Modern Hexane-Extractable (Oil & Grease) Analysis of Wastewater Samples

Vinson Leung, Michael Ebitson and Zoe A. Grosser, Horizon Technology, Inc.
Salem, NH USA
Email SPE@horizontechinc.com • Web www.horizontechinc.com • Tel +1 603.893.3663

n-Hexane-extractable material (HEM), often termed oil & grease, is an operationally-defined general measurement used around the world to help assess water pollution due to a variety of hydrocarbons, including dissolved aromatics, benzene, toluene, xylene and dispersed polynuclear aromatic hydrocarbons (PAHs), aliphatics, naphthenic and fatty acids. (1) The commonly recognised sources include fats, soaps, fatty acids, hydrocarbons, waxes, and oils. (2) It is also used to determine the input into water treatment plants to ensure their continued good operation and to help keep sewer systems from becoming clogged with fats, oil and greases. The measurement of the extracted material is done using a balance in regulatory methods US EPA 1664, ISO 11349 and Standard Methods 5520G, providing a simple and inexpensive detection step. (3,4,5) A further silica-gel treatment can be used to isolate the nonpolar material in the n-hexane extract.

Hexane extractables can be used to regulate allowable pollution in the US. This is done through a system known as the National Pollutant Discharge Elimination System (NPDES) where allowable pollution is listed by industrial category for regulation. For example, in the US Code of Federal Regulations part 40 section 408.12, Subpart A—Farm-Raised Catfish Processing Subcategory, oil & grease, the federal effluent limitation is based on the amount of seafood processed and cannot exceed 10 kg/kkg of seafood on any one day or an average of 3.4 kg/kkg of seafood over the course of a month. Similar regulations are seen in Brazil, Malaysia, the Philippines and other countries.

Method 1664 allows use of solid phase extraction (SPE) instead of liquid-liquid extraction with hexane and this has been widely adopted in the US. In addition to using less solvent, there is less chance of an emulsion forming during extraction with SPE, making the process more predictable. The SPE process can be more easily automated, reducing exposure to solvent and improving reproducibility and we will discuss the results from an automated analysis in this work.

Experimental

The extraction 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) (a smaller one is also available) in anticipation of samples containing more particulate matter. 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 (100 mm) were used for this work (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 and Oil & Grease Snip and Pour (20 mg hexadecane and 20 mg stearic acid) standards were used for detection limit and spiking purposes (Horizon Technology, Inc.).

The Initial Demonstration of Compliance, required when starting up the method, specifies that the method detection limit (MDL) and recovery of spikes should be determined. The method detection limit is determined by evaluating the precision of a set of seven spikes at low concentration. The MDL must be 1.4 mg/L (or better) or 1/3 the regulatory compliance level.

Precision is assessed by measuring four replicate spiked reagent water standards and evaluating the standard deviation and recovery. All samples were 1000 mL and the original sample bottle was dispensed and rinsed by the SPE-DEX 3100 system.

Results and Discussion

The criteria for quality control requirements in method 1664 are shown in Table 1.

Table 1. Acceptance Criteria for Hexane Extractable Performance Tests

Acceptance Criteria	Limit (%)
Initial Precision and Recovery	
HEM Precision (s)	11
HEM Recovery (x)	83-101
Matrix Spike/Matrix Spike Duplicate	
HEM Recovery	78-114
HEM RPD	18
Ongoing Precision and Recovery	
HEM Recovery	78-114

The MDL was determined from 7 replicates of 1 L of reagent water, each spiked with 4 mg/L of standard. The concentrations and statistics are shown in Table 2. The MDL is well below the requirement stated in the method, ensuring that low concentrations of HEM can be measured with the precision necessary.

Table 2. MDL Results

Sample	Conc (mg/L)
1	3.0
2	3.2
3	3.2
4	2.5
5	3.0
6	2.6
7	3.1
Blank	0.6
Standard Deviation:	**0.28**
MDL	**0.89**

Initial precision was demonstrated by spiking 4 1-L volumes with one Snip and Pour pre-measured standard each (40 mg). The data for the four replicates is shown in Table 3. The average percent recovery is excellent and meets the criterion specified in Table 1 of 83-101% recovery. The standard deviation is better than the criterion specified of 11%.

Table 3. Replicate Recoveries

Sample	Recovery (mg)	Recovery (%)
1	39.3	98.2
2	39.8	99.5
3	37.9	94.7
4	38.7	96.8
	Average:	**97.3**
	Standard Deviation:	**2.0**

Several wastewater treatment plant influent source samples were measured and spike recoveries calculated to evaluate the effect of matrices on the method. As shown in Table 4, the spike recoveries were within the 78-114% recovery limits for samples with both a low and high original hexane extractable content.

Table 4. Wastewater spiked with 40 mg standard

Sample	Unspiked (mg)	Spike Recovery (mg)	Recovery (%)
Wastewater 1	14.5	35.5	88.8
Wastewater 2	161	32.1	80.3

Conclusion

The automation of HEM (oil & grease) analysis using SPE for extraction meets the challenging and specific criteria set forth in US EPA Method 1664. The SPE-DEX 3100 automated extraction system provides reproducibility and reduces operator exposure to solvent. Less solvent is used and the formation of emulsions is limited. Additional features of the system provide the ability to handle heavily particulated samples reliably. Overall, automated SPE provides advantages even for smaller laboratories with fewer samples and increases productivity for larger labs with many samples to run.

References:

1. Produced Water, Chapter 2, Ming Yang, Springer,2011.

2. M.K. Stenstrom, S. Fam, and G. Silverman, Env. Tech. Letters, 7, 625-636 (1986).

3. Method 1664, Revision B: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, available at www.epa.gov, (2010).

4. ISO 11349, Water quality — Determination of low-volatility lipophilic substances — Gravimetric method, First edition 2010-09-15, available at http://www.iso.org/iso/home.htm.

5. Method 5520G, Standard Methods for the Analysis of Water and Wastewater, 21 Edition, available at https://www.standardmethods.org/.