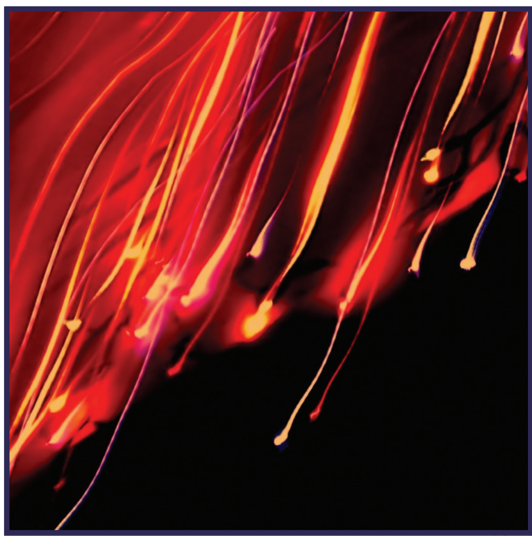


Modern EDXRF in the Petroleum Industry

Scott Fess, Product Manager – EDXRF, Applied Rigaku Technologies, Inc.
9825 Spectrum Dr. Bldg. 4 Suite 475, Austin, TX 78717
Tel: 512-225-1796 ext. 0963 • Fax: 512-225-1797 • Email: info@RigakuEDXRF.com • Web: www.RigakuEDXRF.com

Energy-dispersive X-ray Fluorescence (EDXRF) is a common technique used throughout the petroleum industry for elemental analysis. In the XRF technique, source X-rays are directed into the sample, which can eject the innermost electron of an atom, leaving a hole. As an electron in an outer shell transitions to fill the hole, it releases its extra energy as a new X-ray called a characteristic X-ray. The characteristic X-ray is then collected by a detection system. Because the energy difference between any two electron shells is unique to the atom that produced the X-ray, the number of fluorescent X-rays detected can be related to the concentration of that atom in the sample. Signals from the detection system are then processed by electronics and displayed as a spectrum, showing intensity peaks that indicate the elements in the sample based on energy position. Software then relates intensity of a peak to elemental concentration via prior analyser calibration, usually using a set of assayed standards to develop the relationship.

Types of EDXRF Instrumentation

Basically, EDXRF systems are available in two types -- direct excitation and indirect excitation -- depending on the particular analytical need. The X-ray tube produces source X-rays from the tube's anode, as desired, as well as a broad spectrum of background X-rays that may or may not be desired. Direct excitation aligns the tube directly into the sample illuminating with characteristic lines from the X-ray tube anode and/or Bremsstrahlung "white" radiation. Filters may be employed to shape or cut quiet spots in the Bremsstrahlung. Indirect excitation systems focus the tube X-rays onto a secondary target, which then directs monochromatic X-rays of one energy into the sample, eliminating almost all of the background. Polarisation can also be used, which is a special case of secondary targets. A crystal is used as the secondary target to produce polarised X-rays, placing the X-rays all in the same plane, and by setting the target-sample-detector angles at 90o Cartesian geometry, the background can be reduced even further.

EDXRF systems use various silicon semiconductor chips or Noble gas enclosed in a tube to detect the energies of incoming characteristic X-rays. Modern Si-based detectors include Si PIN diodes and the SDD (Si Drift Detector). Semiconductor detectors allow for sharper, better resolved elemental peaks than the older gas-filled proportional counters, and the SDD type detector yields much higher X-ray throughput than other detector types.

Benefits of EDXRF in the Petroleum Industry

While the XRF technique can be used to measure most of the elements in the periodic table, one of the chief uses in the petroleum industry is to measure the sulphur content of oils, from crude to fuels.

The benefits of EDXRF for measuring sulphur and other elements are many. Chief among these are ease of use, analysis speed on the order of 30-300 seconds, exceptional reproducibility, and the ability to measure a wide range of sulphur concentrations from low ppm to % levels.

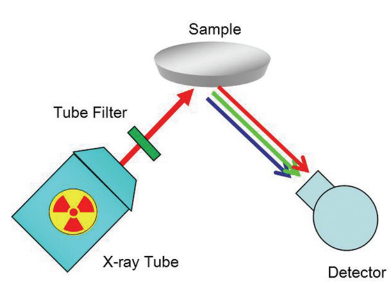


Image 1

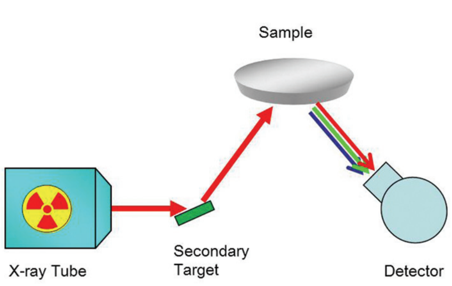


Image 2

Advances on the source excitation side of EDXRF systems include the use of secondary targets and polarisation, giving EDXRF the ability to quantify very low levels of sulphur. Direct excitation advances in more versatile filter sets that allow for the ability of more elements being measured more rapidly. Advances in detector technology over the past decade allow for the use of the higher resolution Si-based detectors, giving the operator the ability to measure more elements with a single analyser and scan or screen for unusual elements that may be present. Modern semiconductor detectors also provide vastly improved stability and reliability.

