

# Automated Handling Techniques for the Analysis of Elevated Volatile Organic Compound (VOC) Concentrations in Soils Utilizing the Atomx Concentrator/Multimatrix Autosampler

## Application Note

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### Abstract

This application note discusses the processes used in USEPA Method 5035 for solid waste as it pertains to concentration levels that exceed the working calibration range used for low level analysis. Typically 200µg/kg is chosen as the highest calibration level. Any sample that exceeds this level must be reduced in response to fall within the calibration range. In this case, the high level soil is to be extracted using methanol as the extraction solvent. After the extraction is complete an aliquot of the methanolic portion of the sample is diluted in 5mL of de-ionized water. The sample is then transferred to a purge and trap for concentration under USEPA Method 5030. The determinative method for this paper is USEPA Method 8260b for use with a gas chromatograph coupled with a mass spectrometer. Several challenges arise from the implementation of this technique such as methanol interference and contamination, dilution error, extraction interference and carryover. The potential for human error and loss of volatiles during the extraction and dilution process are greatly reduced with this new automated technique.

### Introduction

In USEPA Method 5035 there are two sample collection options for samples containing high levels of Volatile Organic Compounds (VOCs). The first method involves collecting a bulk soil sample in the field. In the lab, the bulk soil is dispersed in a water miscible solvent. Next, an aliquot of the solution is added to 5mL of water and finally, the sample is purged using Method 5030. The second option is to collect 5g soil sample and add it to a pre-weighed vial containing a prescribed amount of a water miscible solvent. An aliquot of this solution is then purged using Method 5030. Both of these processes are time consuming and have the potential to introduce human error both in the field and in the laboratory.

Teledyne Tekmar has consistently been at the cutting edge of Purge and Trap (P&T) technology. In keeping with this tradition, Teledyne Tekmar has developed a new combination P&T concentrator/Multi-Matrix Autosampler, the Atomx. This new system can not only run waters and soils, but can also automate the sample extraction of high level VOC soils, thus improving laboratory efficiency. The Atomx offers our proprietary #9 U-shaped adsorbent trap, as seen with our Stratum PTC. The autosampler utilizes an 80 position carousel drive platform for proven reliability. The system offers uniform heating throughout the sample gas pathway. Siltek™ coated stainless steel and PEEK™ tubing aid in the reduction of carryover.

In this study, data was collected to evaluate methanol extracted samples utilizing the Atomx in conjunction with an Agilent 7890A Gas Chromatograph (GC) and a 5975C inert XL Mass Selective Detector (MSD). The efficiency, reproducibility, and linearity of compound response were evaluated by comparing the automated Atomx extraction process with the traditional manual extraction technique. The Atomx proved to be an excellent system for performing extractions.

### Experimental-Instrument Conditions

As stated previously, the Atomx, an Agilent 7890A GC and a 5975C inert XL MSD were used for this analysis. The analytical trap used for this analysis was Teledyne Tekmar's proprietary #9 trap. Tables 1, 2, 3, 4 and 5 display the GC, MSD, and the varied Atomx conditions respectively.

GC Parameters	
GC:	Agilent 7890A
Column:	J&W Scientific DB-624 20m x 0.180mm x1.0µm
Oven Program:	35°C for 4 min; 16°C/min to 85°C for 0 min; 30°C /min to 210°C for 3 min, 14.29 min runtime
Inlet:	220°C
Column Flow	1.5mL/min
Gas:	Helium
Split:	80:1
Pressure:	27.49 psi
Inlet:	Split/Splitless

Table 1: GC Parameters

MSD Parameters	
MSD:	5975C inert XL
Source:	230°C
Quad:	150°C
Solvent Delay:	0.5 min
Scan Range:	m/z 35-300
Scans:	5.19 scans/sec
Threshold:	400
MS Transfer Line Temp:	230°C

