

# Methanol Extraction of high level soil samples by USEPA Method 8260C

## **Abstract**

In order to determine the concentration of Volatile Organic Compounds (VOCs) in soil and waste samples the USEPA developed Method 8260C in conjunction with preparative Method 5035. USEPA Method 5035 describes the process for which solids such as soils, are prepared using purge and trap technology. This includes the handling of soils which exceed normal VOC concentration levels (>200ug/kg). For this study a working linear calibration curve and Method Detection Limits (MDLs) for high level soil samples will be analyzed by Teledyne Tekmar's Atomx, an automated VOC sample prep system. The Atomx will utilize an automated methanol extraction process, followed by purge and trap concentrator in conjunction with a gas chromatography mass spectrometer (GC/MS) to determine the concentration of VOCs in high level samples.

## **Introduction**

USEPA Method 5035 has two sample collection options that can be used in accordance with USEPA Method 8260C.<sup>1,2</sup> The first option is to collect 5g of soil into a pre-weighed vial containing a prescribed amount of a water miscible solvent (Methanol). An aliquot of this sample is taken and purged using USEPA Method 5030.<sup>3</sup> The second option involves collecting a bulk soil sample on site. Once back in the lab the bulk soil can be separated into individual samples containing a water miscible solvent. Then, like the first method, an aliquot of this sample is taken and purged using USEPA Method 5030.<sup>2</sup>

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.

This integrated platform of the Atomx allows for analyzing 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 variable internal standard and surrogate volumes automatically and new clean up techniques further improve sample capacity which is critical to the success of environmental testing laboratories.

Since high level soil analysis requires methanol extraction, these extra steps adds time to the analysis. By using the Atomx, the instrument automates the methanol extraction. A soil sample with a VOC concentration of >200ug/kg is sampled in the field and placed into a 40mL VOA vial. The vial is then placed on the carousel of the Atomx. Once the high level soil sample is ready for analysis the vial is raised up on to the three stage needle. Once on the needle, the Atomx adds the prescribed amount of methanol to the sealed vial. Mixing or agitation is applied to the vial to release the VOC from the soil into the methanolic solution. An aliquot of the methanolic solution is added to 5mL of de-ionized water and is analyzed under normal purge and trap conditions.

In this study, methanol extraction was evaluated by USEPA Method 8260C and utilizing the Atomx with an Agilent 7890A CG and a 5975C inert XL Mass Selective Detector (MSD). A linear calibration curve, Method Detection Limits (MDLs) and percent recovery were performed for this application note. Water samples were analyzed using a 5mL sample volume, while the soil analysis required 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		MSD Parameters	
GC:	Agilent 7890A	MSD:	5975C inert XL
Column:	Restek RTX-VMS 20m x 0.18mmID x 1um	Source:	230°C
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	Quad:	150°C
Inlet:	220°C	Solvent Delay:	0.5 min
Column Flow:	0.9mL/min	Scan Range:	m/z 35-270
Gas:	Helium	Scans:	5.76 scans/sec
Split:	80:1	Threshold:	150
Pressure:	21.542 psi	MS Transfer Line Temp:	230°C
Inlet:	Split/Split less		

Tables 1 & 2: GC and MSD Parameters

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.)

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 and Reproducibility Study

A 50ppm working calibration standard was prepared in methanol for all USEPA 8260C compounds. Calibration standards were then serially diluted with de-ionized water over a range from 0.5-200ppb. A 25ppm surrogate 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 to have a final concentration of 25ppb.

The calibration data was processed using Agilent Chemstation Software. The Relative Response Factors (RRF) of all analytes were evaluated for response and linearity. The water calibration curve met all USEPA 8260C<sup>1</sup> performance criteria with results listed in Table 5.

To show the accuracy and precision of the methanol extraction option on the Atomx, a reproducibility study was performed. Five replicate samples containing 10ppm BTEX (Benzene Toluene Ethylbenzene and Xylenes) were methanol extracted to have a final concentration of 100ppb. Figure 1 shows the Total Ion Chromatogram for the final 100ppb methanol extracted sample. This study shows the efficiency of the extraction, the accuracy of the dilution and the reproducibility of the analysis. The results are listed in Table 6.

