS

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## Abstract

The Wisconsin DNR Modified Gasoline Range Organic (Wisconsin GRO) Method was used to determine the concentration of volatile organic compounds (VOCs) in water and soil matrices. The Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with an Agilent 7890B Gas Chromatograph (GC) and 5977B Mass Spectrometer (MS) was used to create a working linear calibration curve, method detection limits (MDLs) and a mid-point verification check for target compounds in water samples, low-level soil samples and high-level soil samples.

## Introduction

The Atomx XYZ is Teledyne Tekmar's most advanced P&T system and is based on the time-tested Atomx instrument platform. The concentrator's efficient trap cooling design reduces sample cycle time by as much as 14% over the previous model. Combined with its 84-position soil and water autosampler, the result is more samples tested per 12-hour period. An innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column life span. In addition to other refinements, the Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

## Sample Preparation

A working 50 parts per million (ppm) (or milligram per liter [mg/L]) calibration standard was prepared in methanol from a Restek® PVOC/GRO Mix (Wisconsin) standard. In total, the standard contained nine compounds.

A nine-point water calibration curve was prepared from 0.5 parts per billion (ppb) to 200 ppb (or microgram per liter [µg/L]) for all compounds, while the eight-point soil calibration curve was prepared from 1 ppb to 200 ppb.

The 1000 ppm nine-compound Restek PVOC/GRO Mix (Wisconsin) standard was used as a working calibration standard to create a five-point methanol extraction calibration curve with the final concentration from 5 ppb to 200 ppb.

The relative response factor (RF) was calculated for each compound using one of the four internal standards: Pentafluorobenzene, 1,4-Difluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Surrogate standards consisted of: Dibromofluoromethane, 1,2-Dichloroethane-d4, Toluene-d8 and Bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 microliters (µL) was then mixed with each 5 milliliter (mL) sample for a resulting concentration of 25 ppb.

Seven 0.5 ppb water standards and seven 2 ppb soil standards were prepared for MDL and precision calculations. Seven 20 ppb water and soil standards were prepared for the assessment of the mid-point verification, accuracy and precision. Also, seven 50 ppb (final concentration) high-level soil methanol extraction samples were prepared for assessment of accuracy and precision. All calibration, MDL, mid-point verification and methanol extraction samples were analyzed with the Atomx XYZ conditions in Table I (water method), Table II (soil method) and Table III (methanol extraction). GC/MS conditions are shown in Table IV.



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## Experimental Instrument Conditions

| Table I Teledyne Tekmar Atomx XYZ Water Method Conditions | | | |
|---|---|---|---|
| **Standby** | **Variable** | **Desorb** | **Variable** |
| Valve Oven Temp | 140 ºC | Water Needle Rinse Volume | 7.00 mL |
| Transfer Line Temp | 140 ºC | Sweep Needle Time | 0.25 min |
| Sample Mount Temp | 90 ºC | Desorb Preheat Temp | 245 ºC |
| Water Heater Temp | 90 ºC | Desorb Time | 2.00 min |
| Sample Cup Temp | 20 ºC | Drain Flow | 300 mL/min |
| Soil Valve Temp | 100 ºC | Desorb Temp | 250 ºC |
| Standby Flow | 10 mL/min | Methanol Needle Rinse | Off |
| Purge Ready Temp | 40 ºC | GC Start Signal | Begin Desorb |
| **Purge** | **Variable** | **Bake** | **Variable** |
| Sample Equilibrate Time | 0.00 min | Methanol Glass Rinse | Off |
| Presweep Time | 0.25 min | Water Bake Rinses | 1 |
| Prime Sample Fill Volume | 3.00 mL | Water Bake Rinse Volume | 7.00 mL |
| Sample Volume | 5.00 mL | Bake Rinse Sweep Time | 0.25 min |
| Sweep Sample Time | 0.25 min | Bake Rinse Sweep Flow | 100 mL/min |
| Sweep Sample Flow | 100 mL/min | Bake Rinse Drain Time | 0.40 min |
| Sparge Vessel Heater | Off | Bake Time | 2.00 min |
| Purge Time | 11.00 min | Bake Flow | 200 mL/min |
| Purge Flow | 40 mL/min | Bake Temp | 280 ºC |
| Purge Temp | 20 ºC | MCS Bake Temp | 180 ºC |
| MCS Purge Temp | 20 ºC | | |
| Dry Purge Time | 0.5 min | | |
| Dry Purge Flow | 100 mL/min | **Trap** | #9 |
| Dry Purge Temp | 20 ºC | **Purge Gas** | Nitrogen |



