



Refinery Applications

for Fluorescence Measurement

Turner Designs Hydrocarbon Instruments

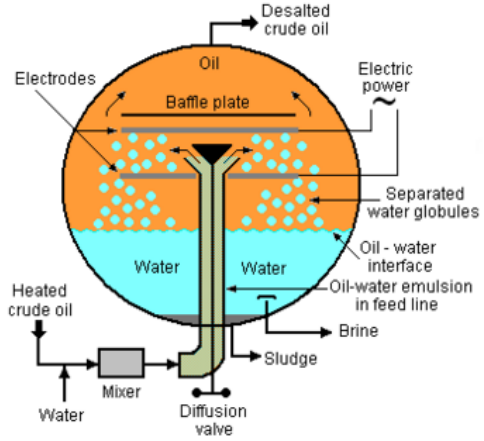
Chip Westaby

Refinery Applications

- Significant Target Customers
- Many requirements for Oil in Water Measurement
- Often same companies as existing Produced Water Customers
- More sophisticated in Oil in Water Measurement than other ‘Industrial’ Customers
- No current best measurement method
- 84 Current Installations – 46 More at Skikda

Refinery Processes

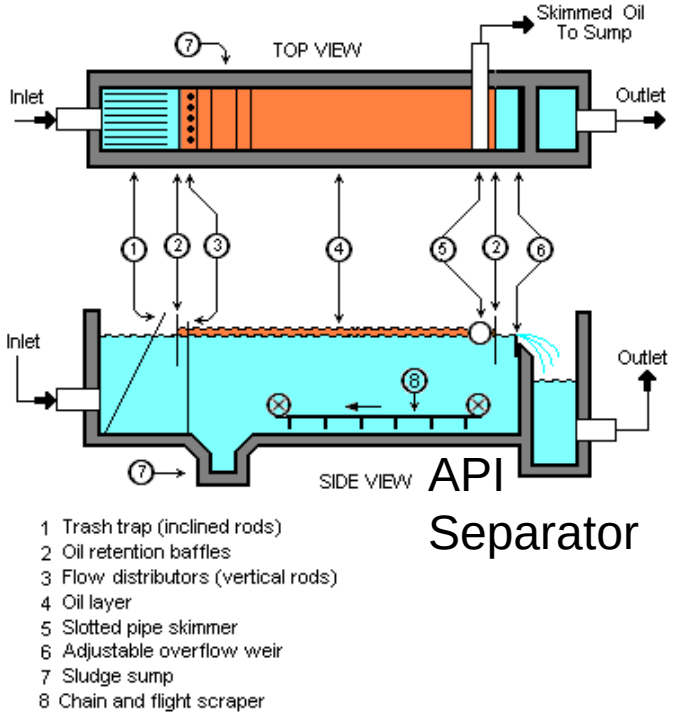
- Storage Tank Farm
  - Dewatering Control
  - Rain Water
- Crude Unit
  - First Process – Water Added to desalt and remove solids
  - Desalter
    - <1% Oil in Water / <0.5% Water in Oil
    - Sample Analysis for chemical optimization



Cross-sectional view of Electrostatic crude oil desalter

Refinery Process

- Waste Water
  - API Separators
  - Dissolved Air Flotation
  - Advanced Processes
    - MBR, DeNitrification, etc.
  - Discharge Compliance
  - Inlet upset Monitoring



API Separator

- Fluidic Catalytic Cracker (FCC)
  - Breaks large molecules into smaller (Gasoline), produces heavy residual oil
  - Catalyst is an abrasive Slurry, heat added
  - Reside Slurry erodes heat exchangers

Refinery Processes

- Hydrotreater
  - Hydrogen and heat added to break large molecules into smaller (Diesel)
- Coker
  - High Heat cracks heavy molecules into light hydrocarbons (BTEX) and almost pure Carbon.
- Utilities
  - Fired Boilers – Low tolerance for hydrocarbons(<1ppm)
  - Unfired Boilers – Heat Exchangers, very common



