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Automated Handling Techniques for the Analysis of Elevated Volatile Organic Compound (VOC) Concentrations in Soils

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Poster Presentation

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Abstract

This poster 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. This process is time consuming and has the potential to introduce human error both in the field and in the laboratory.

Teledyne Tekmar has developed a new autosampler that will improve laboratory efficiency. This new system can not only run waters and soils, but can also automate the sample extraction of high level VOC soils. 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. The Atomx offers our proprietary #9 U-shaped adsorbent trap, as seen with our Stratum PTC. The autosampler utilizes an 80 position carrousel 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 and reproducibility of the extractions were evaluated by comparing the automated Atomx 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, and 3 display the GC, MSD, and Atomx conditions.

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			
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
Sparge Vessel Heater	Off	Desorb Temp	250°C
Sparge 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.)

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 was 11.4% or better. The calibration results of the compounds of interest are listed in Table 5.

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 5.

Reproducibility 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 in two different ways 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 Table 4. 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 5.

Extraction1	5g of baked sand placed in 40mL vial and spiked with 500µl of a 50ppm standard, the extraction and dilution was performed by the Atomx.
Extraction 2	5g of baked sand placed in 40mL vial and spiked with 500µl of a 50ppm standard, the sample was extracted and diluted by the analyst.

Table 4: Extraction Descriptions