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

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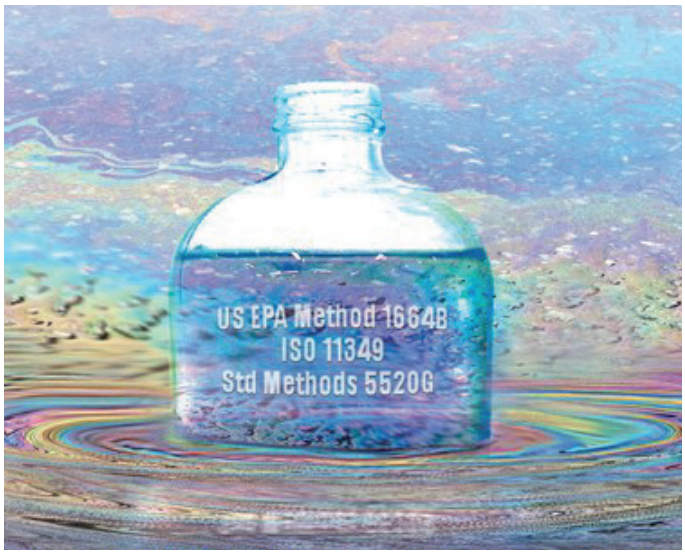
Introduction

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 mand dispersed polynuclear aromatic hydrocarbons (PAHs), aliphatics, naphthenic and fatty acids.[1] Some commonly recognized sources of these compounds include fats, greases, soaps, 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 also be used as a metric 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.



US EPA Method 1664 has allowed use of solid phase extraction (SPE) instead of liquid-liquid extraction with hexane since 2007 and this has been widely adopted in the US. On January 16, 2009, the US EPA released information regarding a modification to EPA Method 1664A. One of the modifications made was to disallow the collection of co-solvents like methanol. It is acceptable to rinse with methanol provided that it is discarded and not eluted into the final eluent. This change was later promulgated into 1664 Revision B. The Biotage® Horizon 3100 (previously known as SPE-DEX 3100) is fully compliant and allows for the methanol to be discarded at the completion of the rinse process.

In addition to using less solvent, there is virtually no 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.

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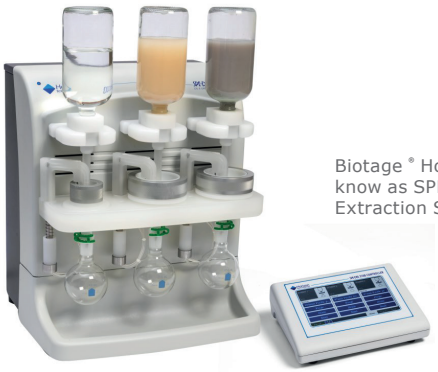
Experimental

The extraction was performed using the Biotage® Horizon 3100 Oil & Grease Extraction System. The Biotage® Horizon 3100 system was set up with either the larger disk holder (90 mm) or the smaller disk holder (47 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). 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 (Biotage part number 50-003-HT) were used for detection limit and spiking purposes. Oil & Grease (20 mg hexadecane and 20 mg stearic acid) standards (Biotage part number 50-021-HT) were used for spiking purposes). Silica gel sorbent material (Fisher Scientific), glass wool, and a glass funnel were used to determine the nonpolar portion of the extract.

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 Biotage® Horizon 3100 system.



Biotage ® Horizon 3100 (previously know as SPE-DEX 3100) Oil & Grease Extraction System with controller.

Speed-Vap® IV Automated Evaporation System with 5-position rack.

Method Summary

Initial Precision and Recovery (IPR)

