# Analysis of Extract Drying Criteria for Oil and Grease Method 1664B

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# Outline

- SPE and Drying with US EPA 1664B
- Limits of Sodium Sulfate
- WaterTrap Membrane Drying Device
- Experimental
- Quality Control Requirements
- Initial Recovery and Precision
- Method Detection Limit
- Matrix Spike /Laboratory Blank
- Results and Discussion
- Conclusion

# Introduction

- US EPA Method 1664 has allowed use of solid phase extraction (SPE) instead of liquid-liquid extraction (LLE) with hexane since 2007 and this has been widely adopted in the US. SPE is an equivalent extraction technique to LLE and produces the same n-hexane extract. The extract, similar to LLE, may contain residual water that must be treated properly and removed from the n-hexane extract.

- In February of 2010, the US EPA released EPA Method 1664B. One of the allowable modifications 1.7.1.12 is the use of solvent phase separation paper or other equivalent means may be used instead of sodium sulfate to remove water from the extract provided all QC requirements are met especially for Sections 9.3 and 9.4, matrix spike and laboratory blanks respectively.

# Limitations of Sodium Sulfate (1 of 2)

- Sodium sulfate is used as a drying agent with nonpolar solvent extracts.
- It has limitations if not properly prepped, stored and used correctly.
- Section 4.4 of EPA Method 1664B emphasizes sodium sulfate has the potential to inflate results for HEM by passing through the filter paper.

# Limitations of Sodium Sulfate (2 of 2)

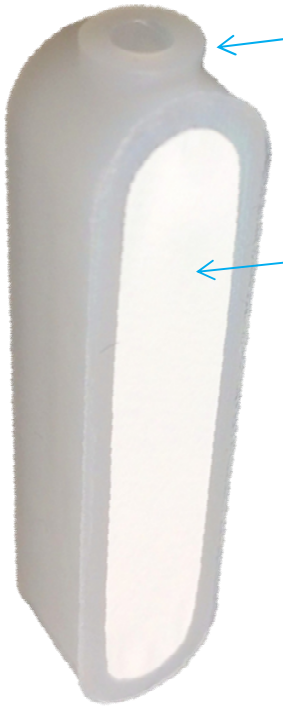
- There are several notes within sections 11.3.6 and 11.3.8 that emphasize the importance of understanding the limitations of sodium sulfate.
  - The amount of water remaining with the n-hexane must be minimized to prevent dissolution or clumping of the sodium sulfate in the extract drying process.
  - The specific properties of a sample may necessitate the use of larger amounts of $Na_2SO_4$.
  - It is important that water be removed in this step. Water allowed to filter through the $Na_2SO_4$ will dissolve some of the $Na_2SO_4$ and carry it into the boiling flask compromising the determination.

# WaterTrap™ Membrane Drying Device

- With several possibilities for failure and false positives with sodium sulfate, Horizon Technology has developed an equivalent means to drying n-hexanes extracts within the method guidelines stated by the EPA within section 1.7.1.12.
- The WaterTrap uses a membrane technology to separate water from nonpolar organic solvents.
- This technique is clean, fast and is not user dependent like sodium sulfate.
- The WaterTrap is designed to specifically mate with the SPE-DEX 3100 and eliminates the sample transfer to the drying step by its in-line installation.

# WaterTrap™ Membrane Drying Device

- **Ready to use**
- **No pretreatment required**
- **Single use disposable**



**Luer Connection Port**

**Hydrophobic Membrane**

- Selectively lets hexane extract to pass through
- Retains residual water up to 5 mL
- The vertical positioning of the membrane allows water to settle to the bottom while leaving exposed membrane for hexane to pass through
- Robust membrane handles up to -25 in Hg vacuum

Full polymeric composition no binders or adhesives

Patent pending

# Installing WaterTrap™

# Brief Review SPE for O&G 1of 2

Before showing a brief video on WaterTrap in operation
the next two slides illustrate the SPE process for O&G