Table 2: MSD Parameters

Atomx Methanol Parameters for 5g of Soil Extracted in 10mL of Methanol			
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
Water Heater Temp	90°C	Methanol Needle Rinse Volume	2.0mL
Soil Valve Temp	125°C	Water Needle Rinse Volume	7.0mL
Standby Flow	10mL/ min	Sweep Needle Time	0.50 min
Purge Ready Temp	40°C	Desorb Preheat Temp	245°C
Condensate Trap Standby	45°C	GC Start Signal	Start of Desorb
Presweep Time	0.25 min	Desorb Time	1.00 min
Methanol Volume	10.0mL	Drain Flow	300mL/min
Spurge Vessel Heater	Off	Desorb Temp	250°C
Spurge Vessel Temp	20°C	Methanol Glass Rinse	On
Prepurge Time	0.00 min	Number of Methanol Glass Rinses	1
Prepurge Flow	0mL/min	Methanol Glass Rinse Volume	3.0mL
Sample Mix Speed	Medium	Number Of Bake Rinses	1
Sample Mix Time	2.00 min	Water Bake Rinse Volume	7.0mL
Sample Mix Settle Time	1.00 min	Bake Rinse Sweep Time	0.25 min
Sample Sweep Time	0.25 min	Bake Rinse Sweep Flow	100mL/min
Sample Sweep Flow	100mL/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	0.50 min		

Table 3: Atomx Methanol Extraction Parameters (parameters highlighted in yellow were not used.)

Atomx Methanol Parameters for 7g of Soil Extracted in 7mL of Methanol			
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
Water Heater Temp	90°C	Methanol Needle Rinse Volume	2.0mL
Soil Valve Temp	125°C	Water Needle Rinse Volume	7.0mL
Standby Flow	10mL/ min	Sweep Needle Time	0.50 min
Purge Ready Temp	40°C	Desorb Preheat Temp	245°C
Condensate Trap Standby	45°C	GC Start Signal	Start of Desorb
Presweep Time	0.25 min	Desorb Time	1.00 min
Methanol Volume	7.0mL	Drain Flow	300mL/min
Spurge Vessel Heater	Off	Desorb Temp	250°C
Spurge Vessel Temp	20°C	Methanol Glass Rinse	On
Prepurge Time	0.00 min	Number of Methanol Glass Rinses	1
Prepurge Flow	0mL/min	Methanol Glass Rinse Volume	3.0mL
Sample Mix Speed	Medium	Number Of Bake Rinses	1
Sample Mix Time	2.00 min	Water Bake Rinse Volume	7.0mL
Sample Mix Settle Time	1.00 min	Bake Rinse Sweep Time	0.25 min
Sample Sweep Time	0.25 min	Bake Rinse Sweep Flow	100mL/min
Sample Sweep Flow	100mL/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	0.50 min		

Table 4: Atomx Methanol Extraction Parameters (parameters highlighted in yellow were not used.)

Atomx Parameters for a Manual Extraction			
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	0.50 min
Soil Valve Temp	125°C	Desorb Preheat Temp	245°C
Standby Flow	10mL/ min	GC Start Signal	Start of Desorb
Purge Ready Temp	40°C	Desorb Time	1.00 min
Condensate Trap Standby	45°C	Drain Flow	300mL/min
Presweep Time	0.25 min	Desorb Temp	250°C
Prime Sample Fill Volume	3.0mL	Methanol Glass Rinse	On
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
Spurge Vessel Heater	Off	Water Bake Rinse Volume	7.0mL
Spurge Vessel Temp	20°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	0.50 min		

Table 5: Atomx Manual Extraction Parameters (parameters highlighted in yellow were not used.)

## Calibration

A 50ppm working calibration standard was prepared in methanol. Calibration standards were prepared in a 50 milliliter (mL) volumetric flask filled to volume with de-ionized water. Each calibration standard was spiked with 1mL of methanol to accurately mimic the final volume of methanol that would occur with the extracted samples. The calibration range was 1.0-200ppb. The calibration standards were transferred to headspace free 40mL vials for analysis. A 25ppm Internal Standard (IS) was prepared in methanol and transferred to the standards vessel of the Atomx, the IS was then delivered in 5µl aliquots to the samples in order to hold the IS concentration at a constant 25ppb.

