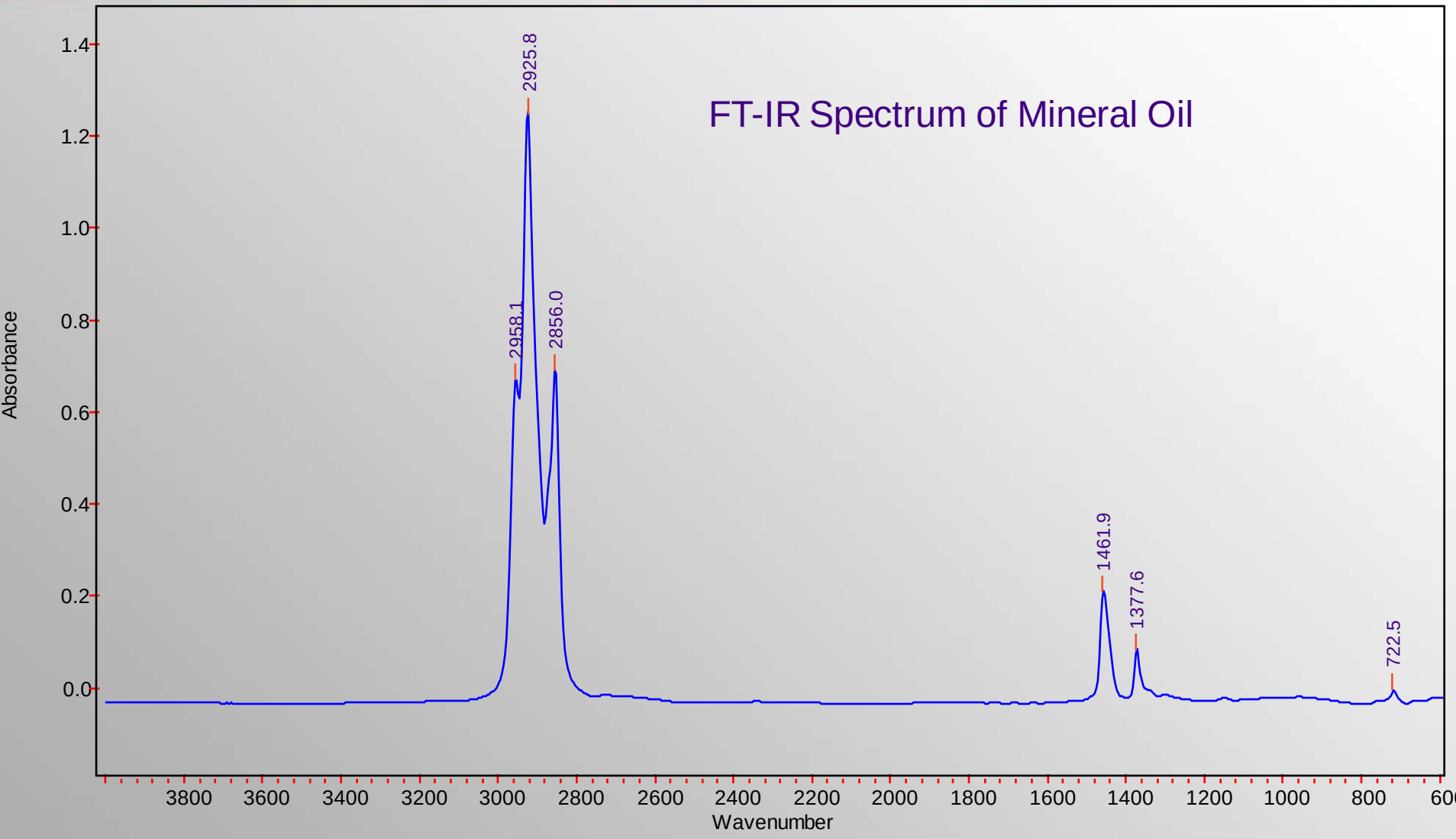
Simple, Fast and Accurate Solvent-free Method for Produced Water Process Monitoring