Skikda Processes

- Isomerization
- Crude
- Naptha Pre-Treatment
- Aromatics Recovery
- Paraxylene Recovery
- Hydropurification
- Hydrotreating
- Flare Systems
- Effluent Treatment
- Xylene Isomerization Units

PERF

- Petroleum Environmental Research Forum
  - To provide a forum to discuss and develop proposals for cooperatively funded projects relating to these areas.
    - Environment
    - Health
    - Safety
    - Waste reduction
    - System integrity
- Members Include
    - Chevron
    - BP
    - ConocoPhillips

- Waste Water Monitoring Study Proposal
  - Multiple Technologies
  - Many process types
  - Process Control



Measurement

- Most applications are for process control, not discharge monitoring purposes.
- Waste Water Processes can have BTEX to Crude in Variable concentrations
  - Approx. 50% of hydrocarbons are crude oil
  - Fluorescence will track crude mostly
- All measurement technologies will measure 100 ppm of BTEX different than 100 ppm crude

Currently used Measurements

- TOC – Total Organic Carbon
  - Regulatory requirement in some cases
  - Slow to respond (2.6-10 Minutes) per sample
  - High Maintenance
  - Measures all organic carbons not just hydrocarbons
  - Consumable Reagents
  - Light HC have lower response than heavy
    - 100ppm crude can be 20% higher than Benzene
- Gas Chromatograph
  - High Sensitivity and selectivity
  - Labor Intensive and expensive to operate
  - Not on line - Samples only
  - Consumable Reagents

TOC Products

- GE Sievers InnovOx
  - .5 to 50,000 ppm
  - Accuracy +/- 3%
  - Precision <5%
  - Response 2.6 to 8.3 minutes
  - Hazardous Area: None
  - Acid, Oxidizer and Water Reagents



- HACH astroTOC
  - 5ppb to 50 ppm
  - +/- 4% accuracy
  - Response: 3-5 Minutes
  - Hazardous Area: None
  - Acid, Oxidize and **CO_2 Free Air needed**



Measurements

- Chemical Oxygen Demand (COD)
  - Lab Method
  - Detect Biofouling in Cooling Towers
  - Surrogate for BOD
- Biological Oxygen Demand (BOD)
  - Lab Method
  - Used in Cooling towers to detect biological build up
  - Chlorine added to kill biologics
  - Hydrocarbons can appear as BOD

Measurements



- Total Suspended Solids / Turbidity
  - Particle Detection
  - Can indicate solids as hydrocarbons
  - Cannot detect dissolved hydrocarbons
  - Low Cost
- Capacitance / Microwave
  - Percentage measurement of hydrocarbons in water 1% to 100% measurement
  - Capacitance cannot measure hydrocarbons below 50%.



