

Maintaining Regulatory Method Compliance while Automating Oil and Grease Analysis

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Regulatory compliance is at the heart of environmental analyses throughout the world. While some regulatory systems provide more flexibility in the methodology used for measuring contaminants, the goal is to gain reliable information that can be used for decision-making. Oil and grease measurement is a simple and important measurement of water quality, but time consuming¹. Methods such as US EPA 1664 (A and B) or ISO 11349 are used around the world to extract oil and grease from water samples and gravimetrically measure the amount present after the solvent is eliminated². As laboratories around the world, in commercial and government sectors seek to implement simpler and more cost effective technologies to gain efficiency in the determination of total hexane extractable material (HEM) or silica gel treated n-hexane extractable material (SGT-HEM) (non-polar) material from aqueous wastewater samples there are some key aspects to consider. And while liquid-liquid extraction (LLE) remains a widely accepted technique, it is cumbersome and prone to numerous limitations and pitfalls due to the complex nature of wastewater sample matrices. The goal for most labs seeking to automate this procedure remains consistent regardless of geographical region, an automated method consistent with regulatory requirements, meeting or exceeding the quality control of existing methods and offering lower cost and faster turnaround time.

First some facts about US EPA Method 1664 and a review of recent advancements...

- As outlined in the introduction of the method...The US EPA withdrew all oil and grease methods using chlorofluorocarbon-113 (CFC-113 & Freon-113) as acceptable extraction solvents in the final rule published March 7, 2007. As such EPA Method 1664, Revision B (Feb. 2010): n-hexane extractable material (HEM; oil and grease) and silica-gel treated n-hexane extractable material (SGT-HEM; non-polar material) is the only US EPA approved method for the measurement of oil and grease in wastewaters.
- Method 1664B is a performance-based method applicable to the measurement of the method defined parameters HEM and SGT-HEM from aqueous matrices and requires the use of n-hexane as the extraction solvent, gravimetry, as the determinative technique and includes additional QC procedures designed to monitor precision and accuracy.
- The 'B' modifications promulgated in February 2010 were designed to provide additional information for labs to improve performance and more importantly define modifications that are now allowed for nationwide use without prior EPA review (40 CFR 136.6) and to also define clearly any modifications that are not allowed...These 'modifications' are found in section 1.7 of the method and take into account advances occurring in analytical technology, provide options to improve separations and consider the reduction of overall costs for measurements.

- Options now included: Continuous Liquid-Liquid Extraction (CLLE) and Solid Phase Extraction (SPE) as accepted separation techniques as well as Kuderna-Danish as an alternative concentration technique.

The method also specifies that:

- “Alternate determinative techniques, such as immunoassay and infrared spectroscopy, and changes that degrade method performance or change the chemistry of the method including the use of extraction solvents other than n-hexane (85% minimum purity, 99% min. saturated C6 isomer, residue less than 1 mg/L) are not allowed.”

Solid phase extraction was incorporated into method 1664 for a variety of reasons including:

- Less solvent is used, reducing waste disposal and improving technician safety
- Emulsions do not form, reducing variability and speeding completion of the extraction step

EPA method 1664 B allows the use of a co-eluting solvent such as methanol so long as this solvent is immediately discarded and not collected. The methanol step is essential in order to maximize the recoveries of HEM and SGT-HEM using n-hexane. The reason for this is that residual water tends to encompass oil and grease molecules not allowing all of the oil and grease molecules to be extracted by the hexane solvent. Figure 1, steps 1 through 4 shows schematically what is occurring at a molecular level.

