Complying With EPA Method 1664A and 1664B by Automated Solid Phase Extraction Utilizing the SPE-DEX® 4790 with Envision® Platform v1.02

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Introduction

The purpose of this application is to demonstrate the viability of a solid phase extraction (SPE) method utilizing the Horizon Technology SPE-DEX® 4790 Extractor with the Envision® Platform software version 1.02 to extract samples for EPA Method 1664A/B and fulfill all QC requirements.

EPA Method 1664 is a performance based method which is used to find the total n-hexane extractable material (HEM) and the silica-gel treated n-hexane extractable material (SGT-HEM) within a sample. The method specifically outlines the steps needed to perform the liquid-liquid extraction (LLE) and details the process to determine if an alternative method may be used.

On January 16, 2009, the US EPA release information regarding a modification to EPA Method 1664A. One of the modifications made was to disallow the elution of co-solvents like methanol. It is acceptable to rinse with methanol provided that it is discarded and not eluted. This modification was later promulgated into Revision B of the method. The SPE-DEX 4790 Extractor with the Envision Platform software version 1.02 is fully compliant and allows for the methanol to be discarded at the completion of the rinse process. For more information, the EPA memorandum can be accessed on their website:
http://www.epa.gov/waterscience/methods/method/oil/1664a-mod.html

The SPE-DEX 4790 extractors are specifically designed to automatically extract oil and grease from a wide range of clean and dirty aqueous samples using the EPA 1664 method. The Speed-Vap III Solvent Evaporation System allows for consistent and gentle heating and air flow over the sample to prevent the loss of volatile compounds. The Solvent Trap Recovery System is designed to recover up to 70% of the n-hexane solvent vapors for reuse or disposal. The Horizon Technology Pacific Premium disks were designed to obtain the accuracy and consistency of data needed to comply with method 1664A/B QC specifications.

Horizon Technology Pacific™ Premium SPE Disk

Horizon Technology Speed-Vap™ Evaporation System, SPE-DEX® 4790 Extractor System, Envision® Platform v1.02, and Solvent Trap™ Solvent Recovery System.

Instrumentation

- Horizon Technology
  - SPE-DEX® 4790 with Envision® v1.02
  - Speed-Vap™ III Evaporation System
  - Solvent Trap™ Recovery System
  - Pacific™ Premium SPE Disks (both 47 mm and 100 mm)
  - 10 mL Oil & Grease Standard containing 2 mg/mL Hexadecane and 2 mg/mL Stearic Acid
  - 26 mL Oil & Grease Standard Containing 4 mg/mL Hexadecane and 4 mg/mL Stearic Acid
  - Aluminum Weigh Pans, 105 mm
- Mettler AE 200 (Balance)
- Silica Gel
- Glass Wool
- Glass Funnel

Method Summary

I. Initial Precision and Recovery (IPR)

1. Obtain twelve 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 to each bottle such that the total concentration is 40 ppm.
4. Extract four samples using the SPE-DEX 4790 with 100 mm Pacific Premium SPE Disks using the method shown in Table 1.
5. Extract four samples using SPE-DEX 4790 with 47 mm Pacific Premium SPE Disks using the method shown in Table 2.
6. Extract four samples by LLE.
7. Pre-weigh twelve aluminum pans and add one extract to each.

8. Use the Speed-Vap III Evaporation System to evaporate each extract.
9. Weigh each extract's pan and calculate HEM recovery (nominally 40 mg).
10. Reconstitute each extract using n-hexane.
11. Place glass wool in glass funnel's downspout.
12. Weigh out 3 g of Silica Gel Sorbent material and place on top of glass wool in funnel.
13. Rinse Silica Gel Sorbent, glass wool, and funnel with n-hexane and discard rinsate.
14. Pass reconstituted extract through the funnel making sure to rinse the pan thoroughly (use clean wool and Silica Gel for each extract).
15. Use the Speed-Vap III Evaporation System to evaporate each extract again.
16. Weigh each extract and calculate the SGT-HEM recovery (nominally 20 mg).

