Sulfur Determination
From Crude Oil to Gasoline

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With federal and international regulations, as well as traded fuel specifications, becoming more and more stringent, the determination of sulfur content is a critical value in quantifying petroleum oils and fuel products. Sulfur determination is increasingly important, affecting not only the environment through sulfur emissions when fuel is burned, but also the price of crude oils and other base products. In 2006 US road fuels will be required to contain no more than 15 mg/kg sulfur, with regulations for off-road fuels soon following suit to this ultra-low sulfur limit. In the coming years regulations and traded specifications may limit sulfur content even more. Accurately measuring and monitoring sulfur is therefore of prime importance, from crude oil and bunker fuels to refined fuel products such as gasoline and diesel. In today's' petroleum market especially, minimizing cost and maximizing profit requires close monitoring of crude oil and fuels in pipelines, shipping transport and crude oil blending, as well as throughout the refining and distribution processes in bringing diesel and gasoline to the consumer. Fuels such as bunker fuel and residual oils are also closely regulated. Accurate measurement of not only sulfur, but also of additive elements or wear metals is essential in the characterization of other petroleum products such as residual oils, lube oils, motor oils and used waste oils. A broad array of instrumentation has been developed to meet the demand of such oil characterization and quality control.

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Monitoring sulfur is important throughout the entire refining process. (Picture licensed for SPECTRO) Monitoring sulfur is important throughout the entire refining process. (Picture licensed for SPECTRO)

Instrumentation for monitoring sulfur in petroleum products is becoming more and more critical as regulations and traded specifications tighten. To meet this need SPECTRO Analytical Instruments has had focussed programme to develop a full product line of analytical analyzers designed for the accurate and precise measurement of sulfur and other elements present in all types of petroleum oils and products, indeed most hydrocarbon matrices. SPECTRO analyzers are designed for use in almost every facet of the refining process, with emphasis placed on the final goal of measuring sulfur in gasoline and diesel. Beginning with the transportation and blending of crude oil, the need for close monitoring of the sulfur content is important throughout refining and distribution processes in order to monitor and track the original sulfur content of the crude oil. Applications include measuring sulfur in crude oil, refinery feed-stocks, refined fuel products and bunker fuels. SPECTRO instrumentation is also employed in the analysis of many elements in addition to sulfur in related oils such as lubricating oil, residual oils and used or waste oils. Uses for sulfur monitoring include pipeline and ship-borne transport of crude oil fuels products, blending operations, refining processes and the sale and distribution of refined oil products. SPECTRO analyzers cover all the day to day refinery and crude operation needs for sulfur analysis, making use of on-line instrumentation as well as analyzers for at-line sulfur measurement and applications in the laboratory.

Techniques

Various techniques are used throughout the refining process to monitor several oil parameters. X-ray and electrochemical techniques are ideal for the measurement of sulfur throughout refining, from the transportation and delivery of crude oils to the consumer products diesel and gasoline. Three techniques are especially useful in monitoring sulfur content: XRT (X-ray Transmission), XRF (X-ray Fluorescence) and P-EC (Pyro-Electrochemical). These techniques encompass the entire spectrum of sulfur monitoring, including on-line, at-line and laboratory measurement. The X-ray techniques make use of low energy "soft" X-rays for safe, efficient monitoring, while the pyro-electrochemical method safely combusts the oil, measuring sulfur content with an electrochemical detection system.

The SPECTRO 682T-HP on-line XRT analyzer is compact and efficient.

XRT

The transmission method, XRT, is a rugged analysis technique used on-line to measure sulfur in the heavier, more viscous oils, such as crude oil and bunker fuels. Because these oils are dense and viscous they are pumped at higher temperatures and pressures than refined fuels, often being pumped with a pressure of up to 800 psig. XRT lends itself well to such a measurement. As the oil flows through a sampling tube, X-rays are passed through the oil to a detector on the opposite side of the flow. Since sulfur blocks and absorbs X-rays to a much greater extent than the hydrocarbon oil matrix, sulfur concentration in the oil is related to the amount of X-ray radiation reaching the detector. Therefore, as the sulfur concentration increases the transmission of X-rays decreases. For this reason the XRT technique is sometimes referred to as XRA (X-ray Absorption) or the transmission-absorption method.