Software and user interfaces have also gone through modernisation in the 21st century. Touch screen computers now allow low cost analysers the ability to offer simple software designs for the non-technical operator, and an array of logging features, including the ability for network logging.

Instrumentation Used

The data shown in this article was generated using Rigaku NEX QC (direct excitation) or Rigaku NEX CG (indirect excitation with polarisation).

Crude Oil as per ASTM D4294

For crude oil, the regulations limiting sulphur content greatly affect the industry. As sweet crude reserves become harder to find, more blending now than in the past is required of sour crude with some sweet, to yield sulphur levels right at the set point for the refinery feedstock. More attention is now taken towards exact and precise blending.

The following shows typical performance of low cost EDXRF using Si detector technology and 100 sec measurement time for the analysis of sulphur in crude over a concentration range used for blending. Comparable performance is achieved measuring sour crudes 0.5-5.0% sulphur.

Element: S	Std Error of Est: 0.0028	
Units: %	Correlation: 0.99995	
Sample I.D.	**Standard Value**	**Calculated Value**
STD 1	0.10	0.098
STD 2	0.30	0.304
STD 3	0.50	0.499
STD 4	0.70	0.698
STD 5	1.00	1.001

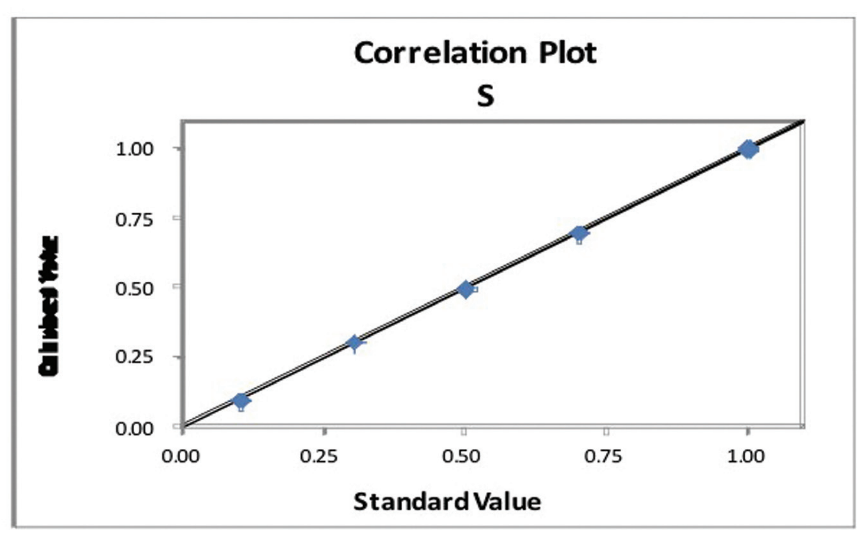


Table 1: Calibration for Crude

And adulteration may be an issue. Crude contaminated with chlorine may foul the refining process, and with more offshore crude being refined, the detection of Cl is more important than

Element: S	Units: %			
Sample I.D.	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
STD 1	0.10	0.0994	0.001	1.0
STD 3	0.50	0.5035	0.003	0.6

Table 2: Repeatability (precision) for Crude

ever. Left undetected or uncorrected, the chlorine content can bias the sulphur reading, in addition to having other deleterious effects on the process. EDXRF with the higher resolution Si-based detectors is ideal for qualitative and quantitative screening. Shown here are typical spectra using EDXRF direct excitation and Si detector.