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| Table II Teledyne Tekmar Atomx XYZ Soil Method Conditions | | | |
|---|---|---|---|
| **Standby** | **Variable** | **Purge** | **Variable** |
| Valve Oven Temp | 140 ºC | Purge Temp | 20 ºC |
| Transfer Line Temp | 140 ºC | MCS Purge Temp | 20 ºC |
| Sample Mount Temp | 90 ºC | Dry Purge Time | 0.5 min |
| Water Heater Temp | 90 ºC | Dry Purge Flow | 100 mL/min |
| Sample Cup Temp | 40 ºC | Dry Purge Temp | 20 ºC |
| Soil Valve Temp | 100 ºC | **Desorb** | **Variable** |
| Standby Flow | 10 mL/min | Methanol Needle Rinse | Off |
| Purge Ready Temp | 40 ºC | Water Needle Rinse Volume | 7.00 mL |
| **Purge** | **Variable** | Sweep Needle Time | 0.25 min |
| Prepurge Time | 0.00 min | Desorb Preheat Temp | 245 ºC |
| Prepurge Flow | 0 mL/min | GC Start Signal | Begin Desorb |
| Preheat Mix Speed | Slow | Desorb Time | 2.00 min |
| Sample Preheat Time | 0.00 min | Drain Flow | 300 mL/min |
| Presweep Time | 0.25 min | Desorb Temp | 250 ºC |
| Water Volume | 10.00 mL | **Bake** | **Variable** |
| Sweep Water Time | 0.25 min | Bake Time | 2.00 min |
| Sweep Water Flow | 100 mL/min | Bake Flow | 200 mL/min |
| Sparge Vessel Heater | Off | Bake Temp | 280 ºC |
| Purge Mix Speed | Medium | MCS Bake Temp | 180 ºC |
| Purge Time | 11.00 min | **Trap** | #9 |
| Purge Flow | 40 mL/min | **Purge Gas** | Nitrogen |



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| Table III Teledyne Tekmar Atomx XYZ Methanol Extraction Method Conditions | | | |
|---|---|---|---|
| **Standby** | **Variable** | **Desorb** | **Variable** |
| Valve Oven Temp | 140 ºC | Methanol Needle Rinse | On |
| Transfer Line Temp | 140 ºC | Methanol Needle Rinse Volume | 2.0 mL |
| Sample Mount Temp | 90 ºC | Water Needle Rinse Volume | 7.0 mL |
| Water Heater Temp | 90 ºC | Sweep Needle Time | 0.25 min |
| Soil Valve Temp | 100 ºC | Desorb Preheat Temp | 245 ºC |
| Standby Flow | 10 mL/min | GC Start Signal | Begin Desorb |
| Purge Ready Temp | 40 ºC | Desorb Time | 2.00 min |
| **Purge** | **Variable** | Drain Flow | 300 mL/min |
| Presweep Time | 0.25 min | Desorb Temp | 250 ºC |
| Methanol Volume | 10.0 mL | **Bake** | **Variable** |
| Sparge Vessel Heater | Off | Methanol Glass Rinse | On |
| Sample Mix Speed | Medium | Methanol Glass Rinse Volume | 3.0 mL |
| Sample Mix Time | 2.00 min | Number of Methanol Glass Rinses | 1 |
| Sample Mix Settle Time | 2.00 min | Number of Water Bake Rinses | 1 |
| Sample Sweep Time | 0.25 min | Water Bake Rinse Volume | 7.0 mL |
| Sample Sweep Flow | 100 mL/min | Bake Rinse Sweep Time | 0.25 min |
| Purge Time | 11.00 min | Bake Rinse Sweep Flow | 100 mL/min |
| Purge Flow | 40 mL/min | Bake Rinse Drain Time | 0.40 min |
| Purge Temp | 20 ºC | Bake Time | 2.00 min |
| MCS Purge Temp | 20 ºC | Bake Flow | 200 mL/min |
| Dry Purge Time | 0.5 min | Bake Temp | 280 ºC |
| Dry Purge Flow | 100 mL/min | MCS Bake Temp | 180 ºC |
| Dry Purge Temp | 20 ºC | **Trap** | 9 |
| | | **Purge Gas** | Helium |