XRF

The fluorescence method, XRF, utilizes an X-ray source similar to the transmission method, however in XRF the X-rays do not pass entirely through the sample. Source X-rays impinge upon the oil or fuel and cause the atoms in the oil to emit their own characteristic X-rays due to the process of fluorescence. Each characteristic fluorescent X-ray detected is unique to the atom that produced it; and so by measuring the energies of the fluorescent X-rays coming from the hydrocarbon matrix, the X-rays emanating from sulfur are counted and sulfur concentration is determined. XRF is used in all areas of refining and distribution, including on-line, at-line and in the laboratory.

P-EC

P-EC is a pyrolosis technique, converting the sulfur in oil to sulfur dioxide gas, which is collected and measured by an electrochemical sensor. Using P-EC, the sample is first flash burned to convert the sulfur to sulfur dioxide. Once in gaseous form, the sample is automatically introduced into an electrochemical sensor which measures the sulfur concentration. P-EC is an ideal method for the reliable on-line measurement of ultra-low sulfur in diesel and gasoline, as well as other light distillate hydrocarbons.

Uses

With regulations tightening this year many refineries and facilities are gearing up now with instrumentation that greatly improves the measurement of sulfur, especially as the crude barrel becomes more sour and higher in sulfur. These higher sulfur crudes requires optimal crude blending with lower sulphur crudes to minimize expensive refinery process plant corrosion problems. XRT instrumentation is used for measuring sulfur on-line in crude oils and bunker fuels, in transport including pipelines and ships, in pipeline terminals both in and out of the refinery and in blending operations. In the X-ray transmission method X-rays are passed completely through the sample volume, thus eliminating such problems as coating build-up on the flow cell window. Coating build-up in flow cells can bias the sulfur result in other techniques, but with X-ray transmission the flow cell is rugged and sturdy, making it an excellent technique for measuring thick oils, such as crude oil or heavy fuels being pumped at high pressures.

The XRF technique, being more comprehensive than XRT, is used throughout the entire petroleum industry. While XRF is used on-line for measuring sulfur in light refined fuels like diesel and gasoline, it is used extensively at-line for monitoring and quality control, as well as in the lab for detailed crude oil analysis and R&D refinery process pre-evaluations. The XRF method is better suited for the measurement of lower levels of sulfur than XRT, while adding the capability for measuring other elements as well.

In order to accurately determine the sulfur content when in ultra-low levels, below 30 mg/kg and especially below 10 mg/kg, more advanced instrumentation is required. SPECTRO's program for ultra-low sulfur determination includes both XRF for at-line and lab measurement and the pyro-electrochemical method for on-line measurement of sulfur in gasoline and diesel.

Instrumentation

The SPECTRO on-line XRT analyzer uses an X-ray tube to generate source X-rays directed through the flowing crude oil or fuel sample. A simple detection system opposite the source X-ray tube is used to count the X-rays that pass through the oil. Because variations in oil density can cause variations in the X-ray transmission independent of the sulfur content, an internal densitometer is used to measure density and the instrument software automatically compensates for density changes between various crude oils. For environments requiring explosion proof instrumentation, internal nitrogen purge is used to evacuate oxygen from the analyzer cabinet and a full explosion proof enclosure is available, to help ensure accidents don't become catastrophic. A simple touch screen interface allows for a non-technical operators to easily check the status of the analyzer. Sulfur results are displayed on the screen and can be sent to an external computer via a 4-20 mA current loop. Optional outputs include standard industrial Bus protocols for use with a LIMS protocol. Recently, in collaboration with a major international oil company, the application of the XRT analyzer has been a proven success for a marine fuel inline supply project for ship fuel bunkering where the use of the ASTM D 6708 statistical tool has shown excellent equivalency of the XRT technology to ASTM D 4294 the industry standard XRF method for marine residual fuels.

