Expanded Clarification of Oil and Grease in Part 136

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Abstract

EPA Method 1664 Revision B was published in February 2010 and was included in Table IB as an approved inorganic test procedure for the measurement of oil and grease in the final Method Update Rule published on May 18th, 2012. EPA 1664B is an updated version of EPA 1664A and specifically identifies a list of allowable method modifications and other modifications that are not allowed. Now that laboratories, auditors and regulators are applying the requirements of EPA 1664B, certain clarifications may be needed due to a misunderstanding or misinterpretation of previous EPA 1664A requirements. The author will address a few of the hotter topics with EPA 1664A/B and will also clarify the requirements of the final decision on an alternative Oil and Grease method published on March 6, 2013.

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Acknowledgement

- Xenosep Technologies would like to thank Mr. Lemuel Walker of the US EPA (Office of Science and Technology, Engineering and Analysis Division) for his review, comment and guidance of the following presentation. Any EPA related questions can be addressed to: Walker.Lemuel@epa.gov.

EPA 1664A – HEM & SGT-HEM (Oil and Grease)

Performance-Based Method

Method-Defined Analyte

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40 CFR § 136.6 – Method Modifications

- Many potentially acceptable modifications but can not change chemistry or determinative technique
- "An analyst may not modify an approved analytical method for a method defined analyte." ((b)(3))
- Wastewater matrix issues
  - Can improve QC recovery with salts and inert surfactants
  - "must not react with or introduce the target pollutant into the sample"

Summary of EPA Methods 1664A and 1664B

- 1 L sample acidified to pH<2
- LLE – 3 x 30 mL extractions n-hexane
- Dry extract with sodium sulfate
- Distill solvent from extract
- HEM is desiccated and weighed
- Proportionate silica gel treatment
- SGT-HEM is desiccated and weighed

EPA Method 1664B Types of Modifications

- Allowable (16)
- Unacceptable (5)
- Limited-Use ATP (1)
- All included in EPA 1664B – § 1.7 & 1.8

EPA 1664A/B Comparison

Method Modification	1664B	1664A
Optimized Extraction Procedure	**Included**	**Allowable**
Alternate Determination Techniques	**Not Allowed**	**Not Allowed**
Analysis of < Collected Sample	**Not Allowed**	**Not Allowed**
Other Reference Standards	**Not Allowed**	**Not Allowed**
Spiking into Extractor	**Not Allowed**	**Not Allowed**
Method 1664 “Cu”	**Included ATP**	**Allowable ATP**

EPA 1664A/B Comparison

Method Modification	1664B	1664A
Alternate Extraction Techniques	**Included**	**Allowable**
Alternate Concentration Techniques	**Included**	**Allowable**
Omit Oven Drying Step §11.4.4	**Included**	**Allowable**
Lower PAR Concentration (20mg/L)	**Included**	**Allowable**
Collect Smaller Sample Volume	**Included**	**Allowable**
Additional Balance Calibration	**Included**	**Allowable**

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EPA 1664A/B Comparison

Method Modification	1664B	1664A
Sample Acidification, pH<2	**Included**	**Allowable**
Prefilter, Filtration Aid Use	**Included**	**Allowable**
SPE Filter Use	**Included**	**Allowable**
Matrix Spike Selection	**Included**	**Allowable**
Silica Gel Treatments	**Included**	**Allowable**
Silica Gel Equivalence	**Included**	**Allowable**

EPA 1664A/B Comparison

Method Modification	1664B	1664A
Solvent Phase Separation Paper	**Included**	**Allowable**
Polar Solvent Cleaning	**Included**	**Allowable**
Polar Solvent SPE Conditioning	**Included**	**Allowable**
Polar Solvent Rinsing/Extraction	**Not Allowed**	**Not Allowed**
Alternate Extraction Solvents	**Not Allowed**	**Not Allowed**
Methanol Rinse Exception	**Included**	**Allowable**

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Summary of 1664A and 1664B Method Modifications

