Oil industry applications using XRF analysis techniques

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Petrochemical Operations at various stages: XRF is mostly used for the Refining and Petrochemical products.
Portfolio Addressing Petrochemical Operating Challenges

- Flow Metering
- Gas Analysis
- Leak Detection
- Lab/Portable Water Quality
- Online Water Quality
- Elemental Analysis
- Overall Process Analysis
- Air/Stack Gas Analysis
- Density, Level Metering
- Positive Materials Identification
Segmentation and *where XRF analysis is targeted*

- **Refinery products**
  - Contract labs
  - Central labs
    - Petrochemicals
      - Vehicle fuels
      - Ship fuels
      - Lube oils
    - Distribution
      - Polymers
        - Polyolefins
      - Fine chemicals
        - Lube blenders
          - Used lubes
          - Biofuels
  - Lube additives
  - Upstream
Why XRF in Petrochemical industry? Why WDXRF?

- WDXRF is the technique increasingly used and recommended in petroleum industry
- Meets all the currently practiced standards or regulations (ASTM; ISO etc.)
- Excellent repeatability
- High degree of flexibility in terms of measurement of analytical lines, background positions and internal references
- High dynamic range (sub-ppm to 100%)
Different instruments for different applications

EDXRF vs WDXRF
Principle of WD-XRF versus ED-XRF

**WD-XRF**
- Superior resolution (15 eV at Mn Ka)
- 2000 kcps per element
- Excellent repeatability and stability
- Low limits of detection (light elements)
- External water cooling required for high power systems
- P10 gas needed for proportional detector
- High end

**ED-XRF**
- Poor resolution (about 135 eV at Mn Ka)
- 125 kcps for all elements
- Continuous display of spectrum
- Robust: no moving parts
- Cooled detector
- Entry-level
Example: Trends for Sulfur regulation in fuels
XRF technique used for the analysis of a large variety of materials in petrochemical industry
Summary of needs in Petroleum industry where XRF is the most suitable technique
Five major areas in general (1 to 30 elements)

- **Low level sulfur analysis:**
  - 2-100ppm in **automotive fuel and gasoline**

- **Blending control for fresh lubricants**
  - 12 additive elements Na, Mg, Si, Ca, S, K, Zn, P, Cl, Br, Mo, Ba etc.

- **Residual heavy fuels:**
  - S 2-4%, Ni, V, Fe, Si, Al etc.

- **Wear metals and Used oils:**
  - Al, Ti, V, Cr, Mn, Fe, Ni, Cu, Ag, Sn, Sb, etc.

- **Catalysts:** new, used and reformed
Elemental analysis for oils and fuels: Regulations and norms

- ISO 14596 (*S using Zr internal standard*)
- ASTM D2622 (*S in WDXRF*)
- *ISO/FDIS 20884 (S in WDXRF)*
- ISO/FDIS 20847 (*S in EDX*)
- *ISO/FDIS 20846 (Fluorescence in UV)*
- Other norms…
  - ISO 15597 (*Cl & Br*)
  - ISO 14597 (*Ni & V*)
  - ASTM D5059 (*Pb*)
  - DIN 51577 (*Cl*)
  - DIN 51391 (*Ca & Zn*)
  - DIN 51431 (*Mg*)
  - DIN 51363 (*P*)
  - …
**Petrochemical industry: Thermo Scientific XRF solutions**

<table>
<thead>
<tr>
<th>ARL QUANT’X</th>
<th>ARL OPTIM’X</th>
<th>ARL PERFORM’X</th>
</tr>
</thead>
<tbody>
<tr>
<td>• EDXRF</td>
<td>• WDXRF</td>
<td>• WDXRF</td>
</tr>
<tr>
<td>• High performance detector</td>
<td>• SmartGonio</td>
<td>• SmartGonio</td>
</tr>
<tr>
<td></td>
<td>• No water cooling</td>
<td>• Universal Gonio</td>
</tr>
<tr>
<td></td>
<td>• Plug and analyse</td>
<td>• 1500W-2500W-4200W</td>
</tr>
</tbody>
</table>
High power Wavelength Dispersive XRF: Central laboratory, method development, advanced applications

