

Gulf Coast Conference
2014

**X-ray Analysis in Petrochemical and
Polymer Industries: Challenges and
Solutions**

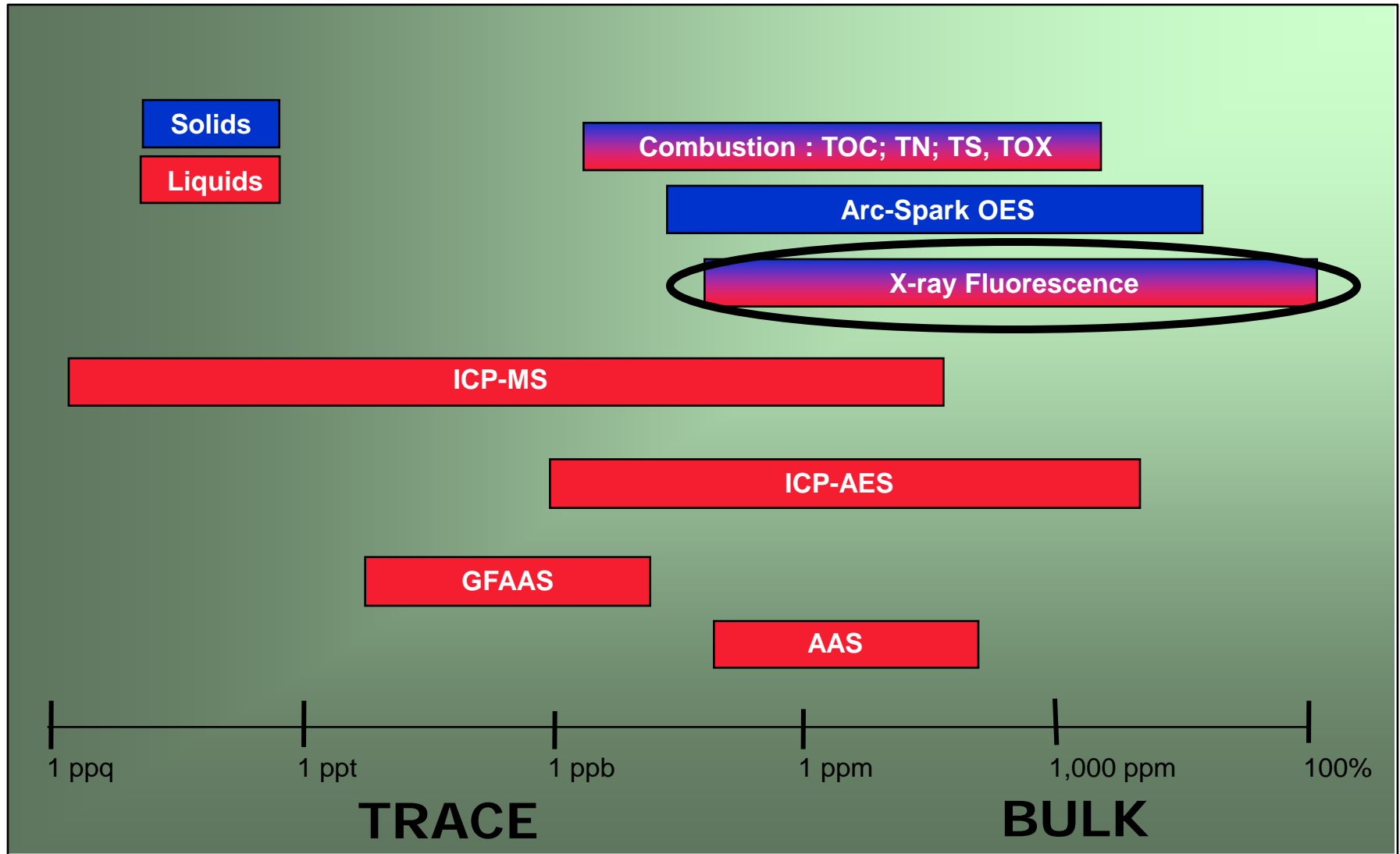
Al Martin

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XRF Petro and Poly Challenges

- Physical forms – liquids, granules, plaques, ??
- Petroleum and polymer industry products continually evolving
 - Chemical makeup of polymers, lubricants, and fuels altered constantly to meet new functional demands
- Today's XRF system must be able to satisfy not only today's requirements but also tomorrows needs:
 - More complex formulations
 - Stricter emissions regulations and norms
 - Catalyst processes
 - Growth of biofuels
 - Never-ending drive for lower costs and improved quality

XRF in the Laboratory: Typical Analytical Ranges



Sample Preparation

- Compared with other analytical methods, XRF is the simplest
- No hot digest or potential dangers through acid use
- Sample cups simple to assemble, liquid handling minimal
- Assortment of sample cups and support films make any analysis safe and easy
- For liquids – assemble sample cup and pour liquid to specific volume or weight
- For solids – same as liquids, or pelletize to form pressed pellet
- Disposal of sample in bulk liquid container or for powder and pellets – simply discard
- Components within instrument offers further protection to optical path

XRF Benefits Summary

- Numerous sample 'types' possible for analysis
- Both solid, solution and in between possible
- Majority of sample preparation fast and relatively simple compared to other techniques
- Not always requiring standards for analysis (discussed later)
- Rapid analysis turn around for single or multi-element procedures