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Potential Compliance Issues for EPA 1664A and 1664B

Horizon letter in March 2009 on www.horizontechinc.com

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1664 METHOD MODIFICATION

Complying with the Modifications to EPA Method 1664A Using Horizon Technology Automated Extraction Systems

On January 16, 2009, the US EPA released information regarding Modifications to Method 1664A. You can access the EPA memorandum referencing these modifications by visiting: http://www.epa.gov/waterscience/methods/method/oil/1664a-mod.html

procedures and seemed to cover a wide range of variations. In an effort to remove confusion, add guidance, and more clearly identify the user's current flexibility to modify the method 1664A, the EPA released their January 16, 2009 memorandum. The memorandum addresses the following topics as Allowable Modifications; PAR Standard, SPE Filters/Prefilters, Smaller Sample Sizes, Alternate Concentration Techniques, Acidification of Sample, Matrix Spike Requirements, and Balance Calibration. The memorandum also addressed Unacceptable Modifications to the Method 1664A, and a Limited Use Modification to Method 1664A, specific to Region 8. See the document for details.

One "Unacceptable Modification to EPA Method 1664A" is the use of co-solvents and/or alternate solvents. Why is this?
One variation the regional EPA auditors found was that people performing SPE were using a variety of solvents to rinse the sample bottle and the SPE disk. While Method 1664A was written as a LLE technique, and was very specific in the sample preparation procedure to be followed, the exact SPE methodology was never included in the written method. It was omitted because SPE was a new technology; and it was determined that the SPE procedure should not be tied to a specific written procedure, that could not be deviated from. The main driver for this action was the fact that there have been previous cases where prescriptive EPA methods have been written and promulgated, but eventually shown not to be properly optimized to ensure good chemistry. However, once a prescriptive method is promulgated, it cannot be changed, which can create a major problem for analytical labs.

With regards to EPA Method 1664A, which was moving towards the performance based approach of method development, it was felt that as long as the MDL, IPR, and OPR requirements of the method were met, the SPE procedure should be able to be optimized, as long as the data quality objectives of the method were met. When the EPA auditors began to find various solvents and techniques being used, they referred back to the written 1664A method, a LLE technique, and made the decision that only n-hexane can be the extracting solvent. Therefore, the January 16th document stated that the "use of CO-solvents or alternate solvents is not allowed because the chemistry of the method has been changed."

How will this modification of disallowing co-solvent impact the recovery values of my O&G samples?
For those doing SPE extractions, it is well known that the optimal approach for maximum extraction efficiency is to rinse the SPE disk with a water soluble solvent, after the water sample has been filtered through the disk. This is important for several reasons.

1. If the residual water left in the pore structure of the SPE disk is not first removed, then any non-polar solvent, such as n-hexane, cannot effectively extract the compounds from the SPE disk, in this case the O&G fraction, which will result in low and inconsistent recoveries. Therefore, all proper SPE methods require a water soluble solvent as a rinse.

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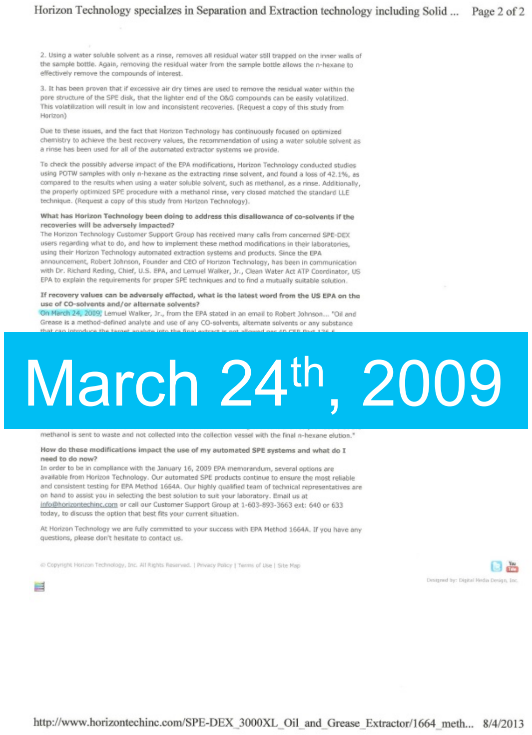
http://www.horizontechinc.com/SPE-DEX_3000XL_Oil_and_Grease_Extractor/1664_meth... 8/4/2013