Compound	Avg RF	Calibration %RSD	MDL	Compound	Avg RF	Calibration %RSD	MDL
Dichlorodifluoromethane	0.329	13.04	0.299	Bromodichloromethane	0.294	4.53	0.252
Chloromethane	0.502	5.62	0.298	2-Chloroethyl Vinyl Ether	0.205	5.42	0.108
Vinyl Chloride	0.374	3.63	0.192	cis-1,3-dichloropropene	0.333	6.07	0.223
Bromomethane	0.304	15.08	0.289	Toluene-d8 (surr)	1.002	0.88	0.809
Chloroethane	0.206	6.10	0.196	4-Methyl-2-Pentanone	0.102	12.13	0.344

Trichloromonofluoromethane	0.524	9.84	0.255	Toluene	1.129	3.36	0.119
Diethyl Ether	0.182	7.63	0.236	trans-1,3-Dichloropropene	0.322	7.10	0.081
1,1,2-trichlorotrifluoroethane	0.325	9.88	0.387	Ethyl Methacrylate	0.351	8.62	0.131
1,1-Dichloroethene	0.293	5.77	0.190	Tetrachloroethylene	0.518	4.46	0.217
Carbon Disulfide	0.635	6.86	1.332	1,1,2-Trichloroethane	0.195	6.24	0.234
Iodomethane*	0.523	0.9989	0.150	1,3-Dichloropropane	0.384	4.68	0.146
Acetone*	0.133	0.9995	1.566	2-Hexanone	0.555	4.65	0.178
Allyl Chloride	0.155	6.44	0.277	Dibromochloromethane	0.381	10.37	0.080
Methyl Acetate	0.726	11.46	0.463	Butyl Acetate	0.758	12.56	0.156
Acetonitrile	0.198	16.12	1.169	1,2-Dibromoethane	0.365	4.14	0.162
Methylene Chloride	0.319	5.23	0.113	Chlorobenzene	1.008	5.12	0.128
Tert butyl Alcohol	0.055	14.11	4.049	1,1,1,2-Tetrachloroethane	0.381	7.57	0.212
Methyl tert butyl Ether	0.961	2.73	0.178	Ethylbenzene	1.361	5.74	0.153
trans-1,2-Dichloroethene	0.339	4.00	0.435	m-p-Xylene	0.627	5.73	0.324
Acrylonitrile	0.352	3.54	0.383	o-Xylene	0.617	5.51	0.078
1,1-Dichloroethane	0.550	4.74	0.206	Styrene	0.985	9.24	0.154
Chloroprene	0.546	4.95	0.185	Bromoform	0.287	16.40	0.099
Vinyl Acetate	0.856	9.18	0.259	Amyl Acetate*	0.614	0.9980	0.133
Ethyl tert butyl Ether	1.136	3.72	0.096	Isopropylbenzene	1.540	7.52	0.122
2,2-Dichloropropane	0.434	3.14	0.110	cis-1,4-Dichloro-2-butene	0.189	11.48	0.345
cis-1,2-Dichloroethene	0.416	3.62	0.292	Bromofluorobenzene (surr)	0.400	2.22	1.050
2-Butanone	0.099	8.34	0.435	Bromobenzene	0.475	4.46	0.168
Methyl Acrylate	0.706	3.03	0.153	n-Propylbenzene	1.526	10.68	0.166
Propionitrile	0.155	10.34	0.388	1,1,2,2-Tetrachloroethane*	0.499	0.9993	0.197
Bromochloromethane	3.510	6.98	0.217	1,2,3-Trichloropropane	0.628	2.00	0.242
Tetrahydrofuran	0.489	4.92	0.134	trans-1,4-Dichloro-2-butene	0.278	10.37	0.211
Chloroform	0.561	4.73	0.113	2-Chlorotoluene	1.560	4.45	0.120
Methacrylonitrile	0.493	5.23	0.143	1,3,5-Trimethylbenzene	2.118	5.76	0.095
1,1,1-Trichloroethane	0.558	5.15	0.135	4-Chlorotoluene	1.556	7.47	0.134
Dibromofluoromethane (surr)	0.371	4.92	1.248	tert-Butylbenzene	2.096	7.24	0.065
Carbon Tetrachloride	0.523	10.00	0.119	1,2,4-Trimethylbenzene	2.168	6.71	0.094
1,1-Dichloropropane	0.380	9.72	0.487	sec-Butylbenzene	2.723	8.63	0.126
Benzene	1.308	3.56	0.128	1,3-Dichlorobenzene	1.460	7.27	0.124
1,2-Dichloroethane	0.444	2.98	0.123	p-Isopropyl toluene	2.608	9.03	0.120
tert Amyl Methyl Ether	0.973	3.50	0.174	1,4-Dichlorobenzene	1.468	7.31	0.249
Isopropyl Acetate	1.232	2.80	0.121	n-Butylbenzene	1.727	10.65	0.193
Trichloroethylene	0.328	8.53	0.185	1,2-Dichlorobenzene	1.504	3.37	0.124
1,2-Dichloropropane	0.233	4.57	0.160	1,2,4-Trichlorobenzene	0.998	12.35	0.260
Dibromomethane	0.179	3.88	0.178	Hexachlorobutadiene	0.322	10.69	0.328