Petroleum Industry Applications



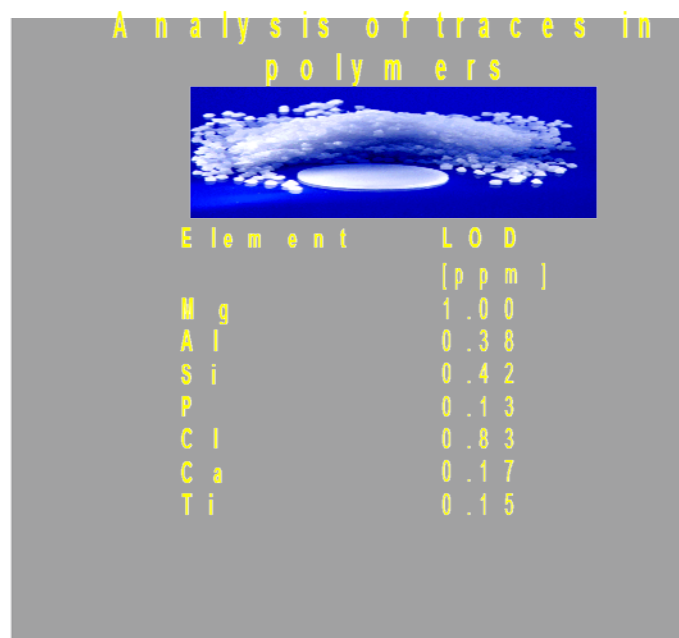
- Gasoline
- Naphtha
- Diesel fuels
- Kerosene
- Jet fuel
- Gas oils
- Residual fuels
- Crude oil
- Biofuels
- Lubricant additives
- Lubricant blending
- FCC catalysts
- Coke
- Additives



Polymer Industry Applications

- Performance of today's polymers is synonymous with additives:

- Accelerants
- Anti-degradants
- Anti-foams
- Anti-oxidants
- Anti-ozonates
- Blowing agents
- Coupling agents
- Cross linking agents
- Fillers
- Flame retardants
- Plasticizers
- Processing aids
- Retarders
- Stearates
- UV stabilizers
- Vegetable oils
- Others



- Low Power EDXRF
- Low Power WDXRF
- High Power WDXRF

EDXRF: ASTM F2617–08

- Chromium, Bromine, Cadmium, Mercury, and Lead by *EDXRF* in polymeric materials
- Application range: from 20 mg/kg (ppm) to ~1% for each element
- Repeatability and reproducibility limit example for Bromine:

TABLE 4 Bromine Content Results from the Interlaboratory Study

NOTE—All values are expressed as mass fractions in mg/kg (ppm).

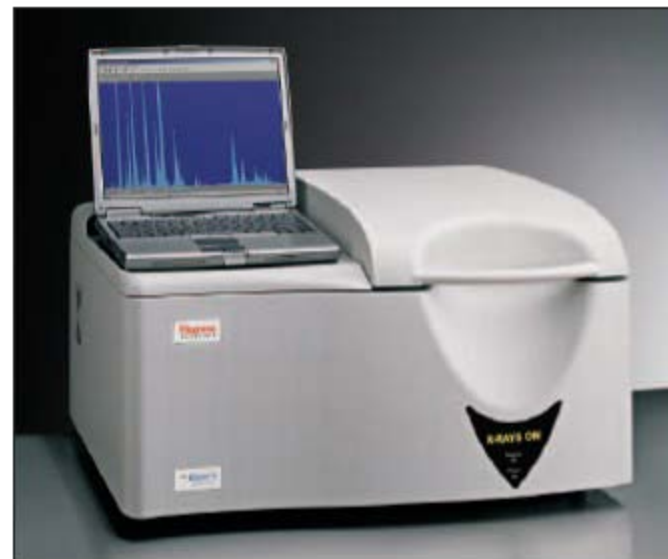
| Material | Certified Value ^{A,B} and Uncertainty | Average | Repeatability Standard Deviation | Reproducibility Standard Deviation | Repeatability Limit | Reproducibility Limit |
|----------|---|-----------|--|--|------------------------|--------------------------|
| | | \bar{X} | s_r | s_R | r | R |
| A | < 0.1 | 2.9 | 0.33 | 4.2 | 0.92 | 11.7 |
| B | 1007 ± 12 | 982.8 | 3.8 | 9.4 | 10.7 | 26.4 |
| C | 51 ± 3 | 52.5 | 1.4 | 3.8 | 4.1 | 10.7 |
| D | 383 ± 14 | 386.4 | 2.3 | 2.9 | 6.4 | 8.2 |
| E | 101 ± 4 | 101.5 | 0.80 | 4.4 | 2.2 | 12.2 |
| F | 808 ± 19 | 781.1 | 2.9 | 61.2 | 8.1 | 171.3 |
| G | 98 ± 5 | 101.5 | 2.8 | 2.8 | 7.8 | 7.8 |

^A The certified values were taken from the certificate of analysis of each material and are typically derived from multiple methods of determination in different laboratories.

^B The uncertainty listed for each certified value was taken from the certificate of analysis of the material. The certificate provides a definition of the uncertainty estimate, typically expressed at a 95 % level of confidence.

