Total Solutions for Sulfur and Metals Analysis in Exploration and Refinery Petroleum Process Intermediates and Final Products

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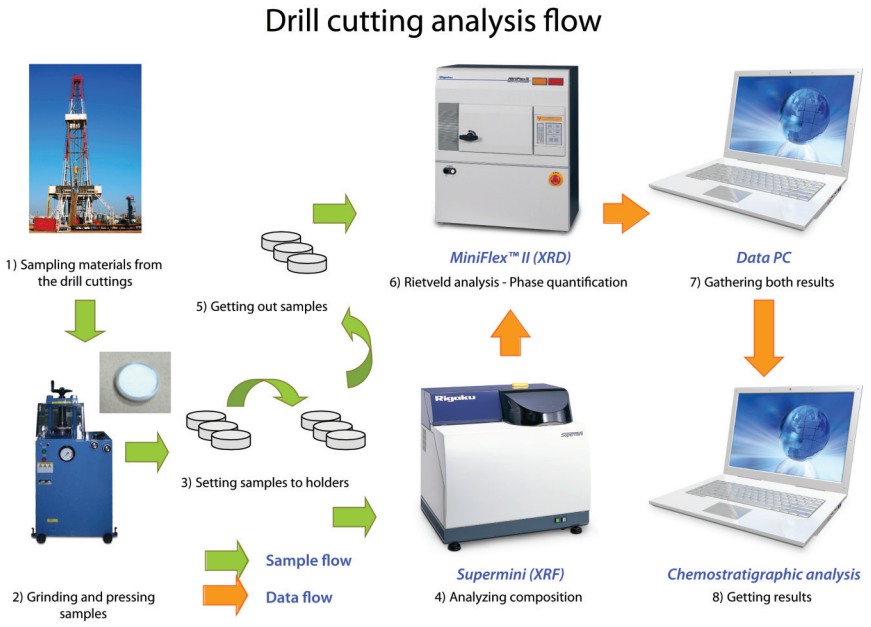
The oil and gas industry is a highly complex conglomerate of "upstream"—the exploration and production sector in the industry—and "downstream"—the sector that deals with refining and processing, distribution and marketing sectors.

Companies operating in the industry may be fully integrated, (i.e., have both upstream and downstream interests), may concentrate on a particular sector (such as exploration and production, commonly known as an E&P company), or may concentrate just on refining and marketing (an R&M company). Many large companies operate globally, the "multi-nationals," while other smaller companies concentrate on specific regions of the world and are often referred to as "independents." In the upstream and downstream sectors, much reliance is placed upon oil field service companies and other contractor companies who provide specialist technical services to the industry.



Rigaku fulfills the role of such a service company, supplying analytical measurement technology to these various vendors based on well founded spectroscopic techniques. Rigaku is pleased to present a view of the integrated role of XRF, XRD and Raman techniques in the oil and gas industry.

Rigaku has long been a supplier of XRF and XRD equipment, focused on high quality, precision engineering to produce instrumentation with outstanding performance characteristics. In keeping with its long history of excellence, Rigaku now offers a complete line of material science solutions for the petroleum industry, from exploration to crude oil production, from transport of the crude oil to final refinery products, and from the blending tanks to the gasoline pumps, the lube oil vending stands and the tire companies.

Exploration and production of crude oil and natural gas is one of the largest-funded single economic markets globally. More than half of all the exploration dollars funded by companies are directed towards finding new reserves of petroleum-based raw materials, be it crude oil deposits, oil shales, or natural gas deposits.

Besides naturally occurring deposits, which seem to be becoming harder to find (and the ones that are being discovered tend to yield oil high in sulfur), there is a quest to use renewable sustainable routes to produce key petrochemicals necessary for our industrialized lifestyle. Alternative oil production (extracting lipids produced by algae, and the use of sugar as a raw material for sustainable production of existing industrial chemicals) offers great potential for cane- and beet-sugar producers to capture added value while helping to transform the chemical industry to a renewable feedstock base.

Large-scale global manufacture of existing industrial chemicals requires approximately 3 billion barrels/year of oil and its equivalents as the primary source of raw materials, heat, and power. In addition to being energy intensive, the chemical industry contributed significantly to the nearly 30 billion tonnes of anthropogenic carbon dioxide emitted globally into the atmosphere in 2008.

The benefits of sustainable chemicals manufacturing for the production of 1,4-butanediol, an existing 1.3 million tonnes/year petrochemical, are self explanatory. Commercial production of 1,4-butanediol from sugar using an engineered microorganism will require much less energy, will release significantly less carbon dioxide, and is expected to be substantially cost advantaged relative to current petrochemical processes.

Each of these processes has intermediate products, with the economic product as well as the inevitable by-products being created. Each of the products, by-products and critical components in the reaction pathways have to be characterized to maximize yield and end-product quality. Analytical equipment, such as XRF, XRD and Raman instruments, can carefully characterize the end products—as well as intermediates—to help control key parameters that affect the quality of the product during the manufacturing process. The end products can then be characterized for certification and or compliance purposes.