- Additives in oils
- Lubrification oils
- Gas oil & Diesel
- Fuel oil
- Traces and Additives in plastics & polymers
- Sedimentary rocks: Petrol prospection
- Perforation tools: High & low alloy steel
- Oil well cements
- Catalysts (FCC) Zeolites
- Residues, waste oils, waters
EDXRF Applications
Analysis of lubricant additive elements under ambient air
Wear Elements in Oil

- 14 wear elements in oil
  - Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Mo, Ag, Cd, Sn & Ba
- Concentration range 0 – 50 ppm
- Measurement Conditions – Analysis in AIR

<table>
<thead>
<tr>
<th>Condition</th>
<th>Filter</th>
<th>Voltage (kV)</th>
<th>Current (mA)</th>
<th>Atmosphere</th>
<th>Live Time (s)</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid Za</td>
<td>Thin Ag</td>
<td>18</td>
<td>Auto</td>
<td>Air</td>
<td>100</td>
<td>Ti, V, Cr, Mn, Fe, Ni, Ba</td>
</tr>
<tr>
<td>Mid Zc</td>
<td>Thick Ag</td>
<td>30</td>
<td>Auto</td>
<td>Air</td>
<td>100</td>
<td>Cu, Zn, Pb</td>
</tr>
<tr>
<td>High Zb</td>
<td>Thick Cu</td>
<td>50</td>
<td>Auto</td>
<td>Air</td>
<td>100</td>
<td>Mo, Ag, Cd, Sn</td>
</tr>
</tbody>
</table>

- Sample presentation
  - 3 grams of oil into a sample cup of 32 mm outer diameter
  - Seal with a 4 micron polypropylene film.
## Calibration RMSE and detection limits

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>Conc. range [ppm]</th>
<th>RMSE [ppm]</th>
<th>LoD, 100s live time [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.59</td>
<td>2.3</td>
</tr>
<tr>
<td>V</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.03</td>
<td>0.7</td>
</tr>
<tr>
<td>Cr</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.48</td>
<td>0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.51</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.03</td>
<td>0.2</td>
</tr>
<tr>
<td>Ni</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.21</td>
<td>0.1</td>
</tr>
<tr>
<td>Cu</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.05</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.22</td>
<td>0.3</td>
</tr>
<tr>
<td>Ag</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.35</td>
<td>0.5</td>
</tr>
<tr>
<td>Cd</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.79</td>
<td>0.7</td>
</tr>
<tr>
<td>Sn</td>
<td>Kα</td>
<td>0 - 50</td>
<td>0.85</td>
<td>1.3</td>
</tr>
<tr>
<td>Ba</td>
<td>Lα</td>
<td>0 - 50</td>
<td>0.95</td>
<td>2.0</td>
</tr>
<tr>
<td>Pb</td>
<td>Lα</td>
<td>0 - 50</td>
<td>0.12</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Sulfur in Mineral Oil
S in Mineral Oil

- S in mineral oil
- Meets ASTM D4294
- Concentration range 0 – 1000 ppm
- Measurement Conditions – Analysis in HELIUM

<table>
<thead>
<tr>
<th>Condition</th>
<th>Filter</th>
<th>Voltage (kV)</th>
<th>Current (mA)</th>
<th>Atmosphere</th>
<th>Live Time (s)</th>
<th>Analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Zn II</td>
<td>Thin Graphite</td>
<td>9</td>
<td>Auto</td>
<td>Helium</td>
<td>100</td>
<td>S</td>
</tr>
</tbody>
</table>

- Sample presentation
  - 3 grams of oil into a sample cup of 32 mm outer diameter
  - Seal with a 4 micron polypropylene film.
- Calibration graph
- Calculated versus Given Concentrations (0 – 1000 mg/kg)
• **Repeatability results:**