EDXRF: F2617-8, Low Power Example (50W)

- Total 500s counting time
 - LOD achieved
 - Cr 2.0 ppm
 - Br 1.0 ppm
 - Cd 1.5 ppm
 - Hg 1.3 ppm
 - Pb 1.3 ppm
- | | Restriction |
|--|-------------|
| | <1000 ppm |
| | <1000 ppm |
| | <100 ppm |
| | <1000 ppm |
| | <1000 ppm |



Thermo Scientific™ ARL QUANT'X™
with Peltier-cooled Si(Li) detector

EDXRF: PVC containing Cd and Pb

- Total 200s counting time
- Difference between 85 ppm and 35 ppm is easy to ascertain

| | Cd | Pb |
|-----------|--------------|----------------|
| LoD | 0.9 ppm | 1 ppm |
| Precision | 1.8 @ 35 ppm | 5.2 @ 89 ppm |
| Precision | 3.7 @ 85 ppm | 14.1 @ 837 ppm |

Table 2: Limits of detection (LoD) and precisions

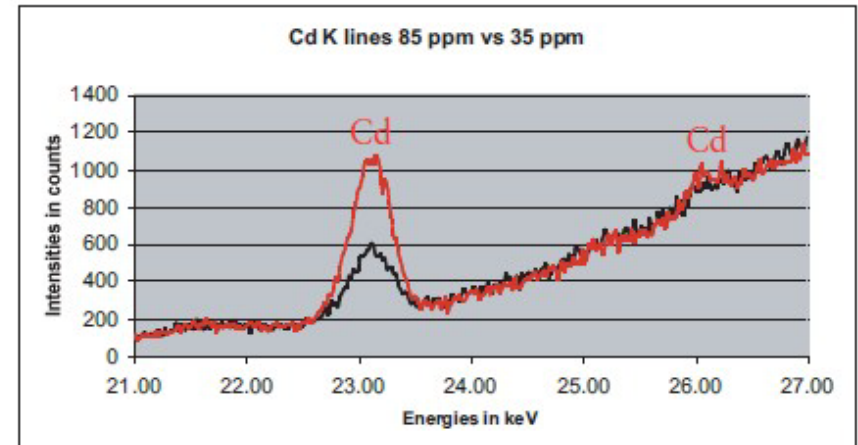


Figure 1: Comparison of the spectrum of PVC containing 35 ppm of cadmium (black) with the spectrum of PVC containing 85 ppm of cadmium (Red)

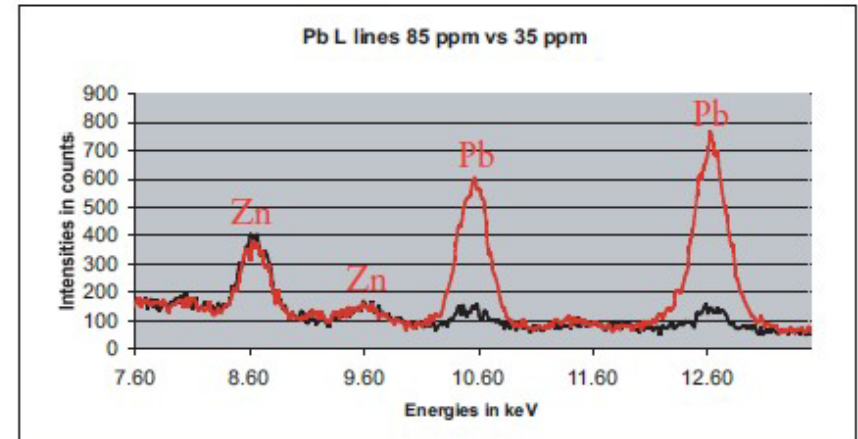


Figure 2: Comparison of the spectrum of PVC containing 35 ppm of lead (black) with the spectrum of PVC containing 85 ppm of lead (Red)

EDXRF: Additional Examples

Analysis of Liquid Hazardous Waste Fuels (LHWF) per ASTM D5839

Cr, Ag, Cd, Sb, Pb

| | Cr (ppm) | Ni (ppm) | Ag (ppm) | Cd (ppm) | Sb (ppm) | Pb (ppm) |
|-------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 1 | 253 | 251 | 260 | 253 | 261 | 259 |
| 2 | 255 | 250 | 261 | 258 | 265 | 267 |
| 3 | 254 | 252 | 258 | 261 | 267 | 263 |
| 4 | 250 | 251 | 261 | 260 | 266 | 268 |
| 5 | 254 | 251 | 261 | 266 | 267 | 267 |
| 6 | 249 | 251 | 261 | 259 | 269 | 269 |
| 7 | 254 | 251 | 264 | 263 | 266 | 269 |
| 8 | 254 | 253 | 260 | 263 | 267 | 269 |
| 9 | 257 | 252 | 260 | 265 | 263 | 270 |
| 10 | 258 | 250 | 259 | 260 | 268 | 268 |
| Average | 254 | 251 | 261 | 261 | 266 | 267 |
| 1-Sigma | 2.7 | 0.8 | 1.6 | 4.0 | 2.3 | 3.4 |
| MDL (240 s) | 1.5 | 0.4 | 1.0 | 0.8 | 2.2 | 0.9 |
| MDL (60 s) | 3.0 | 0.7 | 2.0 | 1.7 | 4.4 | 1.8 |

Table 3: Repeatability results and MDLs for a total analysis time per condition of four minutes. MDLs expected for an analysis time of only one minute per condition are also shown.