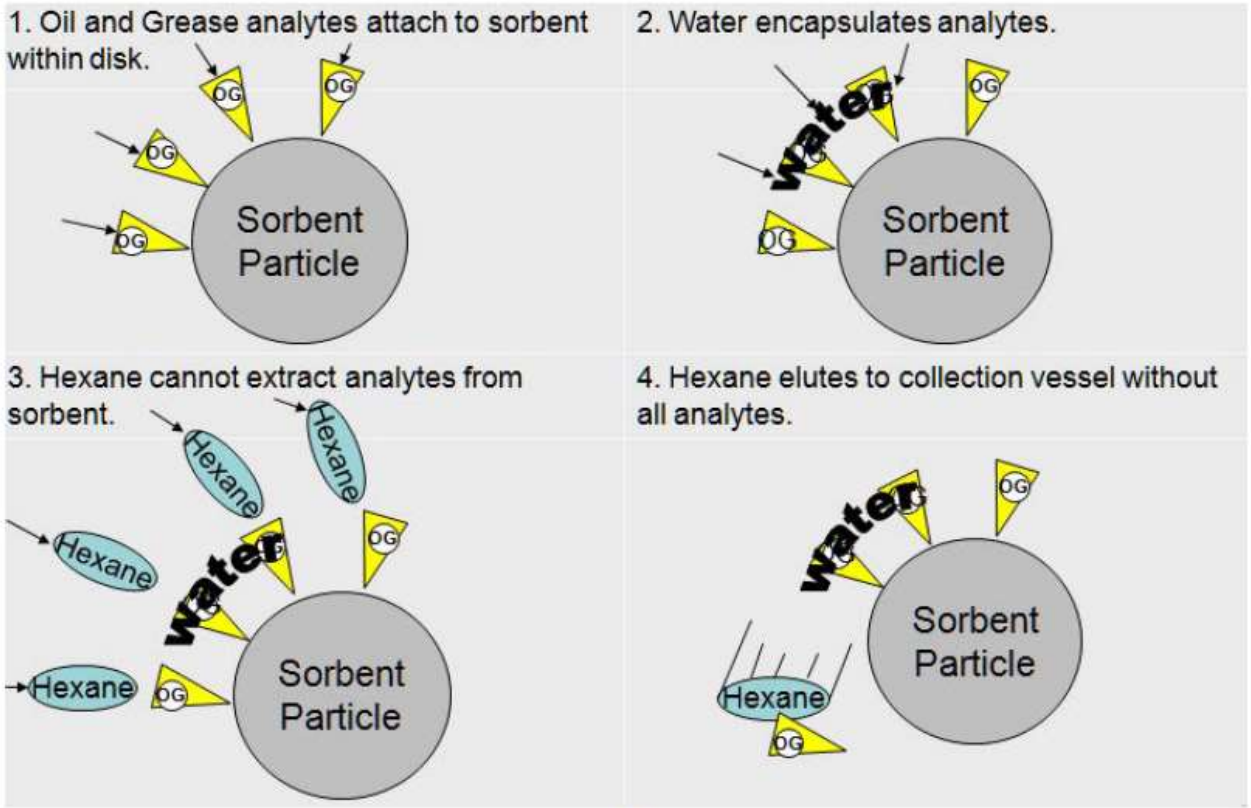



Figure 1. SPE molecular-level processes

# Brief Review