January 16, 2009



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2. Using a water soluble solvent as a rinse, removes all residual water still trapped on the inner walls of the sample bottle. Again, removing the residual water from the sample bottle allows the n-hexane to effectively remove the compounds of interest.

3. It has been proven that if excessive air dry times are used to remove the residual water within the pore structure of the SPE disk, that the lighter end of the O&G compounds can be easily volatilized. This volatilization will result in low and inconsistent recoveries. (Request a copy of this study from Horizon)

Due to these issues, and the fact that Horizon Technology has continuously focused on optimized chemistry to achieve the best recovery values, the recommendation of using a water soluble solvent as a rinse has been used for all of the automated extractor systems we provide.

To check the possibly adverse impact of the EPA modifications, Horizon Technology conducted studies using POTW samples with only n-hexane as the extracting rinse solvent, and found a loss of 42.1%, as compared to the results when using a water soluble solvent, such as methanol, as a rinse. Additionally, the properly optimized SPE procedure with a methanol rinse, very closed matched the standard LLE technique. (Request a copy of this study from Horizon Technology).

What has Horizon Technology been doing to address this disallowance of co-solvents if the recoveries will be adversely impacted?
The Horizon Technology Customer Support Group has received many calls from concerned SPE-DEX users regarding what to do, and how to implement these method modifications in their laboratories, using their Horizon Technology automated extraction systems and products. Since the EPA announcement, Robert Johnson, Founder and CEO of Horizon Technology, has been in communication with Dr. Richard Reding, Chief, U.S. EPA, and Lemuel Walker, Jr., Clean Water Act ATP Coordinator, US EPA to explain the requirements for proper SPE techniques and to find a mutually suitable solution.

If recovery values can be adversely effected, what is the latest word from the US EPA on the use of CO-solvents and/or alternate solvents?
On March 24, 2009, Lemuel Walker, Jr., from the EPA stated in an email to Robert Johnson... "Oil and Grease is a method-defined analyte and use of any CO-solvents, alternate solvents or any substance that can introduce the target analyte into the final extract is not allowed per 40 CFR Part 136.6

methanol is sent to waste and not collected into the collection vessel with the final n-hexane elution."

How do these modifications impact the use of my automated SPE systems and what do I need to do now?
In order to be in compliance with the January 16, 2009 EPA memorandum, several options are available from Horizon Technology. Our automated SPE products continue to ensure the most reliable and consistent testing for EPA Method 1664A. Our highly qualified team of technical representatives are on hand to assist you in selecting the best solution to suit your laboratory. Email us at info@horizontechinc.com or call our Customer Support Group at 1-603-893-3663 ext: 640 or 633 today, to discuss the option that best fits your current situation.

At Horizon Technology we are fully committed to your success with EPA Method 1664A. If you have any questions, please don't hesitate to contact us.

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http://www.horizontechinc.com/SPE-DEX_3000XL_Oil_and_Grease_Extractor/1664_meth... 8/4/2013

March 24th, 2009

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March 29, 2009, EPA to Horizon
February 2010, EPA Method 1664B
May 18, 2012, EPA MUR Final

"However, a methanol rinse may be allowed to remove water residual if:

1. The methanol rinse is immediately discarded to waste.

2. The SPE filter is sufficiently air dried with vacuum to remove any traces of methanol remaining in the SPE filter so as to ensure that no methanol will collocate or be collected with the n-hexane extractions.

3. And, it is the laboratory's responsibility to demonstrate and document the appropriate operating conditions (1 and 2) above to allow this use of methanol.