Methyl Methacrylate	0.234	6.58	0.290	Naphthalene	4.300	9.87	0.042
n-Propyl acetate	0.749	5.18	0.112	1,2,3-Trichlorobenzene	1.002	10.90	0.272

Table 5: Experimental Calibration Results. \* Compound was linear regressed

Compounds	Calibration %RSD	Extraction Results %Recovery
Dibromofluoromethane*	4.92	94.8
Benzene**	3.56	98.5
Toluene d8*	0.88	101.6
Toluene**	3.36	94.6
Ethylbenzene**	5.74	93.7
m-,p-Xylene**	5.73	94.0
O-Xylene**	5.51	96.1
Bromofluorobenzene*	2.22	101.2

Table 6: Results % Recovery (n=5). \*Surrogate compounds recoveries.

\*\* Analytes of interest (BTEX compounds) recoveries

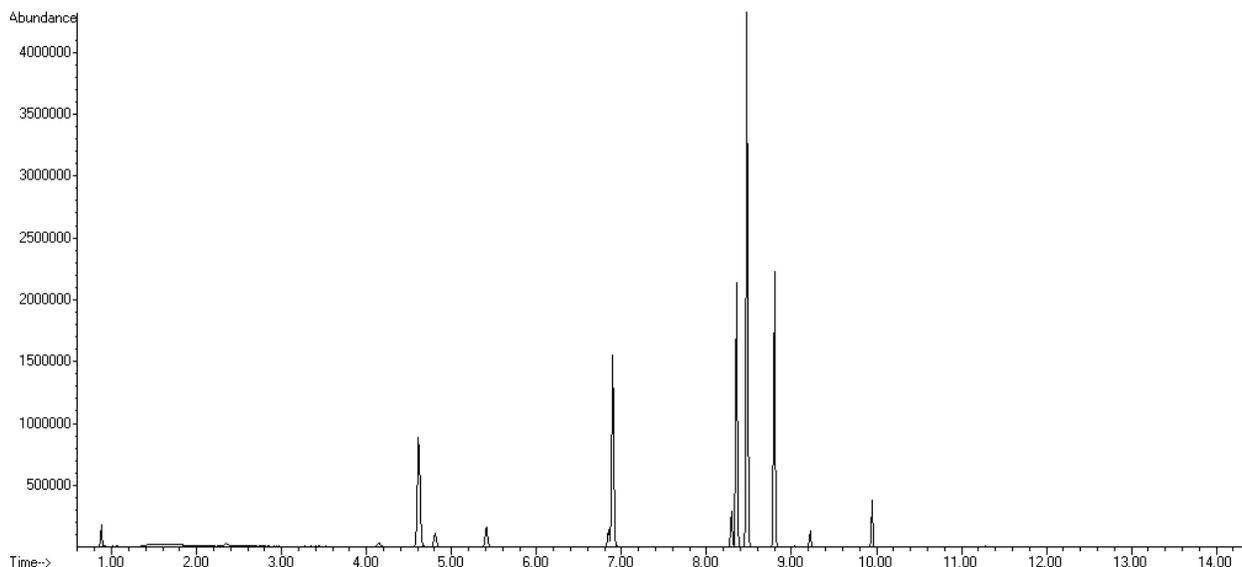


Figure 1: Total Ion Chromatogram (TIC) of a 100ppb BTEX standard Methanol Extracted by Atomx.

## Conclusions

This study validates the use of the Atomx automated sample prep system in conjunction with an Agilent 7890/5975 GC/MS for the USEPA Method 8260C with preparative Method 5035. Calibration and MDLs met all performance criteria of the method. The versatility provided by 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 methanol rinsing function can also help control/eliminate carryover. The Atomx proves to be an excellent system to increase productivity in the lab.

## References

1. USEPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 3, August 2006
2. USEPA Method 5035 Closed-System Purge-And Trap and Extractions For Volatile Organics In Soil and Waste Samples Revision 1, July 2002
3. USEPA Method 5030 Purge-And-Trap For Aqueous Samples Revision 3, May 2003