A NEW APPROACH TO THE DETERMINATION OF OIL AND GREASE IN WATER AND WASTES

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Huffington Post -Background

Summary

- Determination of **OG** in water and *industrial and municipal effluent discharges.*
- ***Evaluation of ASTM D-706 04 - S-316 (Horiba) EXTRACTION AND IR DETECTION (****also* enables analysis of waste samples with silica gel.
- ***Figures of merit -*** LOQs, long-time stability of standard, spiking and sample extracts, and recoveries from laboratory samples.
  - Participation in ***NELAC proficiency test***

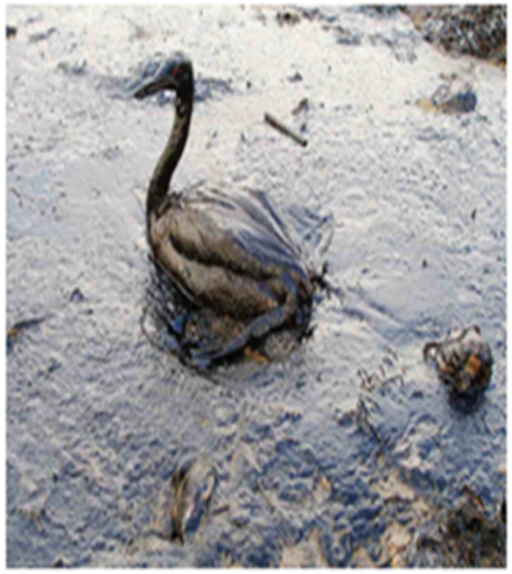


Designation: D 7066 – 04

- Comparison of alternative procedures
  - Analytical problems - solvent used for extraction and method of measurement.

INTRODUCTION

- **Deleterious effect and impact on aquatic life.**
- Cause environmental toxification, and serious difficulties for ***effluent reuse***
- Induce related public health risks when discharged in surface or ground waters.
- **Decision 179182/656/1979** - limit of 40 mg L^{-1} total OG for industrial discharges in sewer systems.





Definitions

- **Oil** - water insoluble organic material - liquid at room temperature.
- **Grease** - water insoluble organic material - solid or semi-solid at room temperature.
- **Extractable materials** - non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials
- ***Oil and grease (OG)*** - a group of organic substances *SOLUBLE IN AN ORGANIC SOLVENT*. In addition to ***OG,*** other organic materials can be extracted.
- ***Nonpolar material*** - *OG* not adsorbed by silica gel

Definitions

- **In food industry**, OG in effluent is composed of edible fats of plant and animal origin.
  - **Fatty acid -** long-chain aliphatic hydrocarbon with a carboxylate group on one end.
  - **Stearic acid**, common name for *octadecanoic acid* - fatty acid with 18 C atoms.
    - $H_3CCH_2CH_2CH_2CH2CH2CH2CH2CH2CH2CH2CH2CH2CH2CH2CH2CH2CH2CO2H$
  - "**Saturated**" - no double bonds in C chain.
  - "**Unsaturated**" - double bonds in C chain

INTRODUCTION

- In past ***OG in water and effluents*** determined by **Trichlorotrifluoroethane (CFC-113, FREON 113) extraction and IR**
- Suspended in 2005 *by law and in accordance with Clean Air Act (**codified at 40 CFR 401.16 and** Montreal Protocol on Substances that deplete Ozone Layer*
- **As a result, until recently, IR was not used**

Summary of procedures for determination of OG in water and wastes

Procedure	Extractant	Extraction	Quantif.	Comments
EPA 413.1	Freon	L-L	E+G	
Unsuitable for low-boiling point fractions that volatilize < 85O C because of evaporation				
EPA 413.2	Freon	L-L	IR	
EPA 1330	Freon	Soxhlet	E+G	
EPA9070, 9070A	Freon	L-L	E+G	
EPA9071A	Freon	Soxhlet	E+G	
EPA 9071B	Hexane	Soxhlet	E+G	Similar to EPA 1664A
SM 5520B	Hexane +MBK	L-L	E+G	
SM 5520C	Freon	L-L	IR	
SM 5520D	Hexane +MBK	Soxhlet	E+G	
SM 5520E	Hexane +MBK	Soxhlet	E+G	Similar to SM 5520D
SM 5520F	Used in conjuction w ith B, C,D,E			
EPA SW 1330A	THF+ Toluene	LL+filtration		
EPA 1664A	Hexane +MBK	Soxhlet or SPE	E+G	Similar to EPA 9071B
Unsuitable for low-boiling point fractions that volatilize < 85O C because of evaporation				
Petroleum fuels from gasoline and low viscosity fuel oils				
ASTM D-7066 04	S-316	L-L +SPE	IR	
Note - E - evaporation				
G - Gravimetry				
L-L Liquid -Liquid extraction				