The calibration data was processed using Agilent Chemstation software. The relative response factors of all of the analytes were evaluated for response and linearity. The %RSD for all of the Wisconsin Gasoline Range Organic (GRO) compounds were 11.4% or better.

## **Carryover Evaluation**

When dealing with high level waste samples, system carryover and contamination can be a major concern. Carryover resulting from the Atomx automated methanol extraction method was evaluated by using a 5g sample of baked sand spiked with 20ppm of GRO standard, the spiked sand was then extracted with 10mLs of methanol. 100µls of the extract was then diluted into 5mLs of de-ionized water for a final concentration of 200ppb to be purged and used as the high level sample. For the three subsequent blanks, 5g of baked sand (unspiked) were extracted and then analyzed for carryover. Following a 20ppm extraction, the Atomx reduced carryover to less than 0.4% in the first blank. This achievement is possible due to the system's methanol rinsing function. The system is capable of rinsing the entire sample pathway with clean extraction solvent (patent pending) in between analyses. The results are listed in Table 8.

## **Extraction Performance Evaluation**

The concentration of analytes in a sample can vary; therefore, five different concentrations were chosen in order to test the linearity of the GRO compound responses when extracted on the Atomx as compared to a manual extraction. The Atomx extractions were tested with two different extraction volumes and sand masses. The automated extractions were compared with their respective manual extractions. See Table 6. Ten replicates of each of the extraction methods were run at all of the five concentrations. All of the methods produced reproducible compound responses resulting in a %RSD of less than 10%. The compound responses over the 5ppb to 100ppb concentration range also proved to be linear. In fact, when comparing the Atomx results to the manual extraction results, the Atomx system proved to be an excellent system for extractions. See Table 7.

## **Precision and Accuracy Study**

In order to demonstrate the precision and accuracy of the methanol extraction option on the Atomx, a reproducibility study was performed. Ten replicates of a 50ppb extraction level of a GRO standard were run on the Atomx. The ten replicate extractions were prepared both by the Atomx and manually so as to evaluate the three key functions of the process; the efficiency of the extraction, the accuracy of the dilution and the reproducibility of the analysis. See Extraction 1 and 2 on Table 6. The results of the study indicate that the automated extraction process of the Atomx is both accurate and reproducible. The results are listed in Table 8.

<b>Extraction 1</b>	5g of baked sand and a pill stir bar were placed in a 40mL vial and spiked with 50ppm GRO standard, the methanol addition, extraction and dilution were performed by the Atomx
<b>Extraction 2</b>	5g of baked sand was placed in a 40mL vial and spiked with 50ppm GRO standard, 10mL of methanol was added and the sample was extracted and diluted by the analyst.
<b>Extraction 3</b>	7g of baked sand and a pill stir bar were placed in a 40mL vial and spiked with 50ppm GRO standard, the methanol addition, extraction and dilution were performed by the Atomx
<b>Extraction 4</b>	7g of baked sand was placed in a 40mL vial and spiked with 50ppm GRO standard, 7mL of methanol was added and the sample was extracted and diluted by the analyst.

*Table 6: Extraction Descriptions*

Compound	Compound Response Linearity (R <sup>2</sup> Value)			
	Extraction 1	Extraction 2	Extraction 3	Extraction 4
MTBE	1.000	1.000	0.999	1.000
benzene	1.000	1.000	0.999	1.000
toluene	1.000	1.000	0.999	1.000
ethylbenzene	1.000	1.000	0.999	1.000
m&p xylene	1.000	1.000	0.999	1.000
ortho xylene	1.000	1.000	0.999	1.000
1,3,5-trimethylbenzene	1.000	1.000	0.999	1.000
1,2,4-trimethylbenzene	1.000	1.000	0.999	1.000
naphthalene	0.998	0.999	0.999	1.000