Given this, the use of methanol to condition the SPE filter or rinsing bottles is allowed provided that the methanol is sent to waste and not collected into the collection vessel with the final n-hexane elution."

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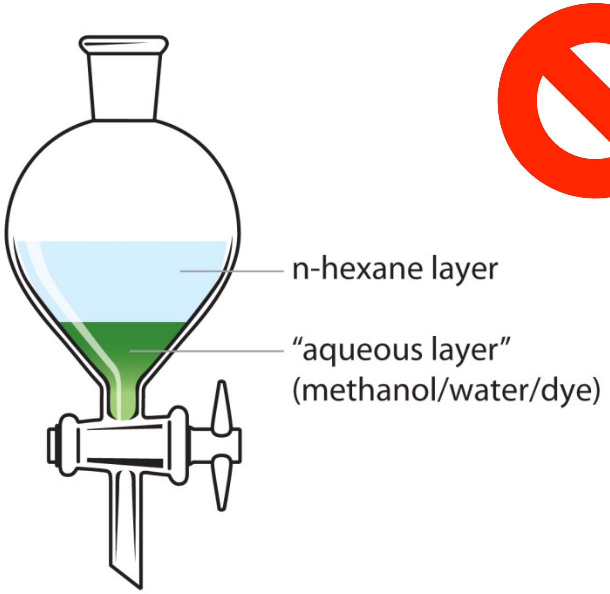
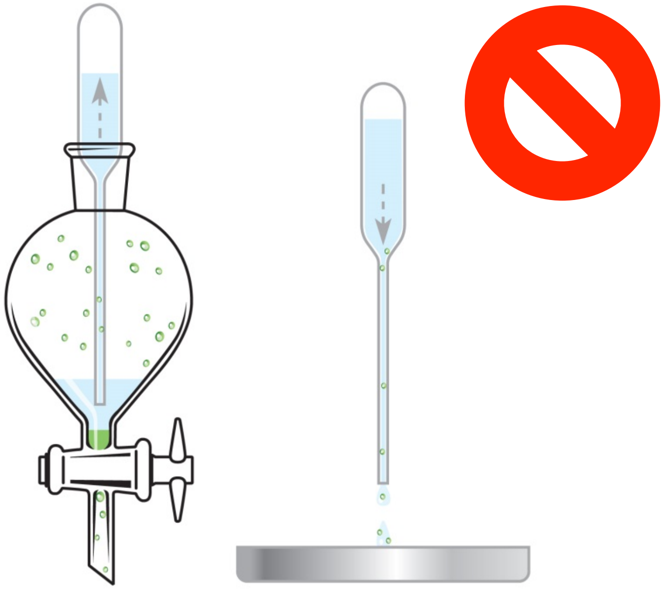
Potential Compliance Issues if your 1664 Extract looks like this



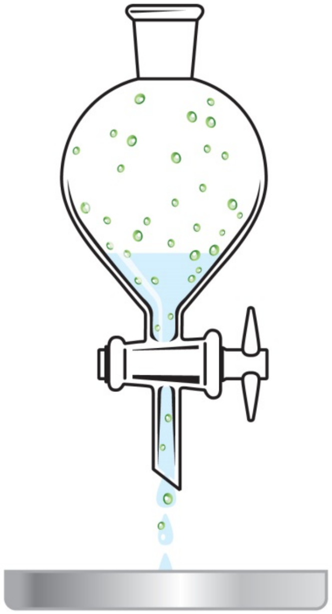
- Methanol in separatory funnel is not allowed
- Must use sodium sulfate to remove water from extract
- Solvent Phase Separator Paper an allowable equivalent means for removing water from extract

Replace Sodium Sulfate with Pipetting from Sep Funnel???



- No methanol is allowed to be in the separatory funnel
- No reason to use dye and not use sodium sulfate or equivalent means for removing water from extract
- Pipetting is not an allowable equivalent means for removing water from extract

Replace Sodium Sulfate with Draining from Sep Funnel???