EDXRF: Additional Examples

Analysis of Liquid Hazardous Waste Fuels (LHWF) per ASTM D5839
Cr, Ag, Cd, Sb, Pb

Analysis of lubricant additive elements under ambient air using EDXRF

| Time (s) | Sample 1 | | | Sample 4 | | | Sample 5 | | | |
|----------------|------------|-------------|-------------|------------|-------------|------------|------------|-------------|------------|-----|
| | P 60 | Ca 30 | Zn 30 | P 300 | Ca 30 | Zn 30 | P 60 | Ca 30 | Zn 30 | |
| Given | 710 | 2150 | n/a | 800 | 2440 | n/a | 840 | 2530 | n/a | |
| Average | 716 | 2138 | 6000 | 808 | 2404 | 652 | 827 | 2525 | 694 | |
| 1-Sigma | 36 | 15 | 5 | 12 | 16 | 6 | 52 | 11 | 6 | |
| % RSD | 5.0 | 0.7 | 0.8 | 1.5 | 0.7 | 0.9 | 6.2 | 0.4 | 0.9 | |
| Replicates | 1 | 696 | 2170 | 600 | 790 | 2392 | 654 | 822 | 2532 | 686 |
| | 2 | 747 | 2137 | 605 | 790 | 2403 | 655 | 884 | 2531 | 692 |
| | 3 | 722 | 2127 | 608 | 799 | 2393 | 658 | 814 | 2516 | 701 |
| | 4 | 757 | 2141 | 593 | 814 | 2413 | 651 | 856 | 2523 | 687 |
| | 5 | 732 | 2135 | 596 | 819 | 2406 | 644 | 820 | 2519 | 691 |
| | 6 | 659 | 2112 | 605 | 819 | 2437 | 652 | 797 | 2506 | 697 |
| | 7 | 750 | 2142 | 597 | 807 | 2402 | 651 | 909 | 2542 | 686 |
| | 8 | 658 | 2144 | 601 | 803 | 2417 | 640 | 727 | 2538 | 697 |
| | 9 | 730 | 2126 | 594 | 824 | 2379 | 657 | 788 | 2519 | 698 |
| | 10 | 711 | 2145 | 603 | 810 | 2396 | 652 | 849 | 2525 | 703 |

Table 3. Analytical precision at various measuring times.

EDXRF: Additional Examples

Analysis of Liquid Hazardous Waste Fuels (LHWF) per ASTM D5839
Cr, Ag, Cd, Sb, Pb

Analysis of lubricant additive elements under ambient air using EDXRF

Analysis of sulfur and chlorine in waste oils under air conditions

| | S ppm | Cl ppm | | S ppm | Cl ppm | | S ppm | Cl ppm |
|------------|----------|-----------|------------|----------|-----------|------------|----------|-----------|
| sample1 01 | 156 | 154 | sample2 01 | 231 | 219 | sample3 01 | 425 | 421 |
| sample1 02 | 154 | 158 | sample2 02 | 221 | 220 | sample3 02 | 429 | 432 |
| sample1 03 | 167 | 135 | sample2 03 | 214 | 219 | sample3 03 | 433 | 404 |
| sample1 04 | 148 | 154 | sample2 04 | 221 | 233 | sample3 04 | 410 | 420 |
| sample1 05 | 142 | 170 | sample2 05 | 222 | 210 | sample3 05 | 423 | 431 |
| sample1 06 | 152 | 144 | sample2 06 | 228 | 233 | sample3 06 | 434 | 432 |
| sample1 07 | 151 | 138 | sample2 07 | 209 | 222 | sample3 07 | 441 | 425 |
| sample1 08 | 152 | 154 | sample2 08 | 216 | 215 | sample3 08 | 439 | 401 |
| sample1 09 | 132 | 145 | sample2 09 | 232 | 224 | sample3 09 | 433 | 409 |
| sample1 10 | 156 | 124 | sample2 10 | 253 | 222 | sample3 10 | 434 | 404 |
| average | 151 | 148 | average | 225 | 222 | average | 430 | 418 |
| sigma | 9 | 13 | sigma | 12 | 7 | sigma | 9 | 12 |

Table 2: Precision for S and Cl under air conditions at 150, 225 and 430 ppm

Analytical Solutions

- Low Power EDXRF
- Low Power WDXRF
- High Power WDXRF

Low Power WDXRF: Fuel and Lubricant Analyzer

- ✓ EN ISO 20884 (S)
- ✓ ASTM D2622 (ULS, ULSD)
- ✓ ISO 14596 (S)
- ✓ ASTM D4927 (Lubs and Additives: Ba, Ca, P, S, Zn)
- ✓ ASTM D6443 (Lubs and Additives:Ca, Cl, Cu, Mg, P, S, Zn)
- ✓ ASTM D7085 (Catalysts)
- ✓ ISO 15597 (Cl and Br)
- ✓ ISO 14597 (Ni and V)
- ✓ ASTM D5059 (Pb in Gasoline)
- ✓ ASTM D6334 (S in Gasoline)
- ✓ ASTM D6376 (Traces – Pet Coke)
- ✓ ASTM D6247 (Polyolefins)
- ✓ Heavy fuel analysis
- ✓ ISO 20884, 20847 and 14596
- ✓ Used oil analyses and others