Table 7: Extraction Performance Results

Compound	Extraction Results 50ppb % Deviation		Extraction % Carryover
	Extraction 1	Extraction 2	
MTBE	83.09	88.03	0.00
dibromofluoromethane (surr)	84.92	87.70	0.01
benzene	90.56	87.58	0.07
toluene-d8 (surr)	92.07	92.92	0.17
toluene	90.61	88.48	0.26
ethylbenzene	92.11	92.69	0.18
m&p xylene	92.14	92.59	0.18
ortho xylene	88.23	91.14	0.11
BFB (surr)	85.27	88.51	0.43
1,3,5-trimethylbenzene	93.63	94.30	0.18
1,2,4-trimethylbenzene	92.60	92.77	0.24
naphthalene	84.51	99.32	0.38

Table 8: Results of the Precision and Accuracy and the Carryover Study

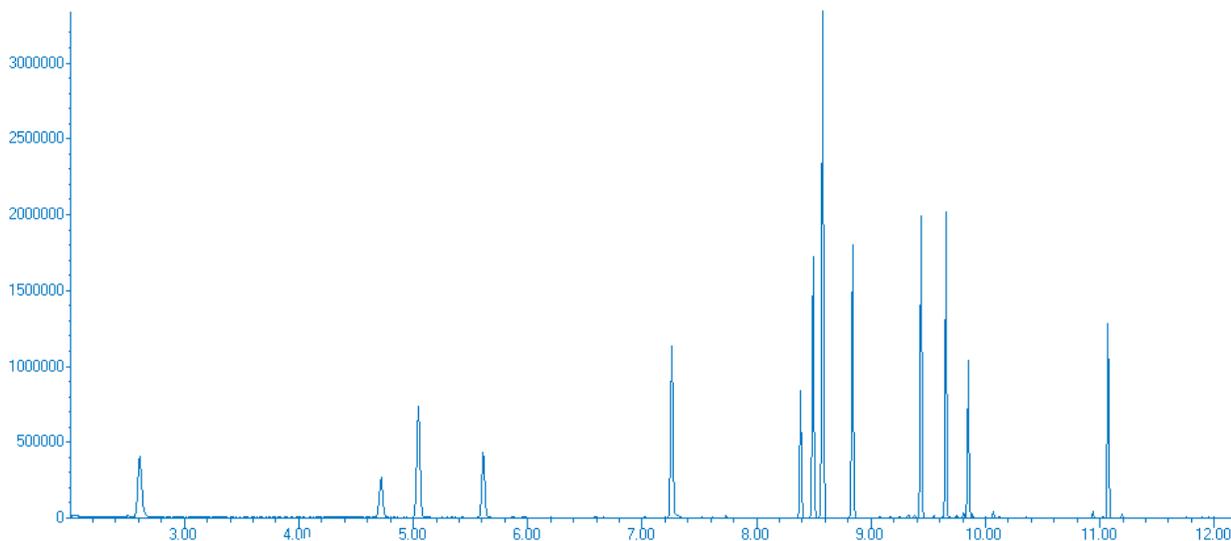


Figure 1: Total Ion Chromatogram of a 50ppb GRO Standard Extracted by the Atomx

## **Conclusions**

The new Atomx offers the best of both worlds, combining the P&T and the autosampler into one system resulting in a shorter sample pathway, improved temperature uniformity and decreased carryover. The concentrator is equipped with Teledyne Tekmar's innovative U-shaped proprietary #9 adsorbent trap; this trap is excellent in the removal of water and is better suited for handling increased volumes of methanol. The system uses a Siltek™ coated stainless steel sample pathway and PEEK™ tubing to aid in the reduction of carryover. The autosampler offers an 80 position carousel driven platform with three standard vessels for more versatility. The system also displayed remarkable reproducibility and accuracy in sample extraction for Gasoline Range Organics. The linearity of the compound response when comparing the Atomx to a manual extraction displayed how well the automated system works at both the low and high levels. The new Atomx system is so versatile that it can run waters, soils and automated sample extractions. The methanol extraction feature can save time and labor by automating sample extraction thus increasing your lab productivity.