Flavors, Odors, and Contaminants in Alcoholic Beverages using Vacuum Assisted Sorbent Extraction (VASE) and GC/MS Analysis

Application Note:

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Overview

A new technique for analyzing the overall full range of volatile to semi-volatile organic compounds in high alcohol containing beverages using Vacuum Assisted Sorbent Extraction (VASE) in headspace paired with GCMS analysis is presented.

A cartridge containing approximately 70mg of Tenax is placed into a sample vial containing either neat or diluted sample containing a high amount of alcohol. A vacuum tight interface allows the vial headspace to be evacuated to less than 0.01 atmospheres, or at least to the point where an aqueous mixture starts to boil at 25°C. The vacuum is only applied for the time it takes to evacuate the vial, about 15-30 seconds depending on vial size. The vial remains under vacuum after removal of the vacuum source, creating a closed system where faster diffusion from the sample/headspace boundary layer to the adsorbent enhances rates of extraction for both low and higher volatility compounds.

Heavy volatile compounds with low vapor pressures which have little to no response by classical SPME are extracted 10-50x more efficiently. Unlike dynamic headspace, which uses an inert gas to sweep the volatiles of a sample through the adsorbent bed

to concentrate and trap analytes, VASE is performed statically. VASE allows the sample and headspace to come to an equilibrium in a closed system, causing analytes to diffuse onto and collect at the very front of the adsorbent bed. Therefore, VASE achieves a much better recovery of heavier compounds while eliminating the common carryover issues.

Once placed under vacuum, the extraction time ranges from minutes to hours until equilibrium between the sample and headspace is reached to produce complete, reproducible extractions. This helps to prevent changes in extraction efficiency when small differences in the sample matrix occur. Additionally, using a packed adsorbent trap for VASE has the advantage of providing 100x more capacity than a GC capillary columns, allowing split injections of 50:1 or more to achieve rapid injection rates while still maximizing the amount that can be loaded onto capillary a GCMS systems for maximum sensitivity and optimum detection limits. In the case of alcoholic beverages, an increased phase ratio is extremely important in dealing with the high affinity of most odor and flavor compounds to the high alcohol containing matrix (up to 40% alcohol by volume).

Data is presented showing rum, whiskey, and wine samples analyzed using VASE, with and without the addition of water or a saturated sodium sulfate solution to determine the optimum approach for recovering volatile to semi-volatile compounds in the sample. Calibration curves of trace level contaminants in wine are also presented showing calibrations from 0.1 to 20 ng/L for Trichloroanisoles, Tribromoanisole, Geosmin, and 2-Methylisoborneol, using Geosmin-d3 as the internal standard. Consistent recovery of

these compounds in spiked and non-spiked drinking water and wine demonstrated the ability to perform measurements in matrices with varied complexity and affinity for the target analytes. The results show the extensive range of compounds extracted using VASE. This demonstrates its potential as a sensitive and routine method for examining aroma compounds relating to flavor analysis and regulated contaminants such as trichloroanisoles and phthalates in alcoholic beverages.

Figure 1 - The vacuum tight seal allows samples to remain under vacuum after a 30 second evacuation, which allows elevated rates of static diffusion to collect significantly more headspace compounds on the adsorbent than can be collected at atmospheric pressure. Sorbent Pens are labeled with a bar code sticker to allow the operator or autosampler to simply scan the Sorbent Pen into the sequence table. The bar code also allows the tracking of each Sorbent Pen through its lifetime of hundreds to thousands of extractions and desorptions.
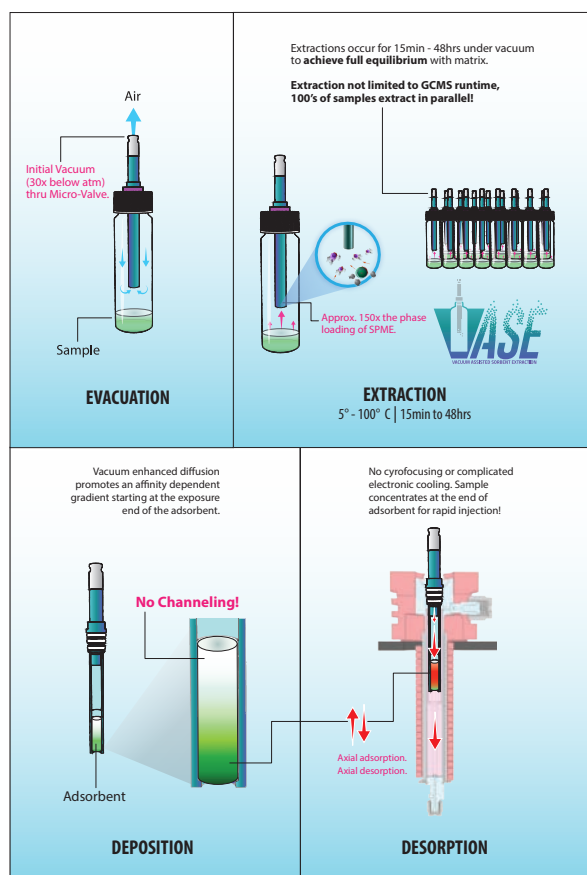

Figure 2 - Processes of a VASE sample from placing the vial under vacuum to desorption.

Introduction

Samples containing large amounts of alcohol (15-40% alcohol by volume) present a challenge for headspace analysis. Before aroma compounds and contaminants can be separated and analyzed, they must be extracted from the alcoholic beverage matrix. Extraction techniques often used for this purpose include purge and trap (dynamic headspace), solvent extraction, solid-phase extraction, and solid-phase micro extraction (SPME). Most of these techniques have several disadvantages, including extensive equipment requirements, environmentally unfriendly solvents, multiple handling steps that increase error, and/or the need for concentration of target analytes to achieve detection levels. Furthermore, headspace techniques such as SPME are affected by matrix interferences leading to poor quantitation, while headspace techniques in general can show poor recovery of heavier components. Matrix affinities for volatile chemicals such as flavor and odor compounds are rather high and the excessive amount of ethanol may saturate adsorbents and create interferences. Many odor producing compounds have been difficult to measure down to olfactory detection limits due to a combination of low vapor pressure and high solubility in the water or beverages that require analysis. Such odor producing compounds include Trihalogenated Anisoles found in wine, and compounds such as Geosmin and 2-Methylisoborneol in drinking water that are produced by bacteria and blue-green algae. Classical methods such as purge and trap have been minimally effective due to low recoveries and poor precision leading to unacceptable method detection limits. SPME methods recover so little of these compounds from the sample that isotope dilution is typically required for every target compound to make quantitative measurements, and carryover as much as 2-10% makes it impossible to establish method detection limits that are reliable.

A new headspace technique call VASE, or Vacuum Assisted Sorbent Extraction, greatly improves upon headspace analysis of high alcohol containing samples by both improving extraction efficiency and by reducing matrix related interferences.

The technique involves placing an adsorbent cartridge, or Sorbent Pen, (SP) into the headspace to minimize transfer losses. A vacuum is created through the adsorbent, and the vacuum is maintained long after removal of the vacuum source to increase the rate of transmission from the sample matrix to the sorbent surface. Extraction can continue from 15 minutes to 24 hours, with 4-20 hours being typical to recover semi-volatile range compounds. During extraction, the sorbent and vial are a closed system, so breakthrough does not occur. Unlike dynamic headspace where a carrier gas can push compounds far into the adsorbent where recoveries are reduced, static extraction under a vacuum tends to keep the collected compounds optimally close to the front of the trap, maximizing their recovery upon thermal desorption, and reducing the levels of contamination that can show up in subsequent runs. This yields both improved reproducibility and extremely low carryover in the following analysis. Additionally, static extraction allows lower desorption temperatures relative to dynamic sampling, and therefore longer lifetimes for each vacuum sampling Sorbent Pen.