- No methanol is allowed to be in the separatory funnel
- No reason to use dye and not use sodium sulfate or equivalent means for removing water from extract
- Draining is not an allowable equivalent means for removing water from extract

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Replace Sodium Sulfate with Pouring from Sep Funnel???

- No methanol is allowed to be in the separatory funnel
- No reason to use dye and not use sodium sulfate or equivalent means for removing water from extract
- Pouring is not an allowable equivalent means for removing water from extract

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February 2010-EPA Method 1664B Alternate Extraction Solvents - 1

- Unacceptable modification
- HEM and SGT-HEM are method-defined analytes and the only solvent that can introduce the target pollutants into the sample is n-hexane, otherwise the chemistry of the method is changed (i.e., legal issue).
- SPE filter conditioning (prior to sample filtration) with a polar solvent is acceptable

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February 2010-EPA Method 1664B Alternate Extraction Solvents - 2

- Special methanol “rinse” exception
- Requirements
  - Methanol rinse immediately discarded to waste
  - Sufficiently air dried with vacuum to remove any traces of methanol remaining in the SPE Filter
  - No methanol will introduce analyte, collocate or be collected with the n-hexane extraction
  - Laboratory responsibility to demonstrate and document the operating conditions above

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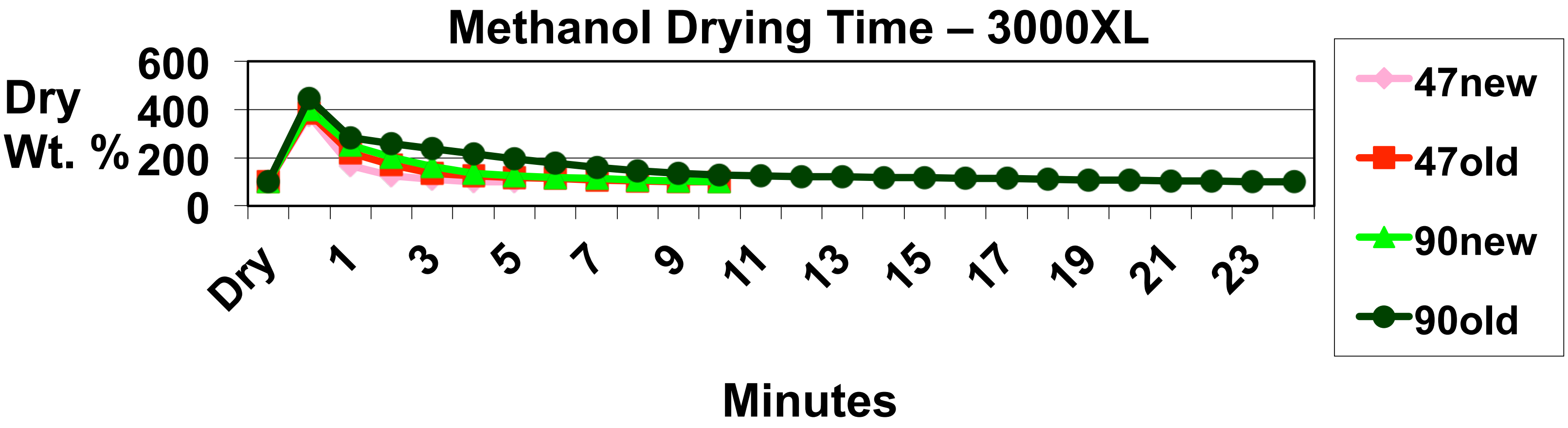
February 2010-EPA Method 1664B Alternate Extraction Solvents - 3