Fluorescence Advantage

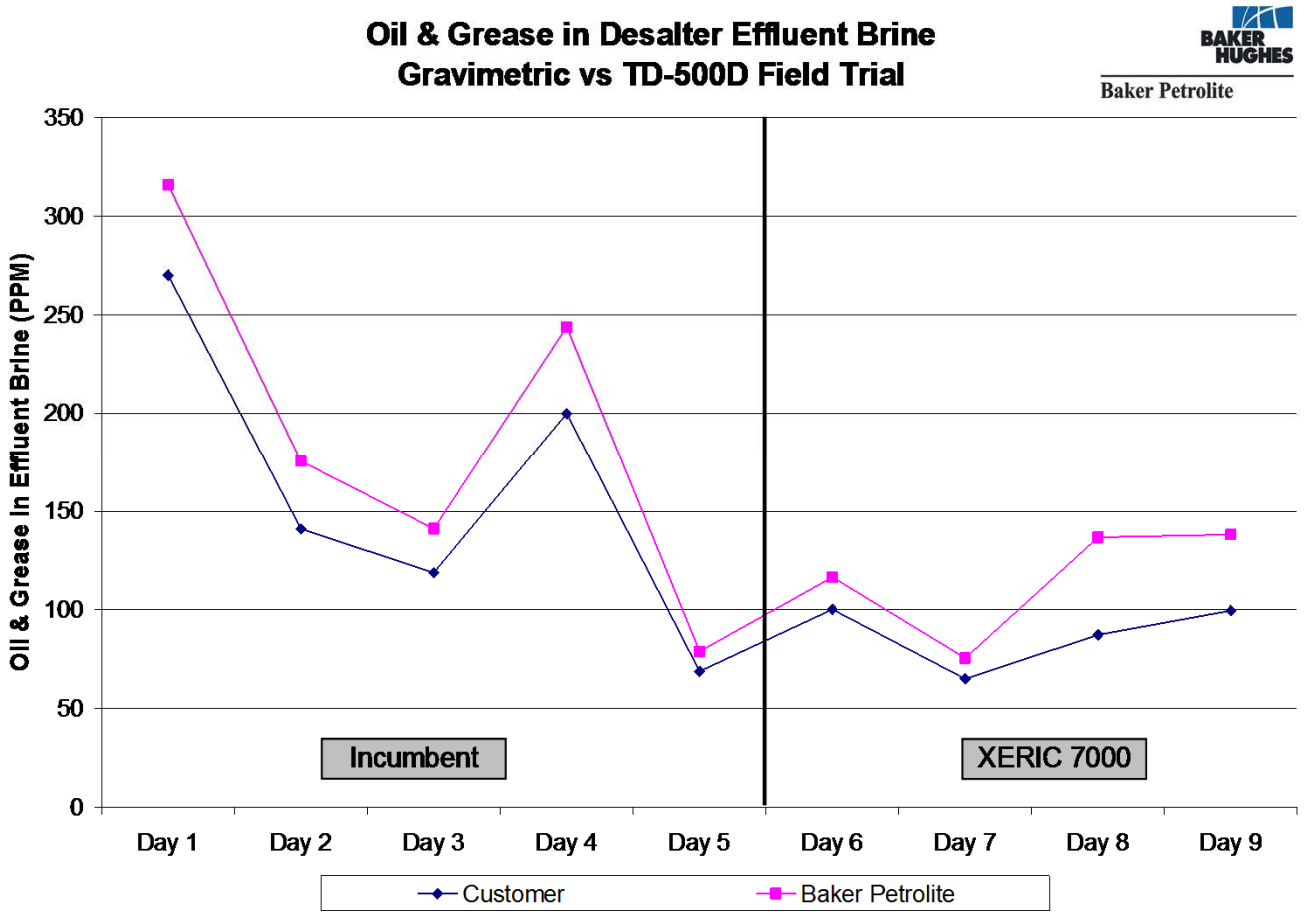
- Fast on line measurement
  - Good for process control
- Specific to hydrocarbon measurement
- Low Maintenance / No reagents
- Works well in combination with other technologies
- In Waste Water process, primarily tracks the most significant contaminant (Crude)

Applications

- Crude Unit – TD-500D
  - Most major Chemical Suppliers use TD-500D to monitor crude unit water
  - No Solvent Method allows for fast on site analysis
    - Fast process optimization
  - Dilution with Distilled water allows for measurement up to ~10%
  - Correlates Well with Lab Method