All SPECTRO XRF analyzers employ EDXRF (Energy-dispersive XRF) and use various XRF techniques to measure sulfur and other elements. The benchtop XRF models used at-line make use of an X-ray tube with polarized excitation to fluoresce the atoms in the oil. Polarized excitation eliminates much of the background noise in order to measure the sulfur X-rays more efficiently. The gas-filled proportional counter in the SPECTRO PHOENIX II is a highly reliable detection system that yields high X-ray count rates for excellent precision of measurement. The polarization technique is coupled with a high resolution SDD (silicon drift detector) in the SPECTRO iQ. The solid-state SDD detector yields extremely sharp elemental peaks, ideal for multi-element analysis, especially when measuring elements that are adjacent in atomic number, like sulfur and chlorine. The SPECTRO iQ is the ideal technology for ultra-low sulfur applications. All SPECTRO analyzers are rugged and designed for use by non-technical personnel.

Powerful tool (or "instrument") for scientists, the SPECTRO PHOENIX II benchtop XRF analyzer is also user friendly for non-technical operators.

Applications requiring the on-line analysis of sulfur are served by SPECTRO's on-line XRF analyzers, while SPECTRO offers the pyro-electrochemical on-line analyzer for ultra-low sulfur determination in diesels and gasolines. The on-line XRF instrument uses the same system as the benchtop analyzers, engineered to accept on-line flow through a sample flow cell. XRF is a non-destructive technique that does not change the atoms or atomic structure of the crude oil or fuel, and so the sample can be returned to the main line after analysis. The P-EC technique is of course destructive, since it combusts the sample. Here a slip stream is set-up to divert a small portion of the main oil stream to the instrument. Once combusted, the sulfur in the crude oil or fuel is converted to sulfur dioxide. The sample is "washed" of nitrogen dioxide through the conversion of NOx to NO, before entering the electrochemical sensor for sulfur concentration determination. Like the XRT analyzer, this instrument is equipped with an easy-to-use interface and sulfur results are displayed on the screen, and can be sent to an external computer via a 4-20 mA current loop, with the optional outputs for use in a LIMS protocol.

Performance

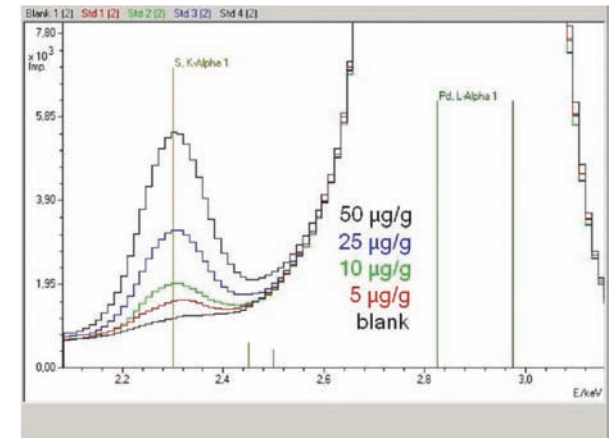
Since so much depends on the sulfur analysis, both through regulation and pricing, high-performance instrumentation is vital. Precision and accuracy are key for a quality sulfur monitoring program. Precision, often referred to as repeatability, is a measure of how closely an analysis result repeats over several analyses, while accuracy is defined as how closely a sulfur measurement relates to the "true" sulfur value.

Precision is mainly dependent on the reliability and repeatability of the analysis instrumentation. The measurement of precision is the observed standard deviation of several repeat analyses of a sample without operator interaction. Closely related to the precision repeatability is reproducibility, which is a measure of how an analyses repeats when different operators, sample aliquots, instruments and locations are involved. While precision is highly dependent upon the instrumentation, accuracy, or closeness to the "true" value, is mainly dependent on the samples used to calibrate the analyzer, the accuracy of their assay values and proper calibration. The S.E.E. (standard error of estimate) is often used as the measure for accuracy for building a calibration fit: the lower the S.E.E., the more accurate the calibration model. (The S.E.E. is a number closely related to the R.M.S. deviation of the calibration fit: the R.M.S deviation takes into account the total number of samples minus one used in the calibration, while the S.E.E. takes into account the degrees of freedom in the calibration fit. Either is good measure of the quality of the calibration.)

Long-term stability is achieved in the SPECTRO instruments through the use of automatic internal stabilization protocols, while calibration drift is held in check through the use of stable and rugged detection systems, as well as with simple standardization routines. If required for an application, the need for standardization is infrequent (monthly or every other month, for example) and easily implemented by an operator in less than a few minutes. Such standardization is automated with on-line analyzers.

