



# Oil & Grease Measurement Improvement for Better Auditability

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# Definition of Oil and Grease

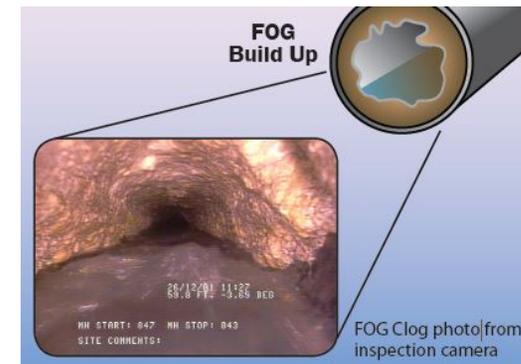


- ▶ Oil and Grease is a “method defined parameter”.
- ▶ In determining “oil and grease”, one does not measure a specific substance. Rather one quantifies all substances in the sample that have similar solubility and volatility characteristics.
- ▶ The principal types of compounds included in oil and grease analyses are fats, soaps, fatty acids, hydrocarbons, waxes, and oils. (M.K. Stenstrom, S. Fam, and G. Silverman, Env. Tech. Letters, 7, 625–636 (1986))
- ▶ In addition to these common materials, “Oil and Grease” includes other organic soluble materials such as sulfur compounds, certain organic dyes and chlorophyll.

# Role of Oil & Grease Testing



- ▶ Identify instances of soil and water contamination by hydrocarbons
- ▶ Protect wastewater treatment facilities
- ▶ Prevent sewer line failure
- ▶ Control pollution



# Example Applications in US Environmental Programs



- ▶ Clean Water Act's National Pollution Discharge Elimination System
- ▶ Leaking Underground Storage Tank regulatory program
- ▶ Petroleum exploration



# US EPA NPDES Program



- ▶ National Pollutant Discharge Elimination System (NPDES)
- ▶ Developed under authority of the Clean Water Act passed in 1973
- ▶ Industrial categories specify general regulations that are refined in negotiation for a permit based on discharge characteristics and the waterway accepting the discharge
- ▶ 40CFR part 400
  - §403.5 National pretreatment standards: Prohibited discharges.  
(a)(1) *General prohibitions.* A User may not introduce into a POTW any pollutant(s) which cause Pass Through or Interference. These general prohibitions and the specific prohibitions in paragraph (b) of this section apply to each User introducing pollutants into a POTW whether or not the User is subject to other National Pretreatment Standards or any national, State, or local Pretreatment Requirements.

# NPDES Federal Limits



## ▶ Subpart A—Farm–Raised Catfish Processing Subcategory

§408.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

Except as provided in §§125.30 through 125.32, any existing point source subject to this subpart shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

Effluent characteristic	Effluent limitations	
	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed—
	Metric units (kg/kg of seafood)	
TSS	28	9.2
Oil and grease	10	3.4
pH	(1)	(1)
	English units (lb/1,000 lb of seafood)	
TSS	28	9.2
Oil and grease	10	3.4
pH	(1)	(1)

<sup>1</sup>Within the range 6.0 to 9.0



# Previous Methods



1. US EPA Method 418.1: Petroleum Hydrocarbons (Spectrophotometric Infrared) 1978.
2. Standard Method 5520C Partition–Infrared method: Standard method for the examination of Water and Wastewater, 1999
3. ASTM® D7066–04: Standard test method for dimer/trimer of chlorotrifluoroethylene (S–316) recoverable Oil and Grease and Nonpolar material by Infrared determination, 2004.



# Why Change?

- ▶ The most common solvents used were 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) or tetrachloromethane.
- ▶ However, these solvents are known ozone-depleting compounds
- ▶ Under the Montreal Protocol, the use of CFC-113 was phased out by 1996 and the
- ▶ use of tetrachloromethane become illegal in 2010



# Health Concerns



- ▶ Additionally chlorinated solvents:
  - Health concerns
  - Disposal concerns

## **Hazard Summary—Created in April 1992; Revised in January 2000**

Carbon tetrachloride may be found in both ambient outdoor and indoor air. The primary effects of carbon tetrachloride in humans are on the liver, kidneys, and central nervous system (CNS). Human symptoms of acute (short-term) inhalation and oral exposures to carbon tetrachloride include headache, weakness, lethargy, nausea, and vomiting. Acute exposures to higher levels and chronic (long-term) inhalation or oral exposure to carbon tetrachloride produces liver and kidney damage in humans. Human data on the carcinogenic effects of carbon tetrachloride are limited. Studies in animals have shown that ingestion of carbon tetrachloride increases the risk of liver cancer. EPA has classified carbon tetrachloride as a Group B2, probable human carcinogen.