TD-500D used in Desalter



Applications

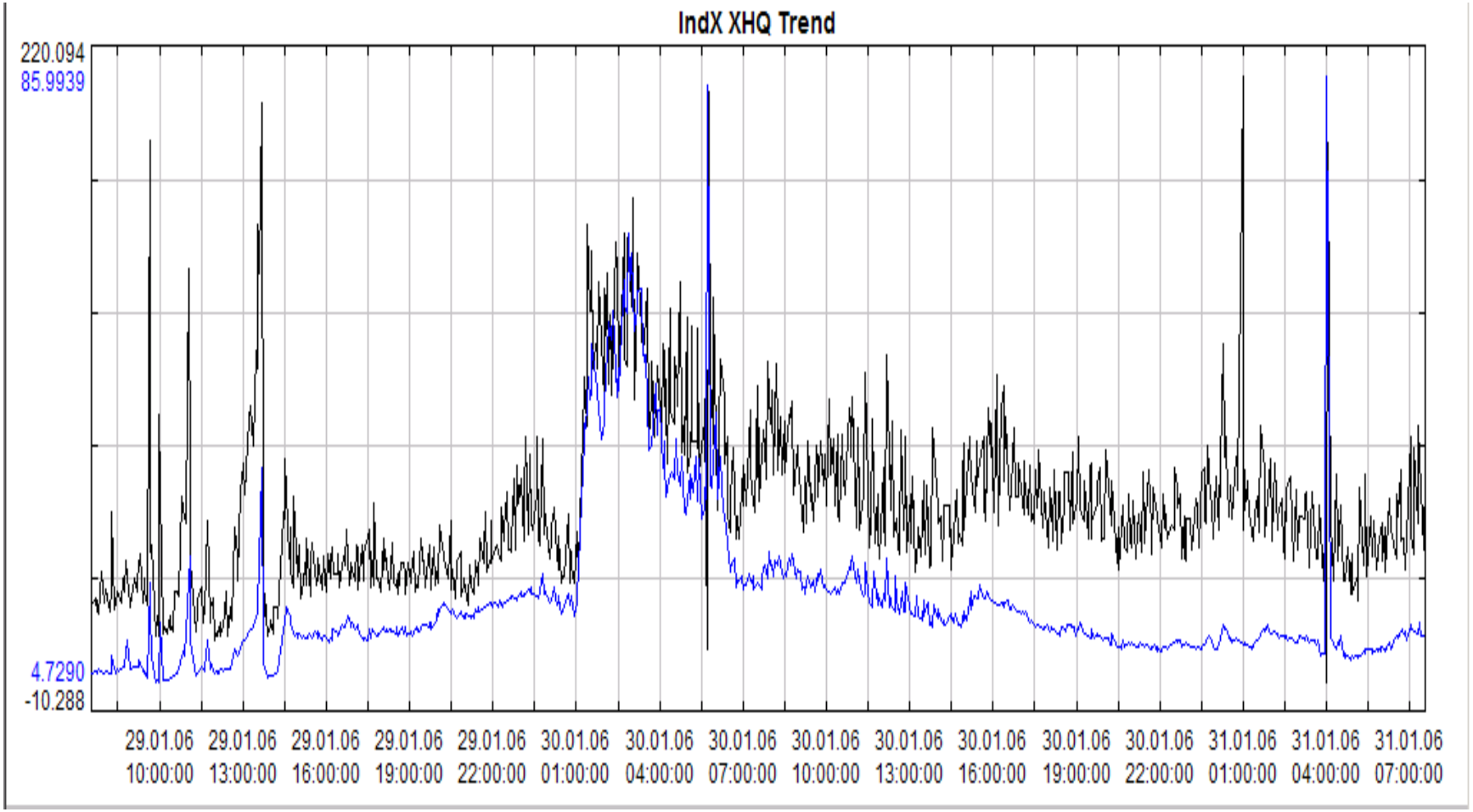


- Leak Detection
  - Steam Condensate
    - Protect Condensate Polisher
    - Can be Non Hazardous
    - Can be Chemical Vendors supplied
  - Cooling Tower
    - Prevent Tower Fouling
    - Reduce Chlorine use
    - Reduce Air Emissions
    - BOD / COD Surrogate measurement

Applications

- Fluorescence used with other technologies
  - Turbidity
    - Able to detect when solids, free hydrocarbons or dissolve hydrocarbons are present
  - TOC
    - Able to differentiate hydrocarbons from naturally occurring organics in boiler feed water

