Analysis of Ni and V in diesel fuel oils with Thermo Scientific ARL PERFORM'X Series Advanced X-Ray Fluorescence Spectrometers

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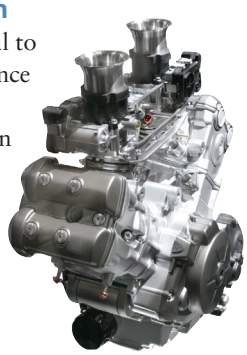
Key Words

ARL PERFORM'X 4200 W, Corrosion prevention, Diesel fuels, X-ray fluorescence, XRF

Goal

A quick and simple analysis of nickel and vanadium in fuels using WDXRF as a direct measurement for routine process and quality control.

Introduction to corrosion



Preventing corrosion is essential to decreasing expensive maintenance and replacement costs for the large industrial engines found in marine vessels, industrial boilers, power facilities and similar operations. Such engines typically consume diesel fuel oils (also called gas oil) which may retain natural contaminants from crude oil even after refining. In particular, traces of metals vanadium (V) and nickel (Ni) in fuel oils react with other contaminants in aggressive engine environments to form vanadium oxides and other corrosive compounds.

Various industrial diesel oil specifications typically restrict traces of V and Ni to 100 ppm or less, in some cases setting limits at sub-ppm levels, for example, V less than 0.5 ppm and the sum of V + Ni + other metals less than 1.0 ppm. Per international standard test methods such as ISO 14597, WDXRF is a preferred technique for analyzing trace metal contaminants in petroleum products due to its ease of sample preparation, multi-element analysis and high sensitivity and precision. This study focuses on analyzing sub-ppm traces of V and Ni in diesel fuel oils.

Instrument

Thermo Scientific ARL PERFORM'X series spectrometer used in this analysis was a 4200 watt system. This system is configured with 6 primary beam filters, 4 collimators, up to nine crystals, two detectors, helium purge and our 5GN+ Rh X-ray tube for best performance from ultra-light to heaviest elements thanks to its 50 micron Be window. This new X-ray tube fitted with a low current filament ensures an unequalled analytical stability month after month.

The ARL PERFORM'X offers the ultimate in performance and sample analysis safety. Its unique LoadSafe design includes a series of features that prevent any trouble during sample pumping and loading. Liquid cassette recognition prevents any liquid sample to be exposed to vacuum by mistake. Over exposure safety automatically ejects a liquid sample if X-ray exposure time is too long.

The Secutainer system protects the primary chamber by vacuum collecting any loose powders in a specially designed container, easily removed and cleaned by any operator. For spectral chamber protection, the ARL PERFORM'X uses a helium shutter designed for absolute protection of your goniometer during liquid analysis under helium operation. In the "LoadSafe Ultra" optional configuration, a special X-ray tube shield provides total protection against sample breakage or liquid cell rupture.

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Samples and methods

A series of 4 petroleum standards containing vanadium and nickel were chosen for the analysis. 10 grams of each sample were poured directly into a special liquid cell fitted with a 6 micron thick polypropylene film. The liquid cell was placed into a metallic sample holder for loading into the XRF spectrometer. A helium gas environment was used to analyze all samples.

Results and discussion

Table 1 shows the analytical conditions used, while Table 2 demonstrates the good sensitivity of the method and the limits of detection achieved.

Element/ Line	Crystal	Detection	Analysis Time
V / Kα	LIF200	FPC	150 sec.
Ni / Kα	LIF200	SC	150 sec.

Table 1: Analytical conditions

Element/ Line	Sensitivity (KCPS/%)	BEC (%)	LOD (PPM)
V	973	0.00095	0.076
Ni	5954	0.00071	0.028

Table 2: Performance and limits of detection
KCPS = thousand counts per second
BEC = background equivalent concentration (noise-to-signal)
LOD = limit of detection

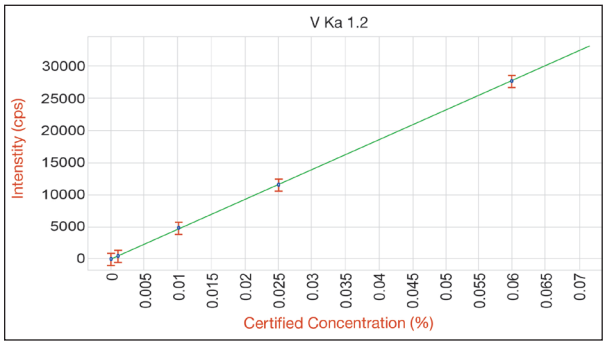

Figure 1: Calibration for vanadium in diesel fuel oil
SEE = 0.020 ppm

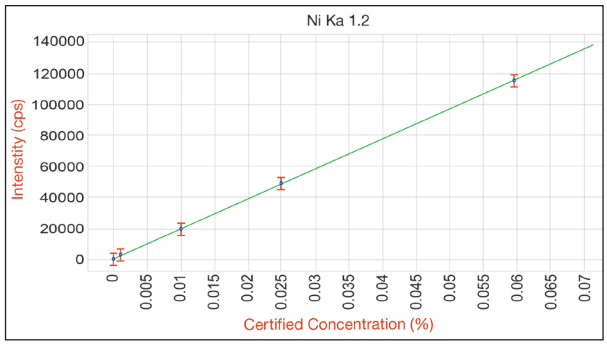

Figure 2: Calibration for nickel in diesel fuel oil
SEE = 0.025 ppm

Figures 1 and 2 show the calibration lines obtained without the need for any matrix correction. The Standard Error of Estimate (SEE), a measure of accuracy, of 0.020 ppm for vanadium and 0.025 ppm for nickel confirms the excellent accuracy of analysis obtained.

Precision at low ppm levels

The repeatability of nickel analysis at the ppm level is shown in Table 3 where four different liquid cells were filled with the same diesel oil sample and introduced into the spectrometer at 3-minute intervals. A counting time of 120 seconds per analysis was used.

Cell Nr.	Ni Concentration
1	1.6 ppm
2	1.6 ppm
3	1.7 ppm
4	1.7 ppm
Average	1.7 ppm
SD	0.06 ppm
RSD	3.1 %

Table 3: Precision of analysis at low Ni levels

Conclusion

The very high sensitivity achieved with the ARL PERFORM'X XRF spectrometer allows the analysis of corrosion-inducing contaminants Ni and V below ppm levels in diesel fuel oil with excellent precision using short analysis times, thereby ensuring quick and easy compliance with even the tightest specifications for industrial diesel fuels.

To see our full X-ray product portfolio, please visit **www.thermoscientific.com/xray**

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