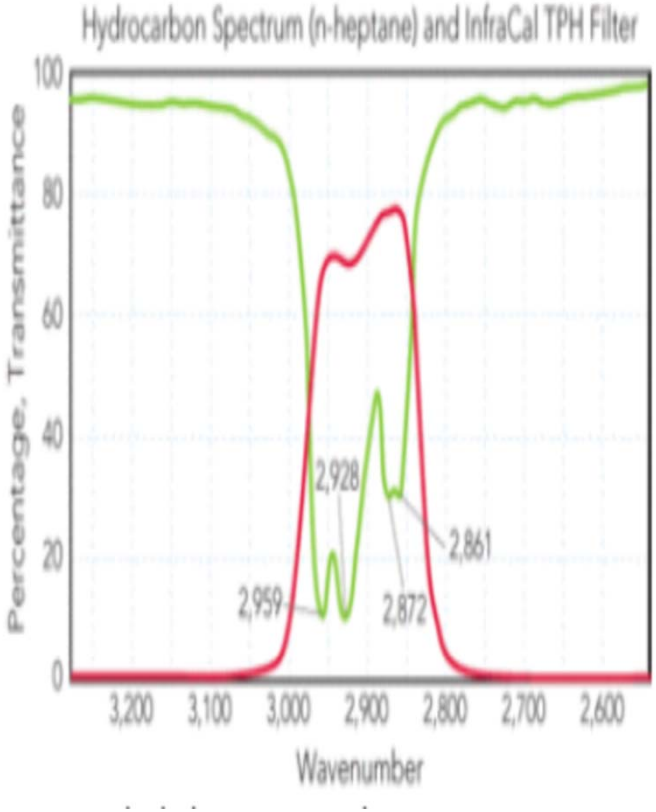
Hexane extraction and gravimetry

- **EPA Method 1664A**
  - ***"N-hexane extractable material" (HEM)*** method - applied to materials other than oils and greases.
  - ***"Silica gel treated n-hexane extractable materials" (SGT-HEM)*** method. Applied to materials other than ***aliphatic petroleum hydrocarbons that are not adsorbed by silica gel.***
- **EPA SW 9071B.**
  - Low concentrations of OG in sludge and sediments
  - **Procedure similar to EPA 1664 A.**

- Replaces Freon-based procedures
- Labor intensive and tedious **SOXHLET** extraction.
- SPE
- Uncertainty of weighing very low amount of residue in a very large collecting flask.
- **Not applicable to materials that volatilize < 85°C.**
  - ***Petroleum fuels from gasoline and low viscosity fuel oils may be lost in Soxhlet extraction***
- ***Crude and heavy fuel oils contain materials that are insoluble in n-hexane - recoveries low.***

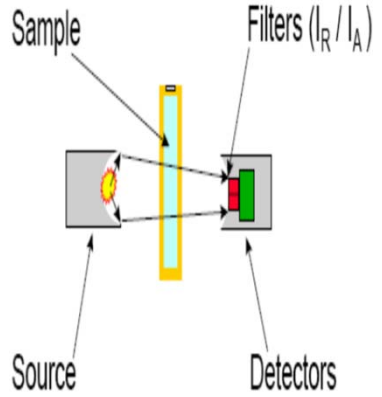
IR -spectrophotometry

- IR absorbance of C–H bond i.e. stretching of aliphatic CH_2 groups at 2930 cm^{-1}, CH_3 groups at 2960 cm^{-1} and aromatic C–H bonds at 3010–3100 cm^{-1}
  - **TOG is measured at these C-H absorption bands**
  - *Measurements can be made only with solvents that **do not possess C–H bonds.***

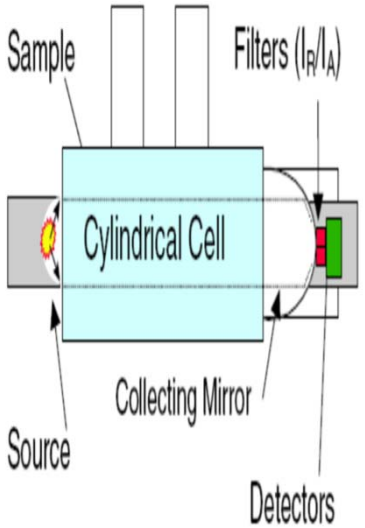


Principle of operation

- OG extracted sample placed in quartz cuvette on sample stage
- IR beam passes through extract sample and focused directly on **dual detector** for IR transmission measurement
- Filter/detector set for C-H absorbance measures hydrocarbon content in extract
- Energy collected at analytical wavelength (IA), is reduced when compared to energy collected at reference wavelength (IR)
  - Oil concentration determined by calculating logarithm of ratio of light transmission at reference wavelength to light transmission at analytical wavelength
  - Beer-Lambert law assumes linear relationship between absorbance and concentration.
  - Dilution factors taken into account during calibration
  - Display reads directly in concentration units



