

# Apply online analyzers to monitor ‘sulfur-free’ fuel

## New x-ray fluorescence methods enable real-time detection of low sulfur concentration in hydrocarbons

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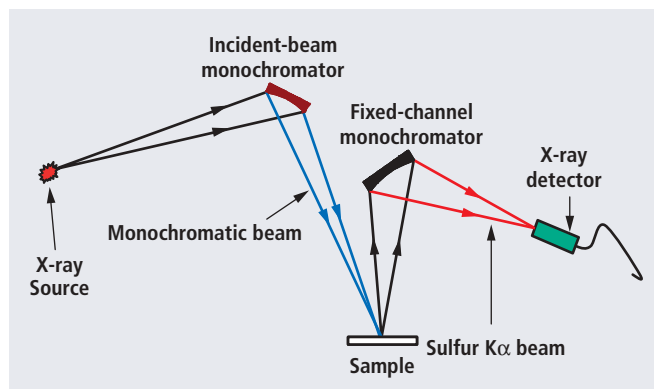
Globally, refiners worldwide are dramatically reducing the sulfur content of onroad gasoline and diesel fuels. Some European refiners are producing diesel fuels below 10-ppm sulfur (S) content, and highway diesel sold in the US must be less than 15 ppm by 2006.

To comply with the ultra-low-sulfur fuel regulations, refiners and pipeline operators will apply online and laboratory-based sulfur-test techniques. These tools are undergoing significant improvements. Online sulfur monitoring enables using closed-loop process control; thus, refiners and pipeline operators can quickly detect out-of-spec fuel, take corrective action and identify root causes of fuel-quality problems. Pipeline operators are evaluating technology-based solutions for the successful transport of ultra-low-sulfur fuels to minimize batch contamination, downgrading and reprocessing.

**New techniques.** Several technologies are currently used for online sulfur determination in motor fuels. These methods, including UV fluorescence (UVF), gas chromatography (GC) with flame photometric detection, and energy dispersive x-ray fluorescence (EDXRF), have shortcomings in online applications, particularly in pipeline applications where response time is a critical requirement. Table 1 lists the benefits of several techniques.

Historically, XRF techniques are proven, reliable analysis tools for laboratory S determination. However, EDXRF has a significant limitation for detecting low level S in fuels due to its poor signal-to-background ratio (S/B). XRF with wavelength dispersive spectrometry (WD XRF) can improve sensitivity and precision. However, conventional WD XRF is not practical for online applications due to system complexity. Useful WD XRF measurements require x-ray tube powers in excess of 1,000 watts and must collect fluorescence from large area samples to obtain data in a reasonable time. High-pressure fuel in the sample cell restricts this technique to laboratory applications.

Recent developments have led to a new x-ray analytical approach, monochromatic wavelength dispersive XRF (MWD XRF) that enables robust, low-maintenance, online analyzers with dramatically lower detection limits and faster response times. Diffraction-based x-ray optics enable highly intense monochromatic x-ray beams using low-power, air-cooled x-ray tubes. These



**FIG. 1.** Analyzer engine configuration for new x-ray analytical techniques.

**TABLE 1.** Online sulfur detection techniques for fuels

	MWD XRF	UVF	GC	EDXRF
Lower detectable limit	<1 ppm/wt	<1 ppm/v	<1 ppm/v	<5 ppm/wt
Repeatability	<1% FS	<1% FS	<2% FS	5% FS at Tier 2 levels
Measurement response time, sec	10–300	120–300	300	60–300
Consumables	Air (purge)	Inert carrier, O <sub>2</sub> , air (purge)	Inert carrier, zero air, hydrogen	Air (purge)
Measurement type	Direct, no conversion mg/kg	Pyrolysis, measure SO <sub>2</sub> volumetric	Pyrolysis, heart cut, measure SO <sub>2</sub> volumetric	Direct, no conversion mg/kg
Preventive maintenance interval, months	6	1–2	1–2	1

three dimensionally shaped x-ray optics selectively reflect a very narrow band of x-ray wavelengths for sample excitation, according

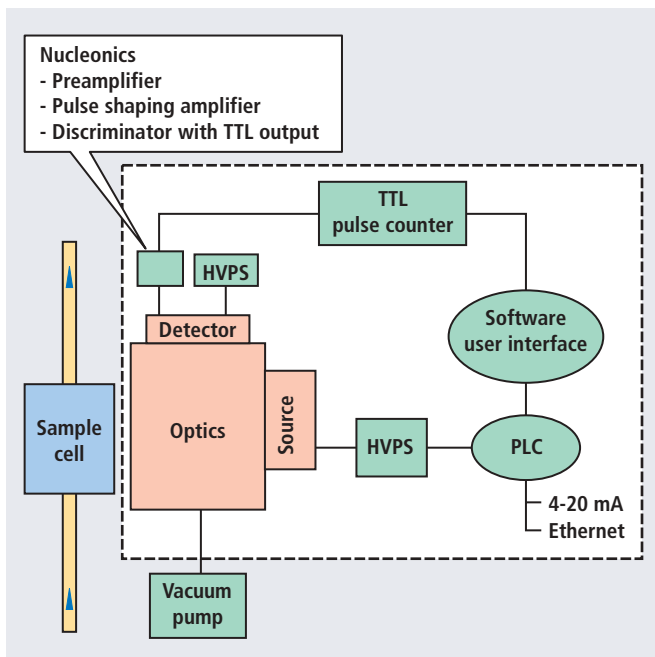


FIG. 2. Block diagram of the online MWD XRF.

to Bragg diffraction laws. MWD XRF eliminates the scattered background peak caused by the x-ray tube and improves the S/B by a factor of 10 compared to conventional WD XRF.