II. 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 Oil and Grease Standard to seven bottles such that the total concentration is 4 ppm. The eighth will serve as a blank.
4. Extract all samples using SPE-DEX 4790 with 47 mm Pacific Premium SPE Disks using the method shown in Table 2.
5. Pre-weigh eight aluminum pans and add one extract to each.
6. Use the Speed-Vap III Evaporation System to desiccate each extract.
7. Weigh each extract's pan and calculate HEM recovery (nominally 4 mg except for blank).

Table 1: 100 mm Pacific Premium Disk Method

Step	Solvent	Soak	Air Dry
1. Prewet	Hexane	30 s	10 s
2. Prewet	Methanol	30 s	10 s
Sample Process			
1. Wash	1:1 MeOH: DI Water	10 s	40 s
Air Dry 3 min			
1. Rinse	Hexane	45 s	30 s
2. Rinse	Hexane	45 s	30 s
3. Rinse	Hexane	45 s	30 s
4. Rinse	Hexane	45 s	30 s

Table 2: 47 mm Pacific Premium Disk Method

Step	Solvent	Soak	Air Dry
1. Prewet	Hexane	30 s	10 s
2. Prewet	Methanol	30 s	10 s
Sample Process			
1. Wash	Methanol	20 s	20 s
Air Dry 45 s			
1. Rinse	Hexane	30 s	30 s
2. Rinse	Hexane	30 s	30 s
3. Rinse	Hexane	30 s	30 s
4. Rinse	Hexane	30 s	30 s

Results

Each laboratory is responsible for operating a formal quality assurance program that complies with the minimum requirements outlined in EPA Method 1664A/B. For this method, there are three requirements:

1. An initial precision and recovery (IPR) study.
2. A method detection limit (MDL) study.
3. An ongoing precision and recovery (OPR) study.

In addition, because we are qualifying a new test, an equivalency demonstration must be performed to show that the new method can recover an equivalent amount of material as the liquid-liquid method. This application note outlines the IPR, MDL, and equivalency demonstrations.

Table 3 shows the results for a seven replicate MDL study. The nominal recovery for HEM is 4 mg/L. A student t-value of 3.143 was used based on a 99% confidence and 6 degrees of freedom. The EPA dictates that the results for an MDL study be below 1.4 mg/L. Accordingly, the SPE results are well below this limit.

Table 4 shows the SPE and LLE data for an IPR study done using 100 mm disks. The data shows that, not only are the recoveries for the SPE method better than the LLE method, but the deviations are smaller too. The biggest benefits of SPE though is that the LLE takes about 40 minutes for one extract and about 120 mL of solvent while SPE takes about 20 minutes and 30 mL (for the 47 mm disk) meaning throughput can be increased substantially and cost decreased.

Table 4 can also be used as a proof of equivalency demonstration. The HEM recovery results for SPE are 102% of the HEM LLE recovery results while the SGT-HEM SPE results are 106% of its LLE counterpart. This is a substantial increase in recovery and both are well within EPA criteria meaning the SPE methodology is an acceptable alternative to LLE.

Table 3: MDL Results for HEM Using 47 mm Disks

Sample	SPE (mg/L)
1	2.8
2	3.2
3	2.9
4	3.4
5	3.1
6	3.1
7	3.0
Blank	0.1
Standard Deviation	**0.1976**
MDL	**0.6211**

Table 4: IPR Comparison Data Using 100 mm Disks

Sample	LLE (mg/L)	Recovery %	SPE (mg/L)	Recovery %
HEM				
1	38.5	96.3	39.9	99.8
2	39.0	97.5	40.0	100.0
3	38.6	96.5	39.8	99.5
4	39.9	99.8	40.2	100.5
Average		**97.5**		**99.9**
Standard Deviation		**1.6**		**0.4**
SGT-HEM				
1	19.6	98.0	18.7	93.5
2	18.7	93.5	20.2	101.0
3	16.9	84.5	19.7	98.5
4	18.8	94.0	19.7	98.5
Average		**92.5**		**97.9**
Standard Deviation		**5.7**		**3.1**

Conclusions

This application note shows that the Horizon Technology SPE-DEX 4790 Automated Extraction System, coupled with the Speed-Vap III and Solvent Trap Solvent Recovery System fulfill all the necessary requirements put forth within the EPA Method 1664A and 1664B.

Automated SPE will not only allow you continual compliance with the EPA but will reduce labor and solvent cost, allow faster turnaround times, and improve on both laboratory precision and accuracy.

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