

What's New in Sulfur Analytical Technology

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EPA/API ULSD Workshop

New Orleans, LA - November 15, 2004

Outline

- Review of current technology
- New ASTM methods
- On-line analyzers needed
- Advances in sulfur measurements
- Other interface detection devices

Current Laboratory Techniques

Laboratory

- UV Fluorescence (UVF) (ASTM D 5453)*
- Wavelength Dispersive X-ray Fluorescence (WDXRF) (ASTM D 2622)
- Electrochemical (ASTM D 6428)
- Microcoulometry (ASTM D 3120)
- Monochromatic Wavelength Dispersive XRF (ASTM D 7039)

*Precision of ASTM D 5453 UV Fluorescence Method

- Petroleum refining industry needs to work to improve the precision of the method.
- Current reproducibility of 6 ppm at a sulfur content of 15 ppm.
- Cost \$MM annually in lowering unit sulfur targets. (Control at 5 ppm or less).

Current On-line Technology

On-line

- GC/Flame Photometric Detector
 - ABB (ASTM D 7041)
 - Siemens
- UVF
 - Antek
 - Thermo
- MWDXRF
 - X-ray Optical Systems/Horiba

New ASTM Methods and Practices

Recently Approved

- D 7039 – Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry (XOS lab method)
- D 7041 – Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by On-line Gas Chromatography with Flame Photometric Detection (ABB)

New ASTM Methods and Practices

Under Consideration

- On-line UV Fluorescence (Antek)
- Standard Guide for Establishing and Validating the Relationship between On-line Analyzer and Primary Test Method Results using relevant ASTM Standard Practices