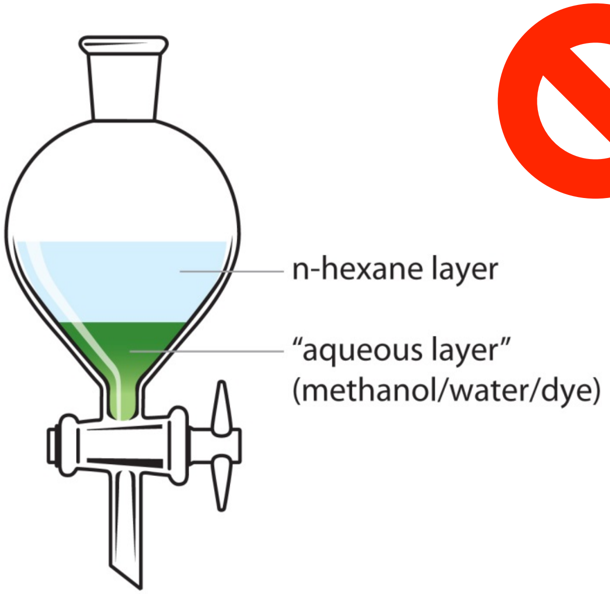
- Meeting “exception” vacuum air dry requirements
  - 47mm SPE filter & 90mm SPE filter (Wet wt. = Dry wt.)
  - Many variables – vacuum, free air flow, SPE filter, etc.
- 2-3 Vacuum air dry steps & GC Analysis?



EPA 1664B Section 1.7.2.1 Note

- **NOTE**: The use of a polar solvent to condition an SPE filter or SPE device in a modified method prior to sample filtration is allowed. The use of methanol or another polar solvent after sample filtration to remove water residual may be allowed provided the polar solvent is immediately discarded to waste and the SPE filter or SPE device is sufficiently air-dried with vacuum to remove any residual polar solvent to trace amounts so at no time will residual polar solvent introduce the target analyte into the sample, collocate with or be collected with the extraction solvent, n-hexane. A simple test to determine sufficient residual polar solvent removal from an SPE filter by vacuum air drying would be to weigh and record the weight of a dry SPE filter to the nearest 0.1 mg. Then analyze a blank using the dry SPE filter, conditioning the SPE filter and filtering the blank sample per the modified SPE method. Immediately after discarding the polar solvent to waste (and prior to addition of the n-hexane extraction solvent), stop the vacuum, remove the SPE filter from the apparatus and weigh the wet SPE filter saturated with residual polar solvent to the nearest 0.1 mg. Record this wet SPE filter weight. Reassemble the wet SPE filter into the apparatus and **continue vacuum air drying the SPE filter until the weight of the wet SPE filter is less than 101% of the dry SPE filter weight.** For example, if the weight of the dry SPE filter is 1,000.0 mg, continue vacuum air drying the wet SPE filter until the final weight is less than or equal to 1,010.0 mg before contacting the SPE filter with the extraction solvent n-hexane. This simple test could be used by the laboratory to demonstrate and document removal of residual methanol from the SPE filter to trace amounts so as to ensure residual methanol will not introduce the target analyte into the sample and at no time will residual methanol collocate with the n-hexane extraction solvent or be collected in the collection flask.

Methanol in Sep Funnel Vs. Methanol Rinse Requirements



- Methanol in separatory funnel is not allowed
  - Lab Responsibility
  - Co-Solvent
  - Collected
  - Collocated
  - Not discarded
  - Not dried to trace amounts

February 2010-EPA Method 1664B Alternate Determinative Methods

- Unacceptable modification
- Examples listed at § 9.1.2 include:
  - Infrared spectroscopy
  - Immunoassay
  - Changes that degrade method performance
- Must be gravimetric determination

ASTM D7575 – Oil and Grease

- Membrane Extraction – IR Detection
  - Green Chemistry Approach – April 2009
  - Technical Concerns RE: Equivalence to 1664A/B

- Method Defined – (new ATP Process TBD in 2013)
  - Chemistry - changed
  - Determinative step - changed
  - IR specifically prohibited in 1664, 1664A, 1664B

- Final Determination – March 6, 2013
  - Results Not Equivalent to EPA 1664A/B
  - Permit by Permit approval if applicable – ATP Tier 1

Questions? More information?

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