

METHOD 1664A

Nicholas Bertrand, Environmental Enterprises USA Inc.



THE PRODUCED
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What is Method 1664a

- This method is applicable to various waste water samples containing a range of 5 – 1000 mg/L solvent extractable material.
- This method is not specific to petroleum hydrocarbons.
- Any material in the sample that is soluble in n-Hexane will be extracted and may contribute to the final result.
- This method is commonly applied as a monitoring tool in NPDES permits.



Summary of Method 1664a

- Sample acidified to <2 pH is transferred to separatory funnel, 30 ml n-Hexane added, then shaken vigorously for 2 minutes.
- Settle for 10 minutes to allow n-Hexane and water phases to separate.
- Water phase returned to sample container.
- n-Hexane extract is filtered through anhydrous sodium sulfate and collected in a boiling flask.



Method 1664a Summary Continued

- After each extraction, n-Hexane and solvent soluble material is collected in boiling flask.
- After third extraction, the flask is placed in a hot water bath (85°C) and the solvent evaporated leaving behind the solvent soluble residue.
- The flask is then dried, vacuumed, allowed to cool and weighed and reweighed until a final stable weight is recorded. After a simple calculation the results are reported in mg/L.
- Produced water and completion fluids for permit compliance must have a daily maximum of 42 mg/L and a monthly average of 29 mg/L or less.



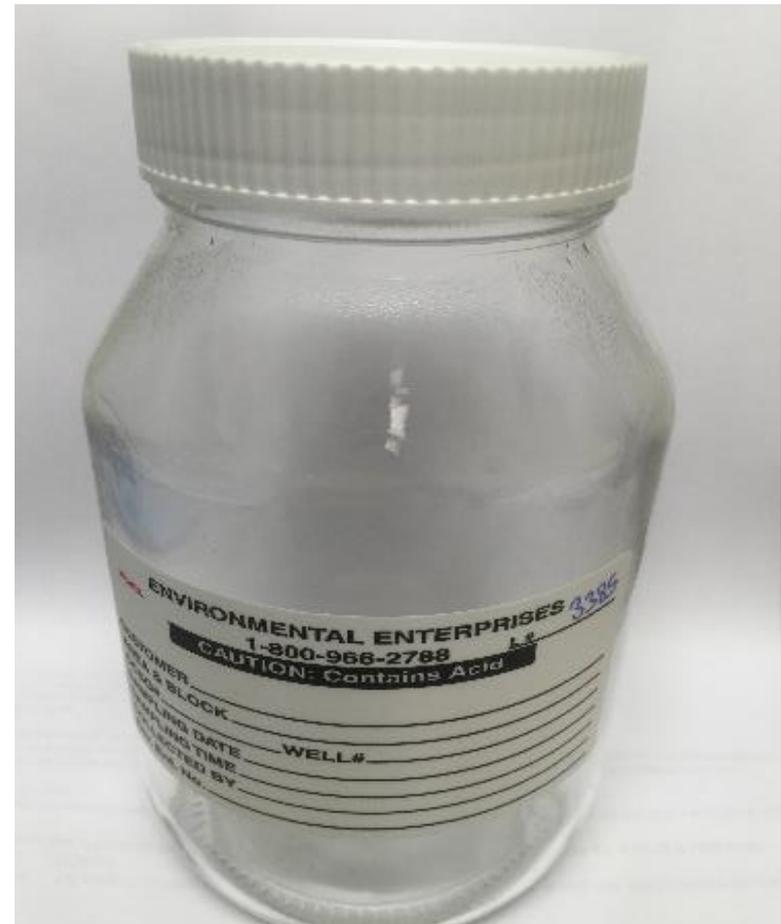
Oil and Grease Sample Collection

- Collect from permitted discharge prior to addition of seawater or splitting for multiple discharge points.
- Collected in 1-liter glass jars with 5 ml 6N HCl preservative and Teflon lined caps.
- Do not rinse out sample container when collecting samples.