Figure 3 shows a C8-C30 standard being utilized to ensure proper recovery during VASE sampling and subsequent desorption using a 5800 Sorbent Pen

Desorption Unit (SPDU) (**Figure 7**) from run to run. A 1μl aliquot of the standard was injected into a 20mL vial, into which the Sorbent Pen was inserted, followed by an overnight extraction at 70° C to obtain recovery out to C30. This standard may also be used to verify proper extraction completeness and reproducibility for new Sorbent Pens after the conditioning step in the 3801 Sorbent Pen Thermal Conditioner (SPTC) (Entech Instruments, Simi Valley, CA) (**Figure 4**).

This innovative approach utilizing this self-contained vacuum extraction system allows the vial and adsorbent to be placed in an agitator with or without heat. The vacuum allows recovery of headspace compounds at lower temperatures (4-25°C) preventing changes to any heat sensitive sample matrices or creating artifacts in samples being studied. Wine, rum, cognac, and whiskey are generally consumed at room temperature or below, therefore these samples were not exposed to heat.

This simple sample preparation procedure of VASE allows the samples to be analyzed unaltered at room temperature, without the use of solvents, addition of heat, or salts. However, if analysis of heavy semi-volatiles is desired, recovery has shown to improve if the vial is subject to heat or with the addition of a salt solution.
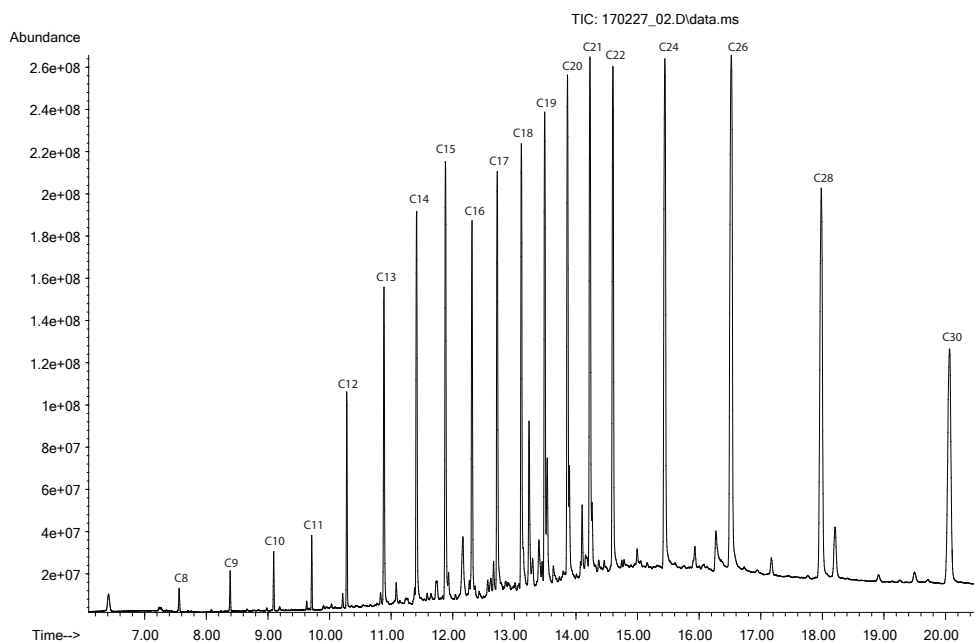

Figure 3 - C8 to C30 Calibration Standard, used to verify proper system operation after installation, including recovery out to C30 prior to sample analysis.

Figure 4 - To prepare new Sorbent Pens for extraction, the 3801 Sorbent Pen Thermal Conditioner (SPTC) is used to condition Sorbent Pens prior to use up to 350°C depending on the sorbent type. During the analysis, the Sorbent Pens are both desorbed to the GCMS and thoroughly baked out, eliminating the need for additional thermal conditioning before reuse. However, if a Sorbent Pen was not isolated after extraction or if it contained unusually high concentrations of extracted compounds not completely removed during the previous analysis, the 3801 SPTC can be used for a quick cleanup of the Pen.

Figure 5 - Sample vials and agitator used to perform VASE. The 5600 Sorbent Pen Extraction System (SPES) provides a convenient way to perform vial extractions using 30-position trays, allowing for significant sample throughput. The sample to be extracted is loaded into the vial, the Sorbent Pen is inserted, a vacuum is created through the MicroQT seal at the top of the Pen, and the sample is loaded onto the tray. The extraction time, temperature, and RPM can be programmed on the 5600 SPES and the vacuum extraction process begins. The Sorbent Pen Extraction System agitates the samples at 30-300 RPM to speed up transfer of volatiles to the headspace, while controlling the sample temperature from 4°C to 70°C. Extractions can be completed in 1–48 hours depending on the application.
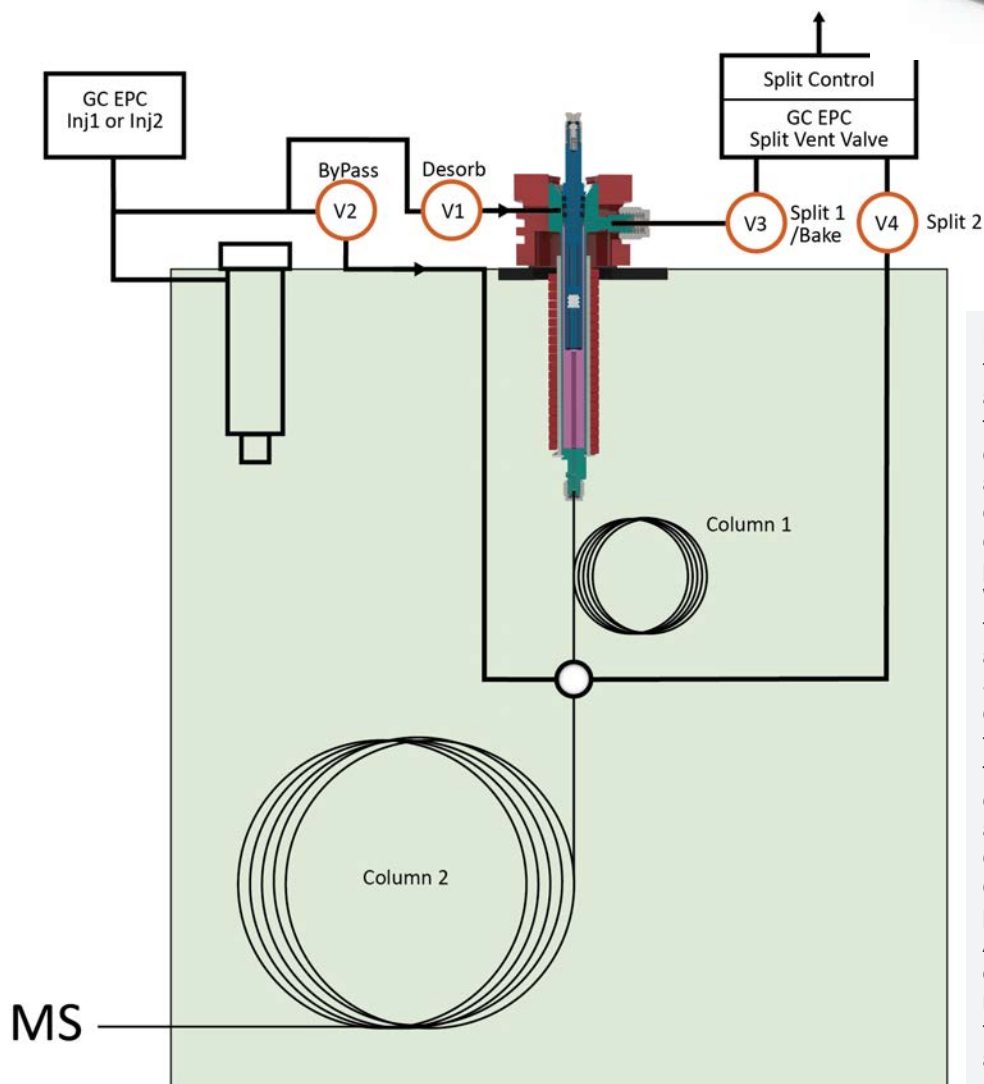

Figure 6 - Using a series of two columns in the flow path after thermal desorption, with forward and backward flushing capabilities for the first column, a wide range of applications can be performed to analyze compounds ranging in boiling points from -100°C to 500°C. Water management is performed through condensation, splitting, and back flushing. The 5800 SPDU uses a series of two columns in the flow path after thermal desorption. With forward and backward flushing capabilities for the first column, a wide range of applications can be performed to analyze compounds ranging in boiling points from -100°C to 500°C. A series of 4 valves controls each method process. Water management is performed through condensation, splitting, and back flushing.