Low Power WDXRF :Limits of Detection in Oils

| ELEMENT | SMARTGONIO CONFIGURATION | SEE [ppm] | SMARTGONIO™ | FIXED CHANNEL |
|---------|--------------------------|-------------|-------------|---------------|
| | | | LOD [ppm] | LOD [ppm] |
| Mg | AX06/FPC | 1.7 | 8 | 8 |
| Al | PET/FPC | 1.8 | 4.2 | 3.1 |
| Si | PET/FPC | 2.1 | 4 | 3.2 |
| P | PET/FPC | 0.7 | 2 | 1.5 |
| S | PET/FPC | 0.7 | 1.7 | 1.2 |
| K | LIF200/FPC | 0.9 | 1.4 | n.m. |
| Ca | LIF200/FPC | n.a. | 1.5 | 1.7 |
| V | LIF200/FPC | 1.1 | 1 | n.m. |
| Cr | LIF200/FPC | n.a. | 1 | n.m. |
| Mn | LIF200/FPC | n.a. | 1 | n.m. |
| Fe | LIF200/FPC | n.a. | 1.1 | 0.8 |
| Ni | LIF200/SC | 0.7 | 0.6 | n.m. |
| Cu | LIF200/SC | n.a. | 0.8 | n.m. |
| Zn | LIF200/SC | n.a. | 0.6 | n.m. |
| Pb | LIF200/SC | 1.2 | 1.7 | 1 |

Fixed Channel vs Goniometer

Analysis time: 120S

FPC: Flow proportional counter
 SC: Scintillation counter
 SEE: Standard error estimate = a measure of accuracy
 LOD: Limit of detection = $3\sqrt{(BEC/Qt)}$
 n.a.: not available as only two samples were available for this element
 n.m.: not measured as this fixed channel was not fitted on the test instrument.

Table 1: Analytical results

Exceeds the requirements of ISO 8217 and other international standards for sensitivity, range and reliability of heavy fuels analysis

Low Power WDXRF: Limits of Detection Examples

| Element | SmartGonio configuration | 50W | 200W |
|-----------|--------------------------|--------------------------|--------------------------|
| | | Typical LoD in 60s [ppm] | Typical LoD in 60s [ppm] |
| Al | AX06/FPC | 5.9 | 3.7 |
| Si | InSb/FPC | 5.0 | 3.0 |
| P | InSb/FPC | 2.8 | 1.8 |
| S | InSb/FPC | 2.6 | 1.7 |
| K | LiF200/FPC | 2.0 | 1.2 |
| Ca | LiF200/FPC | 2.1 | 1.3 |
| V | LiF200/FPC | 1.4 | 0.9 |
| Cr | LiF200/FPC | 1.4 | 0.9 |
| Mn | LiF200/FPC | 1.4 | 0.9 |
| Fe | LiF200/FPC | 1.5 | 1.0 |
| Ni | LiF200/SC | 0.8 | 0.5 |
| Cu | LiF200/SC | 1.1 | 0.7 |
| Zn | LiF200/SC | 0.8 | 0.5 |
| Pb | LiF200/SC | 2.4 | 1.5 |

Oil matrix
60 s counting time
Comparison at 50W and 200W

FPC : Flow proportional counter
SC : Scintillation counter

Low Power WDXRF: Pre-Programmed Analysis

| Element | Goniometer configuration | 200W | in a counting time of (s) | 200W |
|---------|--------------------------|----------------------|---------------------------|--------------------------|
| | | Typical LoD in [ppm] | | Typical LoD in 60s [ppm] |
| Na | AX06/FPC | 104 | 40 | 84.9 |
| Mg | AX06/FPC | 12.7 | 40 | 10.4 |
| Al | AX06/FPC | 8.4 | 36 | 6.5 |
| Si | InSb/FPC | 2.7 | 36 | 2.1 |
| P | InSb/FPC | 3.2 | 36 | 2.5 |
| S | InSb/FPC | 3.9 | 36 | 3.0 |
| Cl | InSb/FPC | 6.9 | 36 | 5.3 |
| K | LiF200/FPC | 1.6 | 16 | 0.8 |
| Ca | LiF200/FPC | 2.5 | 16 | 1.3 |
| Ti | LiF200/FPC | 2.6 | 16 | 1.3 |
| V | LiF200/FPC | 1.6 | 16 | 0.8 |
| Cr | LiF200/FPC | 1.5 | 16 | 0.8 |
| Mn | LiF200/FPC | 1.4 | 16 | 0.7 |
| Fe | LiF200/FPC | 1.5 | 16 | 0.8 |
| Ni | LiF200/SC | 1.6 | 16 | 0.8 |
| Cu | LiF200/SC | 1.3 | 16 | 0.7 |
| Zn | LiF200/SC | 1.1 | 16 | 0.6 |
| Mo | LiF200/SC | 1.4 | 16 | 0.7 |
| Sn | LiF200/SC | 9.3 | 24 | 5.9 |
| Sb | LiF200/SC | 4.7 | 24 | 3.0 |
| Ba | LiF200/SC | 7.1 | 16 | 3.7 |
| Pb | LiF200/SC | 4.9 | 16 | 2.5 |

e.g. PetroilQuant
22 elements

Practical limits of detection obtained by repeated analysis on blank oil

- LoD = 3 x Standard Deviation
- Counting time shown

FPC : Flow proportional counter

SC : Scintillation counter

Low Power WDXRF: Polymer Applications

Polymers



Low Power WDXRF: Heavy Elements in Polymers

Limits of detection for heavy elements in polymers at 200W

Factory Calibrations:

Calibration for Heavy metals
in Polymers (RoHS + As)

6 Elements: Br, Cr, Cd, Hg, Pb,
and As

Element Range [ppm]