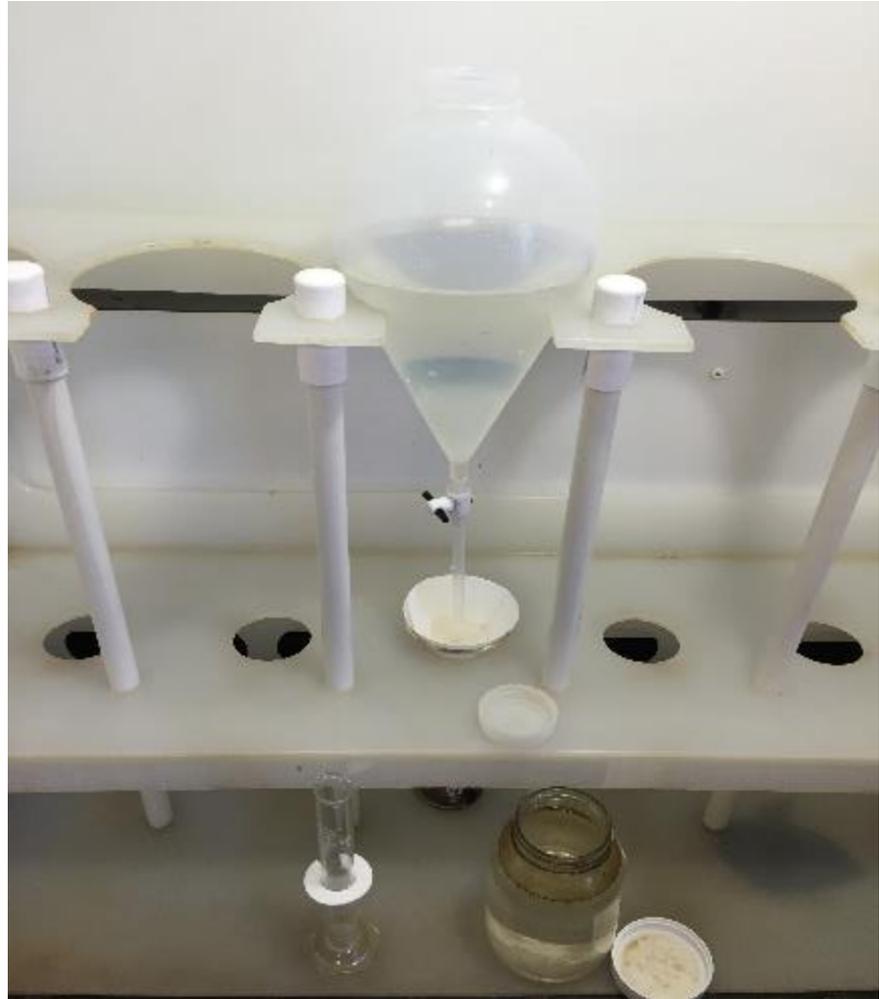
Sample Collection Continued

- Ship on ice and should be received by lab at 0.1 to 6° C.
- Samples should not be frozen.
- Sufficient ice should be used to maintain temperature until received by the laboratory.



Equipment & Set Up

- Fume hood.
- 2-liter separatory funnel.
- 1-liter sample with $\text{pH} < 2$ su at room temperature before analysis.
- Silicon treated filter paper.
- pH indicator paper.



Equipment & Set Up Continued

- Approximately 10 grams of sodium sulfate.
- Clean 125-ml boiling flask and initial flask weight.
- Hot water bath @ 85°C.
- Drying oven @ 70°C.
- Vacuum pump.
- Desiccant and vacuum desiccators.



Equipment & Set Up Continued

- Class A graduated cylinder for measuring solvent.
- Analytical balance capable of measuring 0.1 mg.
- n-Hexane 85% minimum purity, residue <1 mg/L.
- Anhydrous sodium sulfate (NaSO_4) dried at 200 to 250°C for at least 24 hours.



Quality Control Criteria

- An analytical batch consists of laboratory performance controls and a maximum of 20 field samples in a 12-hour shift.
- The laboratory performance controls in each analytical batch include a blank, laboratory control sample (LCS), LCS duplicate, matrix, and matrix duplicate spike.
- LCS's and Matrix samples are spiked with spiking solution.