Comparison of Needed On-line Sulfur Analyzers

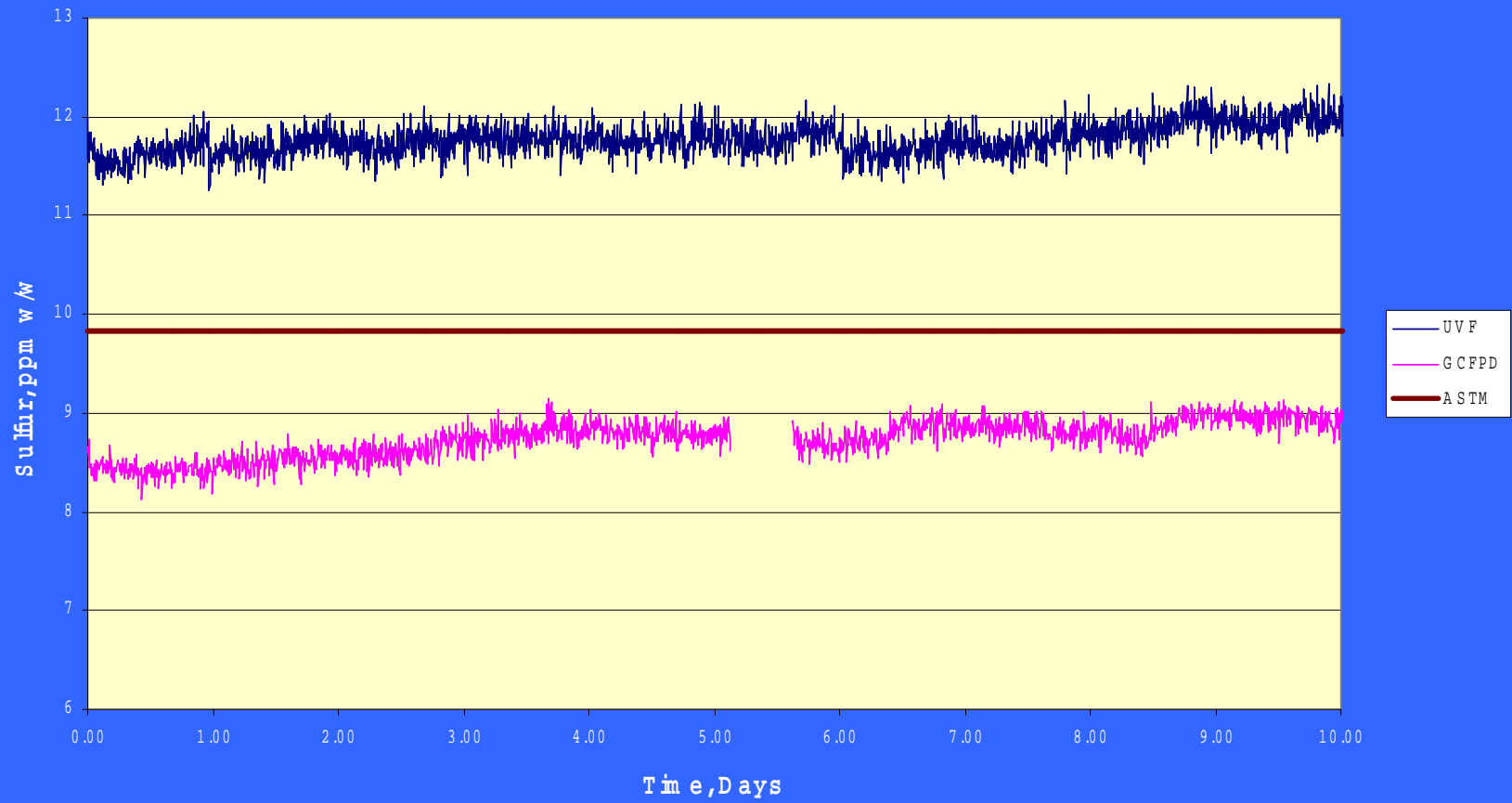
Refinery

- 5-minute analysis time sufficient to control units
- Utilities are prevalent
- Comparison of results to lab method
- Maintenance groups already exist

Pipeline

- Remote locations
- Very quick response time needed to detect interfaces
- Few utilities
- Very few analyzer maintenance personnel