# US EPA Method 1664



- ▶ Proposed in the Federal Register January 1996
- ▶ 1664, Revision A, developed February 1999
- ▶ 1664, Revision B, developed February 2010
  
- ▶ Uses hexane for extraction
- ▶ Allows the use of solid phase extraction
  - Can be automated



# Other Methods



- ▶ Standard Methods 5520
  - 5520 B Partition–Gravimetric Method
  - 5520 D Soxhlet Extraction Method
  - 5520 E Extraction Method for Sludge Samples
  - 5520 F Hydrocarbons
  - 5520 G SPE– Gravimetric Method
  
- ▶ ISO 11349 Water quality — Determination of low–volatility lipophilic substances —Gravimetric method
  
- ▶ OSPAR Method, GC–FID
- ▶ SW–846 Method 8015, GC–FID
- ▶ Extractable Petroleum Hydrocarbons (EPH)



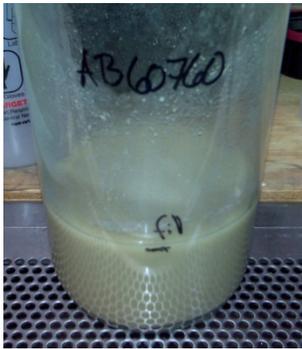
# Preparing for Audits



- ▶ In the US, accredited laboratories are audited to ensure they are following their SOPs and methods accurately
- ▶ We will go through some of the issues that have been raised about method 1664 and how to be prepared



# Matrices



Wastewater

## Industrial Waste



Saline Water



# Extraction Techniques

## Liquid-Liquid

Extraction:

- ▶ 3x shake using n-hexane



## Solid-Phase

Extraction:

- ▶ Filter sample through disk and elute using n-hexane



# Other Extraction Techniques



- ▶ What does the method say?

*1.7.1 “Allowable Modifications”*

*1.7.1.1 “Alternate extraction techniques including continuous liquid–liquid extraction, solid–phase extraction, solid–phase–heated extraction, solid–phase–Soxhlet extraction, and others.”*

*9.1.2 “In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve separations or lower the costs of measurements, provided that all performance specifications are met. These options include alternate extraction and concentration devices and procedures such as continuous liquid–liquid extraction, evaporation, Kuderna–Danish concentration, and solid–phase extraction.”*

- ▶ Method 1664 Rev A made me prove waste stream equivalency. Do I need to prove equivalency with LLE if I use SPE under Rev B?

# What is needed to prove equivalency?



- ▶ IPR –(initial precision and recovery) to demonstrate that the results are equal or superior to LLE.
- ▶ MDL – if the detection limit is affected
- ▶ Matrix Comparison on each Waste Stream – if used for compliance monitoring
- ▶ Matrix Comparison (9.2.3.1):
  - SPE HEM = 103% of LLE HEM
  - Requirement: 78–114%
  - SPE SGT–HEM = 108% of LLE SGT–HEM
  - Requirement: 64–132%
- ▶ Better accuracy and precision.

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

# Other Extraction Techniques



- ▶ Do I need to prove waste stream equivalency with LLE if I use SPE under Revision B?

**No!**

*Section 9.1.2.1 “...(not required for modifications allowed under Section 1.7.1)”*

*1.7.1.1 “Alternate extraction techniques including continuous liquid-liquid extraction, **solid-phase extraction**, solid-phase-heated extraction, solid-phase-Soxhlet extraction, and others.”*

(IPR and MDL are still required)

# Solvents and Co-Solvents



- ▶ What does the method say?

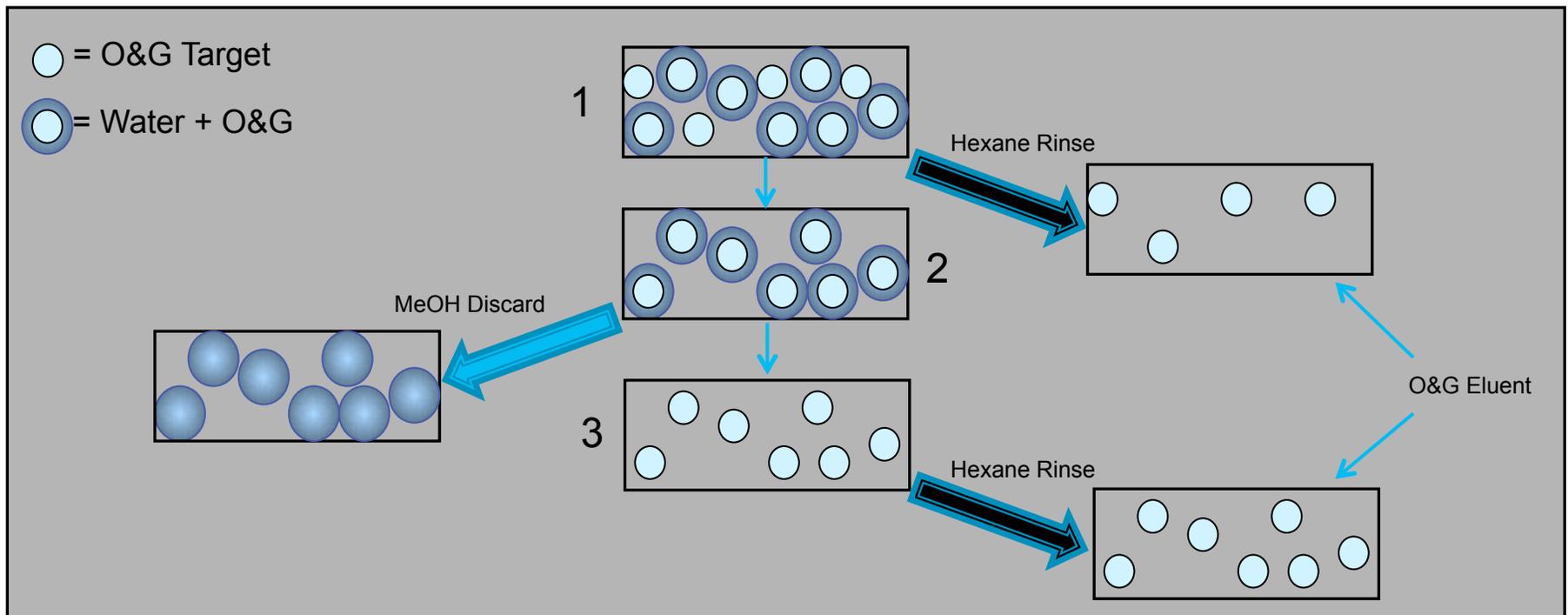
*1.7.2 “Unacceptable Modifications”*

*1.7.12.1 “The extraction solvent must be n-hexane. Alternate extraction solvents or co-solvents including methanol, acetone and others that react with or introduce the target pollutant into the sample are not allowed.”*

- ▶ Most SPE systems use a co-solvent, does this mean I’m not in compliance?



