Application Note: 41714

Elemental analysis of heavy (residual) fuel oil

ARL OPTIM'X Wavelength Dispersive X-Ray Fluorescence Spectrometer

Key Words

- ARL OPTIM'X
- Heavy fuel oil
- Residual marine fuel
- WDXRF
- X-ray fluorescence

Introduction to heavy fuels

The broad term "heavy fuel oil" refers to the highest boiling-point distillate fractions and non-boiling residuum of refined crude oils, used as fuel for industrial heaters, boilers and engines. Of the total recent global production of 530 million metric tons of heavy fuel oil, 54 % was consumed in the marine fuel market to power the huge compression ignition engines of the world's ocean-going ships.[1] Terms such as residual marine fuel, marine fuel oil and bunker fuel oil are used in industry for the 10 different fuel grades described by the ISO 8217 (2005) marine fuel standard.

Natural contaminants found in crude oil such as sulfur, vanadium, nickel and iron are largely tied up in complex non-volatile asphaltene and porphyrin molecules. These elemental contaminants thus remain and concentrate in the heaviest distillate fractions associated with heavy fuels; refining process contaminants also concentrate in these streams. In a high temperature, oxygen-rich combustion engine environment, the concentration and interaction of these variously abrasive and corrosive elemental contaminants can become virulent and highly damaging, reducing equipment service life up to 80 %.[2] Therefore despite relatively inexpensive market prices, marine residual fuels must adhere to comprehensive quality specifications also guarding against used oil dumping during storage (Table 1).

Element	Performance factors	Limit (max)†
Sulfur (S)	Corrosive wear, greenhouse emissions	1.0-4.5 % m/m
Vanadium (V)	Corrosive wear, particulate emissions	100-600 mg/kg
Aluminum (Al) + Silicon (Si)	Abrasive wear	25-80 mg/kg total
Zinc (Zn)	Used oil contaminant	15 mg/kg
Phosphorous (P)	Used oil contaminant	15 mg/kg
Calcium (Ca)	Used oil contaminant	30 mg/kg

Table 1. Elemental contaminants controlled by ISO 8217 marine fuel standards

†- ranges include lighter Distillate Fuel grades (low limits) to heaviest Residual grades (higher limits)

Standard test methods

The ISO 8217 marine fuel standard specifically references wavelength dispersive X-ray fluorescence (WDXRF) as a preferred analysis method for sulfur, vanadium and nickel analysis per ISO test methods 14596 and 14597. The WDXRF technique provides well-known advantages in overall speed of analysis owing to ease of sample prep (no dilution required) and excellent precision and stability from ppm to percentage concentrations across multiple elements. In addition, the British Institute of Petroleum (IP) proposed a new industry test standard in 2009 specifically for WDXRF analysis of residual fuel oil covering ten elements of interest mentioned above.

In this study we evaluate the suitability of the Thermo Scientific ARL OPTIM'X spectrometer for analysis of heavy residual fuel oil per typical international test protocols.

Instrumentation

The ARL OPTIM'X is a wavelength dispersive XRF instrument designed for ease of use, rapid deployment, and minimal lifetime operational costs. Its low power 50W Rhodium target X-ray tube provides equivalent sensitivity to conventional 200W instruments due to its unique Ultra Closely Coupled Optics™ (Figure 1). The resulting analytical sensitivity for even ultra-low contaminant concentrations rivals that of higher-powered and more expensive WDXRF instruments, while also providing full capabilities at high concentrations, e.g., 4.5 % sulfur. In addition, the efficient low power system of the ARL OPTIM'X does not require the same auxiliary water cooling as larger instruments.

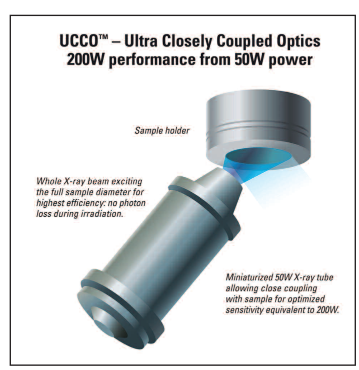

Figure 1. Innovative UCCO technology

[1] *International Sustainable Energy Exchange, Residual Fuel Oil and Residual Marine Oil (2008)*

[2] *Jones, R.L., US Patent 5312585: Corrosion inhibition in high temperature environment (1993)*

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The sequential analysis capabilities of the patented SmartGonio™ miniaturized goniometer cover all elements of interest in heavy fuels from Na (Z=11) to Zn (Z=30) or heavier. The goniometer also provides spectral resolution 10 times better than high-end EDXRF instruments. An additional advantage of the ARL OPTIM'X unique design includes optional enhanced performance on selected elements through configuration of two MultiChromator™ fixed channels, in which specially curved and focused crystals further improve sensitivity or reduce analysis time.