Calibration & Accuracy

In all three techniques, XRT, XRF and P-EC, calibration is used to initially configure the instrument for the measurement of sulfur concentration. Once calibrated, the calibration does not need to be updated for several months to a year, depending on the application. Calibration is achieved by analyzing a set of assayed reference samples and obtaining a relationship between concentration and X-ray intensity, or in the case of the pyro-electrochemical method between concentration and electrochemical potential. Reference samples for calibration in most petroleum products are available commercially and are often traced to a NIST SRM (Standard Reference Material, SRM is a registered trademark of NIST). When commercial calibration samples are not available, actual product samples are used that evenly cover the sulfur range of interest. For such calibration samples assays must simply be determined using techniques such as an established XRF analyzer already calibrated, or a different method.



The advanced polarized X-ray optics of the SPECTRO iQ are ideal for measuring ultra-low levels of sulfur.

Limit of Detection, Limit of Quantification

The detection limit is the point at which a sample first becomes distinguishable from the background in the measurement and gives an indication of how sensitive a certain technique is capable to acheive. In the empirical method the detection limit is defined as 3X the standard deviation of ten repeat analyses of a blank sample containing no sulfur. The lowest concentration level that can be more reliably measured is called Limit of Quantification. The Limit of Quantification is generally taken to be 10X the standard deviation of ten repeat analyses of a blank sample containing no sulfur and is the lowest concentration at which two differing concentrations can be reliably distinguished from each other with a 95% certainty. When selecting analytical equipment, one of the criteria certainly has to be the Limit of Quantification or the Limit of Detection, as this should fit to the purpose of the analysis.

Precision and accuracy requirements are often described in international standard test methods. SPECTRO products fulfill these requirements perfectly.

	EDXRF	EDXRF	Online EC	Online LP	Online HP
	SPECTRO iQ	SPECTRO PHOENIX II	SPECTRO 682P-EC	SPECTRO 682T-LP	SPECTRO 682T-HP
ASTM D7220	X				
ASTM D4294	X	X		**	*
IP 532	X				
IP 496	X	X			
IP 336	X	X			
ISO 8217	X	X			
ISO 20847	X	X			
ASTM D6920			X		

* Meets performance criteria of ASTM D4294 above 2000 ppm sulfur
** Meets performance criteria of ASTM D4294

Conclusion

Regulations and specifications are getting tighter and cost optimization of reducing "product giveaway" is becoming more and more critical. Now more than ever monitoring sulfur in petroleum crude oils and fuels is of the utmost importance, with even stricter rules coming in the near future. The wide range of improved instrumentation options makes it possible to accurately and precisely measure and track sulfur in oil. Almost every aspect of petroleum shipping, blending, refining and production for consumer use are affected. This makes a comprehensive sulfur analysis regime imperative in the changing petroleum industry. With analyzers designed for on-line and at-line use, SPECTRO Analytical Instruments meets the industry needs with a full line of analyzers ideally suited for sulfur analysis. From the XRT on-line method for measuring sulfur in heavy crudes and bunkers, to various XRF and P-EC techniques for on-line, at-line and laboratory analysis of refined petroleum products, SPECTRO has the key to a high-quality instrumentation program of hydrocarbon product monitoring and control. Ease-of-use is a cornerstone for at-line use by non-technical operators, while SPECTRO analyzers offer the scientist in the laboratory versatile analysis methods for measuring more than just sulfur content. But sulfur is the key, and minimizing sulfur content in fuels is the goal to be achieved. In order to maximize profit and meet regulatory demands, sulfur measurement and monitoring is essential for success in the petroleum industry.

Footnotes:

SPECTRO is one of the worldwide leading suppliers of analytical instruments for optical emission and X-ray fluorescence spectrometry. As a member of the AMETEK Materials Analysis Division, SPECTRO manufactures advanced instruments, develops the best solutions for strongly varying applications and provides exemplary customer service. Innovation, instrument concerns and customer relations are its main activities. From its foundation in 1979 until today, more than 24,000 analytical instruments have been delivered to customers around the world. AMETEK, Inc. is a leading global manufacturer of electronic instruments and electromechanical devices with annualized sales of more than 1.6 billion US$.