A compact monochromatic wavelength dispersive x-ray fluorescence (MWD XRF) analyzer uses two such x-ray optics (Fig. 1). The analyzer engine consists of a low-power x-ray tube, a point-to-point focusing optic for excitation, a sample cell, a second focusing optic for collection and an x-ray detector. In this system, the first focusing optic captures a narrow bandwidth of x-rays from the source and focuses this intense monochromatic beam to a small spot on the fuel cell. The monochromatic primary beam excites the sample and secondary characteristic fluorescence x-rays are emitted. The second collection optic, collects only the characteristic sulfur x-rays that are then focused onto the detector.

This MWD XRF analyzer provides several advantages. This technique not only achieves sub 1-ppm S detection, it also enables a much simplified and highly robust online x-ray technique. The focusing geometry of the analyzer illuminates only a small area of the sample stream, which allows a high-pressure flow through the sample cell (up to 100 psi) even with thin x-ray windows. The analyzer engine has no moving parts and does not require consumable gases or high temperature operations.

The S/B is improved by using the monochromatic excitation of the x-ray source characteristic line. Secondly, the focusing ability of the collection crystal also allows using a small-area x-ray counter, which results in low detector noise and enhanced reliability. Further, the unit has no moving parts in the analyzer engine thus raising the analyzer's robustness and reliability.

Monochromatic excitation provides another important advantage over polychromatic excitation: simplified quantification and matrix effect correction. By using a single wavelength for the primary beam, the fluorescence intensity of an element in a sample can be related to its concentration by simple equations relying on the fundamental parameters of materials at only two wavelengths.

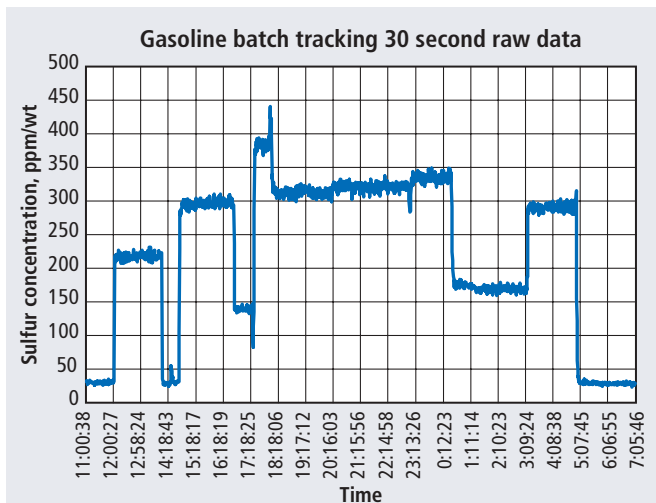


FIG. 3. Raw data collected with online MWD XRF analyzer on gasoline pipeline over a 20-hour monitoring period.

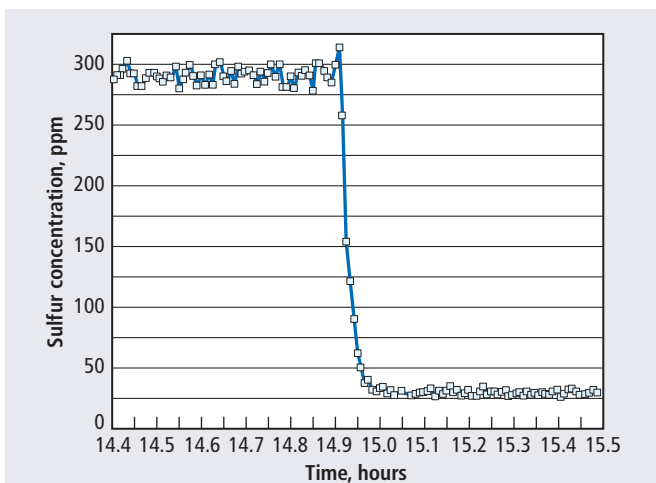


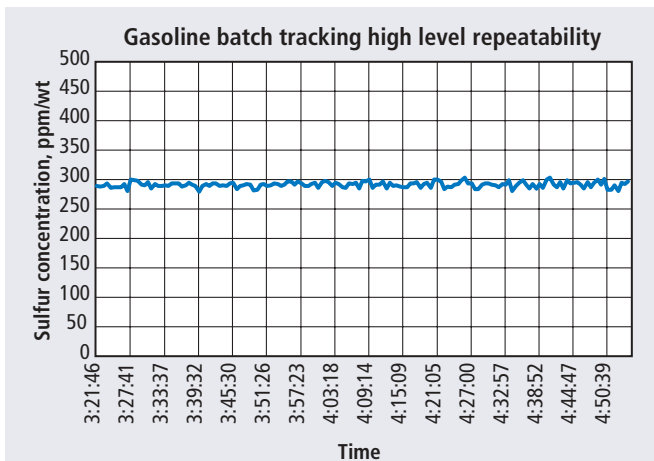
FIG. 4. Transition time from high to low sulfur levels in gasoline with 30-second measurement time.