Methods

Rum, whiskey, cognac, and wine samples were chosen to study how VASE would perform with high alcohol matrices. Tenax was chosen as the adsorbent for this study to specifically target volatiles to semi-volatiles.

Rum and wine samples were prepared neat and with the addition of water to show the effects of diluting alcohol samples. Water was added to increase the affinity of ethanol to the sample matrix. Additionally, water was added to investigate how making the matrix more polar might decrease the affinities of other compounds for the liquid phase to enhance extraction. Samples were evacuated through the MicroQT valve at the top of the Sorbent Pen. An oil free, dual stage diaphragm pump capable of achieving a vacuum of <0.01 atmospheres was used with the Vial Evacuation Tool to create a vacuum through a micro seal at the top of the Sorbent Pen. A restrictor on the Vial Evacuation Tool ensures the vial is evacuated slowly enough so samples do not boil or foam up too much so liquid never contacts the adsorbent. With this tool, 20-40mL vials evacuate in about 15-30 seconds (**Figure 1**). The Sorbent Pen makes a seal to the liner allowing the vacuum to be retained in the vial after removal of the vacuum source. The vacuum level can be confirmed after the sample extraction period is complete to verify the absence of leaks.

After evacuation, the vials are placed into the 5600 Sorbent Pen Extraction System (SPES) (Entech Instruments, Simi Valley, CA) at 100rpm and allowed to equilibrate at 25°C over a 4-hour period. Agitating the samples at 100rpm was used to both increase the surface area of the sample headspace boundary, while also refreshing the boundary layer to maximize the concentration of compound at the surface through mixing. The 5600 SPES, **Figure 5**, allows temperature control up to 70°C and adjustable agitation (rpm) to further enhance extraction if desired. The outer body of the Sorbent Pen protects the adsorbent from contact with any aerosols kicked up from agitation to ensure only fully volatilized chemicals reach the adsorbent.

Whiskey samples were prepared by adding 50µL of whiskey and 500µL of DI water to 20mL vials. To demonstrate the effects of adding salt, 500µL of sodium sulfate saturated DI water solution was added to 50µL of whiskey in place of the 500µL DI water. Whiskey samples were placed in the 5600 SPES for 10 hours at 25°C at 100rpm.

Analysis was performed by thermally desorbing the Sorbent Pens on a 5800 Sorbent Pen Desorption Unit (SPDU) (Entech Instruments, Simi Valley, CA) to deliver the sample onto a 0.6m filmless pre-column. To get a rapid injection onto the GC column, the adsorbent material must be preheated. However, during the extraction process, a small amount of water and ethanol also get into the adsorbent and must be minimized. To manage the water, a precolumn, labeled in **Figure 6** as Column 1, serves as an expansion area during preheat so nothing is injected while the water volatilizes. During preheat, there is no flow through the thermal desorber (V1 is OFF and V2 is ON), and the GC oven remains cool (e.g. 35°C) allowing expanding water to easily re-condense on Column 1. After the preheat step is complete, the Desorb gas valve (V1) turns ON and the Bypass Valve (V2) turns OFF resulting in a fast injection to deliver the sample past the split and into Column 2 within a couple minutes. This allows part of the sample and water to be split out. To continue clearing out the remaining water that is still condensed in Column 1 from reaching Column 2 and the water sensitive mass spectrometer, Split 1 (V3) also turns ON to create high flow rates. Using a packed adsorbent trap for VASE has the advantage over GC columns in that the Tenax cartridge can carry up to 100x more sample before becoming overloaded, so a 10-50:1 split will achieve a fast injection without requiring Liquid N2 focusing, but still provides optimal sample loading onto the column resulting in maximum sensitivity, even for compounds at low concentrations in the sample.

All analyses in this study were performed on an Agilent 7890/5977 GCMS (Palo Alto, CA). Carrier gas flow was supplied to the 5800 SPDU by teeing off the carrier gas going to the front injector. The return flow, coming from the 5800 Split 1 and Split 2 Union, is connected directly to the GC EPC Split Vent Valve, allowing the EPC to control the split ratio programmed in the GC Method. Connecting directly to the GC Split Vent Valve allows stable flow rates to be maintained when 5800 valves are toggled, resulting in reproducible injections.

Figure 7 - 5800 SPDU shown on Agilent GC. After sample extraction, simply insert the Sorbent Pen into the 5800 SPDU and press START on the 5800 Controller to transfer volatile to semi-volatile compounds onto the column and to the detector for sensitive and accurate analysis.

The 5800 SPDU was set to an idle temperature of 70°C. Once in place, the Sorbent Pen is desorbed for 20 minutes at 260°C and delivers the sample onto a 0.6m pre-column (Silonite coated stainless steel, filmless) with a split vent (Split 2) downstream prior to the primary column to allow higher flow rates during desorption of the cartridges. Following the pre-column and after passing Split 2, the compounds flow through the primary column (DB5MS UI, 30m length x 0.25mm ID, 0.5µm film) to the MS detector. The initial GC temperature was 35°C which after a 5-minute initial hold was ramped to 300°C at 10°C/min. Full scan data was collected from 34-450 amu, with approximately 2.5 scans per second. The NIST Library was used to identify the compounds detected. Following the desorption, the Sorbent Pen remains in the SPDU and is subject to a baking period at 260°C while the extracted and desorbed compounds are separated as they flow though the GC analytical column. After the baking period, the Sorbent Pen starts to cool down to the idle temperature of 70°C during post bake step for 3-5 minutes when the run is almost complete. This allows the SPDU to cool down to idle temperature, ready for the next injection.

For alcoholic beverage trace analysis, Column 1 is a GC column containing a thin film which will retain the odor or aroma compounds of interest, while allowing the carrier gas, water vapor, and lighter compounds to pass through Column 1, with most of it being eliminated through Split 2. After the sample

has been desorbed and the target compounds are captured on Column 1, Split 2 is turned off, and the oven is heated to drive the condensed sample onto Column 2 for splitless full separation and detection of trace analytes C8 and above. During this time, V3 is turned on to bake out the adsorbent. As a result, the Sorbent Pen is clean and ready for reuse when the GC run is finished. Geosmin (Supelco) and a mixture of 2-Methylisoborneol, Trichloroanisole isomers, and Tribromoanisole (Veolia Research, France) were obtained in methanol and diluted to working concentrations in filtered water. Geosmin-d3 was used as the internal standard for all compounds analyzed. Sample extraction was performed at 25°C for periods of 1, 3, 8,16, 20, and 24 hours to compare rate of extraction for each compound using 20 ng/L concentrations. An extraction period of 20 hours was selected for this method based on previous results indicating that compounds had reached equilibrium and no further recovery was achieved by longer periods. Analysis was performed by thermally desorbing the Sorbent Pens using a 5800 SPDU on a 7890B/5977 GCMS (Agilent, Palo Alto, CA) to deliver the sample first onto a 5m pre-column (DB1, 0.25mm ID, 0.5µm film) with a split vent prior to the primary column (DB1, 60m, 0.250mm ID, 0.5µm) to allow higher flow rates during desorption of the cartridges. The initial GC temperature was 35°C with an immediate ramp rate of 20°C/min to 280°C with a 4-minute hold. Full scan data was collected from 33-350 amu, with approximately 2.5 scans per second. The calibration data from 0.1 to 20 part per trillion was obtained using SIM with an EM Gain of 8. Detection in both unfiltered tap water and wine were performed by direct analysis and with a 5ng/L spike of the target compounds to verify invariance to the matrix. The red wine was diluted 10:1 with filtered water prior to spiking with 5ng/L to reduce the potential for chromatographic interferences, and because olfactory detection limits are not as low in wine as in drinking water.