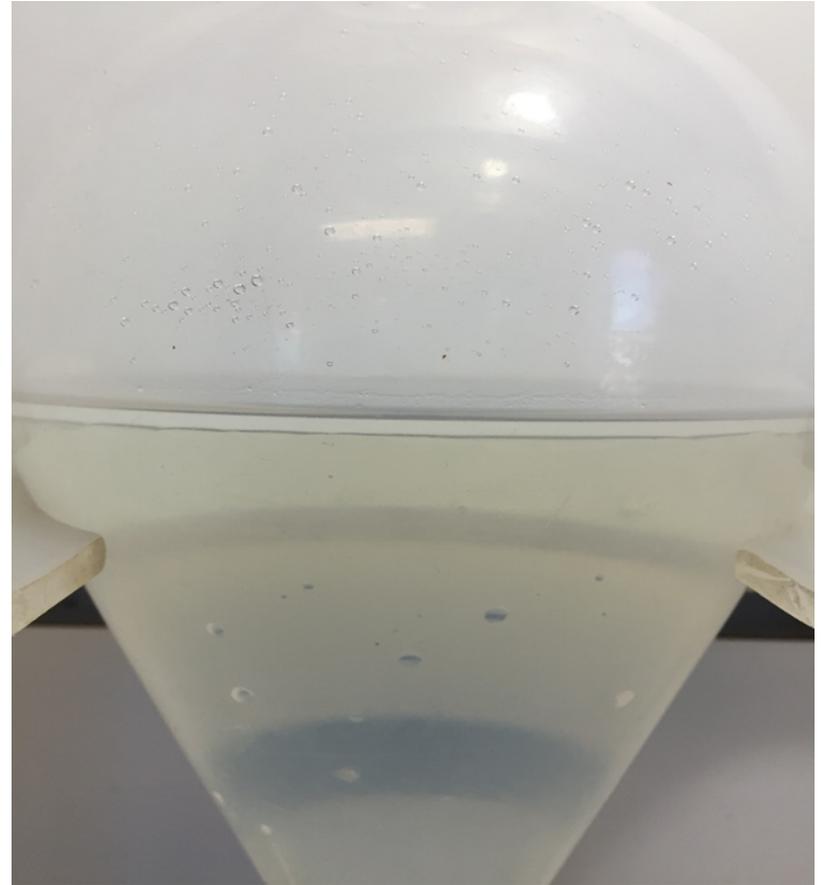


Quality Control Criteria Continued

- Spiking solution is a 1:1 solution of stearic acid and hexadecane dissolved in acetone.
- The concurrent laboratory performance control results must meet acceptance criteria for the results of the other field samples in the batch to be valid.