$A = \log I_R / I_A$



$A = \log I_R / I_A$

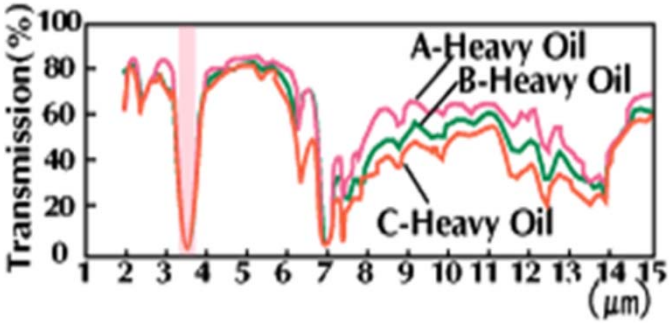
Designation: D 7066 – 04

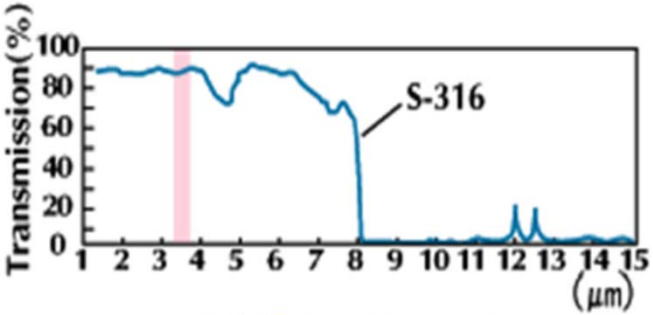
Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination[1]

- ***OG and nonpolar material in water and wastewater determined by infrared (IR) using chlorotrifluoroethylene (S-316) extractable substances from acidified sample.***
- Extraction of hydrocarbons such as fats, oil, and grease from water or soil using **ozone-friendly S-316** - **avoids hexane and FREON *extraction***
- ***No*** *Soxhlet extraction and gravimetric quantification*
- Wastewater sample collected in glass container.
- S-316 added - **one part solvent to 10 parts sample (WILKS procedure – 1 to 5)**
- Shake 2 min
- Portion of solvent extract is presented to **WILKS InfraCal TOG/TPH analyzer** - result displayed in under a minute.
  - Only a small amount of extract needed for analysis;
  - **100-mL sample requires 10 mL of S-316**
  - S-316 can be reclaimed
- Other compounds soluble in solvent.
- Applicable to measurement of light fuel, although loss of some light components during extraction is possible.
- ***OGs determined by IR absorption spectrophotometry***
  - Extracted hydrocarbons absorb IR energy at a common IR wavelength, and amount of energy absorbed is proportional to concentration of OG in solvent.
  - Directly calibrated or converted to amount of oil in original sample.
- Method covers range of 5-100 mg/L **(WILKS system has larger range)**
- *May be extended to lower or higher level by extraction of a larger or smaller sample volume collected separately.*
- ***"Performance-based"*** method allows analyst to modify procedure to overcome interferences or to lower cost, provided all performance criteria are met

S-316 – Horiba

- ***S-316 solvent*** —dimer/trimer of chloro-trifluoro-ethylene (Horiba, Japan)
- Proprietary, non-hydrocarbon solvent *environmentally safe*.
- **S-316** transparent at analytical wavelength used for hydrocarbon absorption - lacks C-H absorption band
- S-316 heavier than water – extraction sinks to bottom
- Recommended and approved replacement solvent for Freon - ASTM Standard Test Method D7066-04.







Model SR-300 Solvent Reclaimer

- SR-300 **(Horiba)** reduces S-316 cost by up to 90%.
- Double activated carbon and alumina column
- Large filtering capacity, easy to operate - no electricity.