Results

The full volatility range experiments performed on whiskey, rum, and wine samples are shown in **Figures 8-15**. These samples were all run with a 10:1 split. Considering the very large capacity of the Sorbent Pen relative to the capacity of a GC capillary column, the idea of extracting more sample than required for

analysis is an attractive alternative. Preheating and splitting the sample can been used to avoid cryogenic focusing, while still achieving great signal to noise ratios at low levels for method detection limits. **Figure 8** shows good reproducibility, and an extremely clean blank between runs. The addition of water to the rum samples shows a slight reduction of some water-soluble compounds in the rum. This is also apparent in the wine analysis with the addition of water. However, the addition of water reduced the intensity of the ethanol peak in general, allowing a much flatter baseline during the first 10-14 minutes of analysis. The addition of a saturated salt solution increased the recovery of phthalates, which are a highly regulated contaminant in many alcoholic beverages.

The trace analysis experiments performed show calibration curves from 0.1 to 20 ng/L for Trichloroanisoles, Tribromoanisole, Geosmin, and 2-MIB, using Geosmin-d3 as the internal standard (Table 1). Individual isotopes were not needed due to the high recovery for each compound of 60-90%. Analysis of spiked and non-spiked drinking water and wine are performed to verify the ability to perform measurements in matrices with varied complexity and affinity for the target analytes (Table 2). The results show that the ultimate limit of detection was more affected by the ability to chromatographically separate interfering compounds, than in achieving enough signal to reach 0.1 ng/L and below when using a single quadrupole GCMS.
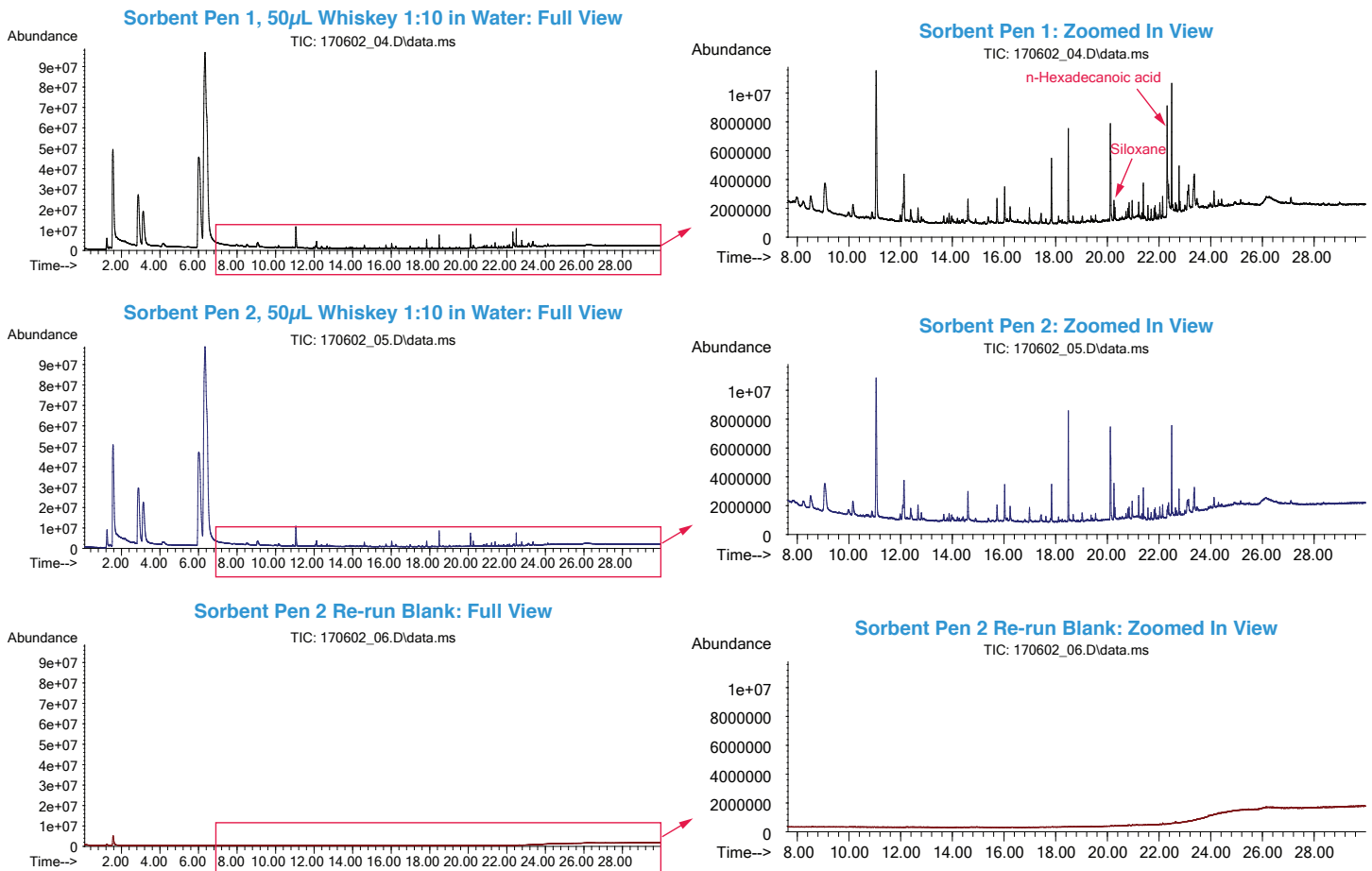

Figure 8 - 50uL of Whiskey with 500uL of water duplicates. Vacuum extracted for 10 hours at 25˚C. The Y axis is scaled equally to show excellent reproducibility considering the difficult matrix. The blank afterwards is totally free of contaminants. A blank run, performed by desorbing the Sorbent Pen a second time without additional cleanup, is completely free of carryover.

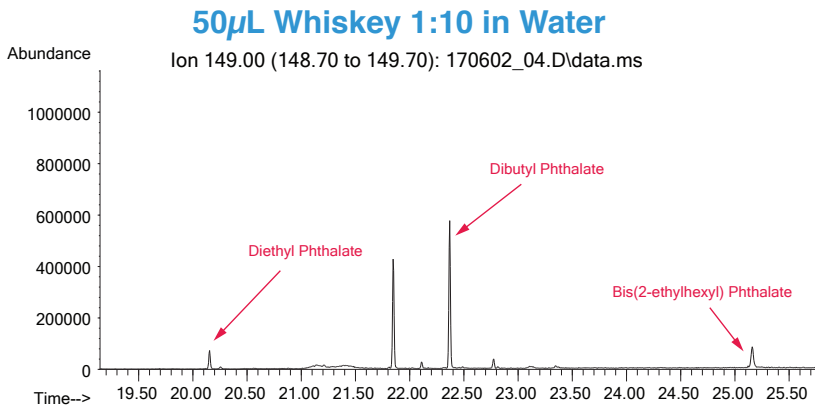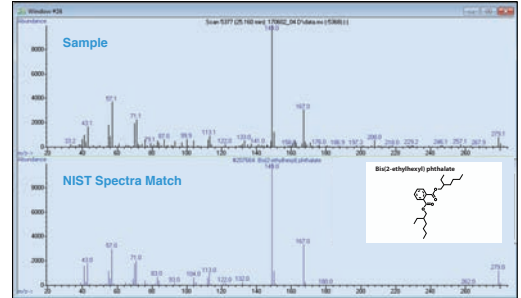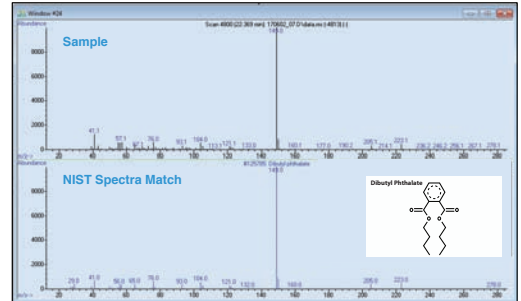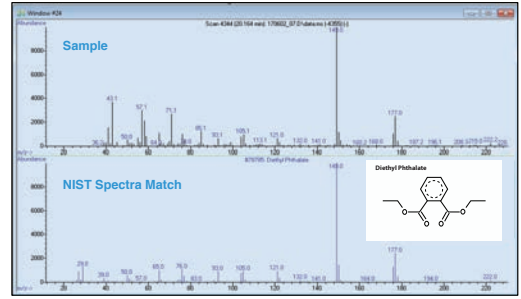## 50μL Whiskey 1:10 in Saturated Salt Water: Increased Phthalate Recovery