<table>
<thead>
<tr>
<th></th>
<th>S Conc. (ppm)</th>
<th></th>
<th>S Conc. (ppm)</th>
<th></th>
<th>S Conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Given</td>
<td>10.40</td>
<td>Given</td>
<td>120.00</td>
<td>Given</td>
<td>499.10</td>
</tr>
<tr>
<td>Rep 1</td>
<td>10.73</td>
<td>Rep 1</td>
<td>120.28</td>
<td>Rep 1</td>
<td>498.45</td>
</tr>
<tr>
<td>Rep 2</td>
<td>10.40</td>
<td>Rep 2</td>
<td>120.75</td>
<td>Rep 2</td>
<td>498.79</td>
</tr>
<tr>
<td>Rep 3</td>
<td>11.50</td>
<td>Rep 3</td>
<td>119.63</td>
<td>Rep 3</td>
<td>499.79</td>
</tr>
<tr>
<td>Rep 4</td>
<td>10.89</td>
<td>Rep 4</td>
<td>120.72</td>
<td>Rep 4</td>
<td>500.44</td>
</tr>
<tr>
<td>Rep 5</td>
<td>10.49</td>
<td>Rep 5</td>
<td>120.88</td>
<td>Rep 5</td>
<td>500.90</td>
</tr>
<tr>
<td>Average</td>
<td>10.80</td>
<td>Average</td>
<td>120.45</td>
<td>Average</td>
<td>499.67</td>
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<tr>
<td>StDev</td>
<td>0.44</td>
<td>StDev</td>
<td>0.51</td>
<td>StDev</td>
<td>1.05</td>
</tr>
</tbody>
</table>

• **Limit of detection in 100s (live time): 1.05 ppm**

• With a longer counting time of 300s, the limit detection decreases to 0.6 ppm
Polymers
Light Elements in Polymers

- NIST SRM 2855 II Polyethylene
- 10kV & thin C filter, 100s Live Time, 50% dead time
Heavy Elements in Polymers

- EC-681 Polyethylene
  50kV & Thick Cu Filter, 100s Live Time, 3% deadtime

![Graph showing elements and their ppm values]

- Br: 306 ppm
- Pb: 22 ppm
Detection Limits Polymers

Detection Limits in polyethylene:

<table>
<thead>
<tr>
<th>Element</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Cd</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quant'X Ref.</td>
<td>9.0</td>
<td>2.6</td>
<td>1.2</td>
<td>0.7</td>
<td>0.6</td>
<td>0.4</td>
<td>0.5</td>
<td>8.8</td>
</tr>
<tr>
<td>New Quant'X</td>
<td>2.2</td>
<td>0.8</td>
<td>0.7</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
<td>10</td>
</tr>
</tbody>
</table>
WDXRF Applications
LoadSafe design:
Analysis of Liquids or Loose Powders made safe

1. Liquid sample recognition sensor
2. Over exposure safety
3. Security container at the pumping/loading stage
WDXRF: UOP 979 – 02 method
Chlorine in catalysts – UOP 979 method

- Scan on chlorine peak and choice of background positions
- 30kV – 50mA
Chlorine in catalysts – UOP 979 method

- Calibration curve for Cl
Chlorine in catalysts – UOP 979 method

- 30kV – 50mA
- Analysis time: Peak and backgrounds at 60s each
- Precision test: Five runs of the same sample
- Analysis under helium as loose powder

<table>
<thead>
<tr>
<th>Run</th>
<th>Chlorine content by WDXRF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0044</td>
</tr>
<tr>
<td>2</td>
<td>1.0093</td>
</tr>
<tr>
<td>3</td>
<td>1.0066</td>
</tr>
<tr>
<td>4</td>
<td>1.0087</td>
</tr>
<tr>
<td>5</td>
<td>1.0086</td>
</tr>
<tr>
<td>Average</td>
<td>1.0075</td>
</tr>
<tr>
<td>Std deviation</td>
<td>0.002</td>
</tr>
</tbody>
</table>
WDXRF: IFP 9303 method
• Scan on sulfur peak and choice of background position
• Calibration curve for S up to 0.4%
• Synthetic samples - Standard error of estimate SEE = 0.004%
Cl and S in catalysts - IFP 9303 method

- Scan on chlorine peak and choice of background positions
• Calibration curve for Cl up to 2%
• Synthetic samples – Standard error of estimate SEE = 0.067%