n-Hexane Separation

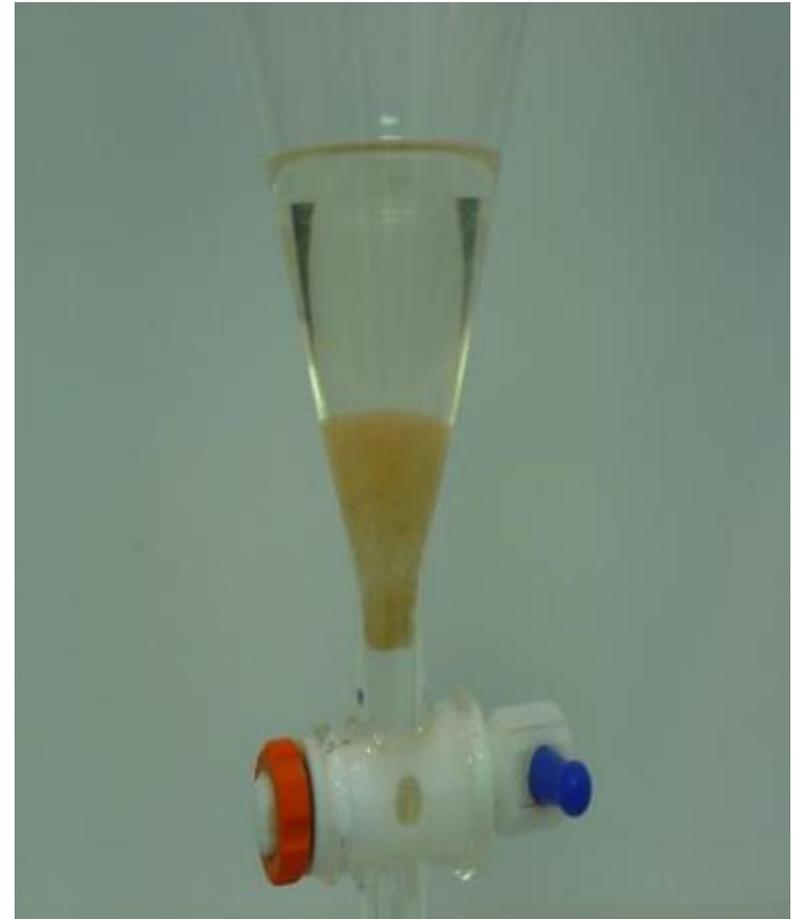


Non-solvent Soluble Material Captured by Filter Assembly

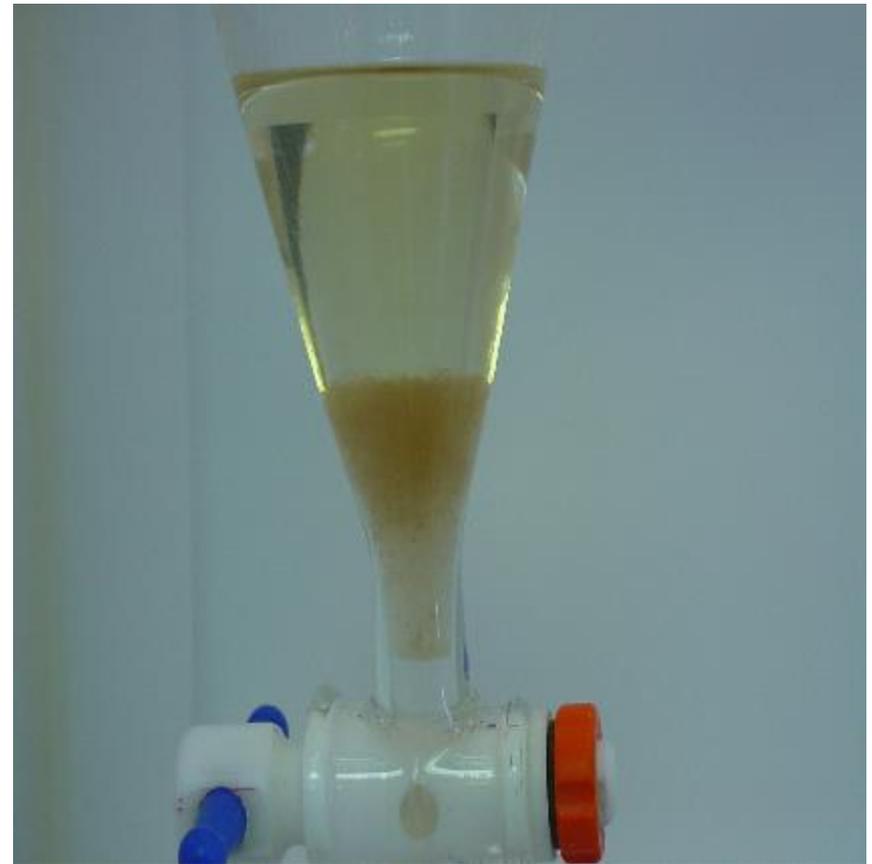
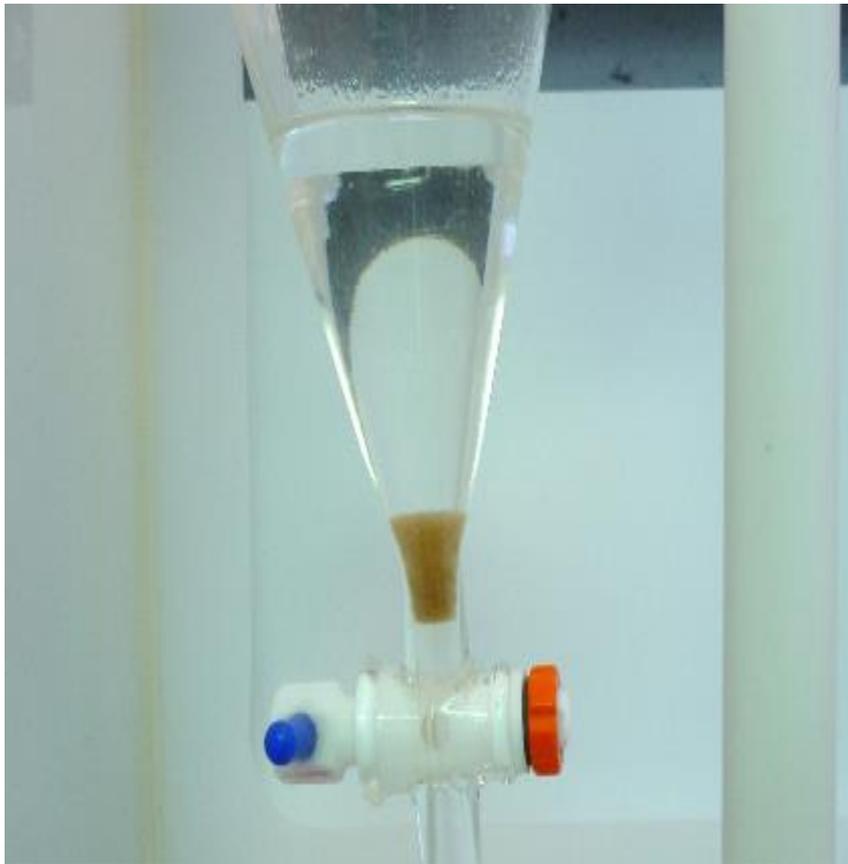


