Measuring sulfur content with pinpoint precision is a demanding requirement within hydrocarbon processing, particularly at refineries and petrochemical plants. In downstream environments, instrumentation for sulfur analysis enables organizations to more efficiently meet regulations regarding low sulfur fuel, motors oils as well as put measures in place that ensure ongoing product quality, catalyst protection, reduction of manufacturing costs and optimization of operational efficiency. Thermo Electron Corporation, a leading manufacturer of process instrumentation, is continuing to install its SOLA II, an online total sulfur analyzer, at a rapid pace within refineries worldwide. The SOLA II eliminates labor-intensive laboratory sampling by providing an online, analytical means for continuous quality control of total sulfur content in liquid hydrocarbon fuel and gaseous process streams. The reliability of the SOLA II has been brought to light by the Consortium of Refineries (COR), a group that monitors and cross-checks sulfur instruments and data amongst quality-driven laboratories. The focus of the COR is to assist and support its members by enabling each to routinely verify their laboratory is capable of meeting new Environmental Protection Agency (EPA) sulfur testing requirements. Lyondell Citgo, a prominent member of COR and one of its primary product evaluators, uses the SOLA II as an authoritative source to verify laboratory sampling.

**Sulfur Analysis Regulations Continue to Put Pressure on Plants**

Clean fuel production requires reliable, accurate and robust real-time chemical analysis. A sulfur analyzer enables pipeline and terminal operators to determine the total sulfur content of fuels entering the pipeline system. Refineries install the SOLA II in gasoline blending and hydrotreating units to provide process engineers with real-time data as well as to monitor the final product during blending operations. The system provides a reliable means to rapidly identify sulfur contamination sources that require corrective action. As a result, refineries prevent downgrading of valuable ultra-low sulfur fuels by fuel blending. The FCCU, the gasoline blend stock that contributes the most sulfur to the final product, is the processing unit monitored most often during each gasoline blend header. Several refineries have certified the SOLA II and can now allow blending directly to the pipeline, eliminating the need for storage facilities. Online sulfur measurements are also commonly used in diesel hydrotreating units to ensure the product is within specification.

While global clean fuel initiatives have brought attention to the amount of sulfur allowed in motor fuels, contracts for many years running have specified the acceptable sulfur content in petrochemical products, including aromatics, olefins and other intermediate products. The SOLA II Trace, an adaptation of the SOLA II that measures sulfur in parts per billion (ppb), provides process engineers with valuable real-time measurements, enabling timely process adjustments before the final product is released. Laboratory measurements are taken several times a day, which facilitates process optimization by ensuring the product’s sulfur content is continuously within specification.

Another common industry concern is catalyst poisoning. Moisture, sulfur and nitrogen compounds that are found in hydrocarbon feed stock or in intermediate stock can adversely affect some types of catalysts. To avoid excessive replacement expenses and even costly shut-downs that also result in lost production, sulfur removal processes are employed prior to the reactors to maintain sulfur levels within operational limits. The SOLA II can conduct a total sulfur analysis on the inlet (feed forward control) or on the outlet (feed back control) of the sulfur removal process to control the sulfur level of the hydrocarbon feed into the reactor catalyst. Sulfur level readings on the outlet are often in the <1 part per million (ppm) measuring range. Online measurement of total sulfur in reforming and isomerization feeds has enabled many plants to take timely corrective actions to prevent catalyst poisoning, resulting in maximum product yield, optimum product quality and improved operational efficiencies. A Thermo customer with plant operations based in Scotland reported a savings of £10 million in catalysts during its first year of SOLA II implementation.

**Evaluation of the SOLA II**

Thermo’s SOLA II has proven to lower costs of desulfurization processes by providing an accurate, reliable process for conducting laboratory analysis in the field. It is an industrialized sulfur analyzer intended for use by non-laboratory personnel. When configured for at-line sulfur analyses, the SOLA II provides a simple, straightforward means of determining grab sample sulfur content. Fully-automated sample preparation negates the need to load vials, syringes or sample cups. The system is equipped with an on-board statistical analyzer that verifies the validity of each analysis.

The SOLA II is an online adaptation of the ASTM Method D4293 “Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence” and the ISO Method 20846 “Petroleum Products – Determination of Sulfur Content of Automotive Fuels – Ultraviolet Fluorescence Method.” It has regularly demonstrated excellent agreement with all laboratory total sulfur measurement methods, including ASTM D4293, ISO Method 20846, lead acetate colorimetry, and ASTM D2622. The major components of the SOLA II include a sample injection valve, a carrier gas flow control system, a mixing chamber, a Pyrolyzer, an optional dryer and a pulsed ultraviolet fluorescence (PUV) detector.
The SOLA II uses an automated sample injection valve to precisely control sample introduction. An air carrier gas is used to deliver the sample from the injection valve to the air bath oven. The air bath oven provides the necessary heat to fully vaporize all components of liquid sample. The hydrocarbon/air mixture next enters the mixing chamber where additional air is added. On exiting the mixing chamber, the sample is fully combusted to carbon dioxide ($CO_2$), water ($H_2O$) and sulfur dioxide ($SO_2$) in the 110°C Pyrolyzer. The Pyrolyzer enables sample combustion using air only and does not require a source of pure oxygen to perform conversions, eliminating oxygen-related safety concerns in a process environment.