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| Table IV Agilent 7890B GC/5977B MS System Conditions | |
|---|---|
| **Agilent 7890B GC Conditions** | |
| Column | Rtx® VMS, 20 m x 0.18 mm, 1 µm Film, Hydrogen – 1 mL/min |
| Oven Profile | 35 ºC, 4 min, 15 ºC/min to 85 ºC, 30 ºC/min to 225 ºC, 2 min Hold, Run Time 14 min |
| Inlet | 180 ºC, 80:1 Split, Purge Flow 0.5 mL/min |
| **Agilent 5977B MS Conditions** | |
| Temp | Transfer Line 225 ºC; Source 250 ºC; Quad 200 ºC |
| Scan | Range 35 *m/z* to 260 *m/z*, Solvent Delay 0.50 min, Normal Scanning |
| Current | Gain Factor 5.00, Autotune |

## Results

The relative standard deviation (%RSD) of the RFs for the calibration curve, MDL, precision and mid-point verification accuracy and precision data are shown in Table V (water), Table VI (soil) and Table VII (high-level soil). Figure 1 (water) and Figure 2 (soil) display a 20 ppb standard, indicating excellent peak resolution with minimal water inference for all VOCs. Figure 3 displays an overlay of seven, 50 ppb (final concentration) 1,3,5-Trimethylbenzene PVOC/GRO Mix (Wisconsin) samples methanol extracted by the Atomx XYZ.

**Table V Wisconsin GRO Method Water Calibration, MDL and Mid-Point Verification Data**

| Compound | Calibration (9-point curve) | | | | MDL (n=7, 0.5 ppb) | | | Mid-Point Verification (n=7, 20 ppb) | |
|---|---|---|---|---|---|---|---|---|---|
| | Retention Time | Target Ion | Linearity RF (%RSD) | Avg. RF | Avg. Conc. | MDL (ppb) | Precision (≤20%) | Accuracy (±30%) | Precision (≤20%) |
| Pentafluorobenzene (IS) | 3.81 | 168 | | | | | | | |
| Methyl tert-butyl ether (MTBE) | 1.85 | 73 | 7.66 | 0.850 | 0.53 | 0.03 | 1.5 | 127 | 3.9 |
| Dibromofluoromethane (Surr) | 3.13 | 111 | 3.84 | 0.394 | 25.3 | | 0.87 | 99 | 1.5 |
| Benzene | 3.55 | 78 | 8.88 | 1.17 | 0.59 | 0.13 | 7.3 | 108 | 2.2 |
| 1,2-Dichloroethane-d4 (Surr) | 3.74 | 65 | 1.91 | 0.406 | 25.1 | | 1.2 | 102 | 2.0 |
| 1,4-Difluorobenzene (IS) | 4.50 | 114 | | | | | | | |
| Toluene-d8 (Surr) | 6.11 | 98 | 4.92 | 1.16 | 24.6 | | 0.71 | 101 | 0.80 |
| Toluene | 6.16 | 91 | 5.49 | 1.10 | 0.79 | 0.09 | 3.6 | 108 | 3.5 |
| Chlorobenzene-d5 (IS) | 7.65 | 117 | | | | | | | |
| Ethylbenzene | 7.73 | 91 | 5.84 | 1.27 | 0.57 | 0.10 | 5.6 | 111 | 3.0 |
| m,p-Xylene | 7.87 | 91 | 8.73 | 0.954 | 1.12 | 0.15 | 4.4 | 112 | 2.9 |
| o-Xylene | 8.19 | 91 | 9.57 | 1.05 | 0.57 | 0.09 | 5.0 | 110 | 2.9 |
| Bromofluorobenzene (BFB) (Surr) | 8.60 | 95 | 2.50 | 0.418 | 25.8 | | 1.8 | 101 | 1.5 |
| 1,3,5-Trimethylbenzene | 8.86 | 105 | 8.96 | 1.08 | 0.54 | 0.12 | 7.1 | 113 | 3.3 |
| 1,2,4-Trimethylbenzene | 9.10 | 105 | 9.06 | 1.11 | 0.54 | 0.08 | 4.9 | 111 | 2.8 |
| 1,4-Dichlorobenzene-d4 (IS) | 9.31 | 150 | | | | | | | |
| Naphthalene | 10.60 | 128 | 15.5 | 1.51 | 0.57 | 0.07 | 3.8 | 118 | 3.1 |