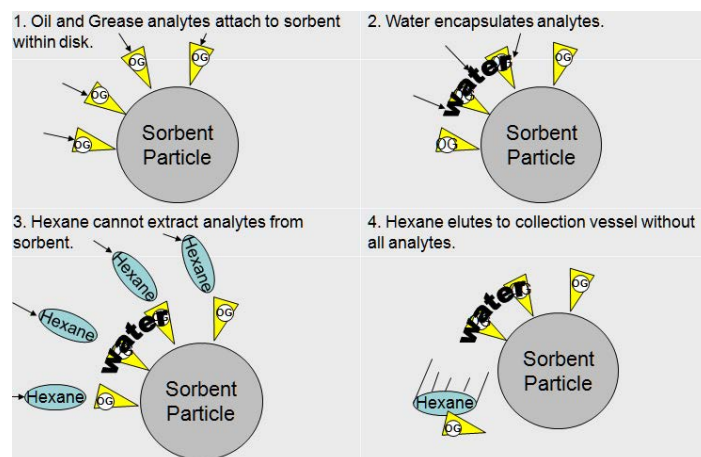


Figure 1. SPE molecular-level processes

When methanol is employed as a co-eluting solvent and then immediately discarded, the methanol will remove any of the residual water encompassing the Oil and Grease molecules and exposing those molecules to the next elution solvent, in this case hexane. Figure 2, steps 5 through 8 shows schematically what is occurring at a molecular level.

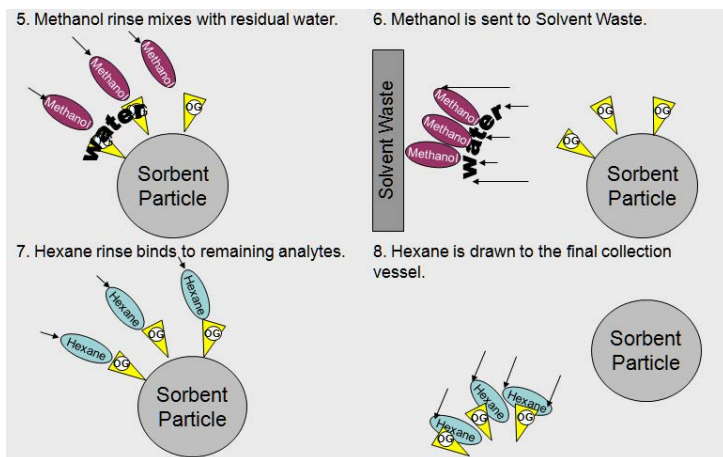


Figure 2. Elution process at a molecular level.

The effect of this methanol pretreatment step was evaluated experimentally. In this experiment, five gallons of influent water from a wastewater treatment plant in the US was thoroughly mixed and divided into 6 one-liter water samples. All samples were acidified and spiked with 20 mg of hexadecane and 20 mg of stearic acid. All samples were processed on the SPE-DEX® 3000 Oil and Grease Extraction System with Pacific™ Premium SPE disks (Horizon Technology). One set of three were extracted without the use of methanol as a co-eluting solvent and the other set of three samples were processed using methanol as a co-eluting solvents and HEM results were determined gravimetrically. The results are shown in Tables 1 and 2 and clearly indicate that those samples not treated with methanol showed 42% less HEM than the samples treated with methanol as a co-eluting solvent. The recoveries with methanol pretreatment were well within the range of 78-114%, method criteria specified for matrix spike recoveries.

Table 1. Extraction with Methanol Pretreatment

Replicate Samples	Begin Weight (g)	Final Weight (g)	HEM (mg)
1-Liter Influent	6.1831	6.2136	30.5
1-Liter Influent	6.2030	6.2359	32.9
1-Liter Influent	6.2015	6.2357	34.2
Avg. Reported Value			32.5

Table 2. Extraction without Methanol Pretreatment

Replicate Samples	Begin Weight (g)	Final Weight (g)	HEM (mg)
1-Liter Influent	6.2473	6.2656	18.3
1-Liter Influent	6.1801	6.2045	24.4
1-Liter Influent	6.2506	6.2643	13.7
Avg. Reported Value			18.8

The use of SPE has been developed and improved over the years since its introduction into this method. In addition, the automation of the method is facilitated by the use of SPE. Automation can reduce the variability that comes from human intervention and error. Table 3 compares the results of SPE with automation (SPE-DEX 3000 Extractor and SpeedVap® III, Horizon Technology) to LLE without automation for simple distilled water samples spiked with standards, an initial demonstration of capability. It can be seen that the recoveries are better and the standard deviations more tightly controlled using the automated process.