# Why Are Co-Solvent Needed?



# Example Influent Wastewater



## With Methanol

SPE Replicate	Begin Wt. (g)	Final Wt. (g)	HEM (mg)
1 – 1 Liter Influent	6.1831	6.2136	30.5
2 – 1 Liter Influent	6.2030	6.2359	32.9
3 – 1 Liter Influent	6.2015	6.2357	34.2
<b>Avg. Reported Value</b>			<b>32.5</b>

## Without Methanol

SPE Replicate	Begin Wt. (g)	Final Wt. (g)	HEM (mg)
1 – 1 Liter Influent	6.2473	6.2656	18.3
2 – 1 Liter Influent	6.1801	6.2045	24.4
3 – 1 Liter Influent	6.2506	6.2643	13.7
<b>Avg. Reported Value</b>			<b>18.8</b>

$$\% \text{ Loss} = (32.5 - 18.8) / 32.5$$

**42.2 % Loss**

## Sample Conditions:

- ▶ 5 Gallon Influent Sample
- ▶ From Lawrence, MA WWTP
- ▶ Thoroughly mixed
- ▶ Acidified to pH 2.0 with HCl
- ▶ Separated into 9 one liter samples
  - 3 LLE
  - 3 SPE with Methanol
  - 3 SPE without Methanol
- ▶ LLE: 2.5 hr/sample
- ▶ SPE: 50 min/sample
- ▶ LLE Results in Avg. HEM = 38.7 mg

## Instrumentation:

- ▶ SPE-DEX® 3000XL Extractor
- ▶ 90-mm Pacific™ SPE Disks
- ▶ Speed-Vap® III Solvent Evaporator

# The Use of Co-Solvents

- ▶ Am I out of compliance if I use a co-solvent?

*Section 1.7.2.1 "...However a methanol or other polar solvent rinse after sample filtration may be allowed to remove water residual when using SPE technology in a modified method provided:*

- 1. The methanol rinse is immediately discarded to waste.*
- 2. The SPE filter is sufficiently air dried with vacuum to remove any residual methanol remaining in 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 or be collected with the n-hexane extractions.*
- 3. The laboratory must demonstrate and document the appropriate operating conditions (1 & 2) above to allow this use of methanol."*



# Proving Co-Solvent Removal

- ▶ The Note given after Section 1.7.2.1 states:

*“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. “*

1. Weigh SPE Disk.
2. Run Blank.
3. Condition SPE Disk.
4. Process Blank.
5. After the Polar solvent is dispensed stop vacuum and weigh disk.
6. Dry disk until weight is 101% of original weight.

# Proving Co-Solvent Removal

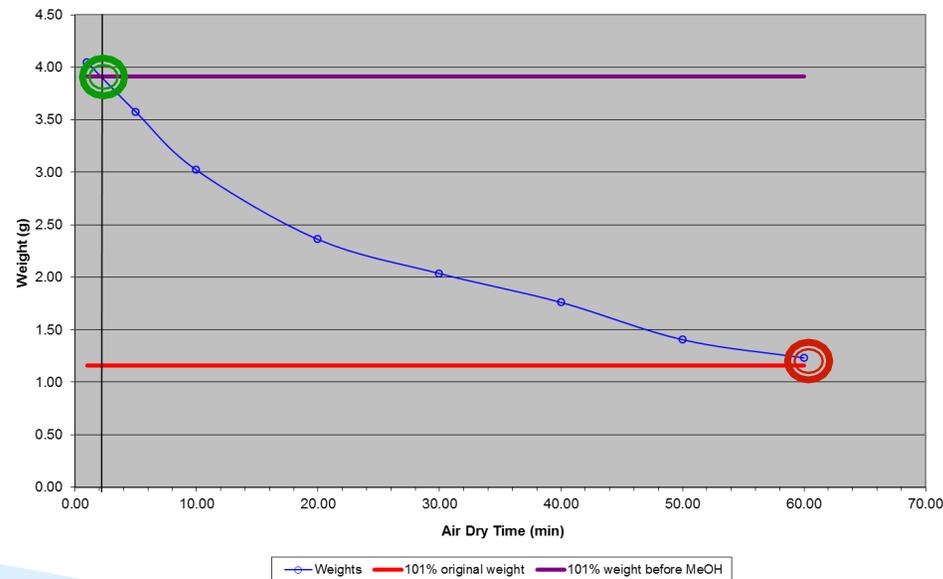
- ▶ But the weight of the disk post-polar-solvent-dispensing consists of:

Hexane + Methanol + Sample Water

**This takes 60+ minutes!**

- ▶ Best to weigh the disk both before and after the polar-solvent-dispense and adjust air-dry time so they are within 101%.