- **Br** LoD – 1050 ppm
- **Cd** LoD – 300 ppm
- **Cr** LoD – 1000 ppm
- **Hg** LoD – 1100 ppm
- **Pb** LoD – 1200 ppm
- **As** LoD – 31 ppm

| Element | Line | LOD in 100 s [ppm] | SEE [ppm] |
|---------|------------|-----------------------|--------------|
| Ba | L α | 2.6 | 17 |
| Br | K α | 1.0 | 6.1 |
| Cd | K α | 3.0 | 18 |
| Cr | K α | 0.5 | 3.6 |
| Cu | K α | 0.5 | 5.6 |
| Hg | L α | 1.2 | 20 |
| Ni | K α | 0.3 | 16 |
| Pb | L β | 0.9 | 24 |
| Zn | K α | 0.3 | 6.2 |

SEE: standard error of estimation with ranges from 0 to 500ppm

ARL OPTIM'X Series: Unique Features

Options when considering low power XRF

- Power - 50 or 200W

Based on requirements

Limits of detection
Precision
Speed of analysis
Budget

Features

ARL OPTIM'X Series: Unique Features

Options when considering low power XRF

- Power - 50 or 200W
- Sensitivity 200W analytical performance from 50W power
500W analytical performance from 200W power



Features

ARL OPTIM'X Series: Unique Features

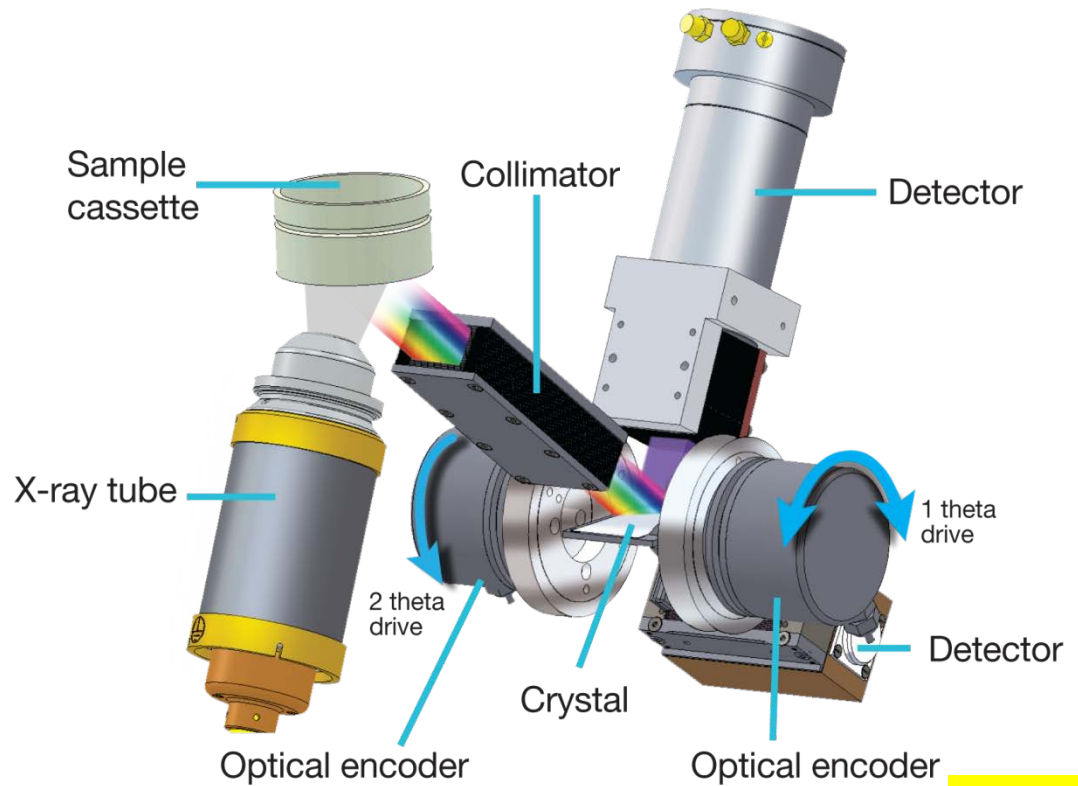
Options when considering low power XRF

- Power - 50 or 200W
- Sensitivity
- Intelligent Design

SmartGonio™

- Compact – Close coupled
- Short optics path
- Optical encoders
- Fixed collimator
- Up to three crystals
- One or two detectors

Access to all elements from **F** to **U**
(3 crystals - 2 detectors fitted)



Features

ARL OPTIM'X Series: Unique Features

Options when considering low power XRF

- Power - 50 or 200W
- Sensitivity
- Intelligent Design
- Speed

Fixed Channel Multichromators

- Greater sensitivities
- Excellent stability
 - Individual temperature control on each crystal
- Individual power supply board
- Sealed detectors from Na to Fe
- Scintillation counter from Fe upwards
- Software control of high voltage and threshold/window settings

Features

ARL OPTIM'X Series: Unique Features

Options when considering low power XRF

- Power - 50 or 200W
 - Sensitivity
 - Intelligent Design
 - Speed
 - Multi-Sample Handling
- 
- The image shows a ThermoFisher ARL OPTIM'X XRF instrument. It is a white and blue machine with a yellow radiation warning symbol on top. The front panel features a digital display, a green power button, and a red emergency stop button. A sample tray with 13 positions is visible, and a detector is mounted above it. The instrument is labeled 'ThermoFisher' and 'OPTIM'X'.
- **13 position automatic sample changer for cassettes**
 - no spring lid
 - centering rings used
 - vacuum/helium option
 - using adequate centering ring

