On-Line Analysis for Transition Metals and Chlorine in Crude Oil and Aqueous Matrices

Berry Beumer
Elemental Analysis Solutions using X-Ray Fluorescence

MWD XRF

- Emitted Characteristic X-rays from Sample
- Detector
- Monochromatic Excitation
- Optics

Polychromatic Incident X-rays from tube
Monochromatic Excitation
Sulfur Kα Beam

HD Maxine
MWD XRF
<table>
<thead>
<tr>
<th>Standard</th>
<th>Gas, diesel 4-500ppm</th>
<th>Gas, diesel 5-500ppm</th>
<th>Gas, diesel 4-500ppm</th>
<th>Gas, diesel 5-500ppm</th>
<th>Petroleum 3ppm-4.6wt%</th>
<th>Gas, diesel 4-500ppm</th>
<th>Gas, diesel 5-500ppm</th>
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<tbody>
<tr>
<td>ASTM D7039</td>
<td>LOD</td>
<td>LOD</td>
<td>LOD</td>
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<td>ISO 20884</td>
<td>0.15ppm 300s</td>
<td>0.4ppm 300s</td>
<td>0.4ppm 300s</td>
<td>0.4ppm 300s</td>
<td>0.4ppm 300s</td>
<td>0.4ppm 300s</td>
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<tr>
<td>r (10ppm)</td>
<td>0.6ppm</td>
<td>0.8ppm</td>
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<tr>
<td>R (10ppm)</td>
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Silicon in Fuels

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<tr>
<th>ASTM D7757</th>
<th>Gasoline, Ethanol 3-100ppm</th>
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<td>LOD ethanol</td>
<td>0.5ppm 600s</td>
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<td>r (10ppm)</td>
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<td>R (10ppm)</td>
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Phosphorus in Fuels and Water

No ASTM method at this time

<table>
<thead>
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<th>LOD ethanol (600s)</th>
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<td>r (10ppm)</td>
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<td>R (10ppm)</td>
<td>2.0ppm</td>
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Chlorine in Fuels and Water Matrices

<table>
<thead>
<tr>
<th>ASTM D7536</th>
<th>0.5-15ppm Aromatics</th>
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<tr>
<td>LOD Crude</td>
<td>0.2ppm @ 300s</td>
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<tr>
<td>r (10ppm)</td>
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<tr>
<td>R (10ppm)</td>
<td>1.4ppm</td>
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</table>
MWD XRF  
Single Element On-line Measurements

LOD in hydrocarbon matrix
ppm in 300 s

- Sulfur 0.6 ppm
- Chlorine 0.3 ppm
- Phosp 1.2 ppm
- Silicon 1.5 ppm
- Vanadium 0.05 ppm

- Low viscosity process streams and finished product blending
  - Diesel
  - Gasoline

Challenge: On-Line Analysis in Crudes and High Viscosity Process Streams
Dynamic Window Module – Low Viscosity Streams
Transition Data

XOS High to Low Cut response

Film advance

Time (seconds):

0:00:00 1:12:00 2:24:00 3:36:00 4:48:00 6:00:00 7:12:00 8:24:00 9:36:00 10:48:00

PPM:

0 5 10 15 20 25 30 35 40
Sulfur in Diesel

28 Hour Data Run on a SINDIE On-Line Analyzer
Average = 8.65 ppmw; SD = 0.31 ppmw
Sulfur in Seawater

Total Sulfur Concentration In Sea Water (3-1/2% NaCl In De-Ionized Water)
40 ppmw Static Sample Measured for 48 hours In a Single Process Analyzer
Avg = 40.99 ppmw ; Std Dev = 0.96 ppmw

Graph showing sulfur concentration over time with data points consistent with 40 ppmw average and 0.96 ppmw standard deviation.
On-line Chlorine Detection in Crude and Water

- **Corrosion Prevention / Mitigation**
  - LOD: 0.6 ppm @ 300s – aqueous matrix
  - LOD: 0.4 ppm @300s – hydrocarbon matrix

- Analysis Time: 10-900s – user adjustable

- Range: 0.4 ppm/wt – 3,000 ppm/wt

- Continuous Measurement
Dynamic Window Module – High Viscosity Streams

- Redesigned DWM:
  - Sample Flow Characteristics Optimized for High Viscosity Streams
  - Quarter inch sample lines
  - Max. Viscosity 160 cSt
  - Sample T > cloud point, max 300 deg. F
  - Filtration: 100um
Analyzer set-up

Diagram showing the flow of raw crude through a desalter and fast loops, with desalted crude exiting and wash water entering.
Cl Repeatability in Desalted Crude Over 72 Hours
5 min integration time / 15 sec integration time
Avg = 5.1 ppmw; Std Dev = 0.21 ppmw
Online Chlorine Analysis in Desalted Crude
5 minute integration time over 10 hours

Avg = 2.63 ppm  Std Dev = 0.13 ppm

Date / Time

Chlorine - 5 min integration
 Chlorine in Raw Crude – 5 hr run time

Gulf Coast Crude

5 ppm Cl addition (Organic Chloride)
Chlorine in Raw Crude – 5 hr run time
Western Canadian Crude – 20API

Sulfur: 2%
Chlorine: by lab extraction/titration: 2 ppm
Chlorine in Crude – 3 hr run time

Crude Sample Chloride Trend, ppmw

- STDEV=1.41
- STDEV=0.64

Crude API = 25

Online Clora Analyzer
Benchtop Clora

Time:
Chlorine in Water – 6 hr run time

Aqueous Sample Chloride Trend, ppmw

STDEV=1.8

STDEV=3.0

Online Clora Analyzer Trend
Benchtop Clora
Multi-Element Analysis

- Emitted Characteristic X-rays from Sample
- Detector
- Monochromatic Excitation
- DCC Optics
- Polychromatic Incident X-rays from Tube

Graphs:
- From Sample
- After DCC Optic
- From Tube Source
<table>
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<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
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*10 minute measurement time in hydrocarbon matrix*
Multi Element On-line Detection

- HDXRF Platform – Multi Element Analysis
  LOD in ppm – 600 s
  - P  25
  - S  15
  - Cl 10
  - K  2
  - Ca 1.5
  - V  1.5
  - Mn 1.5
  - Fe 1.5
  - Co 1.0
  - Ni 0.5
  - Cu 0.3
  - Zn 0.3
  - Hg 0.15
  - As 0.15
  - Pb 0.15
  - Se 0.08
Online Maxine Trends - 6/13 to 6/14/2012

Blend of Canadian Crude

Continuous sample flow with continuously acquired data using a 300 second integration time and 60 second pause time between successive measurements.
Online Maxine Multi-Element Analysis of Various Crudes

Empty cell - Flow stopped (no pressure) during tank clean out and sample change; Added 90 micron filter.

3:

V_avg = 77.6; V_stddev = 0.90;
Fe_avg = 16.2; Fe_stddev = 0.65;
Ni_avg = 14.3; Ni_stddev = 0.10
Cr_avg = 0.2; Cr_stddev = 0.14
Conclusion

• On-line and bench-top single element analysis in crude and water is available for Cl, S, P, Si and V at sub ppm detection limits

• Multi element bench-top analysis of critical (transition) elements can be done by HD XRF

• Multi element on-line analysis in crude and process streams a reality today.
Thank you

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