**This takes 2-3 minutes!**



# Lower PAR Concentrations

(precision & recovery)



- ▶ Why?
  - Introduces half as much spiking solvent into the sample.
  - Allows for users to stretch a batch of standard.

- ▶ Requirements (1.7.1.4)

*“A lower PAR standard concentration such as 20 mg/L may be used to spike matrix samples provided the concentration of the spike is: (a) greater than the background concentration, (b) less than or equal to the regulatory compliance level and (c) all quality control requirements are achieved.”*



# SPE Disk Sizes

- ▶ Some of my samples are clean, so I use 47 mm disks. For dirty samples, I use a 90 or 100 mm disk. Is this ok?
  - I run my QC on 47 mm disks, but my samples on 90 or 100 mm disks.

- ▶ Section 1.7.1.9

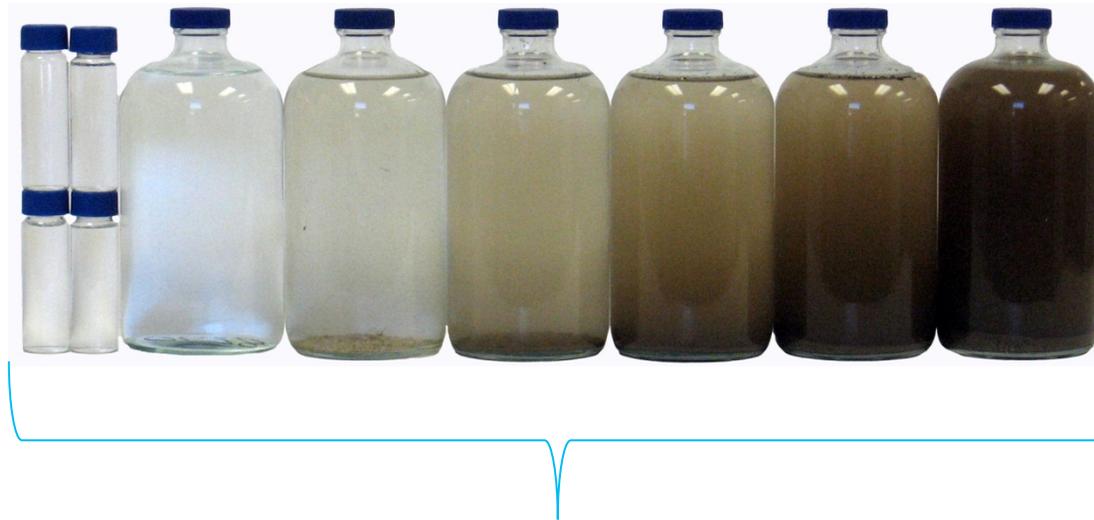
*“If SPE filters are used in the analytical batch, they must all be of the same manufacturer brand and diameter. If different manufacturer’s brand or different diameter SPE filters are used in different analytical batches or methods, each different SPE method must have its own quality control chart.”*

- ▶ One batch = One Size/Brand



# Prefilters

- ▶ The goal is to be able to filter all types of samples through a disk, no matter the particulate content