Features

ARL OPTIM'X: Summary

- **Optimized Configurations**
- Sequential analysis with SmartGonio™
- Sequential-simultaneous analysis: SmartGonio™ + 1 or 2 fixed channels
- Completely simultaneous for 8 elements using 4 multichromators™
- Choice of power – 50w or 200w
- UCCO for greater sensitivity
- SmartGonio for fast F-U analysis
- Option on sample changer
- Vacuum or Helium atmosphere choice



Features

Situation

- Oil, gas, and chemical laboratory for SGS using a 1kW WDXRF for ULS plus wear metals in engine oils and marine fuels
- One of OGC's main daily concerns is analyzing sulfur concentrations in fuels in compliance with various international standard methods such as ISO 20884, ISO 14596 and ASTM D 2622 (note European standard for S is 10ppm)
- Some samples noted as 'aggressive'
- Require an analytical instrument that can measure, aside from other tests, sulfur at ultra-low concentrations in a wide range of fuels with high accuracy within a few minutes
- Existing system presented instability in light elements, sample heating, tube head corrosion, increasing down time, application support lacking

Solution

- ARL Optim'X preliminary tests were encouraging enough for purchase
- System installed and implemented (methods and calibrations) within one week of delivery
- ARL Optim'X proved capable of taking over all the applications
- Small increase in analysis time was acceptable and stability is described as excellent !
- Light element stability especially much improved, corrosion eliminated, down-time eliminated

Client Testimonial

- ARL OPTIM'X met all client requirements in combination with extreme ease of use

“One of the reasons we chose a system from Thermo Fisher Scientific is that—besides the fact that this company is well known in the petroleum industry—we’ve had very good experiences in maintenance and support from them.” - OGC analyst Erwin V



‘The long term stability and reliability of the ARL OPTIM'X have also made a very strong impression on the OGC laboratory staff’

Analytical Solutions

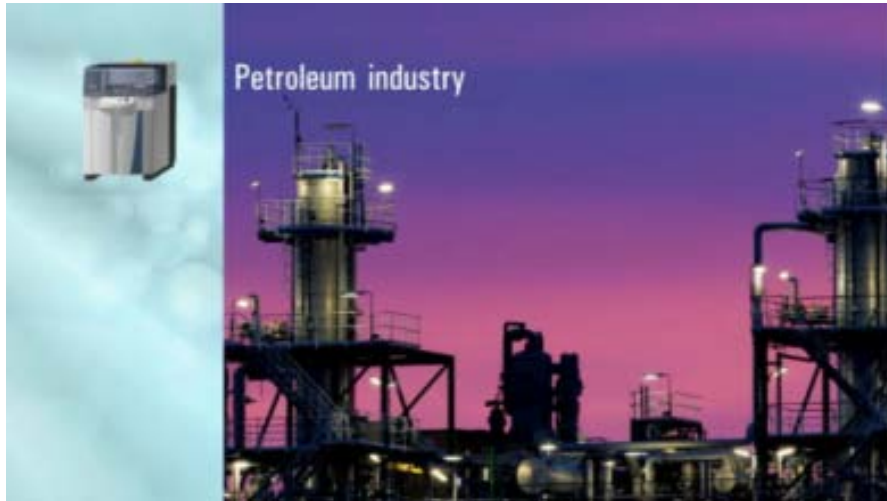
- Low Power EDXRF
- Low Power WDXRF
- High Power WDXRF

Thermo Scientific Solutions in Refineries



- Environmental regulation compliance
- Online sulfur detection
- Refining gas detection
- Corrosion prevention of refinery piping systems
- Complex in-process liquid and gas analysis
- Continuous process monitoring (densities, levels, flow rates, heating values)
- Process optimization
- Quality assurance and control
- Full range of laboratory instruments

Petroleum Product Applications - WDXRF



Requirements

- Safe analysis
 - Liquid sample recognition sensor
 - Security device in case of spilling
 - Tube shield protection (optional)
- Speed of analysis with
 - Dual sample loading
 - Urgent sample position
 - Fastest goniometer
- High precision
 - Accurate goniometer
 - Wider counting linearity
 - Optimized collimator-crystal combinations
 - Optimized filters and X-ray tube conditions

Petroleum Product Applications - WDXRF

- Gasoline
- Naphtha
- Diesel fuels
- Kerosene
- Jet fuel
- Gas oils
- Residual fuels
- Crude oil
- Biofuels
- Lubricant additives
- Lubricant blending
- FCC catalysts
- Coke
- Additives



Thermo Scientific™ ARL™ Perform'X™ in Petrochemicals

Ideal for Central Laboratory

- Versatility for many applications
- Thin window x-ray tube (30 micron) for high sensitivity in light elements
- Flexible software options
- Analysis of any material
- Standard, Standardless analysis
- High throughput to research
- Vacuum/Helium atmosphere
- Optim'X as backup system
- IQ/OQ & Remote Diagnostics for easy installation and serviceability