Ion 149.00 (148.70 to 149.70): 170602_07.D\data.ms

50μL Whiskey 1:10 in Water

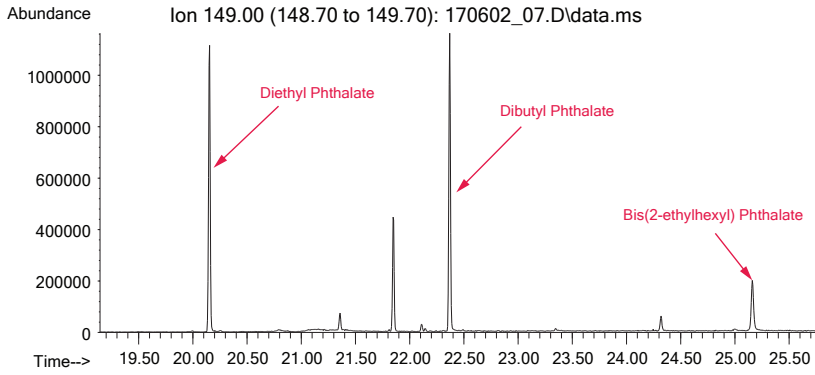Ion 149.00 (148.70 to 149.70): 170602_04.D\data.ms

Figure 9 - 50μL of Whiskey diluted in 450μL of DI water in comparison to 50μL of Whiskey diluted in 450μL of a saturated NaSO4 solution. The recovery of three phthalates found in the whiskey sample, Diethyl Phthalate, Dibutyl Phthalate, and Bis(2-ethylhexyl) Phthalate, increased with addition of the salt solution to the matrix and the NIST Library Spectra match is shown.

50μL Whiskey Diluted 1:10 in DI Water

TIC: 170602_04.D\data.ms

1. Acetaldehyde
2. Ethanol
3. Ethyl Acetate
4. 1-Propanol, 2-methyl-
5. Methane, diethoxy-
6. Ethane, 1,1-diethoxy-
7. 1-Butanol, 3-methyl-
8. Furfural
9. 1-Butanol, 3-methyl-, acetate
10. Ethyl orthoformate
11. Pentane, 1-(1-ethoxyethoxy)-
12. Propanoic acid, 3-ethoxy-, ethyl ester
13. Hexanoic acid, ethyl ester
14. 2-Furancarboxylic acid, ethyl ester
15. Pentanoic acid, 4-oxo-, ethyl ester
16. Propanedioic acid, diethyl ester
17. Butanedioic acid, diethyl ester
18. Octanoic acid, ethyl ester
19. Acetic acid, 2-phenylethyl ester
20. 2(3H)-Furanone, 5-butyldihydro-4-methyl-
21. Decanoic acid, ethyl ester
22. Dodecanoic acid, ethyl ester
23. Diethyl Phthalate
24. 2-Pentadecanone
25. Octadecanal
26. Tetradecanoic acid, ethyl ester
27. n-Hexadecanoic acid
28. Dibutyl phthalate
29. Hexadecanoic acid, ethyl ester
30. Linoleic acid ethyl ester
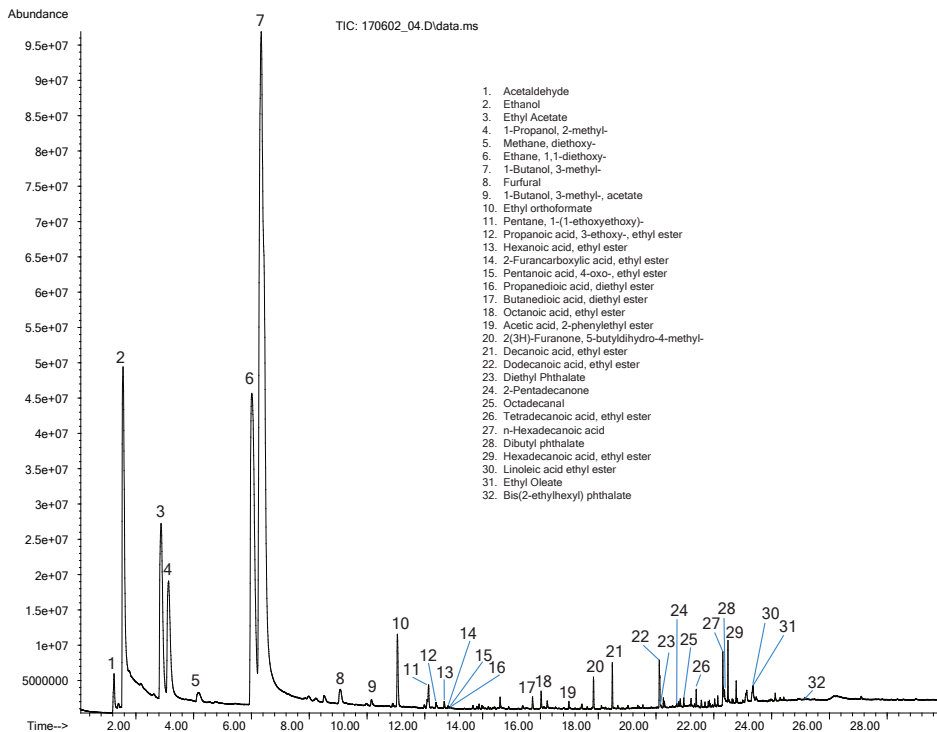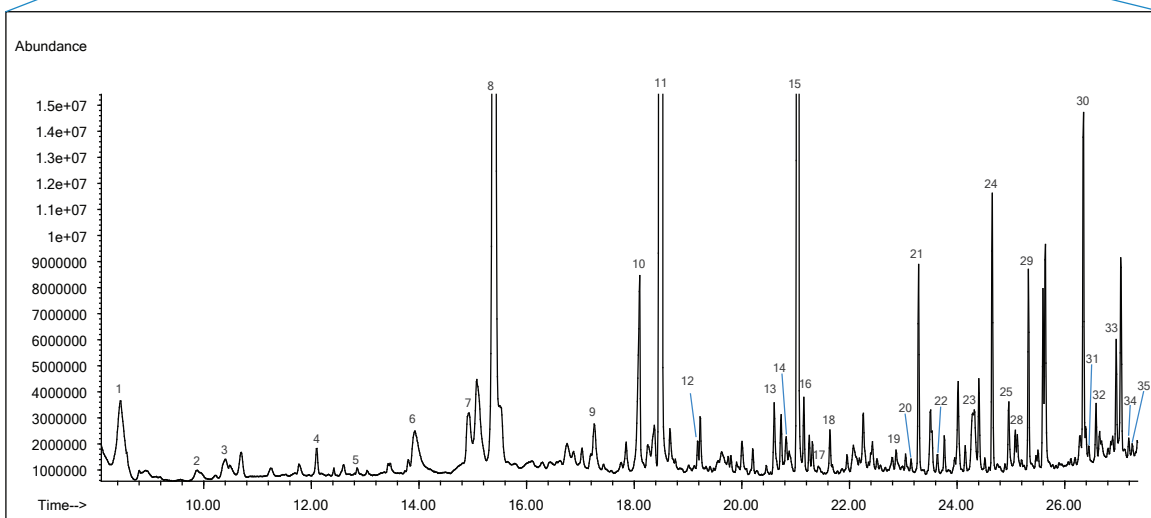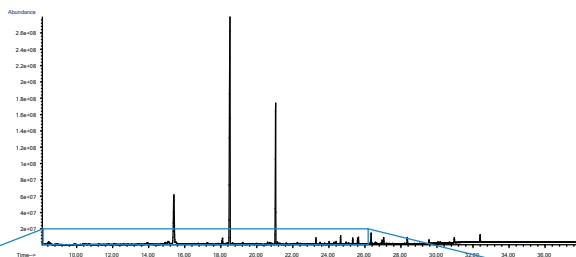31. Ethyl Oleate
32. Bis(2-ethylhexyl) phthalate