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| Table VI Wisconsin GRO Method Soil Calibration, MDL and Mid-Point Verification Data | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | Calibration (8-point curve) | | | | MDL (n=7, 2 ppb) | | | Mid-Point Verification (n=7, 20 ppb) | |
| | Retention Time | Target Ion | Linearity RF (%RSD) | Avg. RF | Avg. Conc. | MDL (ppb) | Precision (≤20%) | Accuracy (±30%) | Precision (≤20%) |
| Pentafluorobenzene (IS) | 3.83 | 168 | | | | | | | |
| Methyl tert-butyl ether (MTBE) | 1.86 | 73 | 9.77 | 0.953 | 1.98 | 0.26 | 4.1 | 97 | 2.6 |
| Dibromofluoromethane (Surr) | 3.15 | 111 | 4.34 | 0.394 | 25.9 | | 2.1 | 101 | 2.8 |
| Benzene | 3.57 | 78 | 9.81 | 1.39 | 2.00 | 0.30 | 4.8 | 93 | 2.6 |
| 1,2-Dichloroethane-d4 (Surr) | 3.76 | 65 | 5.26 | 0.320 | 26.1 | | 2.4 | 102 | 2.7 |
| 1,4-Difluorobenzene (IS) | 4.51 | 114 | | | | | | | |
| Toluene-d8 (Surr) | 6.11 | 98 | 3.97 | 1.20 | 24.4 | | 1.0 | 101 | 1.4 |
| Toluene | 6.16 | 91 | 13.8 | 1.62 | 2.02 | 0.22 | 3.5 | 87 | 3.7 |
| Chlorobenzene-d5 (IS) | 7.65 | 117 | | | | | | | |
| Ethylbenzene | 7.73 | 91 | 9.73 | 1.83 | 1.93 | 0.31 | 5.1 | 90 | 4.3 |
| m,p-Xylene | 7.87 | 91 | 12.1 | 1.39 | 3.99 | 0.26 | 2.0 | 92 | 3.8 |
| o-Xylene | 8.20 | 91 | 9.97 | 1.46 | 1.97 | 0.27 | 4.3 | 91 | 4.0 |
| Bromofluorobenzene (BFB) (Surr) | 8.60 | 95 | 2.00 | 0.421 | 25.7 | | 0.56 | 102 | 1.6 |
| 1,3,5-Trimethylbenzene | 8.86 | 105 | 7.26 | 1.51 | 1.86 | 0.30 | 5.2 | 92 | 3.4 |
| 1,2,4-Trimethylbenzene | 9.10 | 105 | 8.21 | 1.46 | 1.87 | 0.23 | 3.8 | 91 | 3.5 |
| 1,4-Dichlorobenzene-d4 (IS) | 9.31 | 150 | | | | | | | |
| Naphthalene | 10.59 | 128 | 12.3 | 1.72 | 1.96 | 0.40 | 6.4 | 91 | 3.5 |



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| Table VII Wisconsin GRO Method High-Level Soil Methanol Extraction Calibration and Reproducibility Data | | | | | | |
|---|---|---|---|---|---|---|
| Compound | Calibration (5-point curve) | | | | Reproducibility (n=7, 50 ppb) | |
| | Retention Time | Target Ion | Linearity RF (%RSD) | Avg. RF | Accuracy (±30%) | Precision (≤20%) |
| Pentafluorobenzene (IS) | 3.83 | 168 | | | | |
| Methyl tert-butyl ether (MTBE) | 2.01 | 73 | 5.72 | 2.08 | 92 | 10.1 |
| Dibromofluoromethane (Surr) | 3.16 | 111 | 10.3 | 0.272 | 127 | 7.9 |
| Benzene | 3.63 | 78 | 5.28 | 2.05 | 88 | 19.4 |
| 1,2-Dichloroethane-d4 (Surr) | 3.76 | 65 | 6.96 | 0.610 | 107 | 5.2 |
| 1,4-Difluorobenzene (IS) | 4.52 | 114 | | | | |
| Toluene-d8 (Surr) | 6.12 | 98 | 2.05 | 1.13 | 98 | 1.7 |
| Toluene | 6.18 | 91 | 9.66 | 1.24 | 93 | 14.2 |
| Chlorobenzene-d5 (IS) | 7.66 | 117 | | | | |
| Ethylbenzene | 7.74 | 91 | 4.14 | 1.39 | 90 | 10.6 |
| m,p-Xylene | 7.89 | 91 | 5.52 | 1.06 | 90 | 10.6 |
| o-Xylene | 8.20 | 91 | 3.71 | 1.10 | 91 | 8.7 |
| Bromofluorobenzene (BFB) (Surr) | 8.60 | 95 | 3.31 | 0.462 | 95 | 1.6 |
| 1,3,5-Trimethylbenzene | 8.87 | 105 | 4.09 | 1.26 | 94 | 6.1 |
| 1,2,4-Trimethylbenzene | 9.11 | 105 | 3.58 | 1.25 | 94 | 6.2 |
| 1,4-Dichlorobenzene-d4 (IS) | 9.32 | 150 | | | | |
| Naphthalene | 10.59 | 128 | 5.32 | 1.35 | 105 | 3.9 |