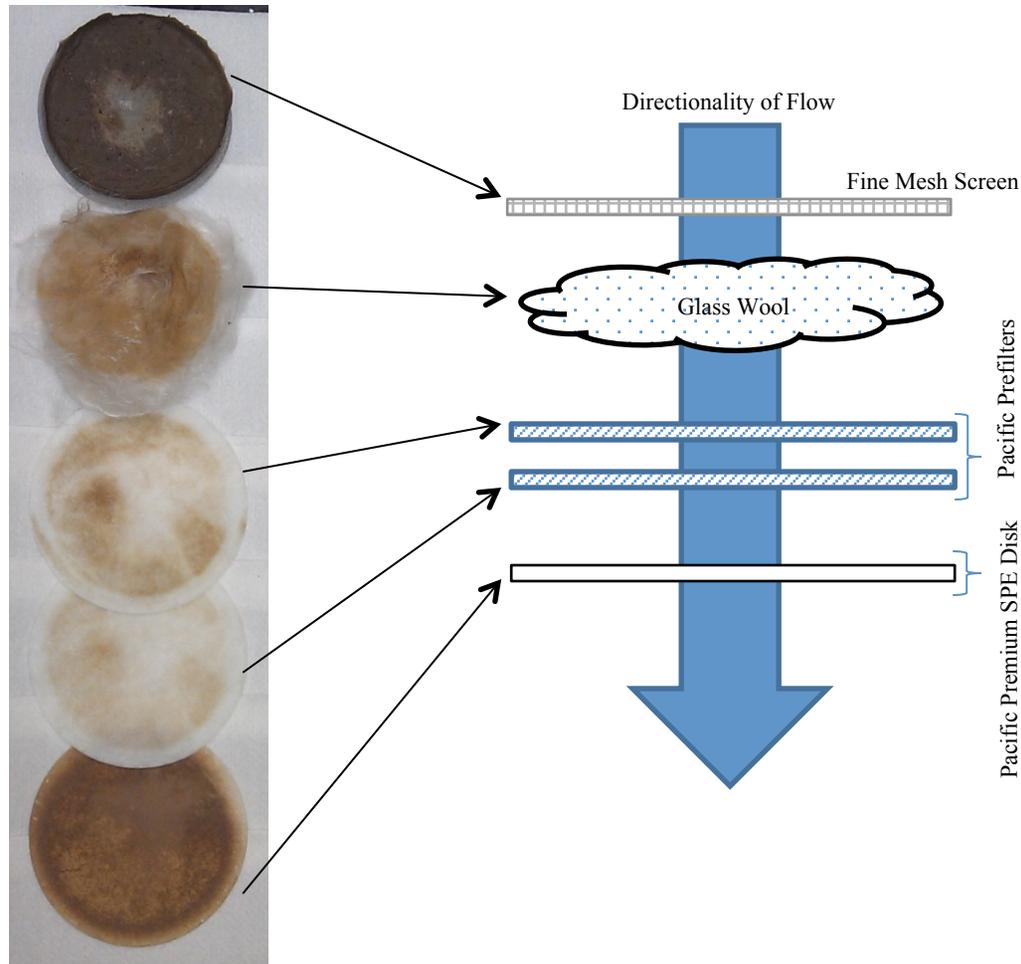


U.S. Penny



Pacific Premium  
SPE Disk

# Dirty Samples: It's All About Layering



# Prefilter Usage



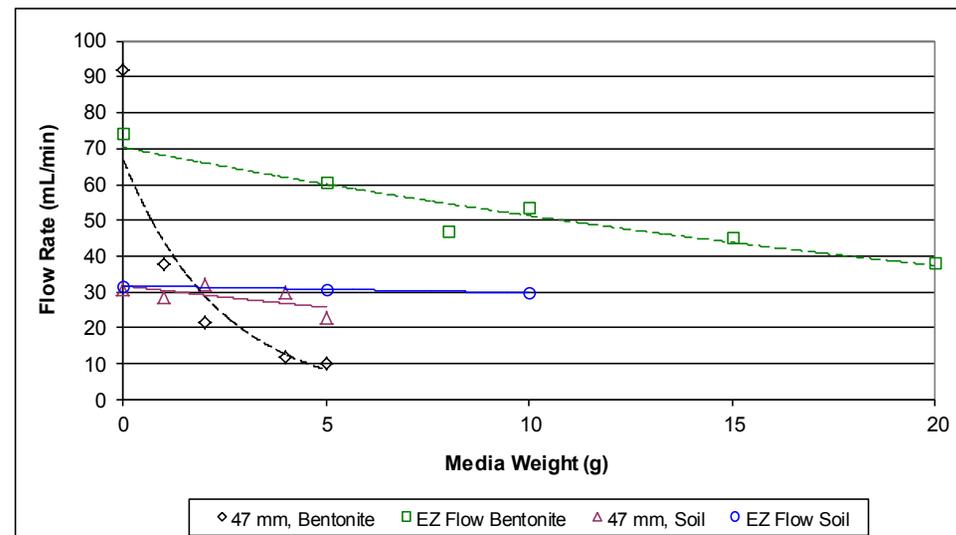
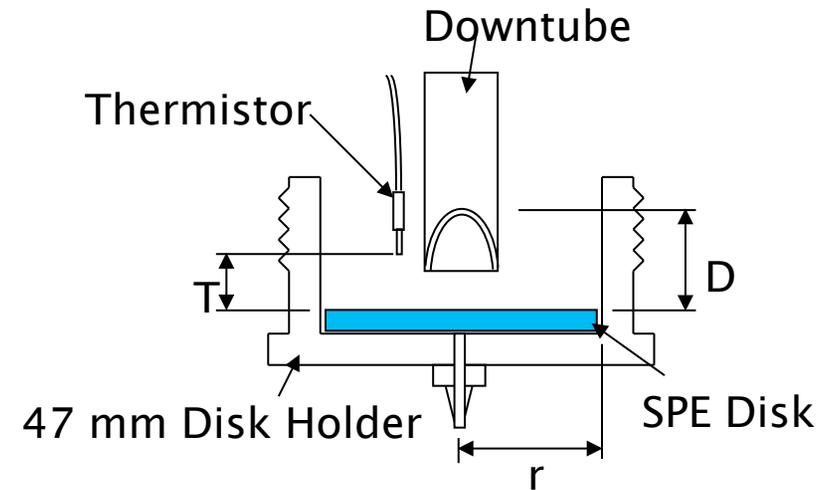
- ▶ What does the method say?

Section 1.7.1.8... *“The use of optional prefilters, filtration aids, glass wool and/or other means including centrifugation and sedimentation to aid processing specific samples is allowed per Section 11.3.5. As appropriate, samples acidified to  $\text{pH} < 2$  which have settled upon refrigerated storage may be analyzed “as is” instead of first mixing and then centrifuging the sample in order to achieve a similar, settled physical state prior to analysis.”*

- ▶ If a sample is dirty, prefilters may be used for that one sample but are not necessary for the entire batch.
- ▶ Important: The use of prefilters allows us to extract the whole sample (sediment and aqueous portions).

# Sediment Limit?

- ▶ How much sediment can I run?
- ▶ Matrix Type
- ▶ Particle Size/Shape
- ▶ Disk Area (diameter)
- ▶ Limits:
  - Volume of Disk Holder
  - Geometry of particles



# Too Much Sediment

- ▶ What do you do with really dirty samples?

Adjust the volume of the sample that you run.