Jim Fitzpatrick

A2 Technologies


FT-IR Spectrum of Mineral Oil
Absorbance
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2925.8
2958.1
2856.0
1461.9
1377.6
722.5
3800
3600
3400
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3000
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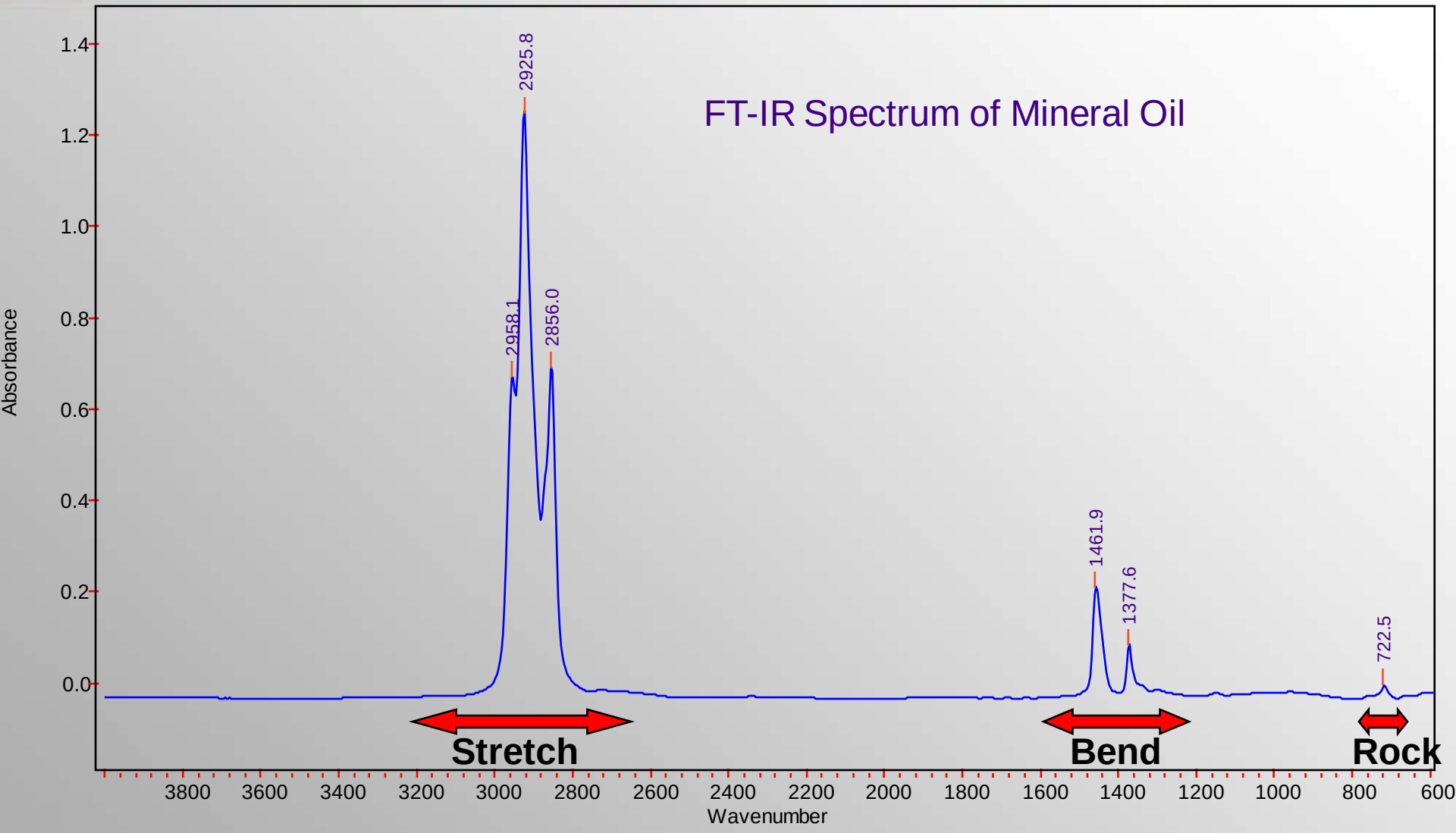
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumber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Stretch
Bend
Rock
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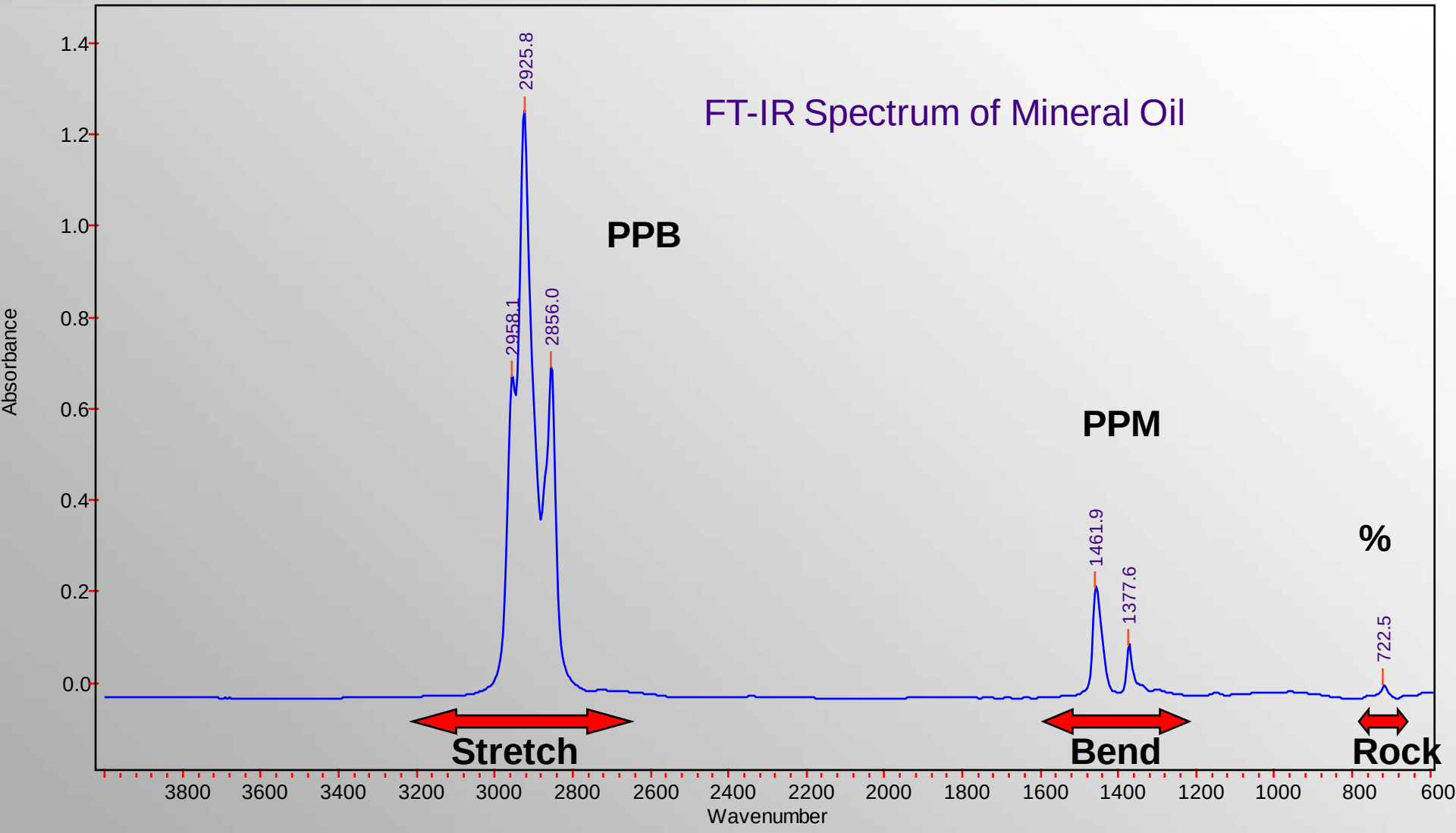
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PPB
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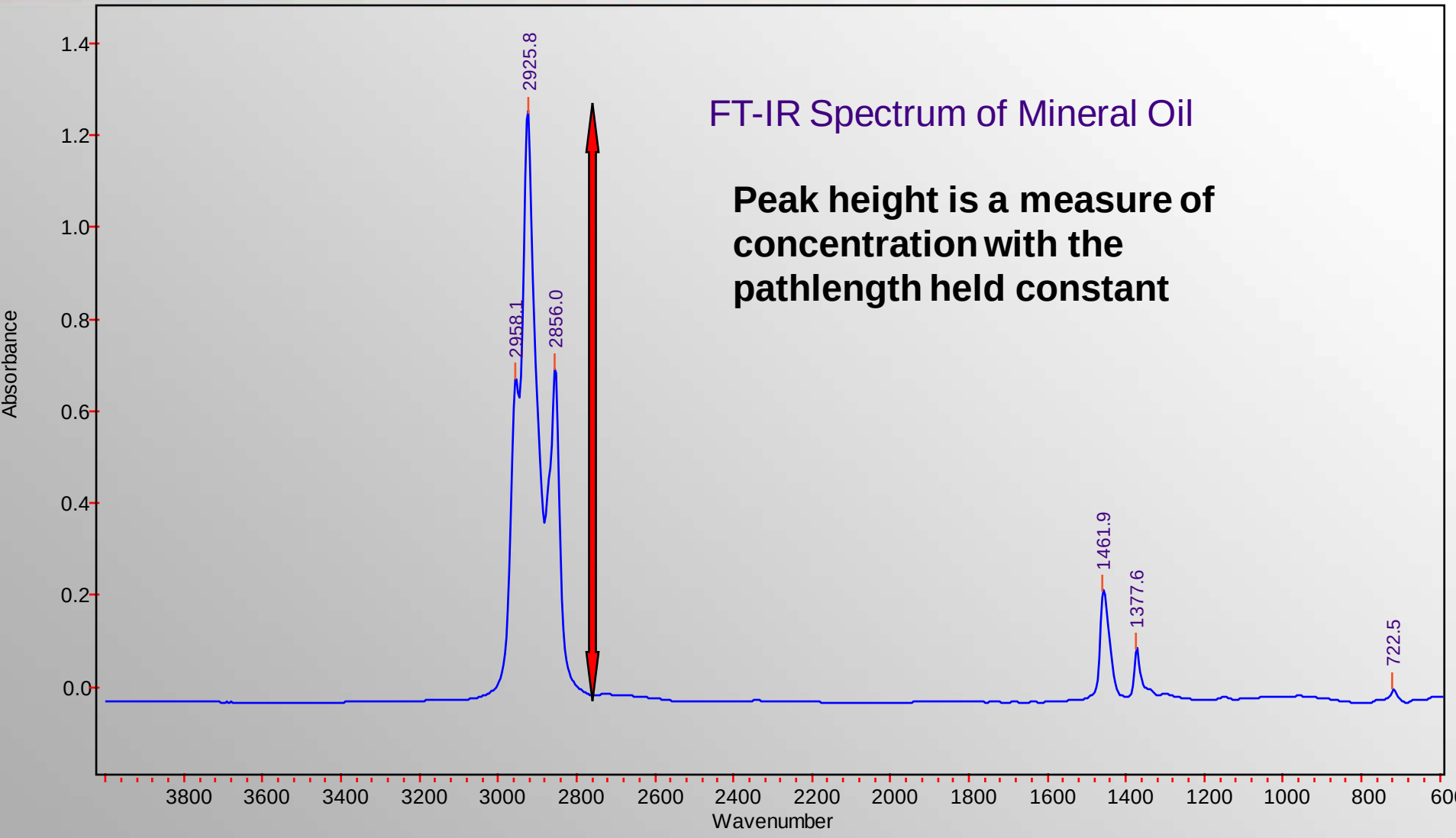
FT-IR Spectrum of Mineral Oil
Peak height is a measure of concentration with the pathlength held constant
Absorbance
1.4
1.2
1.0
0.8
0.6
0.4
0.2
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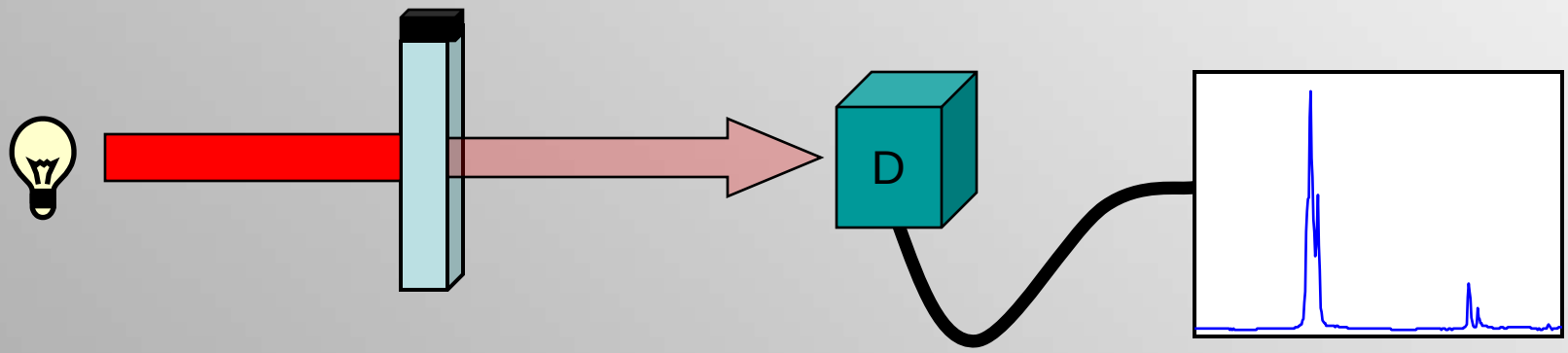
800
600
Wavenumber

