Easy Elemental Analysis of Heavy Fuel Oils Using Wavelength Dispersive X-ray Fluorescence

Robert Hergenrader, Manager, Petrochemicals and Analytical Service Labs, X-ray Elemental Analysis, Thermo Fisher Scientific, Ecublens, Switzerland

Heavy fuel oils are blended products based on the residues from various refinery distillation and cracking processes. They are composed from the highest boiling-point distillate fractions and non-boiling residuum of refined crude oils, resulting in viscous liquid products with a characteristic odor and requiring heating for storage and combustion. Heavy fuel oils are used as fuel for industrial heaters, boilers and engines in industrial plants, marine applications and power stations[1]. Other terms commonly used to describe heavy fuel oils include residual fuel oil, bunker fuel oil, industrial fuel oil, marine fuel oil and black oil. In 2008, 54% of the total global production of 530 million metric tons of heavy fuel oil was consumed in the marine fuel market to power the huge compression ignition engines of the world's ocean-going ships[2].

Natural contaminants found in crude oil, such as sulfur, vanadium, nickel and iron (S, V, Ni, Fe) are largely tied up in complex non-volatile asphaltene and porphyrin molecules. As a result, these elemental contaminants remain and concentrate in the heaviest distillate fractions associated with heavy fuels. Refining process contaminants such as catalyst fines (Al, Si) 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 by up to 80%[3]. Likewise, heavy fuel contamination from used oils including zinc, phosphorous and calcium additives (Zn, Ca, P) can affect oil viscosity and increase volatility, lowering fuel quality and causing safety and reliability problems such as ash fouling, slag and corrosion in engines. High asphaltene levels in particular make fuel oils unstable when stored and result in poor combustion.

New ISO Standard and Test Methods

Despite relatively inexpensive market prices, marine residual fuels must adhere to comprehensive production quality specifications which also guard against used oil dumping during storage. The International Organization for Standardization (ISO) is scheduled in summer 2010 to release the fourth edition of its ISO 8217 standard setting ever tighter specifications for organo-metallics and other contaminants in marine fuels[4].

As in previous editions, the ISO 8217:2010 standard describes ten total grades of distillate and residual fuels. Significant changes from the 2005 edition include a reduction of parts per million (ppm) allowances for elements aluminum and silicon (Al+Si) - indicative of trace catalyst fine contamination - designed to reduce the risk of abrasive particles reaching the engine's inlet. In addition, the 2010 edition reduces the limits for organo-metallic contaminant vanadium (V) for most grades, designed to limit post-combustion deposits.

The ISO 8217:2010 marine fuel standard specifically references wavelength dispersive X-ray fluorescence (WDXRF) as a preferred method for the analysis of sulfur, vanadium and nickel according to the ISO 14596:2007 and ISO 14597:1997 test methods. In addition, the WDXRF technique also provides advantages for easily measuring other organo-metallic contaminants in heavy fuel oils including aluminum and silicon from catalyst fine particles, and zinc, phosphorous and calcium from used oils (Table 1).

Wavelength Dispersive X-ray Fluorescence

The WDXRF technique provides many benefits for determining the elemental composition of a wide variety of samples, both solids and liquids. The technique provides significant advantages in overall speed of analysis owing to ease of sample preparation, which is performed in a non-destructive way and without the requirement for dilution. In addition, WDXRF achieves excellent spectral resolution, precision and stability from ppm to percentage concentrations across multiple elements. Traditional high power WDXRF analysis has long been a staple in petroleum laboratories due to the usefulness of both its full-range sequential elemental analytical capabilities for difficult problem-solving and ease of use for routine yet demanding petroleum quality analysis.

Shifting demands within the petroleum industry have necessitated corresponding changes to WDXRF technology and design. Recent advances in WDXRF technology allow new, lower power instruments to achieve impressively similar results to traditional high power systems with significantly lower hardware and operating costs and less auxiliary support. The design challenge lies in developing such systems to meet ever-tightening regulatory standards. A study was performed to evaluate the suitability of advanced WDXRF technology for the analysis of heavy residual fuel oil according to typical international test protocols.

Table 1: Elemental contaminants controlled by ISO 8217:2010 marine fuel standard

Element	Performance Factors	Limit (max) †
Sulfur (S)	Corrosive wear, greenhouse emissions	1.0-4.5 % m/m
Vanadium (V)	Corrosive wear, particulate emissions	50-450 mg/kg
Aluminium (Al) + Silicon (Si)	Abrasive wear	25-60 mg/kg
Zinc (Zn)	Used oil contaminant	15 mg/kg
Phosphorous (P)	Used oil contaminant	15 mg/kg
Calcium (Ca)	Used oil contaminant	30 mg/kg

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

Experimental

The Thermo Scientific ARL OPTIM'X WDXRF analyzer was used for this study, equipped with a low power 50W rhodium target X-ray tube and Ultra Closely Coupled Optics (UCCOTM) technology greatly increasing X-ray efficiency. The instrument's SmartGonio™ miniaturized goniometer operating sequentially covers elements at ppm levels in heavy fuels from Al (Z=13) to Zn (Z=30). The instrument was also configured with selected MultiChromator™ fixed channel crystals to enhance the performance on particular elements.