How to Handle Emulsions

- Time will usually allow the emulsion to separate.
- Collect the emulsion in a separate boiling flask and continue with the other extractions.
- Transfer the emulsion to the separatory funnel, add 1 liter of deionized water, shake gently, and let settle.
- Drain the solvent soluble phase from the emulsion through the sodium sulfate and filter paper into the boiling flask with the solvent soluble phases from the three extractions.



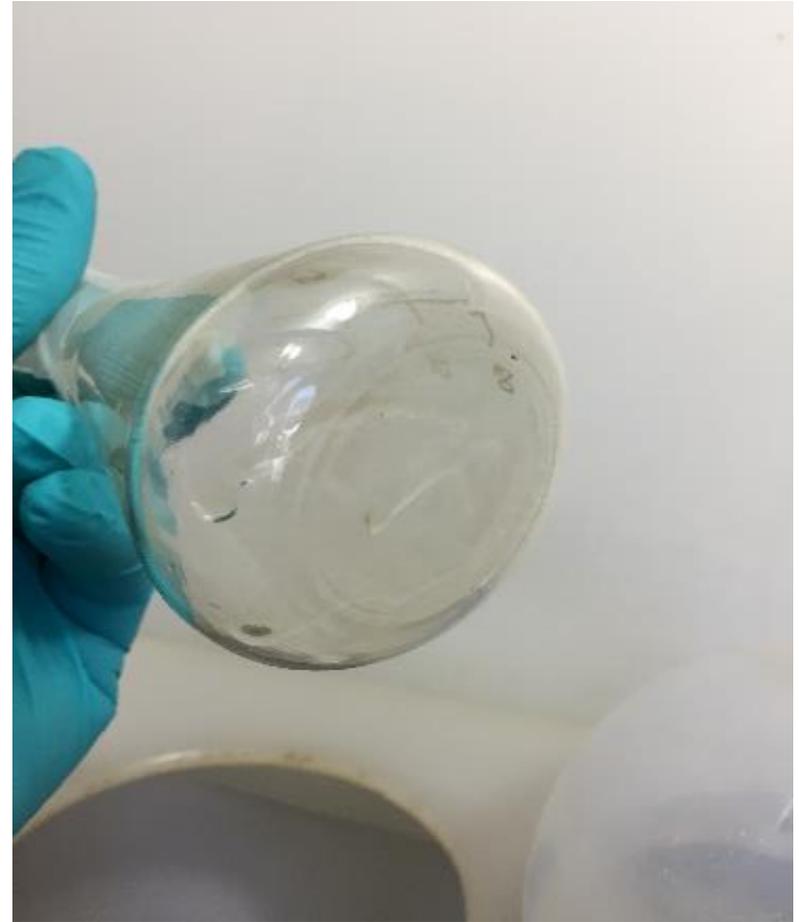
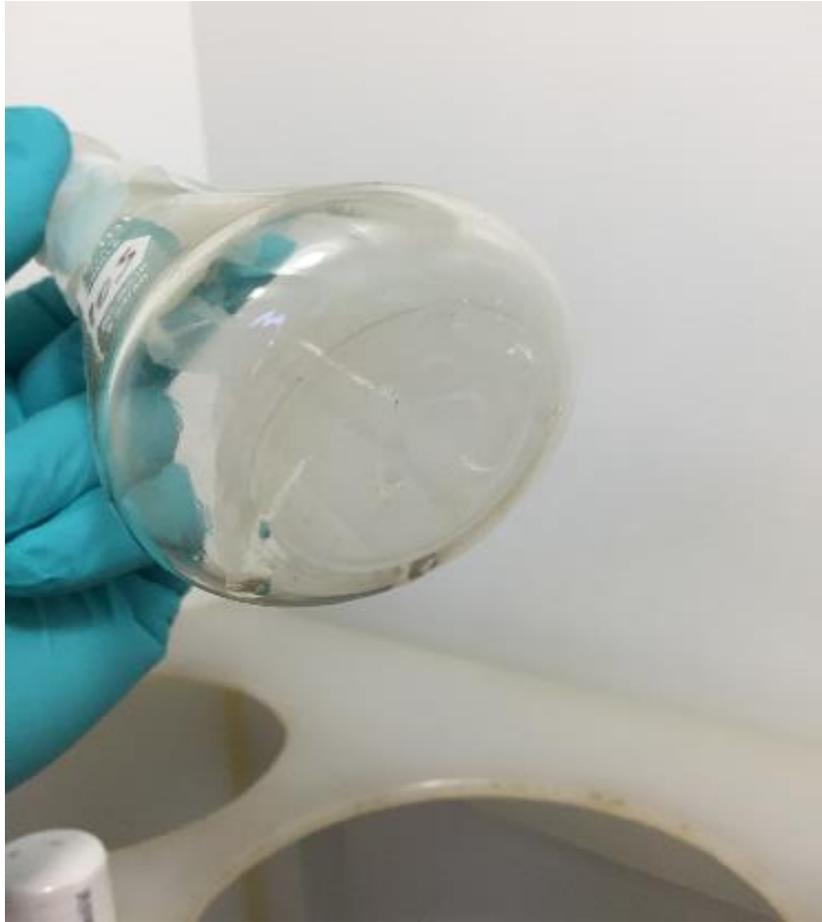
Minor Emulsions