1. Obtain four 1 liter volumes of DI water.
2. Acidify each with 1:1 hydrochloric acid (until pH <2).
3. Add 5 mL of Oil and Grease Standard OR Add one standard to each bottle (total concentration of 40 ppm).
4. Extract four samples using the Biotage® Horizon 3100 with 47 mm or 90 mm Pacific® Premium SPE Disks.
5. Dry the extract using the WaterTrap in-line membrane drying device. (Sodium sulfate and decanting are allowed for some methods, check with your regulatory agency)
6. Pre-weigh eight aluminum pans and add one extract to each of four. The second set of four will be used for the silica gel-treated extracts.
7. Use the Speed-Vap® IV Automated Evaporation System set to 40° to evaporate each extract.
8. Weigh each extract's pan and calculate the HEM recovery (nominally 40 mg).
9. Reconstitute each extract using n-hexane.
10. Place glass wool in a glass funnel's downspout.
11. Weigh out 3 g of silica gel sorbent material and place on top of glass wool in funnel.
12. Rinse silica gel sorbent, glass wool, and funnel with n-hexane and discard rinsate.
13. Pass reconstituted extract through the funnel making sure to rinse the pan thoroughly (use clean wool and silica gel for each extract). Collect in a pre-weighed clean pan.
14. Use the Speed-Vap® IV Automated Evaporation System set to 40° to evaporate each extract again.
15. Weigh each extract and calculate the SGT-HEM recovery (nominally 20 mg).

Method Detection Limit (MDL)

1. Obtain eight 1-liter volumes of DI water.
2. Acidify each with 1:1 hydrochloric acid (until pH<2).
3. Add 0.5 mL of Oil and Grease Standard to seven bottles (total concentration of 4 ppm). The eighth will serve as a blank.
4. Extract all samples using the Biotage® Horizon 3100 with 47 or 90 mm Pacific Premium SPE Disks.
5. Pre-weigh eight aluminum pans and add one extract to each.
6. Use the Speed-Vap IV Automated Evaporation System to evaporate each extract.
7. Weigh each extract's pan and calculate HEM recovery (nominally 4 mg, except for blank).

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Results and Discussion

The criteria for quality control requirements in method 1664B are shown in Table 1.[3]

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
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

Table 2. HEM MDL Results for 47 mm and 90 mm Disk Sizes.

Sample	47 mm Disk	90 mm Disk
1	2.7	3.0
2	2.7	3.2
3	3.0	3.2
4	2.9	2.5
5	3.0	3.0
6	3.3	2.6
7	3.1	3.1
Blank	0.3	0.6
Standard Deviation	**0.21**	**0.28**
MDL (mg/L)	**0.68**	**0.89**

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 in Table 2. The MDL is better than the requirement stated in the method (1.4 mg/L), ensuring that lowconcentrations of HEM can be measured with the necessary precision.

Initial precision was demonstrated by spiking four 1 L volumes with one pre-measured standard, each (40 mg/L). The data for the four replicates is shown in Table 3 for 47 mm Disks and in Table 4 for 90 mm Disks. The average percent recovery is excellent and meets the criterion specified in Table 1 of 83–101% HEM recovery and 83–116% SGT-HEM recovery for both size disks. The standard deviation is better than the criterion specified of 11% For HEM and 28% for SGT-HEM.

Table 3. Replicate recoveries, HEM 47 mm Disk.

Sample	Recovery (mg)	Recovery (%)
1	39.2	98.0
2	39.1	97.7
3	38.7	96.7
4	38.7	96.7
Average		**97.3**
Standard Deviation		**0.7**

Table 3A. Replicate recoveries, SGT-HEM 47 mm Disk.

Sample	Recovery (mg)	Recovery (%)
1	17.7	88.5
2	17.7	88.5
3	18.1	90.5
4	17.5	87.5
Average		**88.8**
Standard Deviation		**1.3**

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Table 4. Replicate Recoveries, HEM 90 mm Disk

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**

Table 4A. Replicate Recoveries, SGT-HEM 90 mm Disk.

Sample	Recovery (mg)	Recovery (%)
1	18.7	93
2	18.6	93
3	17.7	89
4	17.9	90
Average		**91.1**
Standard Deviation		**2.5**

Additionally, to demonstrate performance with complex real samples, two wastewater treatment plant influent samples were measured and spike recoveries calculated to evaluate the effect of matrices on the method. The 90 mm disks were chosen for these extractions because of the particulate matter in the sample. As shown in Table 5, the spike recoveries were within the 78–114% recovery limits for samples with both a low and high original hexane extractable material content.

Table 5. Wastewater Spiked with 40 mg HEM 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, shown in Table 1. The Biotage® Horizon 3100 (previously known as SPE-DEX 3100) automated extraction system provides reproducibility and reduces operator exposure to solvent. Less solvent is used and the formation of emulsions is virtually eliminated. 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.

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