Figure 10 - 50μL of Whiskey in 500 μL of DI water, vacuum extracted onto Tenax at 25°C for 15 hours, no salt. 10:1 split injection.

50µl of Rum with 50µl DI Water

1. 3(2H)-Furanone, dihydro-2-methyl-
2. 1-Hexanol
3. Ethanone, 1-(2-furanyl)-
4. Hexanoic acid, ethyl ester
5. Pentanoic acid, 4-oxo-, ethyl ester
6. Phenylethyl Alcohol
7. Butanedioic acid, diethyl ester
8. Octanoic acid, ethyl ester
9. trans-3-Methyl-4-octanolide
10. n-Decanoic acid
11. Decanoic acid, ethyl ester
12. Octanoic acid, 3-methylbutyl ester
13. Dodecanoic acid
14. Benzoic acid, 4-hydroxy-3-methoxy-, ethyl ester
15. Dodecanoic acid, ethyl ester
16. Pentanoic acid, 2,2,4-trimethyl-3-carboxyisopropyl, isobutyl ester
17. Benzophenone
18. Pentadecanoic acid, 3-methylbutyl ester
19. Tetradecanoic acid
20. Ethyl 9-tetradecenoate
21. Pentadecanoic acid, ethyl ester
22. Isopropyl myristate
23. 1-Hexadecanol
24. Pentadecanoic acid, 14-methyl-, methyl ester
25. n-Hexadecanoic acid
26. Ethyl 9-hexadecenoate
27. Hexadecanoic acid, ethyl ester
28. 1-Tetradecyl acetate
29. Isopropyl palmitate
30. 9-Octadecenoic acid (Z)-, methyl ester
31. Heneicosane
32. Methyl stearate
33. Ethyl 9-hexadecenoate
34. Octadecanoic acid, ethyl ester
35. Benzoic acid, tridecyl ester

Figure 11 - 50µL of Rum and with 50µL of DI water, vacuum extracted onto Tenax at 25°C for 4 hours. 10:1 split injection to improve light end injection rates. The three largest peaks are off scale to enhance smaller peaks for viewing and identification.

50µl of Cognac

Abundance

TIC: 170523_05.D\data.ms

1. Furfural
2. Acetic acid
3. 3-Hexen-1-ol, (Z)-
4. 1-Hexanol
5. Oxime-, methoxy-phenyl-_
6. Hexanoic acid, ethyl ester
7. Octanoic acid
8. Octanoic acid, ethyl ester
9. n-Decanoic acid
10. Decanoic acid, ethyl ester
11. Dodecanoic acid
12. Dodecanoic acid, ethyl ester
13. 2-Pentadecanone
14. Tetradecanoic acid
15. Tetradecanoic acid, ethyl ester
16. Pentadecanoic acid
17. 2-Heptadecanone
18. n-Hexadecanoic acid
19. Hexadecanoic acid, ethyl ester
20. Octadecanoic acid
21. Octadecanoic acid, 4-hydroxy-, methyl ester
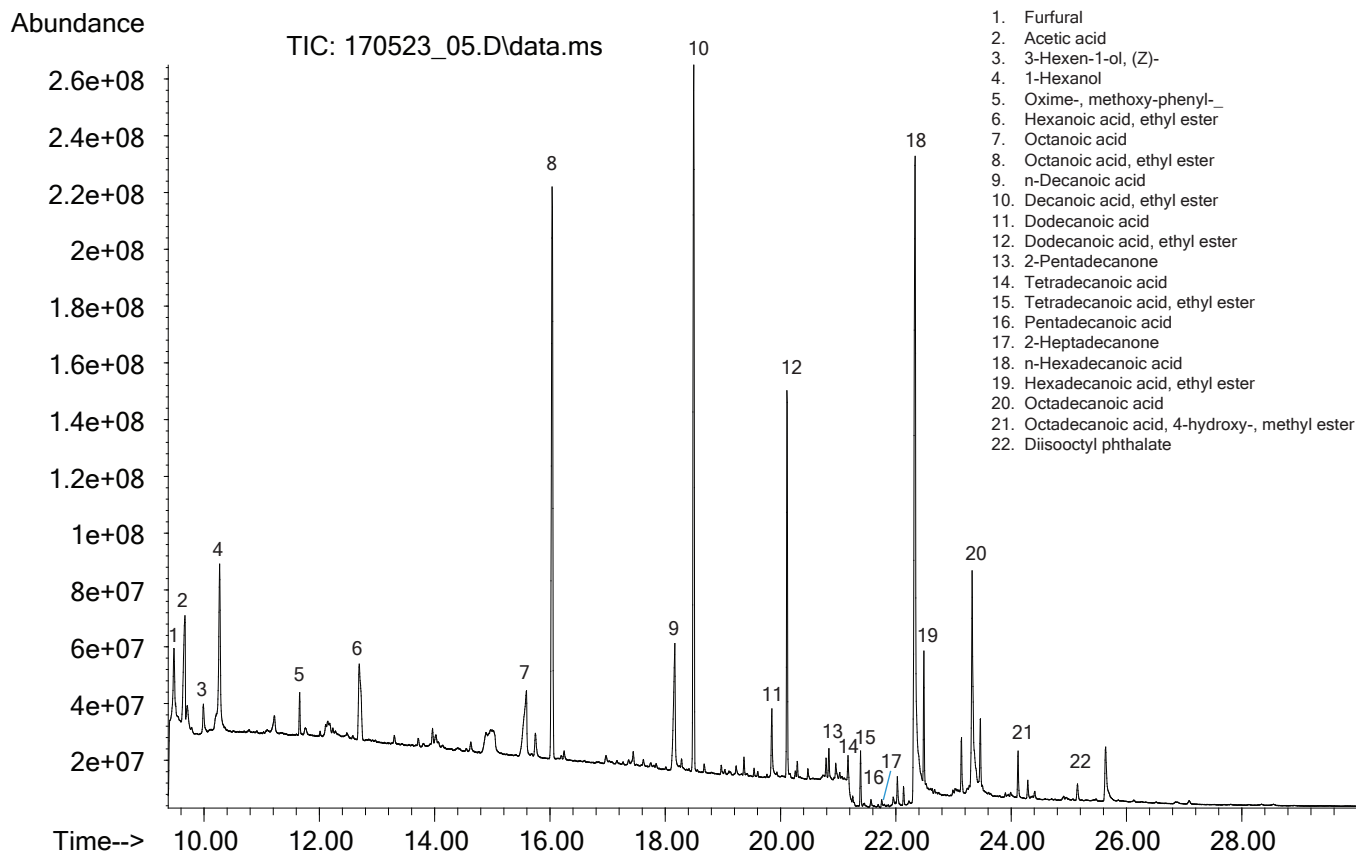22. Diisooctyl phthalate

Figure 12 - 50µL of Cognac, no water, vacuum extracted onto Tenax at 25°C for 6 hours.