Method comparison

- Old protocol
  - IR Technique
  - Freon extraction – kept light ends

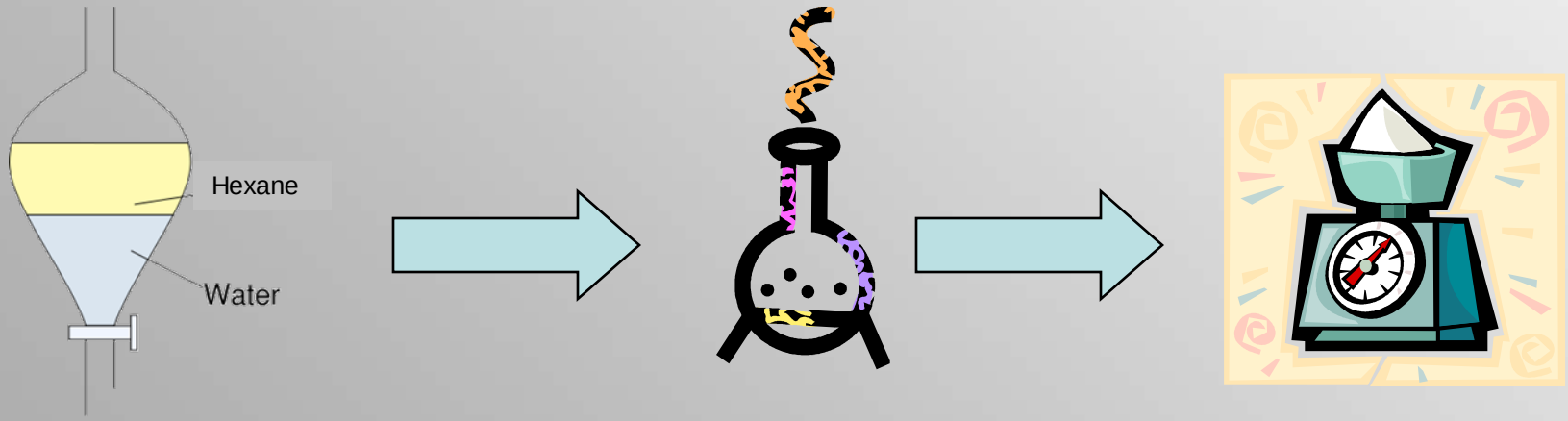


Method

- Extraction left all the insolubles behind in the water phase
- Water soluble substances left behind
- All organic components were measured, including light ends, because they all have a C-H bond.
- Reasonably easy to do

U.S.Method

- New Technique – EPA 1664
  - Hexane extraction
  - Distill off the hexane
    - Loss of light ends
  - Weigh the residue



EPA 1664

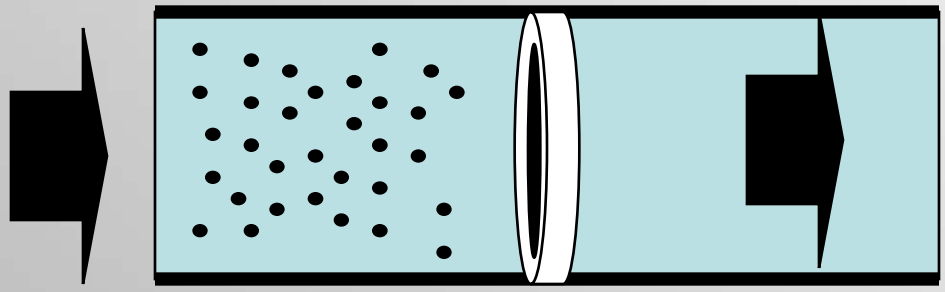
- Requires hexane as a solvent
- Complicated multi-step process
  - Measuring
  - Washing
  - Drying
  - Weighing
- Many opportunities for operator error

Goal

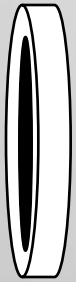
- Introduce a method that:
  - Is very easy to do
  - Requires no solvent
  - Correlates well with regulatory requirements
  - Has inexpensive, disposable consumables