Pyrolysis is used to convert all organically bound sulfur to sulfur dioxide ($SO_2$). At the measurement cell, the sample is irradiated with ultraviolet light, resulting in an electrically excited state. The electronic transition results in the emission of light at a slightly longer wavelength. The photomultiplier tube, PMT, measures the intensity of the resulting fluorescence. Next, the PMT signal is processed to provide data communications to the process control system which should indicate that the intensity of the emitted light is directly proportional to the total sulfur content of the sample. The photodiode serves as the heart of the feedback circuit to ensure that the intensity of the ultraviolet, UV, flashlamp remains constant throughout the useful life of the lamp. Maintaining a constant UV light intensity is a competitive feature of the SOLA II that assures calibrations are held stable over a long period of time. The low maintenance PUVF detector has a longer life and can detect limits at lower levels than non-pulsed UV systems, with the ability to measure as low as 0.25 ppm S. Full-scale measurement ranges from 0.5 ppmv to 0.3,000 ppmv.

A practical application is measuring total sulfur in motor fuel. New samples are introduced to the analyzer every 30 seconds, and each sample is mixed with air and combusted. At this point, sulfur compounds are converted to $SO_2$ and the amount of $SO_2$ is quantified by the PUVF spectrometer. The SOLA II responds to a change in total sulfur concentration immediately following sample injection and indicates the direction of change in the sulfur concentration every 30 seconds, enabling rapid detection of pipeline interfaces and slugs caused by sulfur contamination.

**Determination of Total Sulfur in Reforming and Isomerization Feeds**

The total sulfur content of reforming and isomerization feedstocks is typically controlled to less than 0.5 ppm. To prevent catalyst poisoning, online measurement of total sulfur in these feeds is necessary to obtain precise data that enables detection before any damage occurs. The SOLA II Trace was engineered to detect sulfur levels in ppb to detect very low sulfur concentrations.

During isomerization processes, straight chain hydrocarbons are rearranged into branched isomers. One isomerization process utilizes an n-butane rich feedstock with the resulting goal of converting n-butane to iso-butane. This iso-butane is utilized as a feed component to other reforming processes, such as alkylate.

Light straight run naphtha is a typical feedstock for a common isomerization process. Variations of this isomerization process include benzene hydrogenation capability to meet reformulated gasoline specifications. All isomerization feedstocks are desulfurized to prevent catalyst poisoning. Isomerization of light straight run naphtha results in a valuable, high octane, low sulfur gasoline blend component.

To produce aromatic intermediates for the petrochemical feedstocks and high octane, low sulfur feed components for the gasoline pool, catalytic reforming of naphtha boiling range hydrocarbons, typically $C_6$ to $C_9$ paraffins, naphthenes and aromatics, is used. Normally rich in paraffins and naphthenes, feedstocks undergo a variety of mainly endothermic conversion processes that include dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins, isomerization of paraffins and naphthenes, dealkylation of alkylaromatics, hydrocracking of paraffins to light hydrocarbons, and formation of coke. The heavy products produced in the reforming process is increasingly valuable as refineries work to satisfy the increased demand for clean fuel production processes.

The ability to determine trace sulfur online is critical to maintaining optimal plant performance. Sulfur in the isomerization feedstock is undesirable because it reduces the activity of the isomerization catalyst by forming metal sulfides that eventually reduce the amount of active metal sites needed for the formation of high octane branched chain $C_8$ isomers. For one isomerization catalyst at 98% $C_8$ yields, the presence of 133 ppm sulfur reduces the Activity of the isomerization catalyst by 10%. This 10% reduction decreases the production of high octane isomers and results in lower octane yield. Sulfur components in isomerization feeds are measured in terms of total sulfur (as sulfur) which indicates that the intensity of the emitted light is directly proportional to the total sulfur content of the sample.

The SOLA II Trace enables timely corrective actions and ensures that isomerization and reforming processes produce maximum product yield and optimum product quality.

**Conclusion**

The precision and repeatability of the sulfur content readings enables SOLA II users to make timely process adjustments as needed to ensure desulfurization or blending operations yield product at the targeted sulfur specifications. Repeatability is measured in terms of standard deviation, with long-term repeatability runs of diesel, gasoline and natural gas samples indicating excellent measurement precision.

Lyondell Citgo uses Thermo’s SOLA II to conduct laboratory sample checks with standards that are traceable to the National Institute of Standards and Technology (NIST). “Lyondell Citgo illustrates Thermo’s ability to bring industry leading products to market,” said John Schwin, director of sales for Thermo Electron’s Process Systems business. “We understand the critical needs within the hydrocarbon processing industry, and we are committed to manufacturing reliable products that enable our customers to optimize their operations and achieve a higher quality product.”

**Functionality of the SOLA II**

- **Measurement ranges**: 0.25 ppm S to 0.50 ppm S for exceptional precision
- **Automatic density compensation**: for ppm S (wt/wt) measurements
- **99%+ online time ensures reliability**
- **Sample combustion uses air only; no pure oxygen is required**
- **Longer life and ability to detect lower limits than non-pulsed UV systems**
- **Comprehensive diagnostics maximize analyzer up-time by eliminating the potential for coke or soot formation**
- **Automatic calibration and automatic control of UV light intensity to hold calibrations steady over a long period of time**
- **Semi-continuous operation that indicates the direction of change in sulfur concentration every 30 seconds**
- **Remote operation enabled via the unique web browser interface, SOLAWeb**

**Applications for the SOLA II**

- **Diesel**
- **Gasoline**
- **Kerosene**
- **Jet fuel**
- **Naphtha**
- **Natural gas**
- **Refinery feed gas**
- **Liquified petroleum gas**