SPE for O&G 2of 2

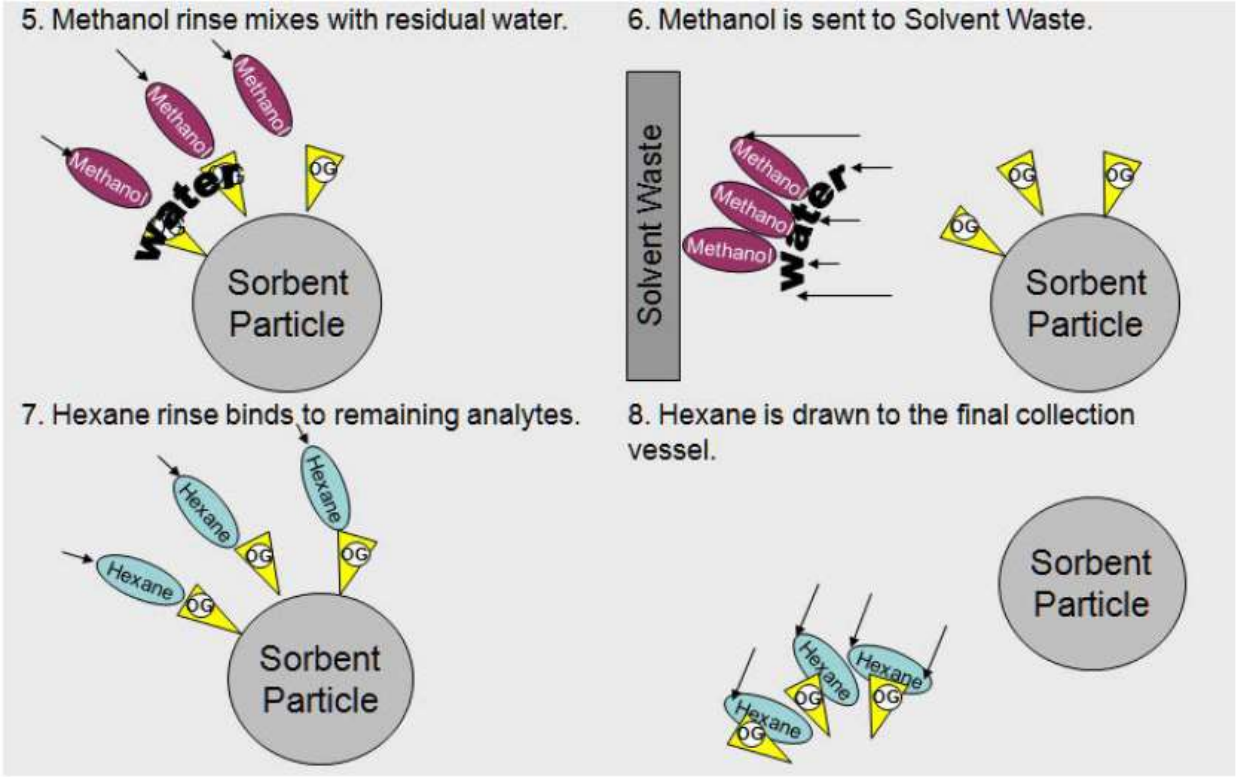
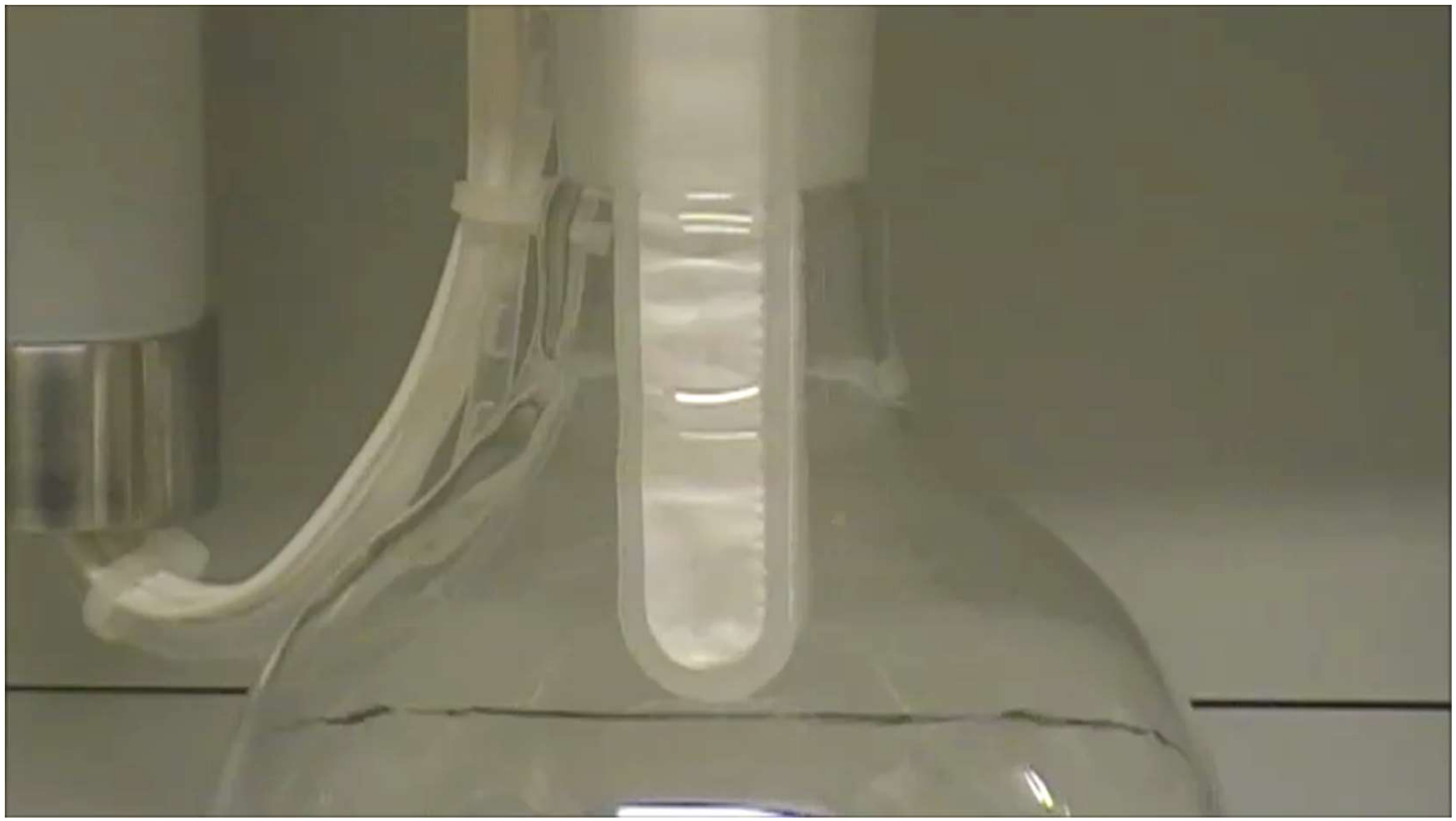