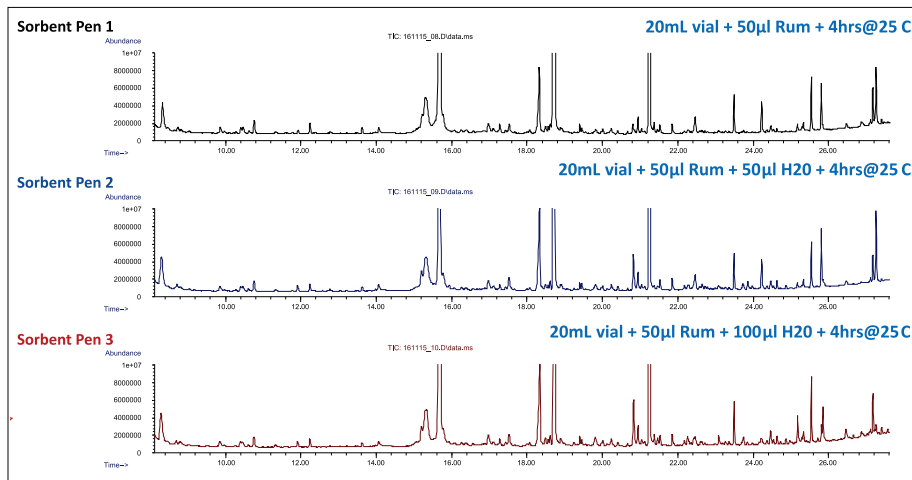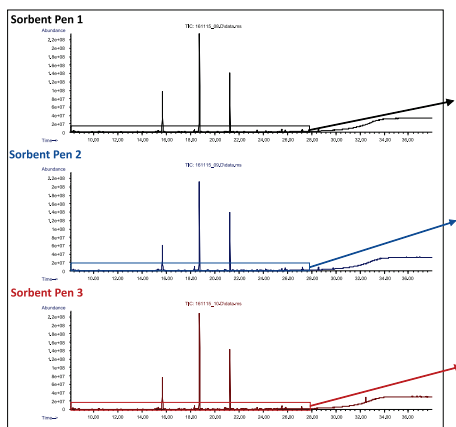**Figure 13** - Rum analysis using 0x, 1x, 2x by volume of added water. 10:1 Split injections. The presence of siloxanes in the 0x and 1x, but not in the 2x runs is being investigated. It is possible that injection of excess ethanol at the start of the run creates a release of trace amounts of siloxane until the ethanol goes completely into the gas phase. Siloxanes are common background peaks in GC/GCMS.

0.5ml Red Wine

TIC: 170601_03.D\data.ms

1. Sulfur dioxide
2. Acetaldehyde
3. Ethanol
4. 1-Propanol
5. 2,3-Butanedione
6. Ethyl Acetate
7. Propanoic acid, ethyl ester
8. 1-Butanol, 3-methyl-
9. Propanoic acid, 2-methyl-, ethyl ester
10. Isobutyl acetate
11. Butanoic acid, ethyl ester
12. Furfural
13. Butanoic acid, 2-methyl-, ethyl ester
14. Butanoic acid, 3-methyl-, ethyl ester
15. 1-Butanol, 3-methyl-, acetate
16. Butyrolactone
17. 2-Furancarboxaldehyde, 5-methyl-
18. Hexanoic acid, ethyl ester
19. Butanedioic acid, ethyl methyl ester
20. Phenylethyl Alcohol
21. Octanoic acid
22. Butanedioic acid, diethyl ester
23. Octanoic acid, ethyl ester
24. Benzeneacetic acid, ethyl ester
25. Acetic acid, 2-phenylethyl ester
26. 2(3H)-Furanone, 5-butyldihydro-4-methyl-, cis-
27. Succinic acid, butyl ethyl ester
28. 2(3H)-Furanone, 5-butyldihydro-4-methyl-
29. n-Decanoic acid
30. 2(3H)-Furanone, dihydro-5-pentyl-
31. Decanoic acid, ethyl ester
32. Butanedioic acid, ethyl 3-methylbutyl ester
33. Dodecanoic acid, ethyl ester
34. Tetradecanoic acid, ethyl ester
35. 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester
36. Ethyl 9-hexadecenoate
37. Hexadecanoic acid, ethyl ester
38. Linoleic acid ethyl ester
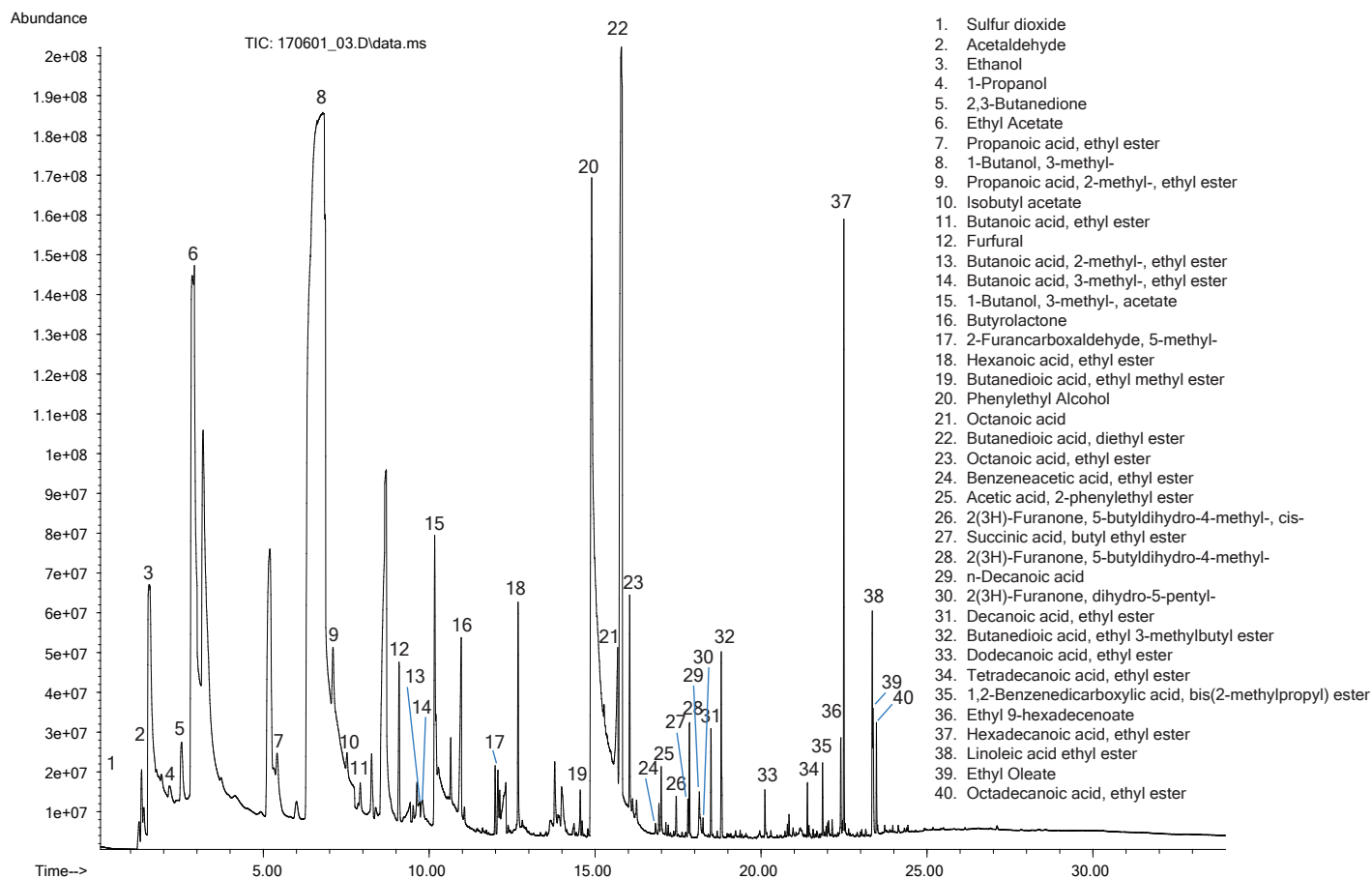39. Ethyl Oleate
40. Octadecanoic acid, ethyl ester