As mentioned, WDXRF provides a notable benefit of direct analysis of even highly viscous liquid samples with no dilution necessary. For this study, sample preparation involved simply pouring (with heating as necessary) fuel samples directly into Chemplex liquid analysis cells sealed with 4 µm polypropylene (Spectrolene®) film. Samples were analyzed under a helium environment to eliminate air interferences; limits of detection were determined for 120 seconds counting time per element.

Results

The SmartGonio crystal and detector combinations used and sensitivities are shown in Table 2, along with some comparison of MultiChromator fixed channel sensitivities. The miniaturized goniometer sequential configuration provided extremely low limits of detection for virtually all contaminant elements in heavy fuels, well within the quality limits set by ISO 8217: 2010. The goniometer also provides spectral resolution ten times better than high-end energy dispersive XRF (EDXRF) instruments. For the lighter elements in particular, the additional MultiChromator fixed channel configurations with specially curved and focused crystals further improved sensitivity or could be used to reduce analysis time. The efficient low power system of the instrument does not require the same auxiliary water cooling as larger instruments, yet provides the good sensitivities shown along with full-range capabilities for high elemental concentrations such as percentage levels of sulfur.

Table 2.

Instrument configurations and analytical 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.

FPC: Flow proportional counter

SC: Scintillation counter

LOD: Limit of detection

n.m.: not measured; fixed channel not fitted for these elements

Further study results demonstrate that the WDXRF technique delivers extremely stable analytical results over time. Reproducibility over a two month period on a sample containing 2.1 % (2,100 ppm) sulfur is shown in Figure 1. With an average value of 2,102 ppm and standard deviation of 9.5 ppm or 0.44 %, the instrument generated reproducible results over time without the need for recalibration.

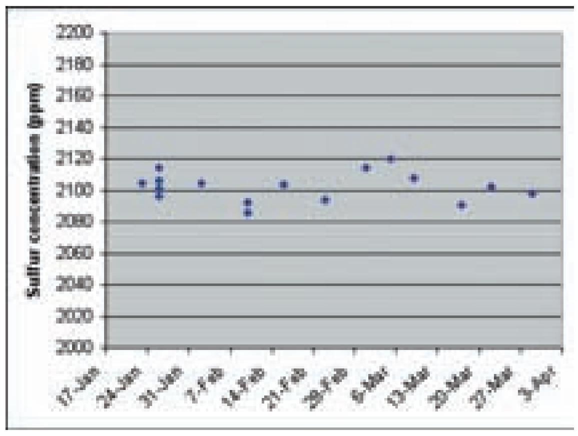

Figure 1:

Reproducibility on high sulfur over a two month period

Conclusion

Despite occupying the low end of the distillate fuel spectrum, heavy fuel oils must adhere to tight quality restrictions to ensure proper marine engine performance. The low ppm levels of contaminants tolerated by current legislative standards require analysis with excellent sensitivity, yet also analytical flexibility to measure percentage element concentrations. WDXRF is a highly powerful technique that is suitable for meeting standards such as the new ISO 8217: 2010 and other international standards for sensitivity, range, reliability and reproducibility for heavy fuel oils analysis.

References

1. Heavy Fuel Oils, prepared by CONCAWE's Petroleum Products and Health Management Groups, Brussels May 1998, HYPERLINK "http://www.accede.org/prestige/documentos/Tox_fuel_pesado.pdf" http://www.accede.org/prestige/documentos/Tox_fuel_pesado.pdf

2. International Sustainable Energy Exchange, Residual Fuel Oil and Residual Marine Oil (2008)

3. Jones, R.L., US Patent 5312585: Corrosion inhibition in high temperature environment (1993)

4. International Organization for Standardization, ISO 8217:2005 and ISO 8217:2010 Petroleum products - Fuels (class F) - Specifications of marine fuels, HYPERLINK "http://www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_detail_ics.htm?csnumber=50613" http://www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_detail_ics.htm?csnumber=50613

Ultra Low Sulpur in Oil Analyser Compliant with ISO 20847 and ASTM D-4294

Horiba (France) is proud to release the SLFA 3000 series of ultra low sulphur analyzer for biofuels, gasoline and petroleum products. It is compliant with current recommended methods: ASTM D4294 - 08a Standard Test Method for Sulphur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry and ISO 20847:2004 specifies an energy dispersive X-ray fluorescence (EDXRF) test method for the determination of the sulfur content of motor gasolines, including those containing up to 2.7% (m/m) oxygen, and of diesel fuels.