- ▶ Section 8.1.2

*“If a sample is known or suspected to contain greater than 500 mg/L of extractable material or consists of complex matrix containing substances (such as particulates or detergents) that may interfere with the extraction procedure, collect a proportionately smaller volume of sample (the volume required will depend upon the estimated amount of extractable material) in a glass bottle.”*

- ▶ Caveat...Section 1.7.2.3

*“...sub-sampling or analysis of less than the total collected volume of sample is not allowed.”*



# Too Much Sediment



- ▶ Sample Volumes less than 1 L are allowed, as long as what you pull is what you run!
  
- ▶ I don't control my sampling, how do I handle the sample I'm given?
  - Run part of the sample on one station and the other part on another station, combine the extracts and concentrate them to get one final weight.
  - You are running the whole sample.
  - You are rinsing the original sample container.
  - Next time, request a smaller volume for that location.



# Cap Rinsing

- ▶ Scenario One:  
The user does not think that a cap rinse is important.
- ▶ Section 11.3.3  
*“...Shake the bottle to rinse all interior surfaces of the bottle, including the lid of the bottle cap. Pour the solvent into the separatory funnel.”*
- ▶ Oil and Grease can be lighter than water. Without rinsing the cap, there is an incomplete extraction.
- ▶ Example:  
Proficiency Test (PT) samples contained vacuum pump oil.



# Cap Rinsing



- ▶ Scenario Two:
  - The user rinsed the cap using n-hexane, and put it into the sample container before running.
  
- ▶ Many interpret as “rinse cap with n-hexane and put into sample bottle.”
  - n-Hexane extracts the O&G in the sample container
  - When the sample is filtered and sent to waste, the HEM goes with it!
  
- ▶ Example:
  - Proficiency Test samples included instructions telling users to rinse the cap and put it in the sample bottle.



# Cap Rinsing: Correct Technique



- ▶ Section 11.3.3

*“...Shake the bottle to rinse all interior surfaces of the bottle, including the lid of the bottle cap. Pour the solvent into the separatory funnel.”*

- ▶ LLE/CLLE: Rinse the sample cap with n-hexane and add to extraction vessel.

- ▶ SPE: Rinse the cap with n-hexane and add to disk holder during the step in the process where the sample container is being rinsed with n-hexane.



# Extract Drying

- ▶ Large variation in techniques:
  - Sodium Sulfate
  - Solvent Phase Separation Paper
  - PTFE or PP Membranes
  - Careful separation using a separatory funnel or pipette
- ▶ AZ Department of Health Services Information Update #117 Released 8/14/2013 gives EPA's official stance.
- ▶ All techniques are acceptable except for "careful pipetting or draining of one immiscible layer from the other"



# Extract Drying

- ▶ What does this mean?  
All extracts **must** be dried.
- ▶ Sodium Sulfate: a cheap and easy procedure, right?
  - How much do you use?
  - Is a pre-packed cartridge always enough for your extracts?
  - Dissolved  $\text{Na}_2\text{SO}_4$  gets into weighing vessel?
- ▶ What happens if this go wrong, are personnel trained to notice?
- ▶ Fool-proof method is to go with membrane drying



# Temperature Settings



- ▶ What does the method say?

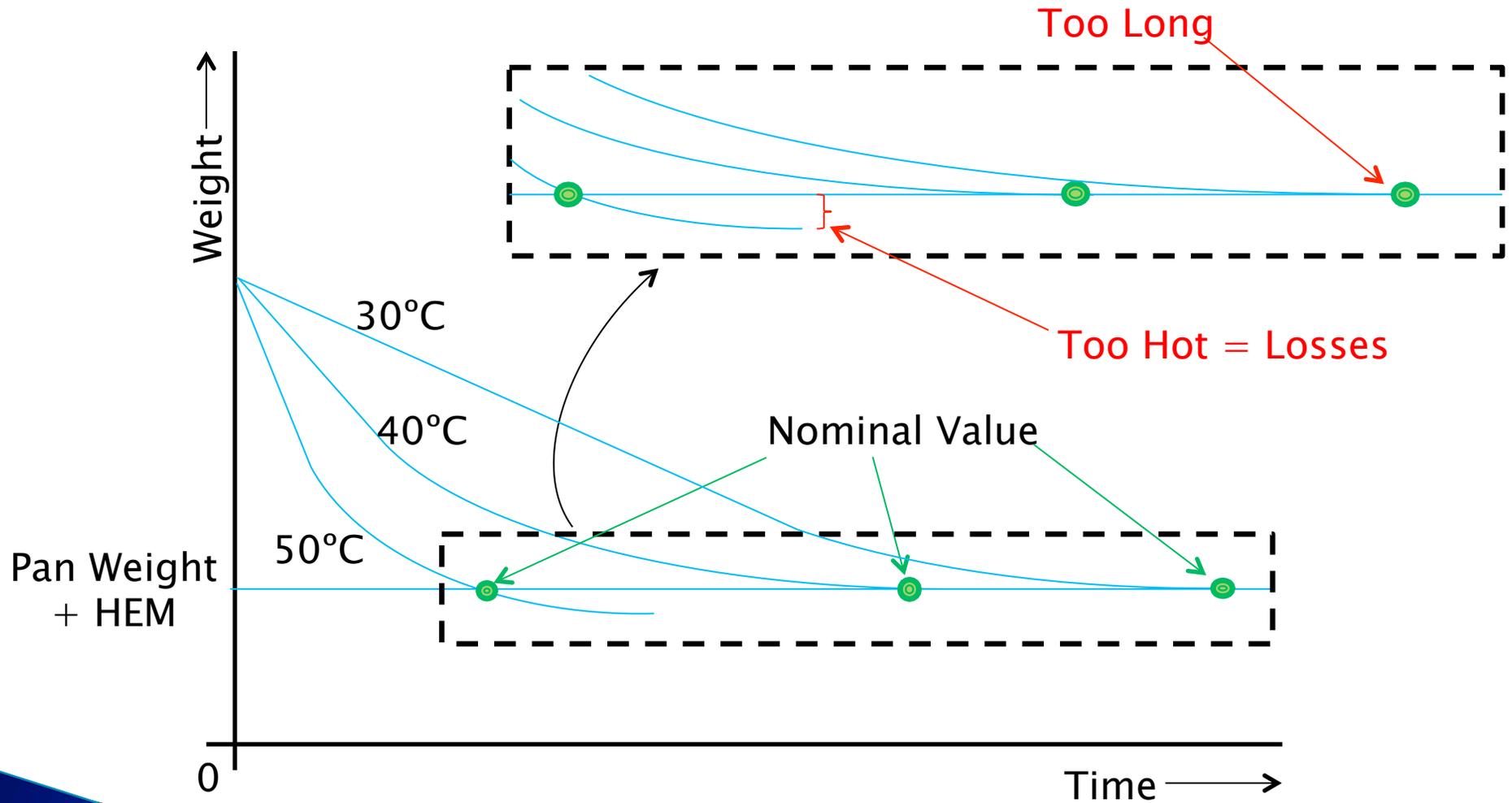
11.4.1 ...“Adjust the water temperature as appropriate to complete the concentration.”