Figure 14 - 0.5mL of Red Wine, no water, vacuum extracted onto Tenax at 25°C for 15 hours. A wide range of compounds were identified, from sulfur dioxide to heavy ethyl esters.
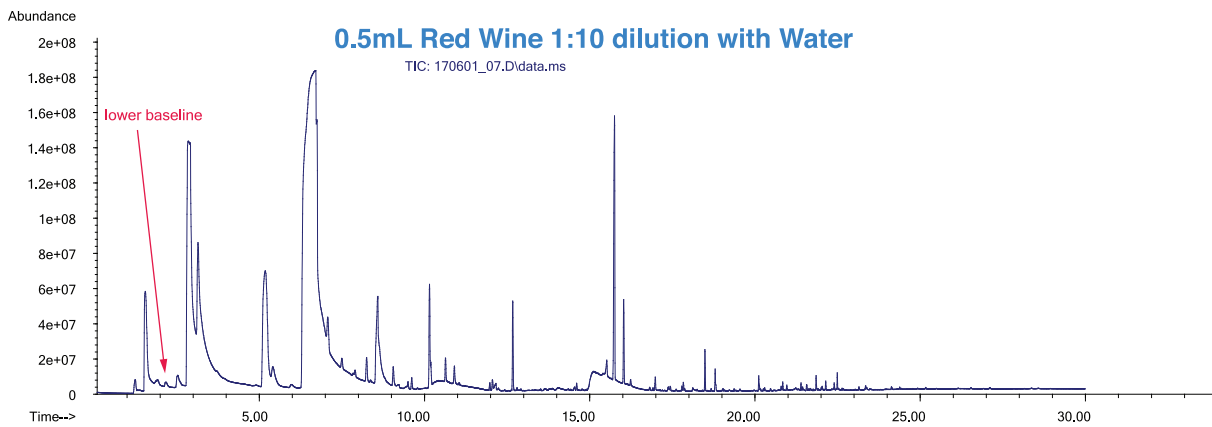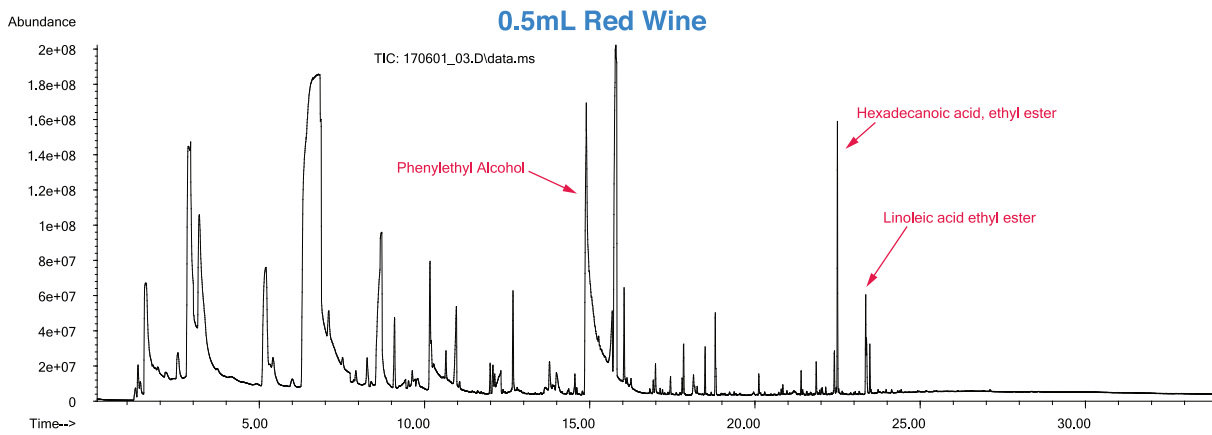
Figure 15 - 0.5mL of Red Wine, no water, in comparison to 0.5mL of Red Wine diluted 10x in DI water. Both samples vacuum extracted onto Tenax at 25°C for 15 hours. Although a few differences in recoveries for compounds with a higher affinity for the ethanol/water matrix, the diluted sample shows a lower baseline as less ethanol was extracted due to the addition of water to the sample matrix.

Calibration (ng/L)							
	0.1	0.3	1	5	20	Average	%RSD
2-Methylisoborneol	0.341	0.346	0.351	0.248	0.309	0.319	13.5
Geosmin			0.362	0.414	0.339	0.372	10.3
2,4,6-Trichloroanisole	0.272	0.283	0.240	0.220	0.218	0.246	12.1
2,3,5-Trichloroanisole	0.367	0.386	0.319	0.299	0.301	0.334	11.9
2,3,4-Trichloroanisole	0.251	0.255	0.198	0.201	0.181	0.217	15.5
2,4,6-Tribromoanisole	0.118	0.111	0.095	0.097	0.089	0.102	11.8

Table 1 - Calibration curves from 0.1 to 20 ng/L showing good linearity over a 200x calibration range. Geosmin points at 0.3 and 0.1ng/L were omitted due to interferences from contaminants in the filtered water.

Analytical Report (ng/L)							
Sample	Area Geosmin-d3	2-MB	Geosmin	2,4,6-TCA	2,3,5-TCA	2,3,4-TCA	2,4,6-TBA
Tap Water	680178	<0.1	<1	<0.1	<0.1	<0.1	0.22
Tap Water = 5ng/L	697602	3.73	5.64	4.02	3.94	3.88	4.38
Wine (1/10 in Water)	284246	<1	<10	0.11	0.20	0.25	0.17
Wine (1/10 + 5ng/L)	497007	4.39	5.03	5.91	5.71	5.64	6.59

Table 2 - Results from Simi Valley, CA tap water and wine samples. The wine was diluted 10:1 prior to analysis. All samples had 10 ng/L Geosmin-d3 added as an Internal Standard. The stability of Geosmin in wine is unclear, and the inconsistent recovery of Geosmin-d3 may be the result of losses.

Conclusions

VASE, or Vacuum Assisted Sorbent Extraction, was shown to be very effective in the analysis of volatiles to semi-volatiles in whiskey, rum, cognac, water, and wine samples. The results show the extensive range of compounds extracted using VASE and demonstrate its potential as a routine method for examining aroma compounds relating to flavor analysis and regulated contaminants in alcoholic beverages. The advantage of VASE extraction over direct GC injection is that it avoids the creation of artifacts that form when injecting the entire matrix including thermally labile compounds into a hot GC injector, resulting in the detection of compounds that do not actually exist in the sample. The VASE technique shows great promise in vastly improving the recovery of low volatility, polar compounds from water and wine for more classical analysis without having to perform isotope dilution for each target compound. This is a huge advantage, as it allows the quantitation of compounds for which no isotopically labeled analogs exist. The decoupling of the extraction and analysis process offers a tremendous advantage over other online extraction techniques, as long extraction times are practical while maintaining a high sample throughput with multiple Sorbent Pens extracting simultaneously. Future VASE work will include heavier semi-volatile compounds such as drugs of abuse including THC, endocrine disruptors, carcinogens in foods and beverages, and PAHs.

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