INSTRUMENTATION - 1

- ***IR instruments - Fourier Transform Spectrometers (FT-IRS) to portable inexpensive fixed filter IR analyzers***
- InfraCal TOG/TPH Cuvette Holder Analyzer Model CVH (Wilks Enterprise Inc.140 Water Street · South Norw CT 06854 USA
  - E-mail info@wilksir.com · www.wilksir.com



- Compact single channel IR spectrometer
- Fixed wavelength IR detector measures C-H absorbance at 2930 cm^{-1}.
- Integrated cylindrical cuvette holder and optics sensing system.
- Sample stage includes modulated IR source and detector system

Instrumentation- 2

- Energy beam transmitted through sample cuvette containing extract
- Focused directly on detector-sensing window
- Reads in relative absorbance units proportional to concentration
- Internal microprocessor - allows calibration to read in desired units.
- Detection limit 2 ppm, with accuracy within 10%.



Field Sampling Extraction Kits for Use with InfraCal TOG/TPH Analyzers

TOG in Water• TOG in Soil• TPH in Water•TPH in Soil

These kits have been specifically designed for use with the InfraCal TOG/TPH Analyzers. Select the kit(s) best suited for your sampling requirements from the following chart based on the InfraCal model and the solvent to be used for the extraction process.

Note: You will also need 15% hydrochloric acid for pH adjustment, in addition to the solvent (Freon-113, a hydro-carbon-free grade of perchloroethylene, hexane, pentane

Rintoul (2005 - A new standard method ASTM D 7066-04 (Test Method for Dimer/Trimer of Chlorotrifluoroethylene S-316 Recoverable Oil and Grease and Nonpolar Material by Infrared Determination and 'New ASTM Test method Offers Quick and Easy Oil and Grease Measurement for Water and Soil Samples', www.eco-web.com/editorial/02675-01.html,accessed December 2007)

Summary of Test Method

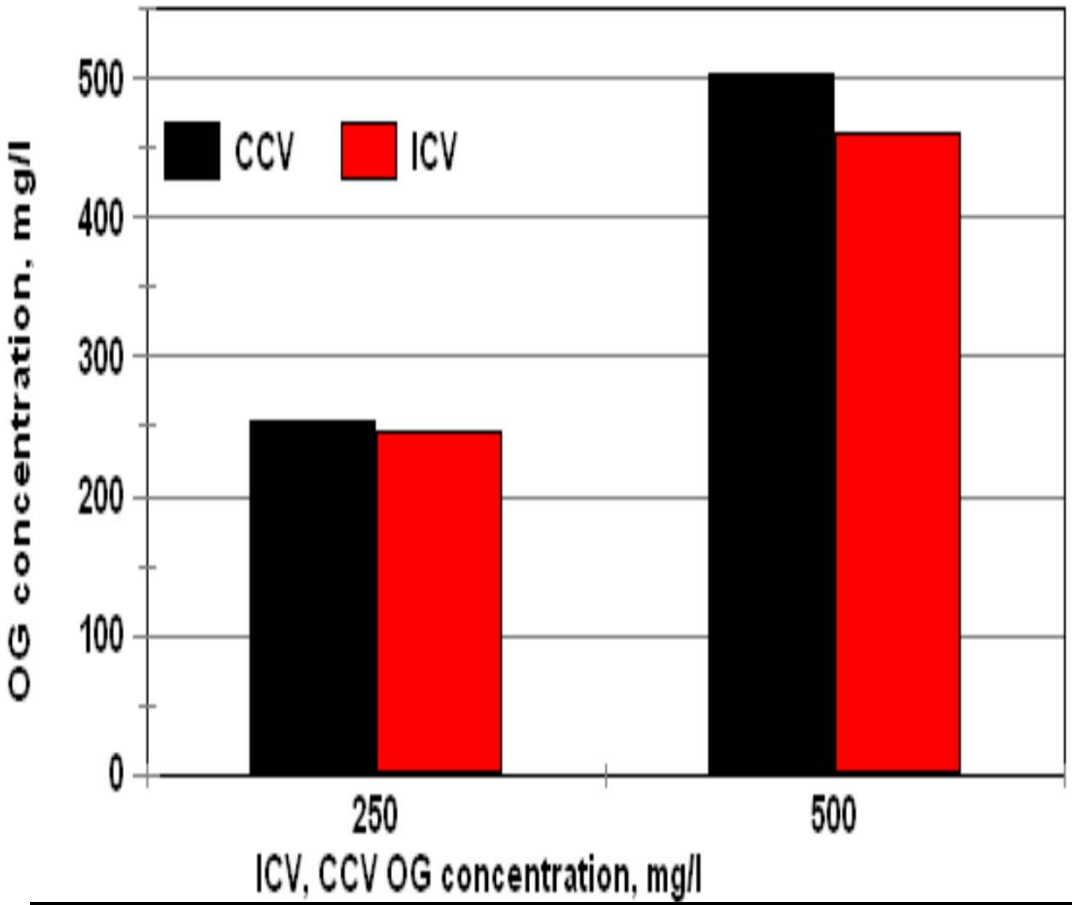
- 1 liter waste water samples acidified to < pH 2 with 6N HCl
- Extracted sequentially - 3 times with 30 ml S-316.
- Extracts filtered through 10 g granulated sodium sulfate.
- After 2 min agitation in separation funnel, extract decanted from bottom of sample and passed through ***Horizon Pacific SPE disks***. (Emulsions reduced using SPE)
- **Portion of** extract passed through silica gel to remove polar organics to produce solution containing nonpolar and then placed in cuvette - determined by IR spectroscopy
  - Difference between TPH (Total Petroleum Hydrocarbon) and TOG (Total Oil and Grease) is polar organics removed from extract using silica gel.
  - Remaining hydrocarbons are non-polar components considered to be TPH.
- LOD - 2 ppm.