A2 Test Methodology

- Filter water through a PTFE filter



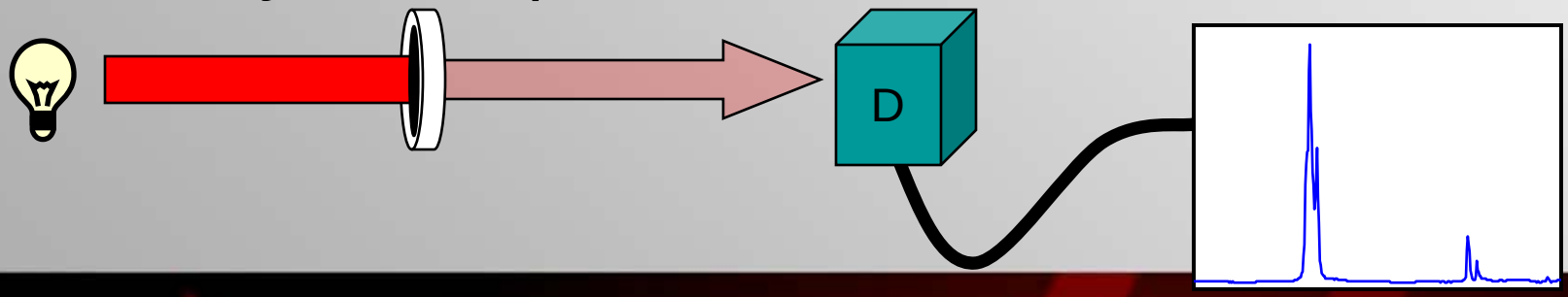
- Mass loading
- Highly efficient
- Even distribution
- Quick drying



We chose a fluorinated polymer for the same reason fluorohydrocarbon was chosen - transparency to IR in the areas of interest

Filter Method

- Time for filtration – 3-4 minutes
- Filter drying time – 2-3 minutes
- Analysis time – 1 minute
  - No solvents
  - Easy disposal
  - Easy cleanup



PAL Spectrometer

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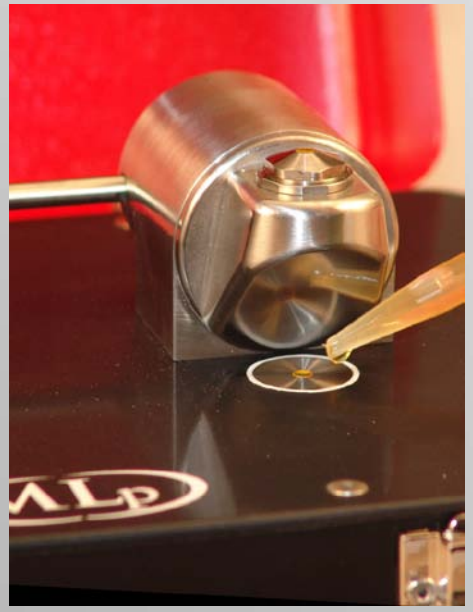
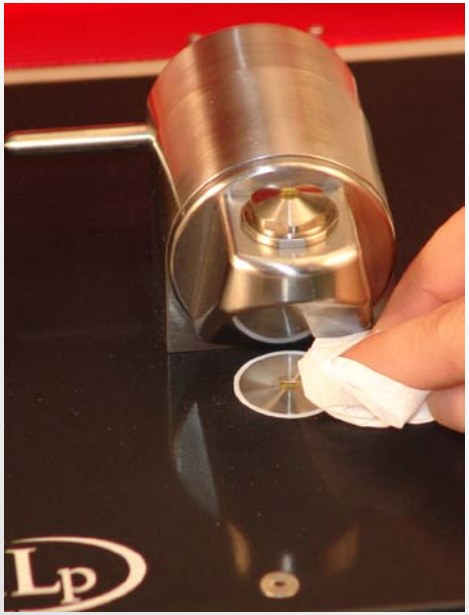


1. Place Sample on window

2. Rotate TumblIR into place

3. Analyze the sample



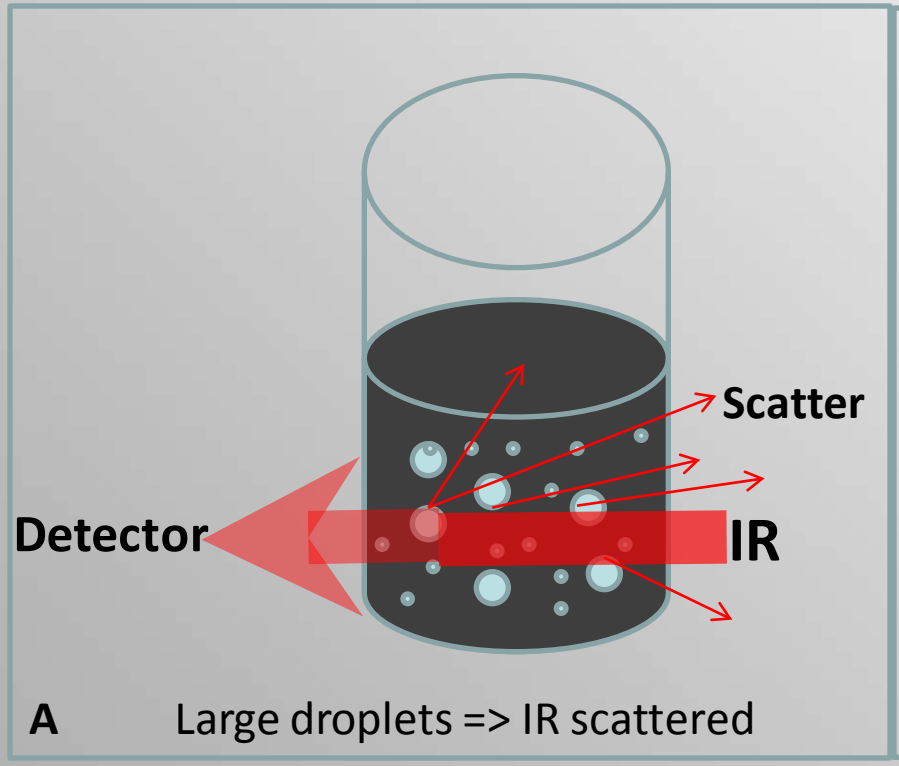
4. Cleaning is easy!

No Sample Prep Required, No Training Required

Why FT-IR for Lubrication Analysis?

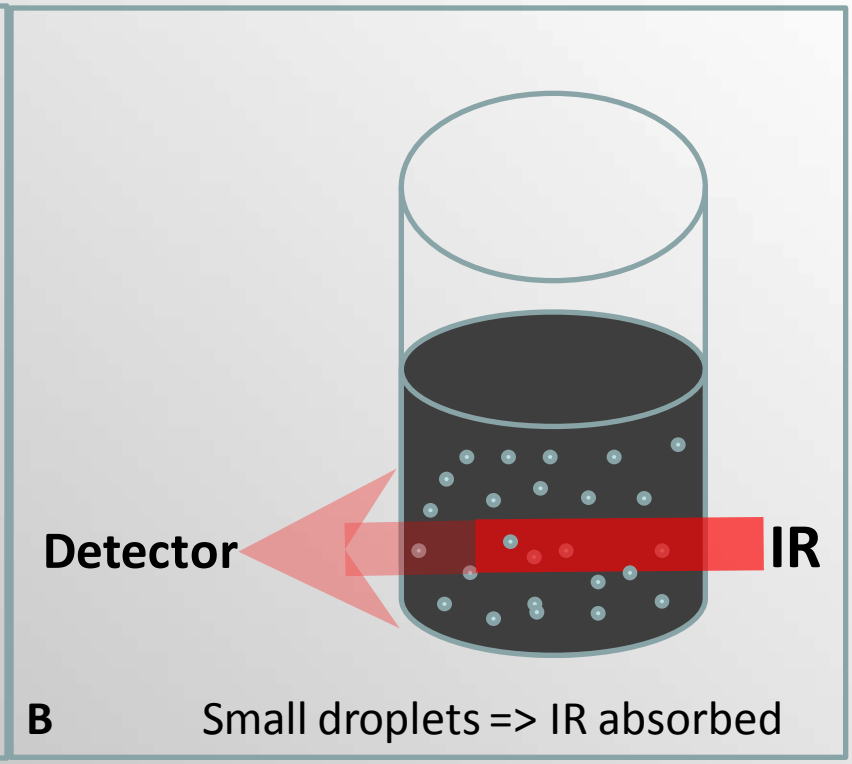
- Water
- Additive depletion
  - Antioxidant
    - Phenolic
    - Aminic
    - EP/AW
- Oxidation
- Nitration
  - Varnish formation