**Figure 1** Total Ion Chromatogram (TIC) of a Water Method 20 ppb PVOC/GRO Mix (Wisconsin) Standard Indicating Consistent Peak Shapes for all Compounds with Minimal Water Interference.
1. Methyl tert-butyl ether (MTBE) 2. Dibromofluoromethane (Surr) 3. Benzene
4. 1,2-Dichloroethane-d4 (Surr) 5. Pentafluorobenzene (IS) 6. 1,4-Difluorobenzene (IS)
7. Toluene-d8 (Surr) 8. Toluene 9. Chlorobenzene-d5 10. Ethylbenzene 11. m,p-Xylene
12. o-Xylene 13. Bromofluorobenzene (BFB) (Surr) 14. 1,3,5-Trimethylbenzene
15. 1,2,4-Trimethylbenzene 16. 1,4-Dichlorobenzene-d4 (IS) 17. Naphthalene.

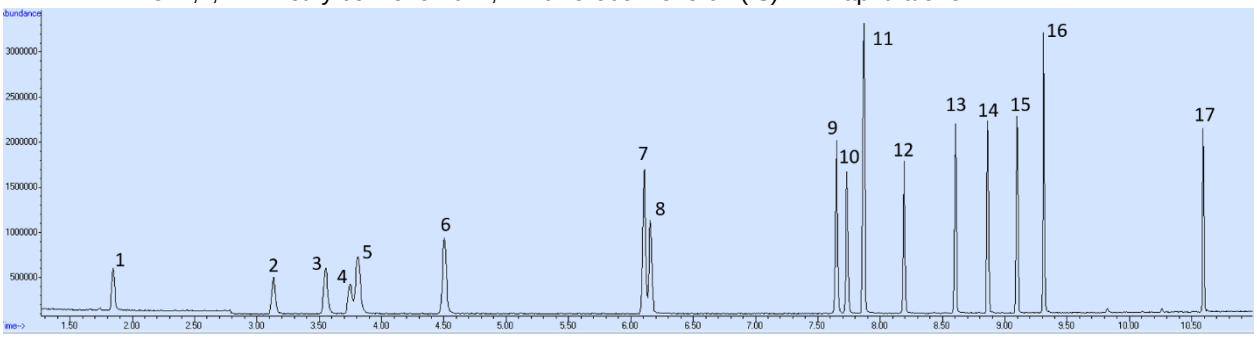



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**Figure 2** Total Ion Chromatogram (TIC) of a Soil Method 20 ppb PVOC/GRO Mix (Wisconsin) Standard Indicating Consistent Peak Shapes for all Compounds with Minimal Water Interference.
1. Methyl tert-butyl ether (MTBE) 2. Dibromofluoromethane (Surr) 3. Benzene
4. 1,2-Dichloroethane-d4 (Surr) 5. Pentafluorobenzene (IS) 6. 1,4-Difluorobenzene (IS)
7. Toluene-d8 (Surr) 8. Toluene 9. Chlorobenzene-d5 10. Ethylbenzene 11. m,p-Xylene
12. o-Xylene 13. Bromofluorobenzene (BFB) (Surr) 14. 1,3,5-Trimethylbenzene
15. 1,2,4-Trimethylbenzene 16. 1,4-Dichlorobenzene-d4 (IS) 17. Naphthalene *Septum bleed from sample vial.