TD-4100XD used in Waste Water Discharge

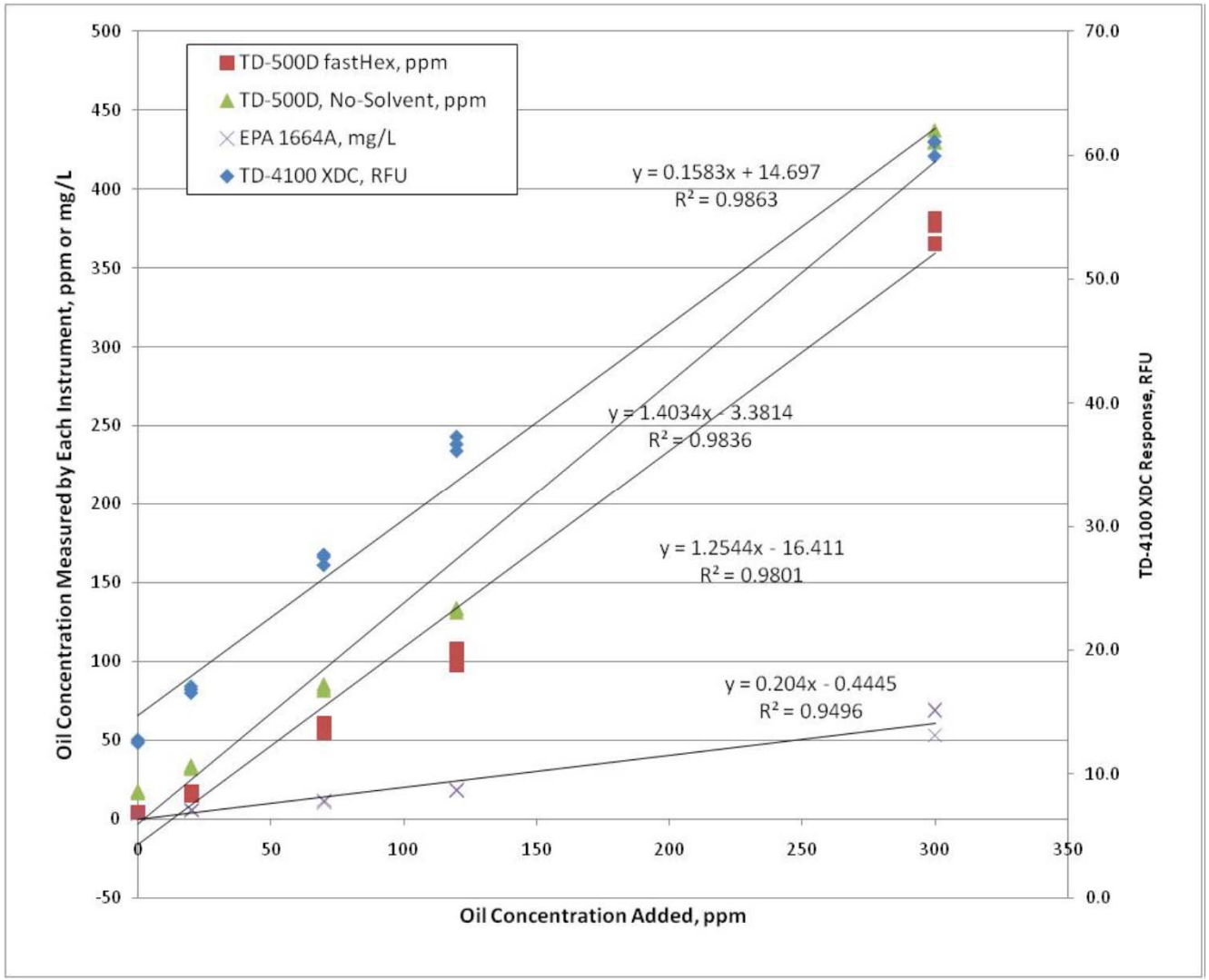


Black is Turbidity, Blue is Fluorescence

TD-4100C used in comparison with



Recent Refinery Ground Water Study



Ethylene Process

- Cracking of Light HC (Ethane, Propane, etc.)
  - Furnace
  - Most common Hydrocarbon Plant
    - Base Stock for plastics
    - Ethylene and Propylene products
  - Heavy Oil, Light HC, and Water By products
  - Large Water separation process
  - Most water is recycled

Industrial Waste Water Trial