Crude Oil Residue



Solvent Soluble Material, Not Crude Oil



Possible Interferences

- Dirty glassware or sample collection container.
- Contaminated solvent.
- Incorrectly calibrated or malfunctioning analytical balance.
- Water bath too hot or too cold.
- Water in solvent extract.



Possible Interferences Continued

- Excessive use of sodium sulfate.
- Too little sodium sulfate could lead to contamination of solvent extract allowing water or solubilized sodium sulfate into extract.
- Leaving boiling flask in water bath > 30 minutes.



FAQ

- Why must samples be acidified prior to analysis and $<6^{\circ}$ C upon receipt by the lab?
 - The acidification serves to halt biological activity in the sample. micro-organisms can degrade oil and grease components.
 - Temperature helps slow down biological activity and keep volatiles from evaporating if any headspace is in the sample container.
 - Adding acid can convert fatty acids from water soluble salts to non-water soluble free acids, increasing solvent soluble oil and grease (OG) result.



FAQ

- What is Total Petroleum Hydrocarbons (TPH)?
 - TPH is the portion of the solvent soluble oil and grease extract that is not absorbed by silica gel (TPH is non-polar hydrocarbons).
 - Silica gel absorbs the water soluble organic acids (WSOs) and other polar components of the OG.
 - Typical produced water OG results can be up to 50% WSOs and other polar materials.



FAQ Continued

- What is a IR Meter and how is it calibrated using OG results?
 - IR meter transmits infrared radiation at a bandwidth that is absorbed by the C-H bond. The amount of IR absorbance is correlated to the OG content.
 - The meter is calibrated at 4 points, 13, 25, 50, & 100 ppm crude oil. The meter range is capable of measuring 10-300 ppm. A representative sample is analyzed using Method 1664a. The OG result is then compared against additional samples analyzed with the IR meter.
 - If the OG result is $\pm 10\%$ of the IR meter results, the meter's calibration is deemed acceptable and recalibration or repair is not necessary.



EE USA Capabilities

- Open 24/7/365
- Turnaround time of 3 hours available for after hours rush samples.
- Normal produced water turnaround time is 7 days.
- Well Fluids are usually analyzed the same day received and certainly within 48 hours.



METHOD 1664A

Method 1664a measures anything solvent soluble and calls it oil and grease.