Stability of calibration standards, calibration, and instrument



Short term precision

< 1% for concentrations > 50 mg/l and 1-10 % at lower concentrations.
Measurements made for 7 replicates of acidified Wibby CRMs in DI water using ASTM procedure.

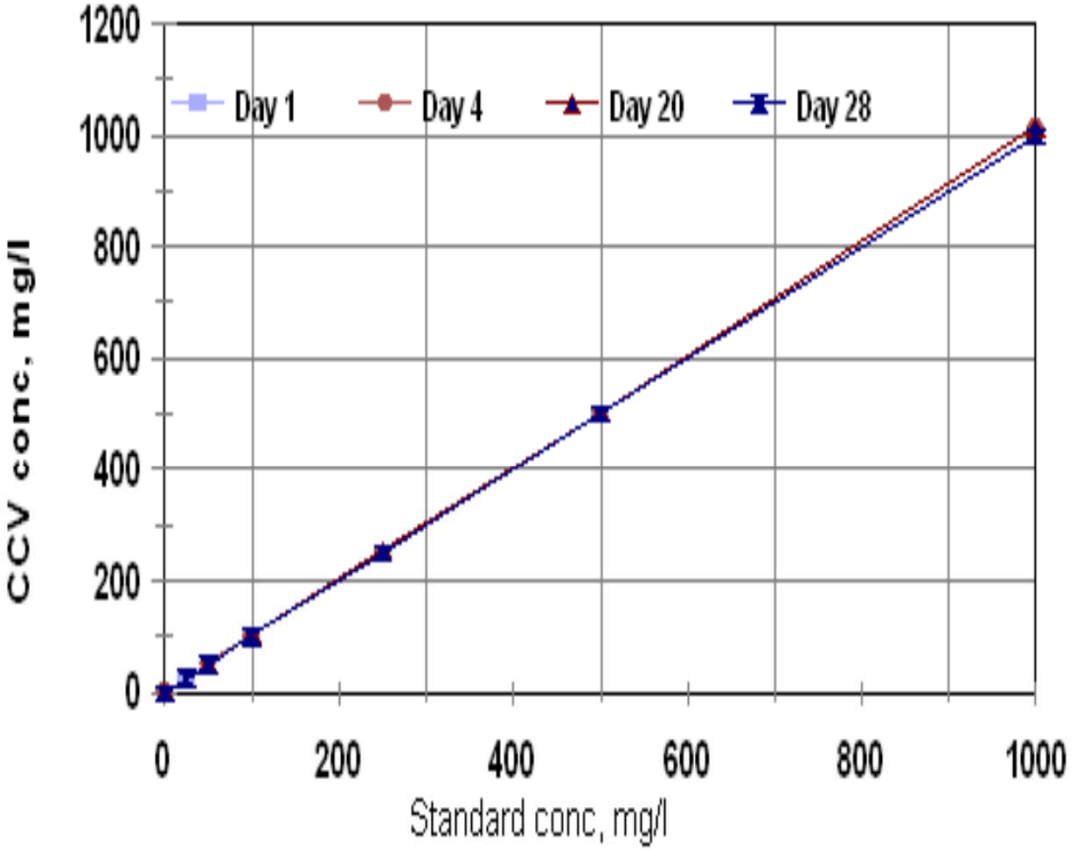
Long term precision

S-316 extractions stored for 30 days at 4°C
Measurements of calibration stability 1-3 % for 50-1000 mg/l
For sample extractions, variations about 10%.

Aim - establish maximum storage period under which valid measurements can be conducted.