Water in oil



A Large droplets => IR scattered

Before surfactant

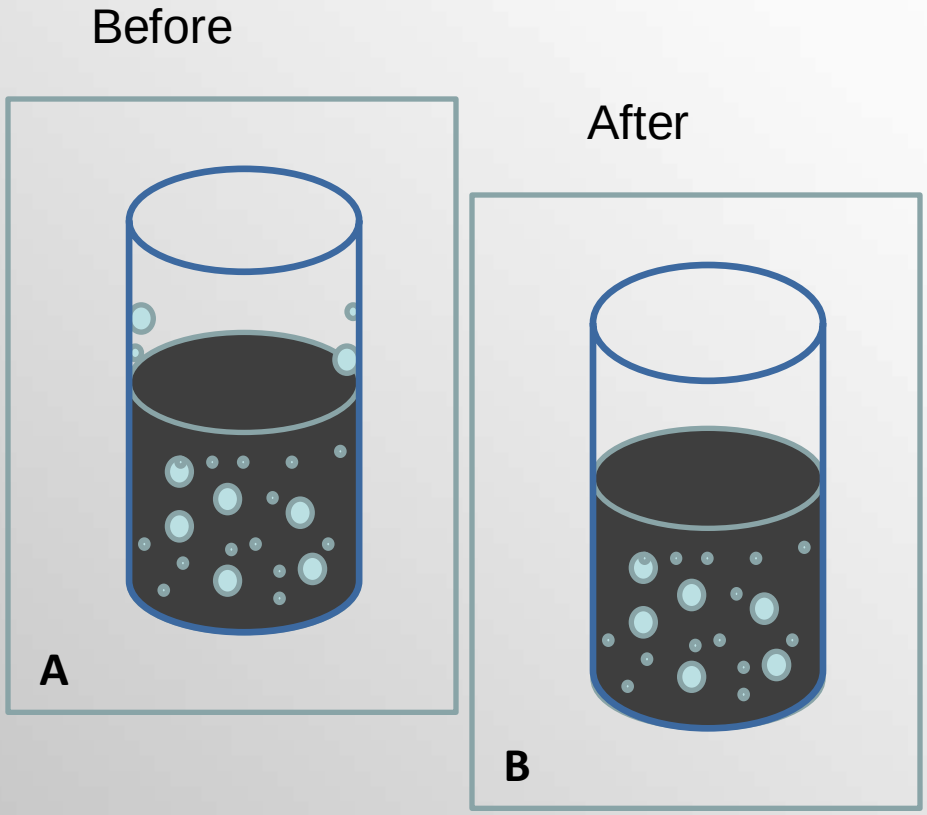


B Small droplets => IR absorbed

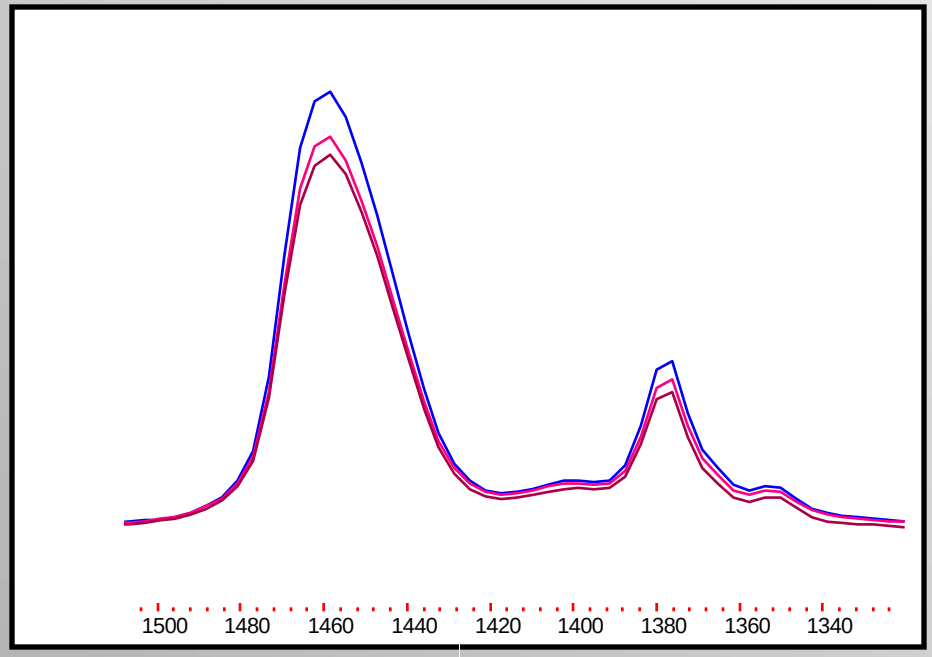
Before surfactant

Surfactant effect

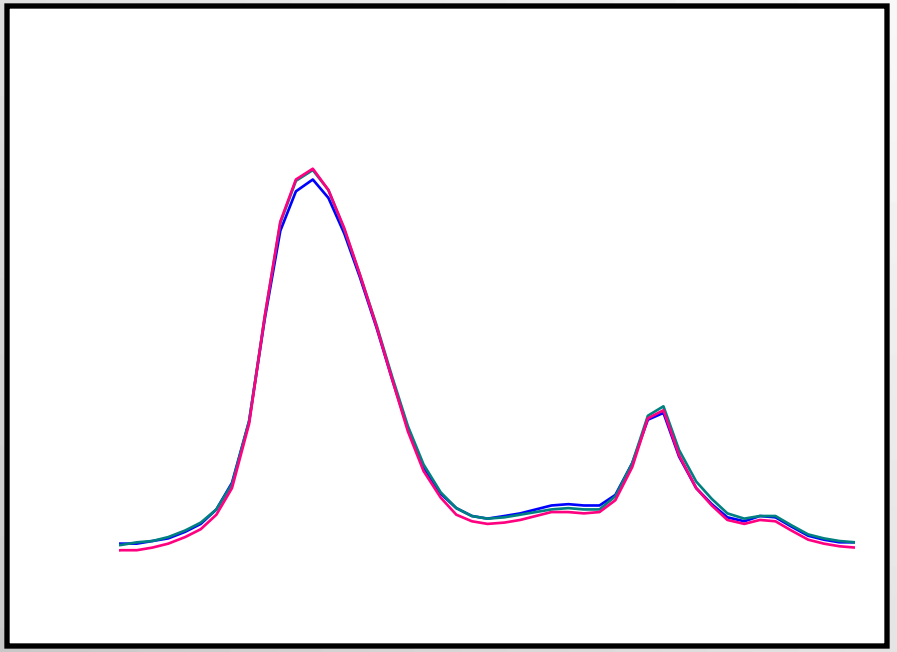
- Minimizes transfer loss from container to container
- Ensures consistency in amount of oil measured