Figure 2. Elution process at a molecular level.

# WaterTrap™ Operation



# Experimental

- SPE-DEX® 3100 Oil & Grease Extraction System [1]
- 100 mm Pacific™ Premium solid phase extraction disks [1]
- Pacific™ Fast Flow Prefilters [1]
- WaterTrap™ for water removal [1]
- Speed-Vap® IV evaporation system [1]
- 105-mm aluminum weighing pans [1]
- AE 200 Balance for gravimetric measurements [2].
- Oil & Grease Standard [1]
  - 4 mg/mL hexadecane and 4 mg/mL stearic acid (PN# 50-003-HT)
  - Used for detection limit and spiking purposes
- Oil & Grease Snip and Pour [1]
  - 20 mg hexadecane and 20 mg stearic acid standards (PN# 50-021-HT)
  - Used for spiking purposes

[1] Horizon Technology, Inc.
[2] Mettler Corp.

# Equipment and Materials

SPE-DEX 3100

SolventTrap
(Optional)

Speed-Vap IV

# Quality Control: Requirements

- To demonstrate that all QC requirements were met using the WaterTrap an Initial Demonstration of Compliance (IDC) was run. It specifies that the method detection limit (MDL) and an initial precision and recovery study (IPR) be determined.

- Section 9.3 (Matrix Spikes) was demonstrated by preparing an ASTM synthetic wastewater sample and spiking it with the concentration of the precision and recovery standard (40 mg/L).

- Section 9.4 (laboratory blank criteria) was demonstrated by running a reagent water blank to demonstrate freedom from contamination.

# Results and Discussion

**Table 1:** Acceptance Criteria for Hexane Extractable Performance Tests

The criteria for quality control requirements in method 1664B are shown

| Acceptance Criteria | Limit (%) |
|---|---|
| | |
| **Initial Precision and Recovery** | |
| HEM Precision (s) | 11 |
| HEM Recovery (X) | 83—101 |
| SGT-HEM Precision (s) | 28 |
| SGT-HEM Recovery (X) | 83—116 |
| **Matrix Spike/Matrix Spike Duplicate** | |
| HEM Recovery | 78—114 |
| HEM RPD | 18 |
| SGT-HEM Recovery | 64—132 |
| SGT-HEM RPD | 34 |
| **Ongoing Precision and Recovery** | |
| HEM Recovery | 78—114 |
| SGT-HEM Recovery | 64—132 |

# Initial Demonstration of Capability

- The MDL is determined from 7 replicates of 1 L of reagent water, each spiked with 4 mg/L of standard. The concentrations and statistics are shown on the next slide.
- The MDL for the water trap is lower than the requirement stated in the method (1.4 mg/L) as well as the MDL with sodium sulfate ensuring that low concentrations of HEM can be measured with the precision necessary.