Assay quantitated by certified primary and QA check standards provided by Wibby (Wibby, Golden, CO, USA).

Long-term stability of calibration standards and instrument stability



Calibration standards prepared in S-316, using different volumes of stock calibration solutions provided by Merck and Wibby in accordance with ASTM procedure.

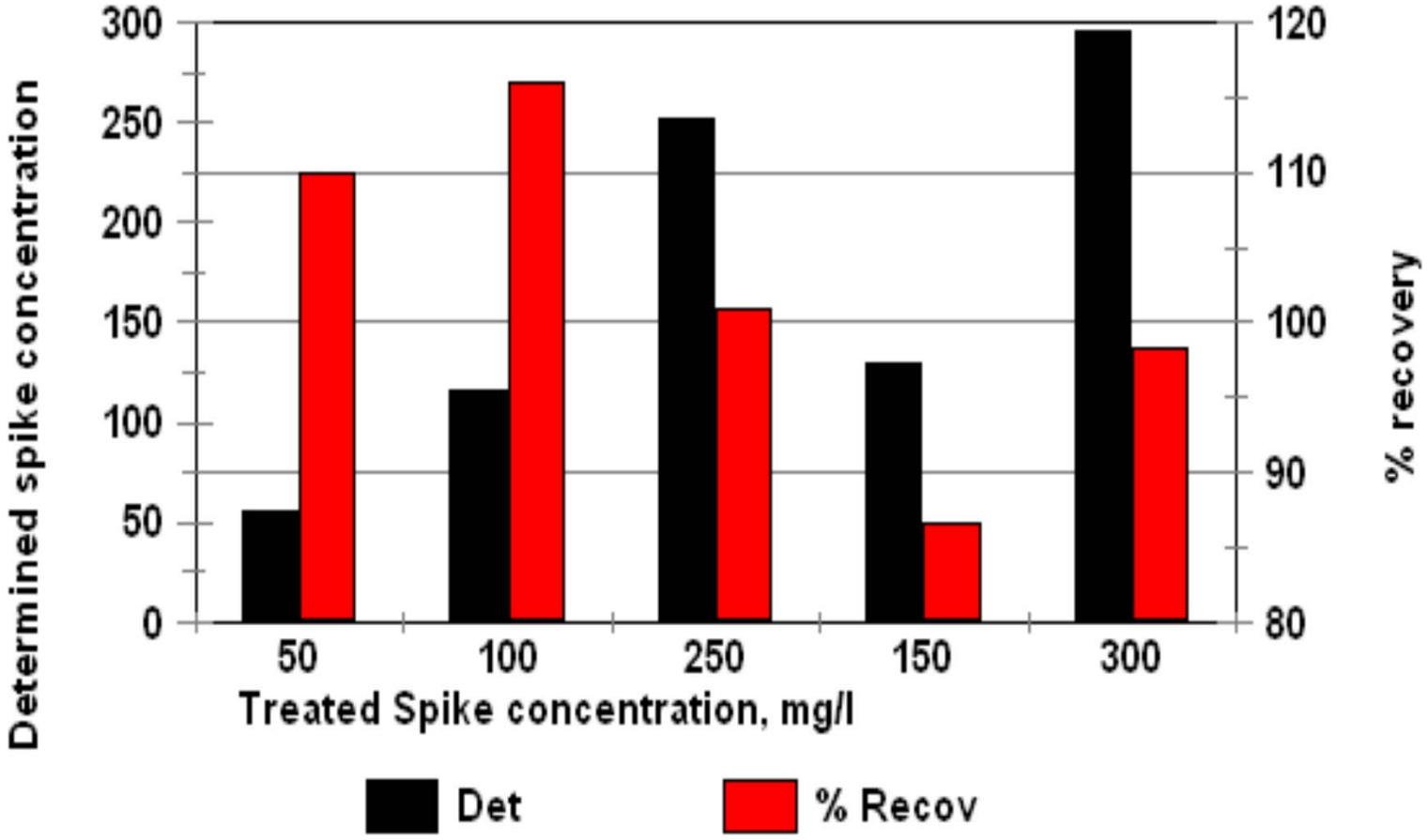
Calibrations 0 to 1000 mg/L.

Data verified using QA check standards provided by Wibby (Wibby, Golden, CO, USA).

0.55 ml Octanoic acid, 0.72 ml Iso-octane (2,2,4-trimethyl-pentane in 10-mL volumetric flask and fill to mark with solvent.

Resulting conc is 50 mg/mL octanoic acid and isooctane (100 mg/mL total OG).