Surfactant Effect

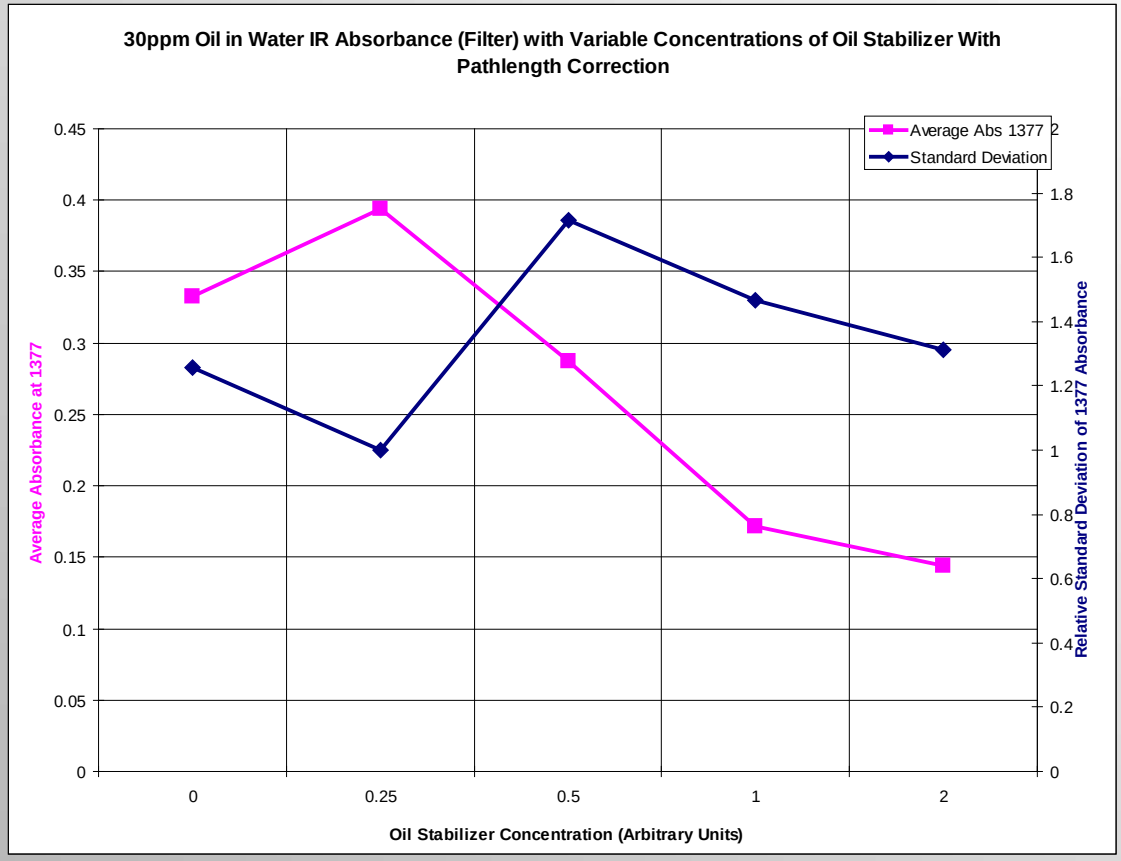


Before surfactant



After surfactant

Surfactant Optimization



Gravimetrically Prepared Oil in Water Standards Used for FT-IR Calibration and Method Development

1. Oil dilution standards gravimetrically prepared in IPA
2. Appropriate volumes added to a thoroughly cleaned 1000mL volumetric flask
3. The IPA solvent is evaporated at 50°C under vacuum
4. Dried flask is filled to the mark with distilled water
5. 250uL of Oil Stabilizer additive is added
6. Sample is vigorously shaken by inversion for 1-2min
7. Transfer solution to cleaned 1L sample jar