Cost containment

In exploration, the costs of locating a viable deposit can be astronomical; therefore, it makes sense for exploration geologists to maximize the information available from the data generated to improve the accuracy of their understanding of the potential deposits and the geomorphology associated with the deposit.

Rigaku XRF and XRD data work synchronistically to feed geo steering data to drilling operations with on-site analysis. For example, the Supermini 200 W XRF spectrometer provides accurate major and trace element data to the MiniFlex™ II Rietveld program for accurate mineral phase identification.

XRF composition data can differentiate between shales, sandstones and other materials. Trace element composition can be used for discriminate analysis and possibly serve as an indicating element for potential hydrocarbon deposits.

XRD phase identification can further refine the geological information to assist in modeling of the exploration area.

Crude oil is readily characterized using XRF for sulfur content and Ni, V and Fe concentrations indicative of the geological environment where the crude is formed.

Refinery controls

There are five critical areas in a refinery where XRF analysis would be of critical use.

Ref No.	Area	Analysis
1	Crude Oil Desalters	Na, Ca, S, Ni, V, Fe, Cu, Zn, Bi, Pb, Hg, and others
2	Atmospheric Bottoms	Al, Si, Na, Ca, P
3	FCC	Metals on spent and regenerated catalysts
4	Reformate	Low level sulfur
5	Sour Water Stripper	Cl

Part of the refining process is dedicated to removing these metals from the process streams in order to minimize unwanted side effects.

Process control limits exist to maximize refinery process yields and to contain costs by maximizing expensive catalysts' lifetimes. Many units have a catalyst regeneration cycle, and process engineers need to quantify the effectiveness of the regeneration cycle. Part of the process optimization requires vigilant analysis of metals in all parts of the refinery streams to meet these process goals.

WDXRF (wavelength dispersive XRF) is uniquely suited for these multiple analytical needs, since the steps to prepare samples for analysis are straightforward and relatively quick. The methods can be extremely sensitive, with limits of detection for most metals being on the order of 0.2 - 1.0 ppm, thus allowing quantification of all metals down to 1 - 3ppm.

The ZSX Petro

The ZSX Petro WDXRF spectrometer is powered specifically to handle volatile liquid samples with the highest sensitivity, while maintaining the integrity of the samples during the analysis time window. The ZSX Petro is a cost-effective variable-power instrument with the full complement of analytical features necessary for all of the routine analyses that today's petroleum refinery laboratory needs to carry out. Whether you are characterizing the sulfur content of incoming crude oil at weight percent levels or qualifying final product sulfur content for the full product line of gasolines, diesels, naphthas, kerosene and jet fuels at single digit ppm levels, or weight percent levels of sulfur, the ZSX Petro will handle the analyses with minimal operator intervention. Just set it up and leave it to do the work. Precise, reproducible data are the trademark of the ZSX Petro XRF. The performance exceeds the guidelines set out by the ASTM procedures by a sizeable margin, enabling very tight process control from 1 ppm to 5 wt% sulfur.

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The Supermini

This powerful benchtop WDXRF instrument can serve as the reserve or overflow unit in your refinery laboratory, or it can serve as your primary ASTM 2622 compliant WDXRF spectrometer at remote or satellite sites. If high volume throughput is not your primary concern, then this benchtop is a very cost effective method of getting top class analytical capability and compliance in a reasonable analysis times. The Supermini, with its multi-position sample changer and intuitive software, will make a welcome ally in your daily sulfur analysis routine. It can be set up in little time to perform these important analyses and be left unattended while the analyst is freed up to take care of more labor intensive analytical tasks.

Results can be sent directly to the Laboratory Information Management System for process control feedback or for reporting purposes. The reliable Rigaku Petro-Pak™ software will ensure that your results are validated and alert you if any out of specification data is encountered. The system helps make you more productive and enhances the reliability and speed of your analytical feedback to process control. This gain in efficiency translates directly into profits for the bottom line.

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Sulfur analysis

One of the major considerations in the cost control process is how much treatment each barrel of crude oil will need to reduce the naturally occurring sulfur to operational levels that will make a product that meets federally mandated standards for sulfur content. Part of the required testing consideration to keep products in specification with the mandated sulfur levels is the overall cost of ownership of testing and measurement equipment for refiners, pipeline operators and product distributors. This cost includes capital expenditure, operating costs and life expectancy.

The Micro-Z sulfur™

The Micro-Z sulfur is designed first and foremost to meet performance requirements of the industry, so this benchtop WDXRF analyzer has the capability of measuring both the sulfur peak and associated background for every analysis as specified in ASTM 2622-08. The instrument has been designed to take advantage of industry-leading optics, using curved crystals to improve X-ray intensity captured by the sealed proportional detector, allowing unparalleled sensitivity and meeting industry mandated detection limits. The close-coupled geometry of the excitation source and sample allows for the use of low-powered X-ray tubes. This excitation system, while still producing high intensity X-ray fluorescence from samples containing sulfur in low concentration levels, has no need for external cooling chillers.

