

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

Michael Ebitson, David Gallagher and William Jones
Biotage, Salem, NH, USA

Introduction

- » US EPA Method 1664 for Hexane Extractable Material (HEM) or Oil and 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 Na₂SO₄.
 - » **NOTE:** It is important that water be removed in this step. Water allowed to filter through the Na₂SO₄ will dissolve some of the Na₂SO₄ and carry it into the boiling flask compromising the determination.

The WaterTrap™ Membrane Drying Device

- » With several possibilities for failure and false positives with sodium sulfate, Biotage 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 Biotage 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 Biotage[®] Horizon 3100 (previously known as 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 Biotage[®] Horizon 3100 Oil and Grease Extraction System (Biotage). The Biotage[®] Horizon 3100 system was set up with the larger disk holder (90 mm). The evaporation step, prior to gravimetric measurement was performed using the Speed-Vap[®] IV automated evaporation system with the 5-position rack and 105 mm aluminum weighing pans (Biotage).

- » Pacific Premium solid phase extraction disks were used for this work (Biotage)
- » Pacific[®] Fast Flow Prefilters were used for this work (Biotage)
- » WaterTrap Membrane for water removal (Biotage)
- » 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 (part number 50-003-HT) were prepared for detection limit and spiking purposes (Biotage).
- » Oil & Grease (20 mg hexadecane and 20 mg stearic acid) standards (PN# 50-021-HT) were used for spiking purposes (Biotage).

Quality Control: Sodium Sulfate vs. Water Trap

- » 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: Na₂SO₄ vs. WaterTrap

Run	HEM Recovery Na ₂ SO 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

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

Table 3. IDC for 90 mm disk, Prefilter: Dried with Sodium Sulfate and WaterTrap.

Run	HEM Using Na ₂ SO ₄ (mg/L)	HEM Using Na ₂ SO 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 Biotage[®] Horizon 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 Biotage[®] Horizon 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 Biotage[®] 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. The Biotage WaterTrap was demonstrated to be equivalent or better than sodium sulfate in the removal of water from the n-hexane extract.