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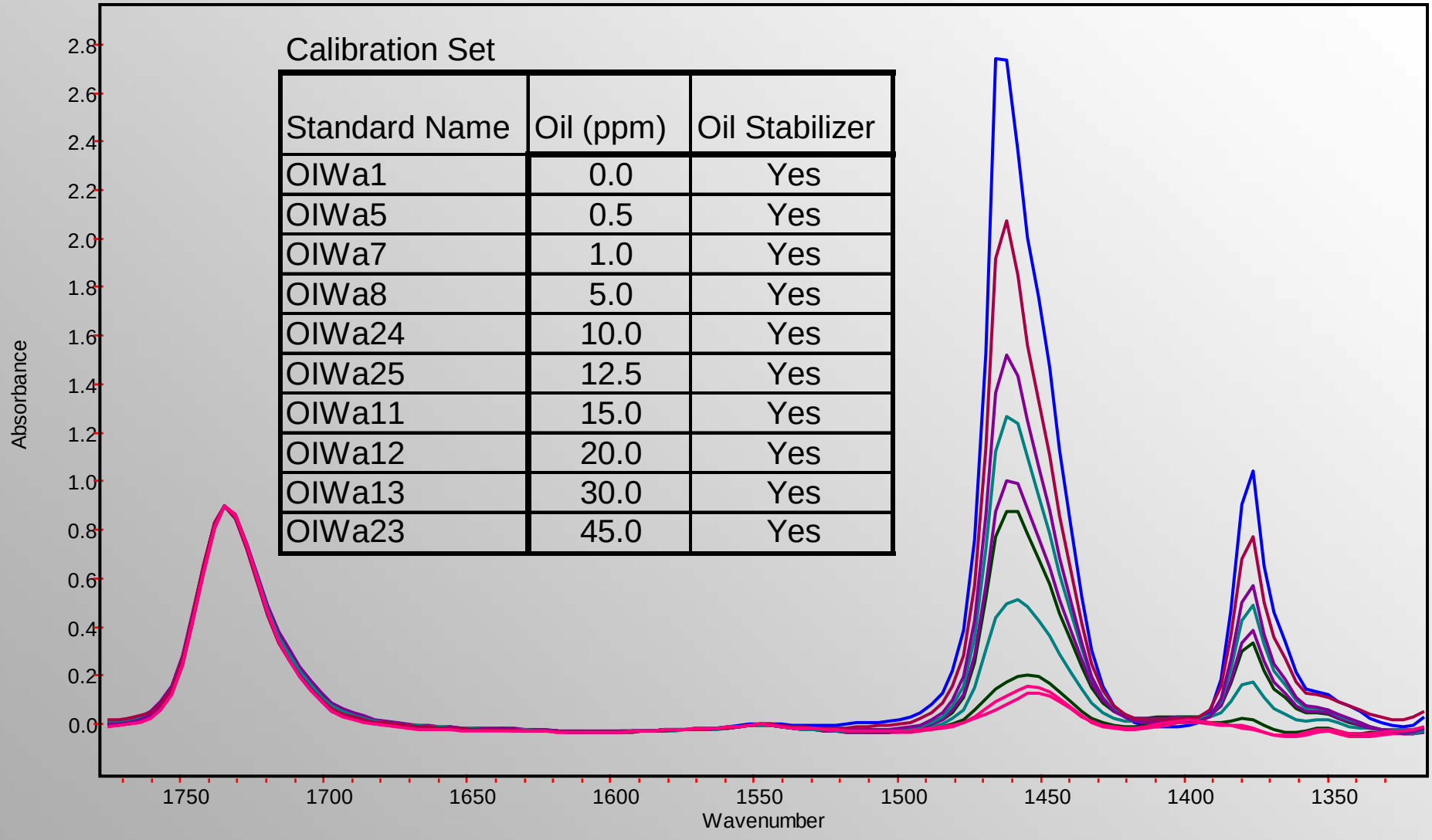
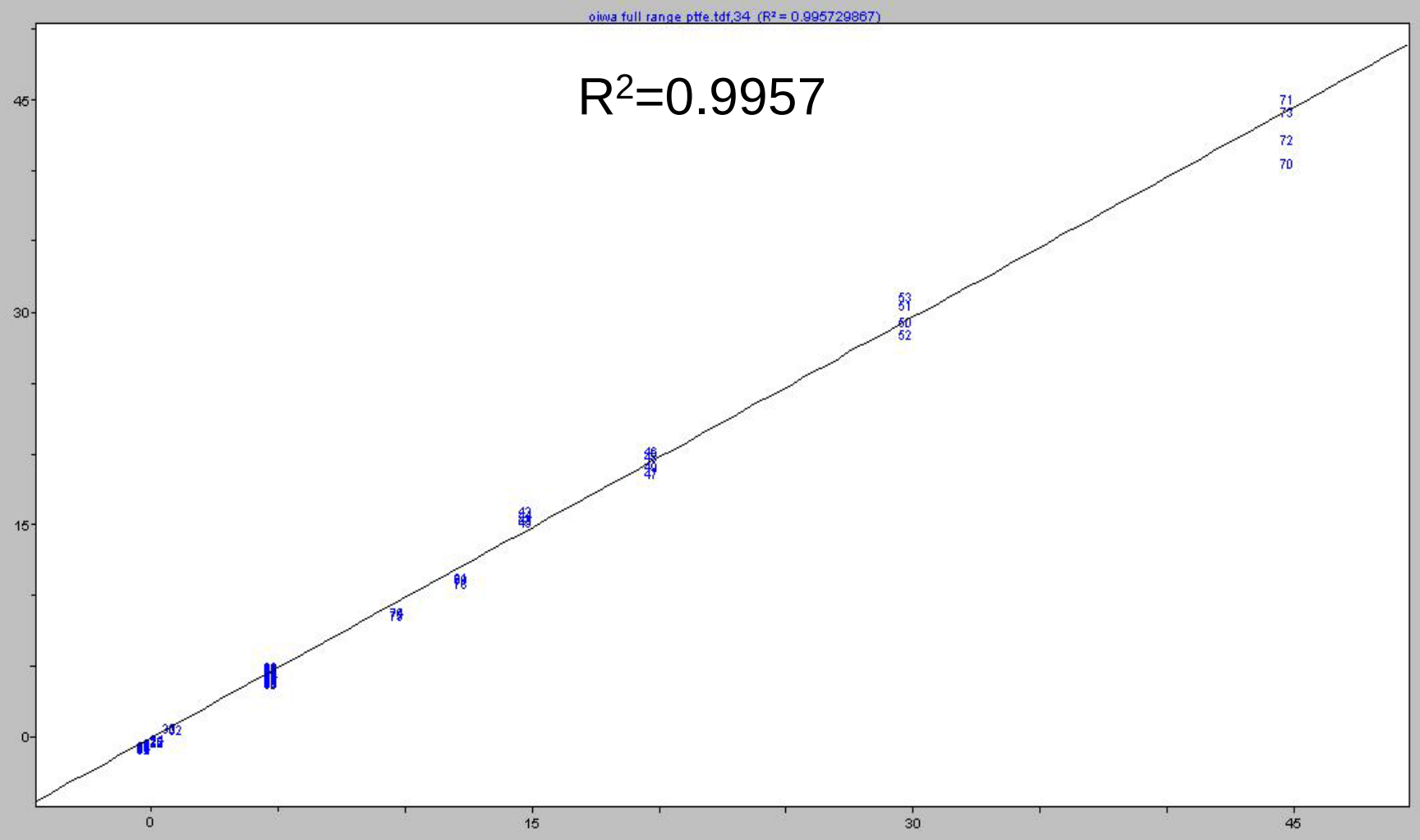
Calibration Set

Standard Name	Oil (ppm)	Oil Stabilizer
OIWa1	0.0	Yes
OIWa5	0.5	Yes
OIWa7	1.0	Yes
OIWa8	5.0	Yes
OIWa24	10.0	Yes
OIWa25	12.5	Yes
OIWa11	15.0	Yes
OIWa12	20.0	Yes
OIWa13	30.0	Yes
OIWa23	45.0	Yes




oiwa full range ptfe.tdf,34 (R² = 0.995729867)
R²=0.9957
Predicted Concentration
Actual Concentration
0
15
30
45

A2 TECHNOLOGIES

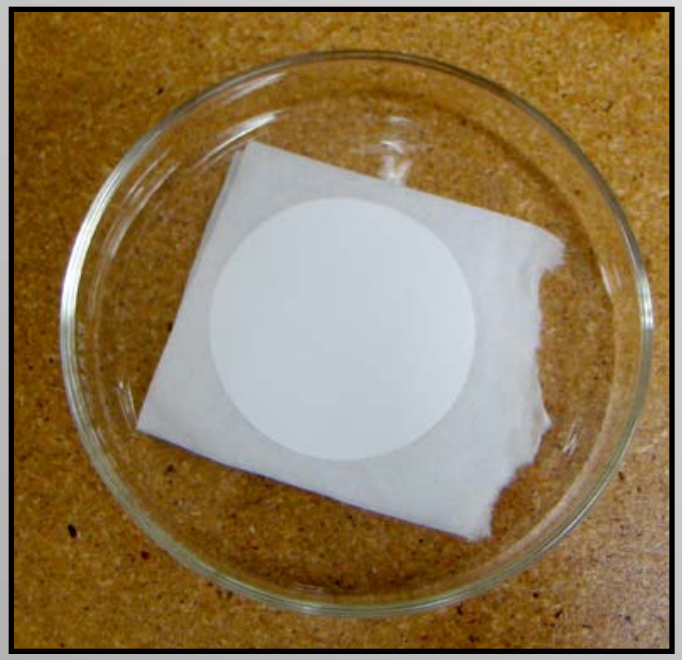
Oil in Water Validation Set Prediction Results

