

Testing for Heavy Metals in a Changing Crude Market



The global crude market is changing. New sources are producing heavier feeds. New production techniques are leaving additives behind. Changing logistics can lead to contamination during transportation. Crude oil producers are blending to meet trading specifications, which create a whole new set of issues for refiners and others downstream.

New elemental specifications will be useful in identifying some low-cost “dumbbell” crudes, which are blended to marginally fall within the current NYMEX Light Sweet Crude Oil Futures specifications but may present other problems during refining. In “dumbbell” blends, the crude has a high content of heavy components on one end and a high content of lighter components on the other, but little in the middle. In these cases, the increased level of heavier components will typically increase the concentration of problem elements. The presence of these elements at elevated levels is therefore a leading indicator of excessive crude blending.

XOS can help meet the needs for low level metals testing in crude. Using the [HD Maxine](#), a user can measure for metals such as nickel and vanadium at sub-ppm levels with the ease of XRF. There is no sample prep or ashing needed as with ICP or AA. Simply pipette the sample into a cup and place it in the analyzer. The HD Maxine uses High Definition X-ray Fluorescence technology (HDXRF®) developed by XOS. With the press of a button, the HD Maxine provides precise multi-element results in ten minutes or less with exceptional levels of detection (LODs), completely eliminating the need for a lengthy and expensive ICP-AES procedure.

For this application, the precise measurement of metals in crude oil is critical as these elements can cause adverse effects at the refinery level. In an attempt to mitigate this issue, the COQA has been pushing for tightening of NYMEX specifications for problem elements due to the increasing presence of “dumbbell” blends. These specifications would help to guarantee that the crudes being sold to refineries will be able to produce the level of middle distillates expected.

Typical Elements of Interest in a Refinery

Vanadium

- High levels produce off-specification coke
- Deactivates cracking catalysts
- May cause corrosion

Nickel

- High levels produce off-specification coke
- Deactivates cracking catalysts
- Can cause emulsions → Poor desalting

Iron

- High levels produce off-specification coke
- Can cause fouling
- Reduces catalyst effectiveness

Zinc

- Can cause emulsions → Poor desalting

Other problem elements: **Chromium** and **Calcium**

In fact, a technical paper presented at the Crude Oil Quality Group (COQG) describes the production of off-specification coke and deactivation of cracking catalysts as possible adverse effects of excess metals in crude oil. Vanadium is one of the common elements causing these issues and laboratories test for it regularly. Although vanadium naturally occurs in crude oil at low levels, contamination from the blending of residual

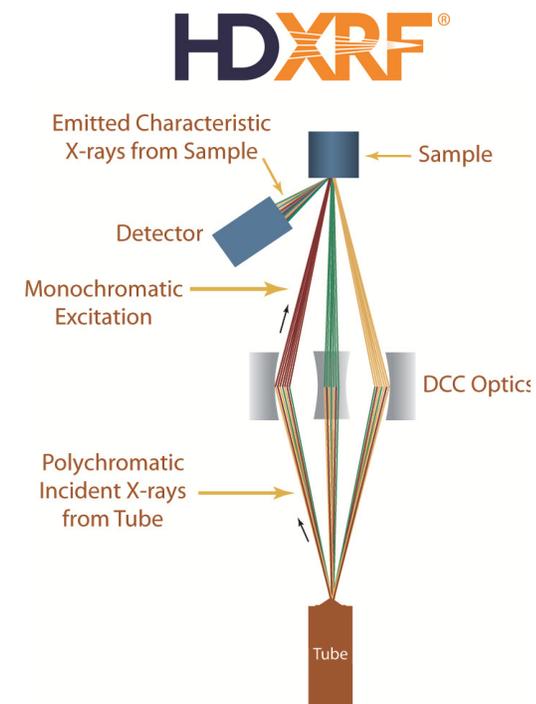
products into the crude oil may result in the elevation of vanadium concentrations. (COQC, 2004, “Crude Oil Contaminants and Adverse Chemical Components and Their Effects On Refinery Operations”)

Additionally, excess iron may cause off-specification coke as well as pump and exchanger fouling, creating potentially severe problems in transportation and processing units. Although trace amounts of iron may naturally occur in crudes, it is predominantly introduced in the field or pipeline as iron oxide and iron sulfide. (COQC, 2004, “Crude Oil Contaminants and Adverse Chemical Components and Their Effects On Refinery Operations”)

The Crude Oil Quality Association (COQA) has recommended additional specifications for Domestic Sweet crude oil that is delivered to the Cushing, Oklahoma terminals (NYMEX: Light Sweet Crude Oil Futures), including nickel at 8 parts per million (ppm) maximum and vanadium at 15 ppm maximum. However, current available analysis, as determined by ASTM Standard D5708, Test Method B, requires a combination ICP-AES procedures (after acid digestion), which can be both expensive and labor intensive.

The exceptionally low LODs delivered by the HD Maxine are the result of state-of-the-art HDXRF technology, a technique based on monochromatic energy dispersive XRF for sample measurement. HDXRF differs from traditional EDXRF in that Doubly Curved Crystal (DCC) optics enhance measurement intensities by capturing x-rays from a divergent source and redirecting them into an intense focused beam to the sample surface. The use of multiple DCC optics enables multiple select-energy excitation beams that efficiently excite a broad range of target elements in the sample. This technique eliminates x-ray scattering background under the fluorescence peaks, greatly enhancing detection limits and precision.

HD Maxine applications include contaminants, additives, wear metals, refineries, lubricant plants, crudes and downstream hydrocarbons.



HD Maxine



Powered by **HDXRF**

Levels of Detection with HD Maxine

Element	Typical LOD (ppm)
Vanadium (V)	0.7
Nickel (Ni)	0.28
Iron (Fe)	0.7
Zinc (Zn)	0.14
Calcium (Ca)	0.7
Chromium (Cr)	0.4
Chlorine (Cl)	6
Sulfur (S)	9

For more information on HD Maxine, or to speak with an XOS field expert, contact info@xos.com or call 1-518-880-1510.