Table 3. Comparison of Recoveries, LLE and Automated SPE

Effluent Replicate	LLE Recovery (%)	SPE Recovery (47-mm disks) (%)
HEM		
1	96.3	100.5
2	97.5	100.3
3	96.5	100.3
4	99.8	99.3
Average	97.5	100.1
Standard deviation	1.6	0.6
SGT-HEM		
1	98.0	104.0
2	93.5	99.5
3	84.5	99.5
4	94.0	95.5
Average	92.5	99.6
Standard Deviation	5.7	3.5

Comparing results with the requirements in method 1664B, Table 1, it can be seen that the recoveries using SPE are well within the limits of 83-101% for HEM and 83-116% for SGT-HEM. The precision requirements are standard deviation of 11 for HEM and 28 for SGT-HEM. In both cases the standard deviation was much less than the criteria.

Additional benefits of using the SPE-DEX 3000 extractor are that it uses less solvent than LLE, it is an automated procedure, and sample process times are more rapid relative to LLE. In this case, SPE methods average 50 minutes per sample versus 2.5 hours for the LLE methods on the treatment plant sample. Since labor costs are often the most expensive part of an analysis this can significantly reduce the labor required and improve turnaround time.

Simple, fast, safe evaporation of n-Hexane solvent...

Since EPA method 1664B is a gravimetric method, it is necessary to further process extracts so that they are evaporated down to dryness while minimizing losses of the volatile components in the extract. The solvent can be evaporated in a hood or desiccator to constant weight, but this can be time-consuming

and it may be difficult to prevent contamination. Automating this part of the process, in parallel to the extraction, can reliably accelerate the evaporation process. One example of an automated system is the Speed-Vap™ III (Horizon Technology) which will quickly and efficiently take the oil and grease extracts to dryness in a controlled fashion. This system operates by applying a vacuum and a gentle heat to individually tared aluminum weighing pans that contain the n-hexane extracts. The Speed-Vap III is covered with a lid that has pin holes drilled into it that allow ambient air to be pulled over the pans as they are evaporating, while minimizing contamination. The pin holes are oriented at an angle that creates a mini vortex in each pan as the heating is occurring. This “constant stirring” of the surface of the hexane extracts accelerates the speed at which the evaporation occurs because the surface of the hexane in the pans is constantly moving, thus reducing the surface vapor tension of the hexane. The system comes supplied with a holder for five 105-mm pans holding 125 mLs of solvent or a holder for 9 pans that are 70 mm that can contain 55-mLs each. Extract volume sizes will vary depending upon how highly particulated the original samples are.

A single robust technique for diverse wastewater samples from dirty to clean...

Solid Phase Extraction disks for adsorption of the oil and grease from water are manufactured to consistent standards to provide reproducible performance. Pacific Premium Disks (Horizon Technology) are available in two sizes, 50 mm and 100 mm, with the choice of size to use depending on how many insoluble solids like soil, sand and small rocks are present in the sample. The cleaner samples with low particulate levels are usually processed using the 50 mm and higher particulated samples often will use the 100 mm disks located in appropriate holders. The instrument uses hexane and methanol as its rinsing (elution) solvents and due to the high efficiency of SPE disks for this application, minimal amounts of solvent are consumed. Based upon the size of the disk chosen the match the sample needs, final extract volumes will vary between 55 mLs and 125 mLs.

A cost effective, versatile and compliant approach to EPA 1664 analysis for any lab...

For those labs performing Oil and Grease analysis in accordance with EPA Method 1664A or B who seek to implement a cost effective automated alternative to traditional liquid-liquid extraction techniques there are in fact, very few viable choices to consider. Infrared solutions simply do not comply with the EPA regulation.

The advantages of automation include:

- Reproducible, providing consistent results
- Requires less attention, freeing analysts for other tasks
- Improve technician safety and reduce exposure to solvents

Using solid phase extraction also provides a number of advantages:

- Fully compliant with method 1664 A and B

- Less solvent is required, reducing costs and waste
- Recoveries and precision is better compared to LLE
- No emulsions form, speeding analysis
- Fewer re-extractions, improving customer satisfaction

Since 1993, Horizon Technology, Salem, New Hampshire, has emerged as a leader in this field providing automated SPE solutions to environmental labs involved in drinking and wastewater analysis world-wide, especially those focused on Oil and Grease monitoring.

In conclusion, SPE and automation of SPE can help maintain compliance with regulatory agency and methodology requirements and deliver better results with faster turnaround time.

References

1. http://water.epa.gov/scitech/methods/cwa/methods_index.cfm
2. Method 1664, Revision B, <http://water.epa.gov/scitech/methods/cwa/upload/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.pdf>, February 2010.