Analysis of Extract Drying Criteria for Oil & Grease Method 1664A/B

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Introduction

- US EPA Method 1664 for Hexane Extractable Material (HEM) or Oil & Grease 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 Sections 9.3 and 9.4, matrix spike and laboratory blanks respectively.

Limitations of Sodium Sulfate

- 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.
- There are several notes within sections 11.3.6 and 11.3.8 that emphasize the importance of understanding the limitations of sodium sulfate.
  - NOTE: 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.
  - NOTE: The specific properties of a sample may necessitate the use of larger amounts of Na_2SO_4.
  - NOTE: 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.

The WaterTrap™ Drying Membrane

- 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 from Horizon Technology 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.

Experimental

The evaluation was performed using the SPE-DEX 3100 Oil & Grease Extraction System (Horizon Technology, Inc.). The SPE-DEX 3100 system was set up with the larger disk holder (100 mm). The evaporation step, prior to gravimetric measurement was performed using the Speed-Vap® IV evaporation system with the 5-position rack and 105-mm aluminum weighing pans (Horizon Technology, Inc.).

- Pacific™ Premium solid phase extraction disks were used for this work (Horizon Technology, Inc.).
- Pacific™ Fast Flow Prefilters were used for this work (Horizon Technology, Inc.).
- WaterTrap Membrane for water removal (Horizon Technology, Inc.)
- An AE 200 Balance (Mettler Corp.) was used for the gravimetric step.
- Oil & Grease standards containing 4 mg/mL hexadecane and 4 mg/mL stearic acid (PN# 50-003-HT) were prepared for detection limit and spiking purposes (Horizon Technology, Inc.).
- Oil & Grease Snip and Pour (20 mg hexadecane and 20 mg stearic acid) standards (PN# 50-021-HT) were used for spiking purposes (Horizon Technology, Inc.

Quality Control: Sodium Sulfate vs. WaterTrap

- 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.

Table 1: Acceptance Criteria for Hexane Extractable Performance Tests (Method 1664B)

Acceptance Criteria	Limit (%)
Initial Precision and Recovery	
HEM Precision (s)	11
HEM Recovery (X)	83—101
cSGT-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

Results and Discussion

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

The method detection limit with the WaterTrap was equivalent or slightly better than the MDL using sodium sulfate for drying

Table 3. IDC for 100 mm 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

The recovery of spiked HEM was equivalent or better with the WaterTrap, when compared with the same procedure using sodium sulfate

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

The laboratory blank contamination was less than specified in the method (must be less than 5 mg/L)

An ASTM synthetic 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 78.5%. We feel that the Triton™ X-100 (soap solution) played a role in the incomplete recovery of the standard

Conclusions

- The MDL for HEM determination using WaterTrap was better than the requirement stated in the method (1.4 mg/L), ensuring that low concentrations of HEM can be measured with the precision necessary. It also out-performs the MDL determined with sodium sulfate drying
- The Initial Precision and Recovery results in Table 2 demonstrated that the WaterTrap is not only equivalent but recovered greater Hexane Extractable Material (HEM) than the samples that were dried with sodium sulfate
- Sodium sulfate required a lot of prep time and glassware in order to filter the extracts. It took time and resources to accomplish this technique by transferring, drying and cleaning up the used glassware and sodium sulfate
- The WaterTrap fits firmly to the tip of the check valve of the SPE-DEX 3100 and requires no user interaction during the run
- 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