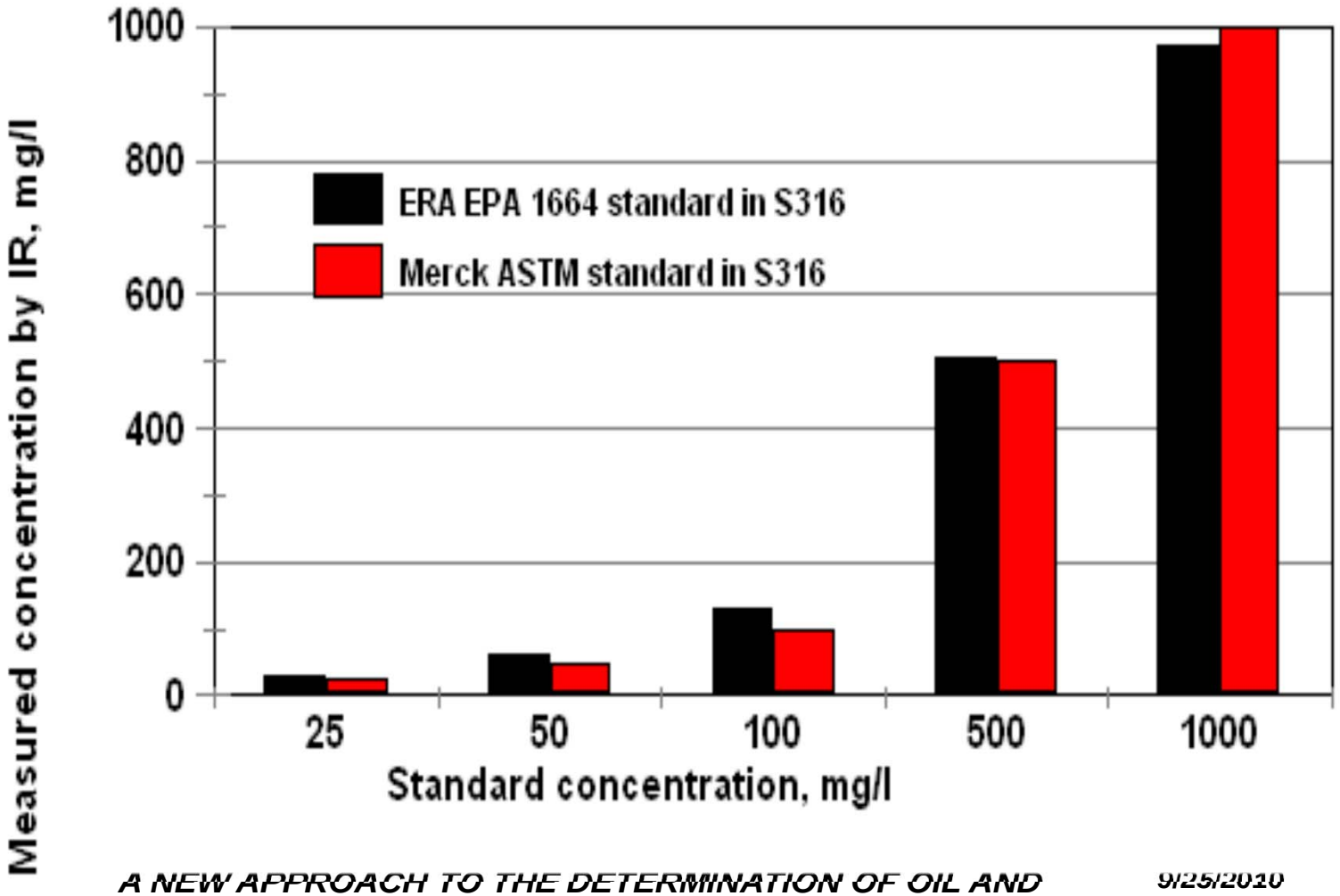
Recovery of OG from spiked samples



Recoveries varied from 85 -115 % with % RSDs from 10% at lowest concentration to 1 % for high levels

Effect of Matrix – "EPA" standards (Hexadecane and stearic acid) vs. "ASTM" matrix *(Octanoic acid, Iso-octane (2,2,4-trimethyl-pentane*

Matrix effects evaluated using **ERA reference standards** containing stearic acid and hexadecane



Comparison of ASTM-S316 sample data

Sample No	ASTM+U Sonic N=1	ASTM+USonic N=3	ASTM+SPE N=3	IG-Sox	BAC-Sox
Total OG					
7801	380		168	660	
7840	570		**234**	1340	**295**
7915	99	176	31	93	
7917	**265**	**294**	**244**	620	530
7937	**498**	**492**	**453**	710	
6012010				738	167
03022010				866	356
Silica gel					
7801	51		10	54	
7840	**53**		**39**	94	
7915	5	6	< LOD	9	
7917	**20**	**19**	**16**	64	0.9
7937	**52**	**61**	**32**	72	