Oil Analysis

- Typical LoD in Oil Analysis

| Element/ Line | Crystal/ Detector | KV-mA | SEE ppm | PBF | LoD (ppm) |
|------------------|----------------------|--------|------------|-----|--------------|
| Na K α | AX06/FPC | 30/120 | 4.1 | | 8.45 |
| Mg K α | AX06/FPC | 30/120 | 1.9 | | 2.21 |
| Al K α | PET/FPC | 30/120 | 0.9 | | 0.99 |
| Si K α | PET/FPC | 30/120 | 0.8 | | 0.58 |
| Si K α | InSb/FPC | 30/120 | 0.8 | | 0.54 |
| P K α | Ge111/FPC | 30/120 | 0.53 | | 0.33 |
| Sn L α | LiF200/FPC | 30/120 | 0.45 | | 0.52 |
| Ca K α | LiF200/FPC | 30/120 | 0.6 | | 0.14 |
| Ba L α | LiF200/FPC | 50/72 | 0.4 | | 0.34 |
| Ti K α | LiF200/FPC | 50/72 | 0.45 | | 0.11 |
| V K α | LiF200/FPC | 50/72 | 0.23 | | 0.1 |
| Cr K α | LiF200/FPC | 50/72 | 0.41 | | 0.1 |

| Element/ Line | Crystal/ Detector | KV-mA | SEE ppm | PBF | LoD (ppm) |
|------------------|----------------------|-------|------------|-----|--------------|
| Mn K α | LiF200/FPC | 50/72 | 0.41 | | 0.11 |
| Fe K α | LiF200/FPC | 50/72 | 0.26 | | 0.12 |
| Ni K α | LiF200/SC | 50/72 | 0.45 | Yes | 0.07 |
| Cu K α | LiF200/SC | 50/72 | 0.34 | Yes | 0.07 |
| Zn K α | LiF200/SC | 50/72 | 0.44 | Yes | 0.07 |
| Hg L α | LiF200/SC | 50/72 | N.A. | Yes | 0.15 |
| Tl L α | LiF200/SC | 50/72 | N.A. | Yes | 0.11 |
| As K β | LiF200/SC | 50/72 | 1.7 | Yes | 0.58 |
| Pb L β | LiF200/SC | 50/72 | 0.56 | Yes | 0.3 |
| Mo K α | LiF200/SC | 60/60 | 0.48 | | 0.22 |
| Ag K α | LiF200/SC | 60/60 | 1.1 | Yes | 0.88 |
| Cd K α | LiF200/SC | 60/60 | 0.54 | Yes | 0.94 |

Standardless Analysis: When none or few standards are available

Thermo Scientific™ UniQuant® Software
for WDXRF

Standardless Analysis: When none or few standards are available

- UniQuant/OptiQuant is peak based so offers greater accuracy and precision compared to scan based standardless routines
- Scan based routines typically hit peak locations for a fraction of a second while scanning – UniQuant sits on locations from 4 – 12 seconds
- All peak and background locations are pre-programmed and maintained by the software
- Total counting time: 14-20 Minutes for 70+ elements
- Drift corrections achieved through supplied control disks
- Able to modify count times or optimize new subroutines to specific matrices
- Standard features of UniQuant/OptiQuant:
 - *Counting time can be adjusted depending on requirements*
 - *Spinning of sample during analysis*
 - *Layer analysis, etc...*

Pre-Calibrated - PetroilQuant

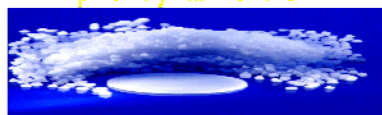
- Factory calibrated package for oils analysis
 - Over 30 elements
 - Calibration maintained using solid drift standards
 - Excellent for fuels, lubricants, and oils



Analysis of Traces in Polymers

LOD (ppm) in 100s counting time

Analysis of traces in polymers



| Element | LOD [ppm] |
|---------|-----------|
| Mg | 1.00 |
| Al | 0.38 |
| Si | 0.42 |
| P | 0.13 |
| Cl | 0.83 |
| Ca | 0.17 |
| Ti | 0.15 |

| Element | High Power (4.2 kW) | Low Power (2.5 kW) |
|---------|------------------------|-----------------------|
| Mg | 0.86 | 1.5 |
| Al | 0.23 | 0.4 |
| P | 0.16 | 0.27 |
| Cl | 0.3 | 0.8 |
| Ca | 0.14 | 0.53 |
| Ti | 0.1 | 0.18 |
| Cr | 0.11 | 0.2 |
| Fe | 0.07 | 0.12 |

Situation

- Special sample types with no commercial reference materials available
- Examples: Biological (DBS – Dried Blood Spots); Cosmetics (Nail Polish); Specially formulated catalysts
- Difficult and costly to manufacture reference materials in-house
- A number of sample components in non-measurable form

Solution

- UniQuant allows for optimization for various components and compounds unique to each sample type
- Analyzed results confirmed by the more labor intensive ICP-MS and ICP-OES methods
- Results produced in a fraction of the time compared to other methods with minimal sample preparation

Client Testimonial

- ARL Perform'X with UniQuant enabled me to quantify diverse sample types that would normally not be considered possible using standard XRF methods
- Nitrocellulose and other volatile organic compounds were accepted into the calculations to provide more accurate results



UniQuant®

‘Working with thin film samples the reliability and precision of primary and duplicate results at trace concentration levels were near identical’

Andrea McWilliams, Research Triangle Institute

Summary

- Many of Petroleum and Polymer analytical X-ray requirements can be handled through lower power systems
- High Power WDXRF are extremely versatile and overcome many challenges
- Combined with a standardless routine such as UniQuant increases the system capability greatly
 - Complimentary technique to existing wet methods
 - Easy sample preparation and system maintenance

Thank You