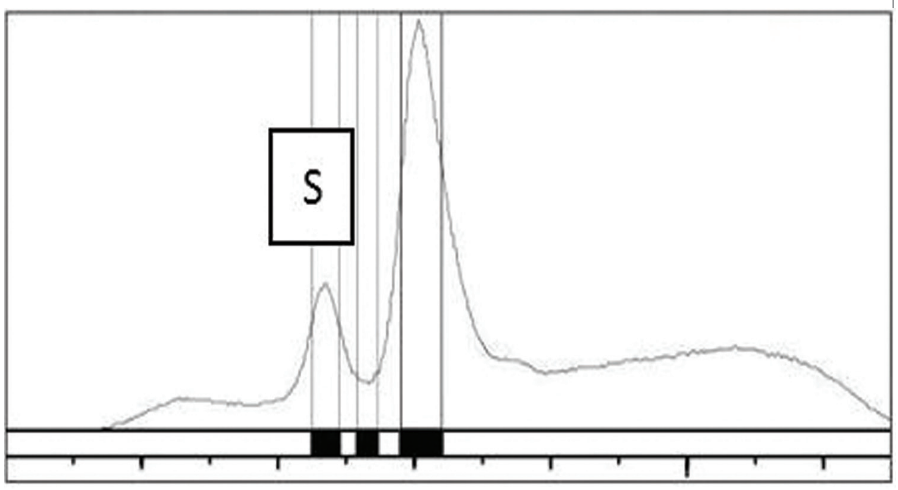


Image 3: Direct excitation spectrum showing S

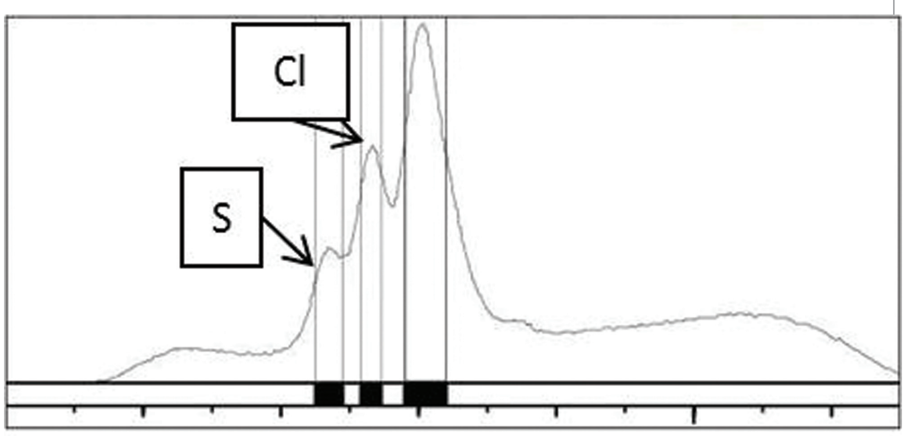


Image 4: Direct excitation spectrum showing S and Cl

Bunker Oil, Residual oil and Marine Fuels

Many countries around the world comply with the ship pollution rules as set out by the International Maritime Organisation (IMO) at the International Convention on the Prevention of Pollution from Ships, known as MARPOL 73/78. In the last decade, in an effort to continue to reduce pollution caused by burning fossil fuels, MARPOL Annex VI directives further limit the allowed sulphur content of bunker fuels by establishing Sulphur Emission Control Areas (SECAs) or ECAs (general Emission Control Area including regulation of carbon gases) near and in major European and Asian ports. ECAs are defined protected areas in which only low sulphur bunker fuels and marine diesels can be used while in or near port. In August, 2012, the US/Canadian ECA goes into effect. It is therefore critical to monitor the sulphur content to ensure regulatory compliance and to improve air quality, affecting those utilising, as well as producing and supplying bunker fuels. Low cost EDXRF instrumentation is essential to meet this industry need.

The previous data shown for crude oil is also applicable to residual oil, bunker fuels and other heavy hydrocarbon oils. The data that follows shows EDXRF direct excitation with Si detector performance using 100 sec measurement time for monitoring diesel fuel at the typical levels found in marine diesels.

Element: S	Units: %			
Sample I.D.	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
STD 1	0.10	0.103	0.001	1.0
STD 3	0.50	0.496	0.002	0.4
STD 5	1.00	1.008	0.003	0.3

Table 3: Repeatability (precision) for Marine Diesel

Diesel and Fuel Oils

The use of EDXRF for the sulphur measurement is also in high demand around the world, as various global regions continue to strive for lower sulphur content in fuel oils. Typically, all the major fuel oils can be measured using EDXRF for sulphur content. These include diesel, off-road diesel, jet fuels, kerosene, heating oils, naphtha and other middle distillates. Gasolines and some biofuel products are also well served by the EDXRF technique.

Several regions in the world have already adopted a maximum limit of 10-15 ppm sulphur in diesel, and as this trend continues more global regions have brought or are bringing the sulphur level down to the 50 ppm level in diesel. The data shown below indicates typical performance over the range 20-100 ppm using EDXRF direct excitation, Si detector, 300 sec measurement time and helium purge for optimum sensitivity.