With the new analyzer, the typical detection limit is 2 ppm which is much below the lowest regulated content of sulfur (10 ppm). While a good detection limit is very useful, the crucial problem with energy dispersive X-Ray fluorescence is the matrix effect. Major developments for the new instrument are automatic matrix corrections with sophisticated algorithms and innovative spectrum analysis. Thanks to these new and unique features, the SLFA 3000 automatically makes matrix corrections for a wide range of sample C/H ratio (from 7 to 9) as well as for oxygen content up to 34 %.

So ultra low detection limits and matrix correction enable these analyzers to be an essential tool for all type of products: From 0 - 10% S in sour crude to sweet crude to straight run gasoline to reformulated gasoline, and specifically all kind of biofuels. SLFA 3000 is your partner for pipeline, refinery or independent test laboratories with its short measurement times, extremely simple use and accurate, reliable results.

Reader Reply Card No 77

3rd Generation of Industrial X-ray Diffractometers Offers More Speed, Applications Power and Automation Potential

PANalytical (Netherlands) has launched CubiX3, the 3rd generation of its successful CubiX X-ray powder diffractometers range. Building on the company's reputation for speed, reliability and reproducible analysis, the CubiX3 introduces new features such as high-intensity data collection as well as extra flexibility in sample handling for automated environments. X-ray diffraction has already reached significant importance as a process and production control method for powdered materials in many industries, including the petrochemical and polymer sectors. Its initial investment is rapidly earned back because of the ease of operation, the independency of operators and the safety for the users, when compared to traditional methods like wet-chemical process control or microscopy methods. The CubiX3 range includes dedicated versions, tailored to the needs of those working in cement, minerals, pharmaceuticals or aluminium production. Dr. Uwe König, Applications Specialist, XRD, highlighted the advantages of XRD analysis with the new CubiX3 range: "X-ray diffraction is recognized as the most efficient method of obtaining direct phase information for many types of materials. Results enable manufacturers to maintain consistency in the quality of their product while optimizing production speeds. CubiX3 is the fastest, most flexible and most accurate diffractometer available for production control. It yields a complete diffraction pattern up to 150 times faster than conventional detection technology". PANalytical was the first X-ray solutions provider to bring 'walk-up' functionality to its line of XRPD systems. The Walk-Up software available for CubiX3 enables a user with no knowledge of XRD to enter urgent samples at any time, even if the diffractometer is already processing a routine batch; and automatically receive a report of results with no user input to the analysis. The Walk-Up / CubiX3 combination provides the perfect analysis tool for multi-user environments. The CubiX3 supports the full analytical X-ray powder analysis methodology from classical data analysis up to full pattern cluster analysis for statistical data interpretation and pass/fail determination.

Reader Reply Card No 78

Replace Dangerous Radioisotope Based Sulphur Gauges with NEX XT Process Sulphur Analyser

Applied Rigaku Technologies, Inc. (USA) is pleased to introduce the new Rigaku NEX XT on-line sulfur. This product represents the next generation of process gauge for high-level sulphur measurement (0.02% to 6% S) of crude, bunker fuel, fuel oils, and other highly viscous hydrocarbons, including residuums.

This versatile, compact and robust X-Ray Transmission (XRT) process gauge is specifically optimized for the sulphur analysis needs of refineries, pipelines, blending operations, bunkering terminals and other storage facilities. Applications include bunker fuel blending to meet MARPOL Annex VI sulphur restrictions, interface detection of different grade fuels delivered via pipelines, refinery feedstock blending and monitoring, and the quality monitoring of crude at remote collection and storage facilities.

The new Rigaku NEX XT system is faster, more sensitive and far more compact than competitive systems and provides continuous, reliable detection of sulphur at pressures up to 1480 psig and 200°C.

The NEX XT can operate as a stand-alone analyser or provide real time closed loop control when tied into a blending or plant wide automation system. Based on the X-ray Transmission (XRT) measurement technique, the hydrocarbon stream travels through a flow cell where the sample is illuminated using a safe low power X-ray tube. A detector on the opposite side of the flow cell measures transmitted X-rays. Signal intensity is inversely proportional to the sulfur concentration. The system contains no radioisotope sources and requires no routine maintenance.

Among its other key features are a simplified user interface, reduced standards requirement, automatic density compensation, automatic water compensation, password protection, and standard platform for communicating sulfur, density, and water content to a plant-wide DCS. Due to its unique design and robust construction, sample conditioning and recovery systems are typically not required.

Reader Reply Card No 79