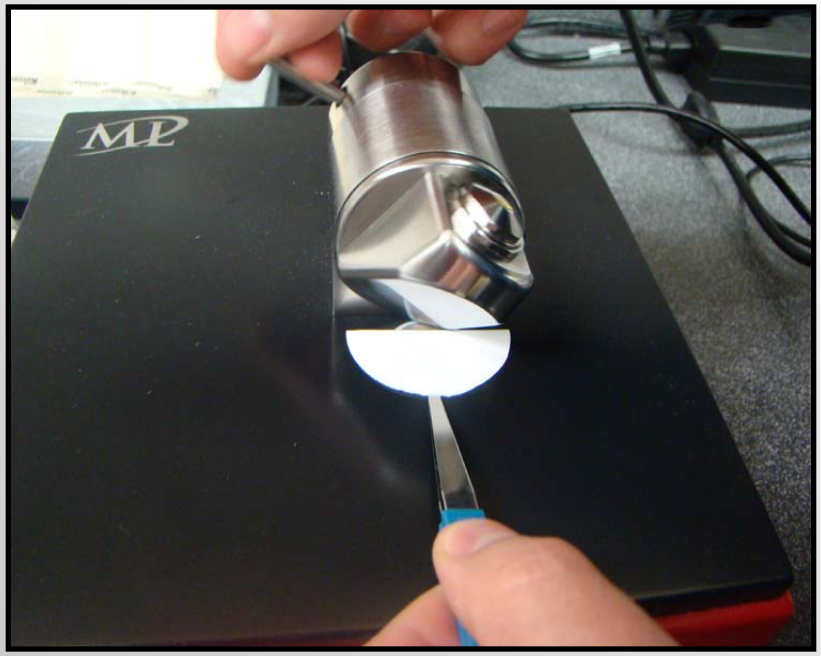
Sample	Predicted Oil Conc. (ppm)	Actual Oil Conc. (ppm)	Absolute Difference	Relative Error (%)
OIWA 6 Instr 1 Rep 1	0.81	0.75	0.06	8.5%
OIWA 6 Instr 1 Rep 2	0.77	0.75	0.02	2.2%
OIWA 6 Instr 2 Rep 1	0.84	0.75	0.09	12.3%
OIWA 6 Instr 2 Rep 2	0.79	0.75	0.04	5.5%
OIWA 9 Instr 1 Rep 1	7.81	7.50	0.31	4.2%
OIWA 9 Instr 1 Rep 2	7.80	7.50	0.30	4.0%
OIWA 9 Instr 2 Rep 1	8.05	7.50	0.55	7.3%
OIWA 9 Instr 2 Rep 2	7.07	7.50	0.43	5.8%
OIWA 15 Instr 1 Rep 1	2.88	3.00	0.12	4.1%
OIWA 15 Instr 1 Rep 2	2.82	3.00	0.18	5.9%
OIWA 15 Instr 2 Rep 1	2.88	3.00	0.12	4.1%
OIWA 15 Instr 2 Rep 2	3.12	3.00	0.12	3.9%
OIWA 19 Instr 1 Rep 1	19.32	17.50	1.82	10.4%
OIWA 19 Instr 1 Rep 2	19.72	17.50	2.22	12.7%
OIWA 19 Instr 2 Rep 1	19.57	17.50	2.07	11.8%
OIWA 19 Instr 2 Rep 2	19.18	17.50	1.68	9.6%
			Total	7.0%

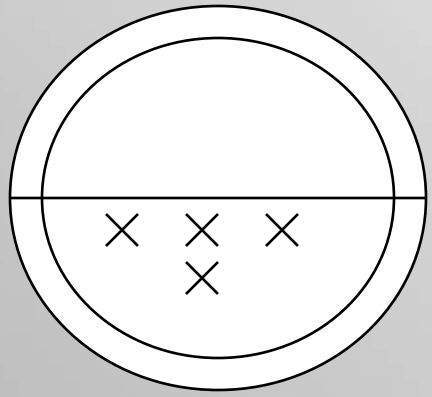
The limit of detection for this method is 0.10ppm (100ppb)

Methodology

Filter

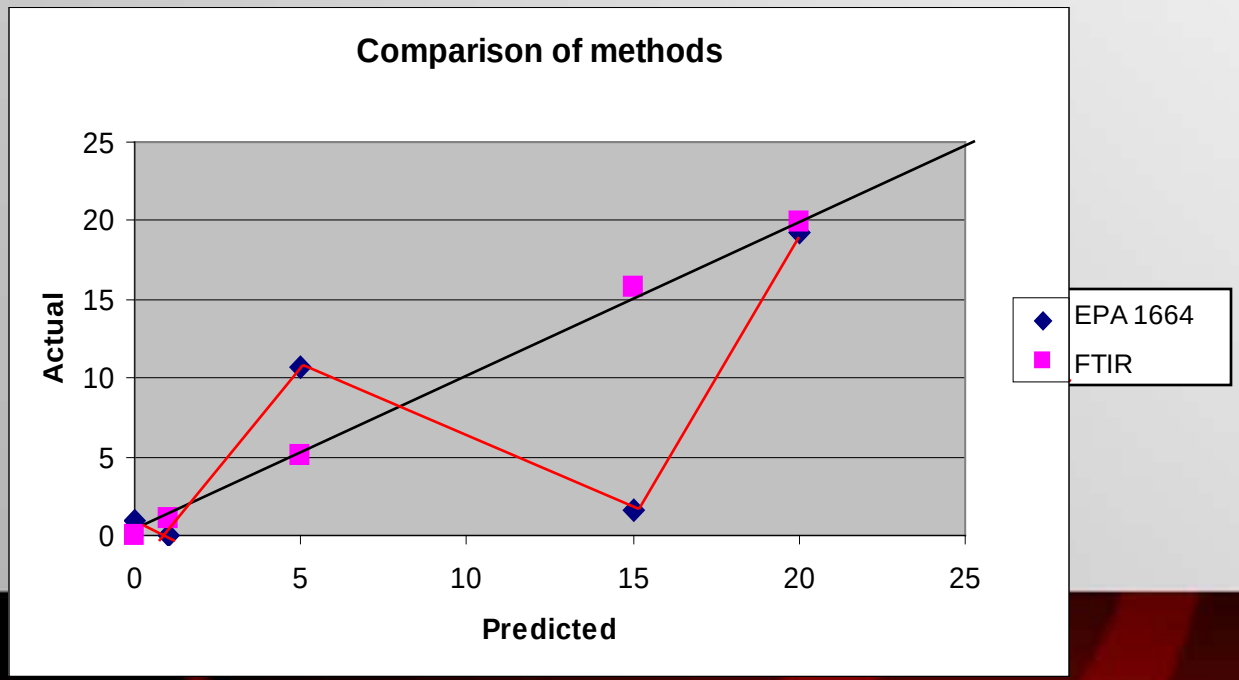






Standard	1463cm-1 Abs	1377cm-1 Abs
30ppm Rep1	2.317	0.399
30ppm Rep2	2.289	0.396
30ppm Rep3	2.269	0.391
30ppm Rep4	2.268	0.391
Rel Standard Deviation	1.004886	1.001287

Sample ID	Actual oil concentrations (ml/L)	1664 Method	FT-IR method
Water #1 A (OIWA, No acid)	0	1	0
Water #1 B (OIWA, No acid)	1	<1	1.1
Water #1 C (OIWA, No acid)	5	10.7	5.1
Water #1 D (OIWA, No acid)	15	1.6	15.8
Water #1 E (OIWA, No acid)	20	19.2	19.9



Additional capabilities

- Water in crude oil
  - 0.1 – 0.3% level
  - Keeps pipes from corroding
- Water in crude oil
  - 1% – 50%
  - Allows dewatering/production validation etc
- Water/Glycol mix analysis
  - Drilling fluid

Work in progress

- All work to date completed with mineral in deionized water
- Need to test effects of:
  - Different oils
  - Salinity
  - Acidification
  - Particulates

Conclusions

- FT-IR used with filter technology to accurately measure oil in water in the range from 0.25 ppm to 45 ppm
- Correlates well with gravimetrically prepared samples
- Good reproducibility independent of filter area measured
- Surfactant minimizes loss due to oil adhering to container surfaces
- More work to be done on real world samples