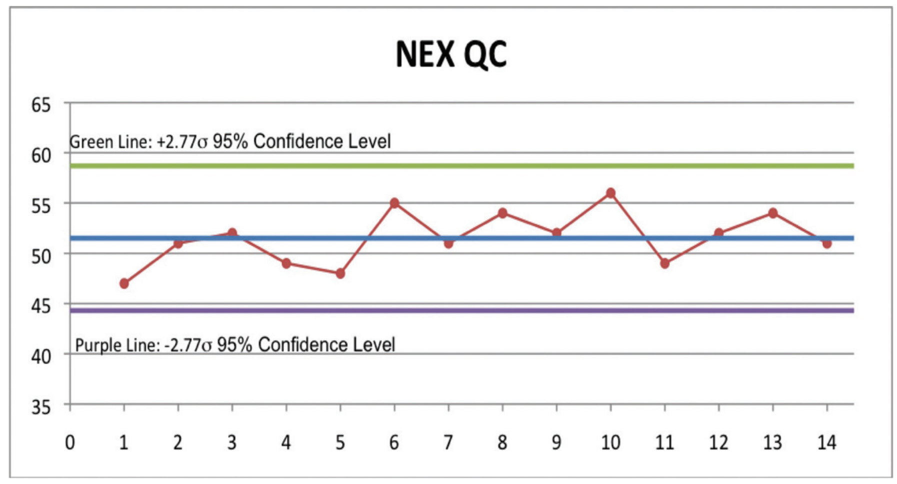
Element: S	Units: ppm			
Sample I.D.	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
STD 1	20	18	3.7	19
STD 2	50	52	2.0	4.0
STD 4	100	102	3.0	3.0

Table 4: Repeatability (precision) for Diesel

EDXRF also provides exceptional long term reproducibility as compared to other atomic spectrometric techniques. The following shows results measuring a 50 ppm sample over a 10-day period using EDXRF direct excitation with Si PIN diode with same measurement conditions as used for Table 5.

Sample: 50.0 ppm S in Diesel	Units: ppm			
	Standard Value	**Average Value**	**Std Dev**	**% Relative**
NEX QC	50.0	51.5	2.6	5.2

Table 5: Reproducibility at 50 ppm sulphur over a 10-day period



Cart 1: Table 6 presented as a control chart

ULSD

Progression towards ultra-low sulphur diesel will continue to proceed around the world over the next several years. Refineries want to control sulphur at levels even lower than the regulatory maximums of 10-15 ppm, to ensure regulatory compliance after as the diesel is transported to consumer locations. EDXRF using secondary targets and/or polarisation is an excellent technique for monitoring sulphur content down to 3 ppm.

ASTM recently published standard test method D7220-12 for use with monochromatic EDXRF instrumentation. Such systems can deliver a sulphur detection limit on the order of 0.5-1.0 ppm, and the method shows an excellent PLOQ (pooled limit of quantification) of 3 ppm across several analysers and different operators.

The data that follows shows ULSD performance for monochromatic EDXRF using polarisation and measurement time of 300 sec.

Element: S	Units: ppm			
Sample	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
2	5	5.2	0.2	4.0
3	10	10.1	0.2	2.0
4	15	14.6	0.2	1.4
7	50	49.6	0.3	0.6

Table 6: Repeatability (precision) for ULSD

International Norms

Shown below are tables of international standard test method norms used in the petroleum industry for measuring sulfur with EDXRF instrumentation.

ASTM D4294	ISO 20847	ISO 8754	IP 496	IP336	JIS K 2541-4
16 ppm – 5%	**30 -500 mg/kg**	**100 mg/kg – 5%**	**100 mg/kg – 5%**	**100 mg/kg – 5%**	**0.01 – 5%**

Table 8: Norms using direct excitation EDXRF instrumentation

ASTM D7220-12	IP 352
3 – 942 ppm	**6 – 50 ppm**

Table 9: Norms using indirect excitation monochromatic EDXRF instrumentation

Conclusion

XRF has long played an important role for elemental analysis in the petroleum industry. With the advent of modern EDXRF instruments, measurement requirements can be met as global regulations continue to bring sulphur levels down in fuels. Low cost EDXRF instrumentation using a Si detector now give the operator a simple means of screening and quantification of other elements, such as chlorine in crude, and is ideal for measuring sulphur in a variety of oils and fuels and in blending operations for crude as well as bunkers to meet expanding MARPOL Annex VI regulations. Monochromatic EDXRF using polarisation offers the industry a reliable means to meet the ultra-low sulphur levels demanded around the world. With such modernisation, EDXRF is well suited to meet the petro demands today and moving forward in the 21st century.

Read, Print, Share or **Comment** on this Article at: **Petro-Online.com/Articles**