Sample preparation and procedure

WDXRF provides a notable benefit of direct analysis of even highly viscous samples without dilution. Sample preparation involves simply pouring (with heating as necessary) fuel samples directly into Chemplex liquid analysis cells sealed with 4 µm polypropylene (Spectrolene) film.

For this study an ARL OPTIM'X was configured with both the SmartGonio for sequential elemental analysis and various fixed channel MultiChromators for enhanced analysis of certain elements. Samples were analyzed for 120 seconds under a helium environment to eliminate air interferences.

Analytical sensitivity

The SmartGonio crystal and detector combinations used and comparison of sensitivities with MultiChromator fixed channels are shown in Table 2. With its SmartGonio configuration, the ARL OPTIM'X provides extremely low limits of detection for virtually all contaminant elements in heavy fuels and well within the quality limits set by ISO 8217. For the more difficult lighter elements, an additional fixed channel configuration provides further sensitivity

ELEMENT	SMARTGONIO CONFIGURATION	SMARTGONIO LOD [ppm]	FIXED CHANNEL LOD [ppm]
Al	PET/FPC	4.2	3.1
Si	PET/FPC	4	3.2
P	PET/FPC	2	1.5
S	PET/FPC	1.7	1.2
Ca	LIF200/FPC	1.5	1.7
V	LIF200/FPC	1	n.m.
Fe	LIF200/FPC	1.1	0.8
Ni	LIF200/SC	0.6	n.m.
Zn	LIF200/SC	0.6	n.m.

Table 2. Instrument configurations and analytical sensitivity

FPC: Flow proportional counter
SC: Scintillation counter
LOD: Limit of detection = $3\sqrt{(BEC/Qt)}$
n.m.: not measured; fixed channel not fitted for these elements

Reproducibility

The design of the ARL OPTIM'X also provides extremely stable analytical results over time. Reproducibility over a two month period on the same medium-range sulfur sample of 2.1 % (2,100 ppm) is shown in Figure 2. With an average value of 2,102 ppm and standard deviation of 9.5 ppm or 0.44 %, the instrument provides reproducible results over time without need for recalibration.

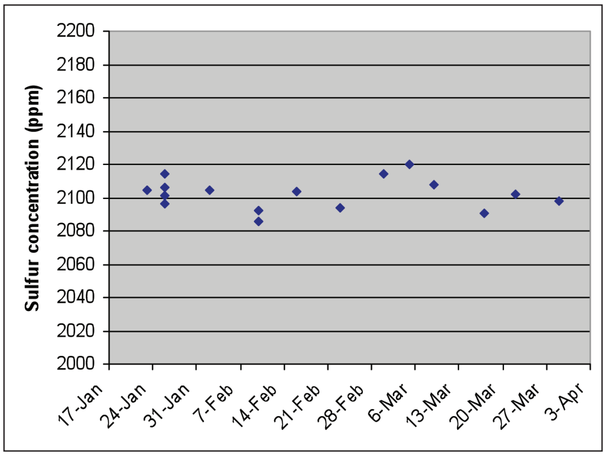

Figure 2. Reproducibility over a two month period

Conclusion

Despite occupying the low end of the distillate fuel spectrum, heavy residual fuels must adhere to tight quality restrictions to ensure proper marine engine performance. The low ppm levels of contaminants tolerated require analysis with excellent sensitivity, yet also analytical flexibility to measure percentage element concentrations. The ARL OPTIM'X is a uniquely designed cost effective WDXRF instrument that exceeds the requirements of ISO 8217 and other international standards for sensitivity, range and reliability of heavy fuels analysis.

For more information on our full range of X-ray instruments, please visit **www.thermo.com/xray**.

[3] *Data courtesy of Institut Français du Pétrole-Lyon, Direction Physique et Analyse, Vernaison, France (2004)*

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