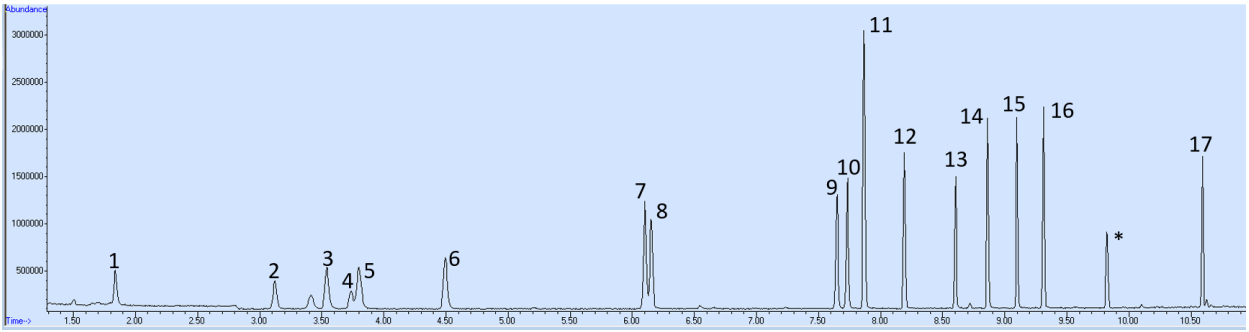
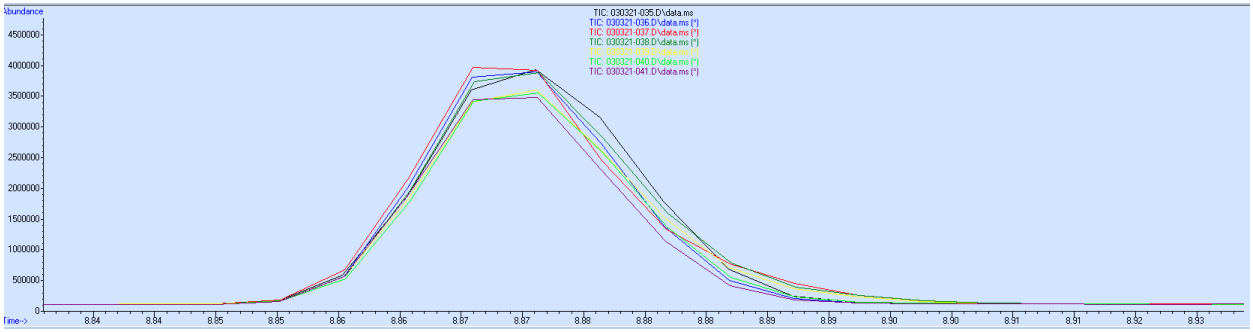



**Figure 3** Total Ion Chromatogram (TIC) of (n=7 replicates) 1,3,5-trimethylbenzene Methanol Extracted High-Level Soil Samples Containing a Final Concentration of 50 ppb PVOC/GRO Mix (Wisconsin) Displaying Excellent Reproducibility with a 6.1% RSD and a 94% Recovery.




## Conclusion

This study demonstrates the Teledyne Tekmar Atomx XYZ P&T system's ability to process VOCs in water, soil and high-level soil samples following the Wisconsin GRO Method with detection by an Agilent 7890B GC and 5977B MS. The %RSD of the calibration curve passed all method requirements. Furthermore, MDL and precision for seven 0.5 ppb standards for the water method, and seven 2 ppb standards for the soil method, showed minimal interference from excessive water. Resulting values were <0.15 ppb for the water method and <0.40 ppb for the soil method. The mid-point verification check with precision and accuracy for seven 20 ppb water standards displayed <4% RSD for all compounds and an average recovery of 109%. The mid-point verification check with precision and accuracy for seven 20 ppb soil standards displayed <4.3% RSD for all compounds with an average recovery of 95%. Furthermore, the Atomx XYZ's automated methanol extraction was able to process high-level soil samples with a >88% recovery and <11% RSD over seven replicates for all but one compound.

By making additional, appropriate changes to the GC oven temperature program, the GC/MS cycle time may also be reduced, increasing laboratory throughput in a 12-hour period.

## References

1. Wisconsin Department Natural Resources (DNR), *Modified GRO Method for Determining Gasoline Range Organics,* September 1995. [Online] https://dnr.wi.gov/regulations/labcert/documents/methods/grosep95.pdf (accessed March 09, 2021)



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