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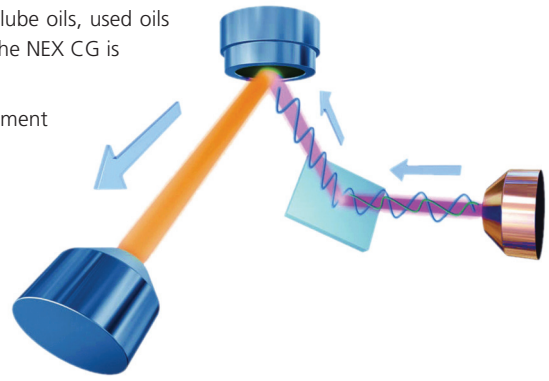
NEX CG - high performance EDXRF

The NEX CG uses secondary targets and polarization for background removal. With a 50 kV, 50 W tube, high performance X-ray source coupled with a state of the art silicon drift detector, the NEX CG represents one of the most advanced energy dispersive XRF (EDXRF) units available today.

The Cartesian geometry optical path allows this instrument to perform at levels not seen before in EDXRF. From ULSD to rapid multi-element analysis for lube oils, used oils and wear metals, the versatility of the NEX CG is unmatched.



Unique features that set this instrument apart from its competition are:

- FP with Rigaku's unique use of Matching Library reduces or eliminates the need for large suites of calibrations standards in many cases.
- ULSD performance with sulfur LLD = 0.5 ppm in 300 seconds for reliable S measurements well below 10 ppm.
- Meets ASTM D7220, IP 532 and EN/ISO 20847 for ULSD.
- In lube oils, measures the basic four P, S, Ca and Zn as well as Mg, Ba, Cu, Mo and other elements in newer blends. Measure low ppm including Cl.
- Lube oils Mg LLD = 45 ppm, with all other elements showing <3 ppm LLD.

This high-end EDXRF has performance characteristics that give it a best in class rating.

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NEX XT - X-ray transmission gauge for real-time analysis of S in crude oil and other heavy hydrocarbon oils

When sulfur in crude and intermediates needs to be determined, the best place to do that is online. To that end, Rigaku has designed and manufactured a unique product: the NEX XT.

This in-line sulfur analyzer provides real time analysis for blending, switching and quality control purposes. With a sulfur LLD = 45 ppm in 60 seconds, and a working range of 200 ppm to 6% S, the versatility of this unit is unmatched. Having typical count times of 30 sec or less means that the flow of product through the processes is virtually seamless. Added functionality of automatic density output and density correction always compensate for these changes, and the correction is seamless for the operators. This ease of use, coupled with consistent results (repeatability <1% relative), streamlines the entire process. The rugged construction and ability to operate under extreme conditions of pressure and temperature – stream pressures up to 1480 psig and temperatures up to 200°C with flow rates up to 53 gal/min (200 L/min) – make the NEX XT an extremely useful online gauge.

The NEX XT can be used in refineries for feedstock blending, process QC, and heavy oil upgrading. It can be used for analyzing marine bunker fuel during blending operations, as it has been qualified for MARPOL ANNEX VI compliance. Finally it has on-line capabilities for pipelines and remote terminals to facilitate real-time blending and remote crude collection QC. It is also used for pipeline interface detection.

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Rigaku FirstGuard™ Raman spectrometer

Finally, Rigaku is pleased to announce its newest product offering. The FirstGuard Raman handheld analyzer makes its debut in our product lineup. It is expected that the Raman handheld will find its analytical niche in the petroleum industry with ease as it helps to identify and quantify both pure materials and mixtures in liquid and solid forms. The non-destructive technique promises to offer analytical information hitherto not available. The Raman handheld family is available in three different laser excitation wavelengths, 532, 785 and 1064 nm, depending upon the application for which it will be used. While the 785 nm source is good for refined oil products, such as methanol content in gasoline, the 1064 nm excitation source is particularly useful for crude and biofuels testing. In crude and biofuels, excessive fluorescence can be problematic with the lower wavelength laser sources, masking the signals of interest. The 1064 nm source offers maximum reduction in fluorescence, making this new handheld spectrometer most useful for crude and biofuels testing applications. Engine oil wear analysis has also proven to be an application that the 1064 nm wavelength is most suited to analyze effectively.

The new Rigaku Raman spectrometer also offers a unique Volume Phase Grating (VPG) that maximizes the efficiency of collected spectra. Until now VPG gratings have only been available in lab and benchtop Raman systems.

Please send all enquiries for further information via www.rigaku.com/contact/pin.html

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