Online Ten-day Stability Test of UVF and GC_FPD



Advances in Sulfur Technology

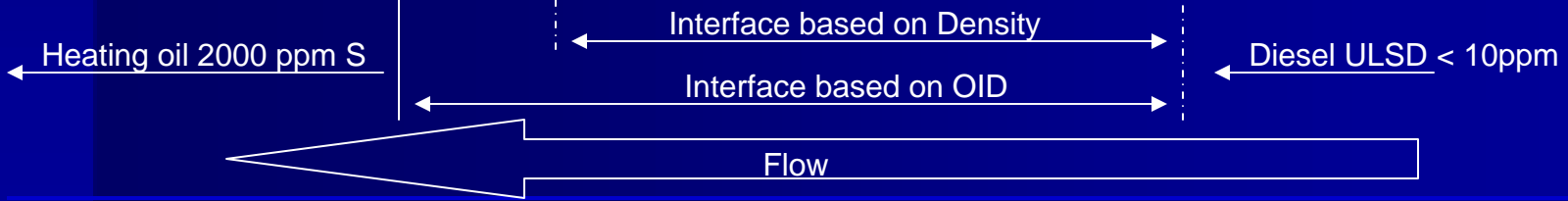
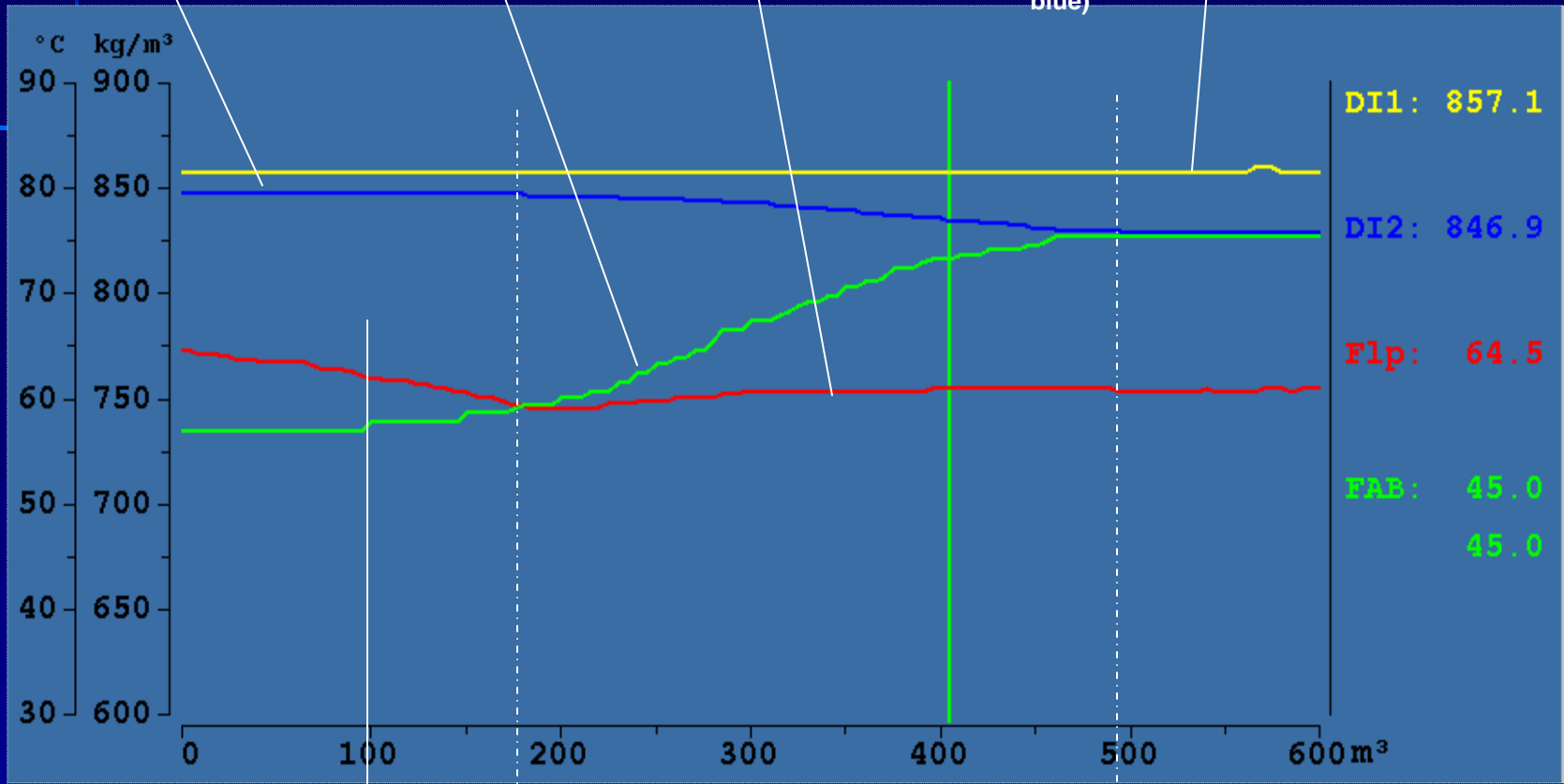
- High-speed analysis down to 1 minute
- Movement to decreased utilities
- Improvements in analyzer communications (OPC)
- Modular sample system designs

Other Detection Devices

- Densitometers – data shows density alone cannot be used to properly make ULSD batch cuts.
- Photometers
 - Optek
 - Optical Solutions
 - KAM

Interface between ULSD (<10ppm S) and Home Heating Oil (2000 ppm S)

Blue = Online-Density Green = OID Red= Flashpoint (not realtime) Yellow= online density (405m³ before Density2 – blue)



Summary

- Work needs to continue in ASTM to approve new methods and improve existing ones.
- On-line analyzer needs are different between a refiner and a pipeline operator.
- Sulfur analyzers cannot be treated as “black boxes” (maintenance, calibration, validation, control charting).
- Correct sample system design is an important component to an on-line sulfur analyzer installation.
- Potential in other on-line technologies.