11.4.2 ... “When the temperature in the distilling head reaches approximately 70 °C or the flask appears almost dry, remove the distilling head.”

1. What Temperature do I use?



# Temperature Settings

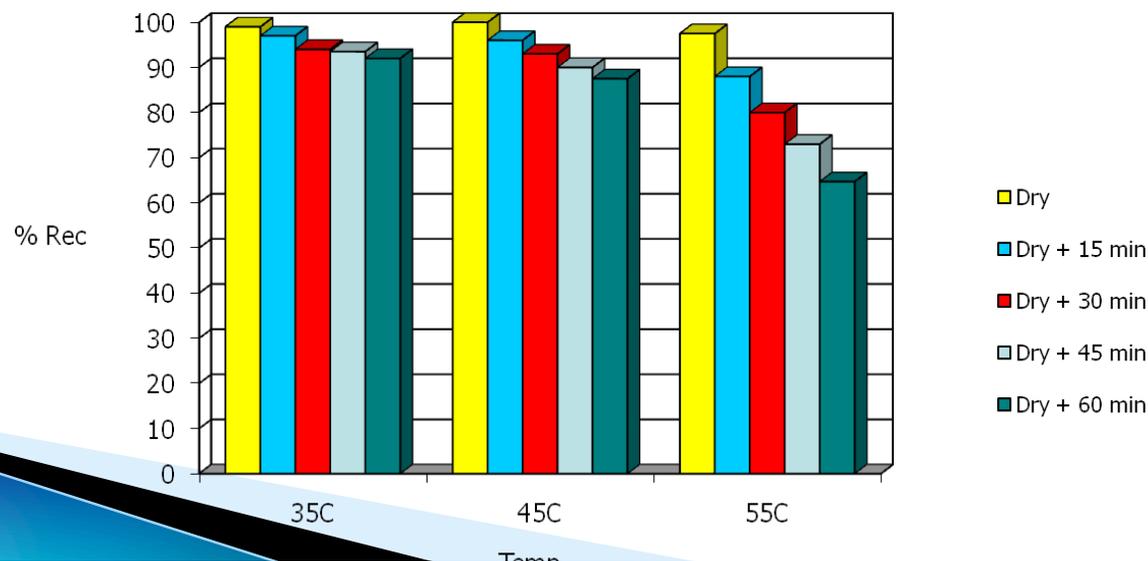


# Temperature Settings

## 1. What Temperature do I use?

Section 1.7.1.2... “Alternate concentration techniques including KD concentration and evaporation using aluminum pans, beakers and flasks as well as user defined temperatures and approximate concentration times.