# Table 2. MDL Comparison of Drying Technique: $Na_2SO_4$ vs. Watertrap

| Run | HEM Recovery $Na_2SO_4$ ( mg/L) | HEM Recovery WaterTrap ( mg/L) |
|---|---|---|
| 1 | 3.0 | 4.3 |
| 2 | 3.2 | 4.3 |
| 3 | 3.2 | 3.9 |
| 4 | 2.5 | 3.8 |
| 5 | 3.0 | 4.2 |
| 6 | 2.6 | 4.1 |
| 7 | 3.1 | 3.8 |
| **Mean** | **2.9** | **4.1** |
| **STD DEV** | **0.28** | **0.22** |
| **MDL** | **0.89** | **0.70** |

# Initial Demonstration of Capability

- The initial precision recovery was demonstrated by spiking two sets of 4, 1-L volumes with one Snip and Pour pre-measured standard, each (40 mg/L).
- The data for each set of 4 replicates is shown on the next slide and was run with 100 mm Disk prefilters.
- The average percent recovery meets the criterion specified in Table 1 of 83-101% HEM recovery for both the sodium sulfate and WaterTrap-dried extracts.
- The standard deviation is better than the criterion specified of 11% For HEM.

# Table 3. IDC for 100mm disk, Prefilter: Dried with Sodium Sulfate and WaterTrap

| Run | HEM Using $Na_2SO_4$ (mg/L) | HEM Using $Na_2SO_4$ (%) | HEM using WaterTrap (mg/L) | HEM using WaterTrap (%) |
|---|---|---|---|---|
| 1 | 33.9 | 84.75 | 35.7 | 89.25 |
| 2 | 33.9 | 84.75 | 35.6 | 89.00 |
| 3 | 34.9 | 87.25 | 35.1 | 87.75 |
| 4 | 34.1 | 85.25 | 34.8 | 87.00 |
| RPD | **1.17%** | | **0.28%** | |
| Average Recovery | | **85.50** | | **88.25** |

# Sections 9.3 and 9.4 Requirements

- The matrix spike sample was generated by creating an ASTM synthetic wastewater sample. (Aquarium salts, kaolin, flour, Triton-X100 and light beer)
- This wastewater sample was spiked with a 40 mg/L standard and run as a normal sample with the SPE-DEX 3100.
- When the sample was calculated it passed Table 1 criteria for matrix spike HEM recovery with a 78.50%.
- We feel that the Triton® –X (soap solution) played a role in the incomplete recovery of the standard.

# Sections 9.3 and 9.4 Requirements (cont.)

- The laboratory blanks with the WaterTrap were well within the method requirements of 5.0 mg/L.
- The average recovery for a set of 4 blanks was 2.3 mg/L when used with the SPE-DEX 3100, Pacific premium disk, prefilter and the WaterTrap.

# Table 4: Laboratory Blank Contamination SPE-DEX 3100

| Run | HEM Recovery (mg/L) |
|---|---|
| 1 | 2.8 |
| 2 | 2.4 |
| 3 | 2.1 |
| 4 | 1.9 |
| Average | **2.3** |

# Conclusions on Ease of Use

- Sodium sulfate required a lot of prep time and glassware in order to filter the extracts.
  - Time and resources were used transferring, drying and cleaning up the used glassware and sodium sulfate.
- It takes only seconds to install a WaterTrap on SPE-DEX 3100 and seconds to remove the device from the system.
  - There was no solvent transferring, rinsing or cleanup required.
  - Once attached all the SPE steps are automated including the drying of the extract.
  - No user interaction and or additional user technique needed to enhance recovery using the WaterTrap it is all automated by the SPE-DEX 3100.

# Conclusions on Performance

- The MDL for HEM determination using WaterTrap was better than the requirement stated in the method (1.4 mg/L).
- WaterTrap had a better (lower) MDL as compared to sodium sulfate.
- The Initial Precision and Recovery results in Table 2 demonstrated that the WaterTrap recovered greater Hexane Extractable Material (HEM) than the samples that were dried with sodium sulfate.
- The requirements for Section 1.7.1.12 in 1664B were demonstrated and met within this study.
- Horizon Technology's WaterTrap was demonstrated to be equivalent or better than sodium sulfate in the removal of water from the n-hexane extract.

# Thank you!