NELAC proficiency test

- Compliant proficiency exercise administered by Libby on behalf of NELAC for determination of OG using the ASTM IR S316 procedure
- Statistically assigned value was **66.3**, our value **54.7** well within range of acceptance - **44.8-79 mg/l**.
- ***Our value accepted by National Accreditation Authority and lab was awarded ISO 7025 accreditation certificate.***

Interferences and problems

- **Sample Collection**
- OGs not stable in water as homogeneous mixture.
- In effluents, OG present as micro droplets or tiny suspended particles
- At high concentrations, as a floating layer varying from semi-solid chunks of grease to gasoline-like sheen
- There are OGs that are heavier than water and settle to bottom of sample plume and container
- Dense OGs composed of halogenated solvents. E.g. chloroform, perchloroethene, and polychlorinated biphenyls.
- For representative sample, collect from area of vigorous mixing.

- **Sample characteristics**
- Soaps, detergents, surfactants, etc., form emulsions that may reduce amount of OG extracted
- ASTM Method only suggests procedures that can break such emulsions.
- Solid phase extraction (SPE) used to overcome emulsions, which affects efficiency of extraction
- Organic compounds and other materials not considered as OG on basis of chemical structure may be extracted and determined as OG.
- Sample extract passes through sorbent bed - OG concentrates on surface, depleted water passes through.
- We used Horizon Technology Pacific™ O&G SPE Disks

QA/QC tests, frequency and acceptance criteria

QA/QC test	Frequency	Criteria	Comments
Calibration verification	every 10 analyses	Recovery within +/- 15 % of concentration	
Cross contamination			
Initial demonstration of laboratory performance			taken through analytical method including sample preservation and pretreatment
Precision and bias	7 replicates of	< 8 %.	independent standard solution
Mean, % recovery of OG		59 % - 100 %	
Method blank - **reagent water**	Each batch	**< 5 mg/L**	
Laboratory control sample (LCS)	**every 20 samples.**		Independent standard spiking solution. Commercial standards acceptable
Matrix spike (MS) - ***aliquot of sample with a known concentration***	**Every 20 samples**	***OG* % recovery 67 and 100**	
Relative Percent Difference (RPD) between matrix spike and matrix spike duplicate		=< 8 % for OG and =< 17 %, l5.5 and 100 for non-polars	
Independent reference material (IRM)	**least once per quarter**		Spiking solution may be used

Oil and grease check list - example

Yes	No	Review Item
		Analytical balance checked with weight standards
		No subsamples taken from sample container
		Calibration verification within limits using CCV and ICV
		Recovery from spiked samples
		Method balnks for contamination for each batch
		Matrix spike and matrix spike duplicate
		RPD
		Precision - sample duplicates
		Analysis of independent CRM
		Holding time limits - 28 days?
		Sample acidified
		Field blanks free from contamination

Conclusions

- Compliant ASTM procedure using S-316 extraction avoids hexane and FREON extraction, and without Soxhlet extraction and without gravimetric quantification. (EPA 1664a) for OG determination
- **Advantages** - no evaporation, extracted light oil and other volatile fractions remain in solvent (petroleum fuels such as gasoline)
- **Convenient and reliable means for compliant determination of O and G making use of cost-effective IR.**
- **Disadvantages** –heavier than water, therefore difficult to separate solvent extraction from sediment and from emulsions.
  - Reduced using SPE
- Considerable differences occur using various procedures.
- Preclude meaningful comparison.
- Nevertheless **ASTM with SPE** appear to produce consistent data. Further examinations are required.
- High cost of S316 - **However time saved and high sample throughput justifies cost of operation.**

- WILKs IR system results in procedural improvements and provides an efficient and cost effective method for compliant determination of O and G in waters and wastes

FUTURE APPLICATIONS

- Spill Protection for Water Intakes
- Water Monitors for crude leakages
- Protection of Desalination Plants
- Cooling Water Intakes
- Potential pollution sources include crude oil drilling and production, ships and barges
- Wastewater from oil carriers
- Lubricating and hydraulic oils
- Crude Oil Tracking Sensors for oil spills
- Refinery effluents
- Biofuel Industry
- Onsite Field Measurement of Oil and Grease
- Monitoring of offshore oil platforms and rigs
- Soil remediation sites.

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