% Recovery as a Function of Elapsed Time after Dryness and Temperature



# Repetitive Weighing

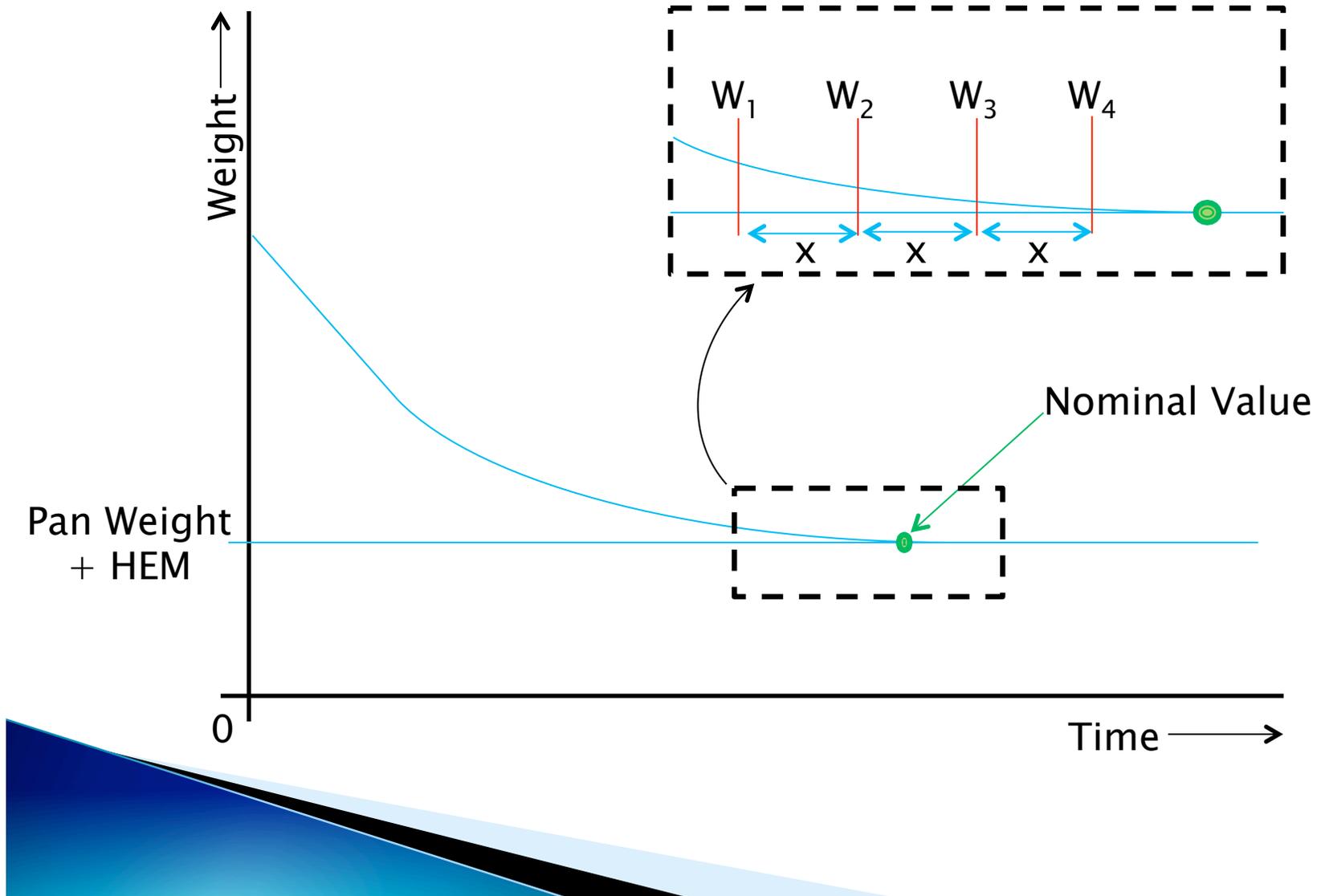
- ▶ What does the Method say?

11.4.4 ... “While at room temperature and without additional heating, repeat the cycle of desiccating and weighing until the weight loss of the flask and dried residue is less than 4% of the previous weight or less than 0.5 mg, whichever is less.”

1. Do I need to take multiple weights?
2. How long do I wait between weight sampling?

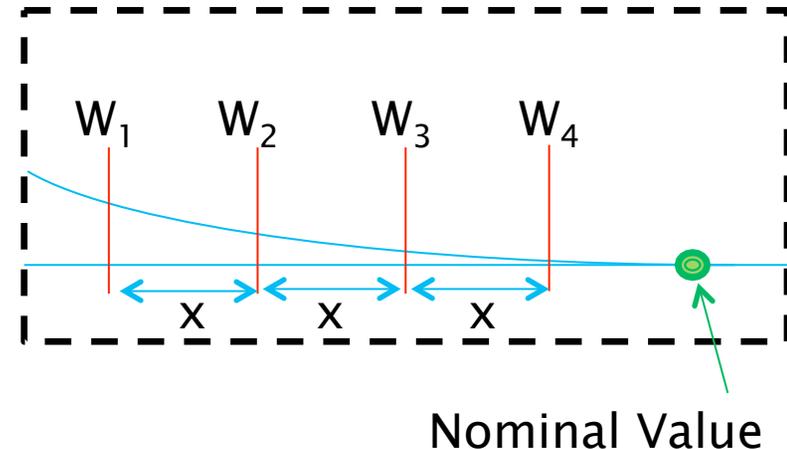


# Repetitive Weighing



# Repetitive Weighing

1. Remove pan from heat prior to full solvent evaporation.
2. Place pan on balance and record  $W_1$ .
3. Place pan in desiccator and wait some time “x”.
4. Repeat steps 2 and 3 to meet criteria:



$$W_{\downarrow f} [mg] - W_{\downarrow i} [mg] < \min_{\tau} (0.5 [mg], W_{\downarrow i} [mg] * 0.04)$$

# Repetitive Weighing

1. Do I need to take multiple weights?  
Most definitely! Sampling multiple times allows for the user to be confident in the final results and ensures that the correct weight is reported.
2. How long do I wait between weight sampling?  
Section 11.4.4 of the method states that 30 minutes minimum should be taken between each weighing. In practice, the incorporation of a drying step and lower distillation temperatures used in most techniques mean that less time is needed for the extract to reach equilibrium with the laboratory conditions.



# Technique Selection Criteria



Easy training and daily use

Are emulsions formed

Flexibility For unique matrices

Able to rinse the cap  
and the sample bottle

Safety

Short ROI

Proven track record

Is equipped for varying solids content

Reliable



Thank you!