This eliminates using sophisticated correction methods and increases the accuracy and reliability of the measurement results.

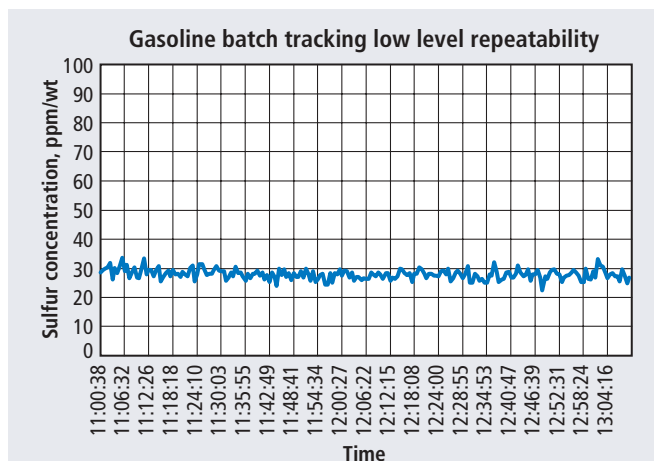
**System design.** Fig. 2 shows a block diagram of an online unit. The analyzer chamber—called the engine—consists of a low-power x-ray tube, two doubly curved crystal optics and a proportional counter detector. The engine is evacuated by a small, oil-free, explosion-proof vacuum pump to minimize the absorption of sulfur x-rays in air. The sample port is sealed to allow the sample to be analyzed at operating pressures. A sample cell contains a high-pressure flow stream with a proprietary x-ray window.

A sample delivery system provides a continuous sample stream to the cell. The maximum inlet pressure of the sample is 100 psi. A calibration inlet is used to introduce a fluid with known sulfur content for the calibration and validation of the system.

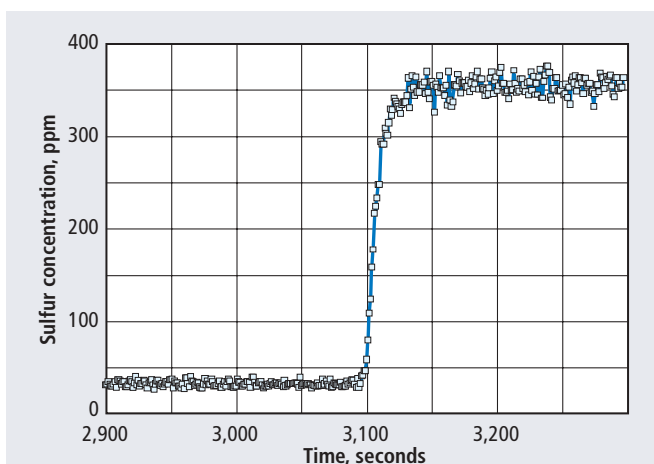
In operation, sulfur x-rays from the fuel stream are collected by the proportional counter. The counter response is converted into a TTL pulse stream by the nucleonics. A counter on the PLC registers the TTL pulses that correspond to the number of sulfur



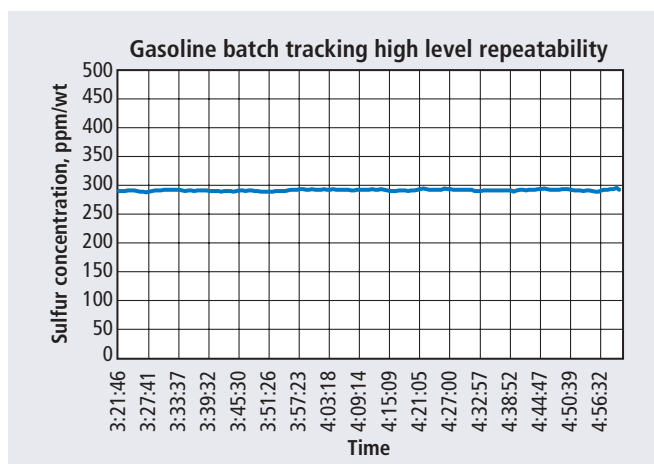
**FIG. 5.** Repeatability of high sulfur concentration levels for gasoline over a 20-hour period; measurement time is 30 seconds.



**FIG. 6.** Repeatability of low sulfur concentration levels for gasoline over a 20-hour period; measurement time is 30 seconds.



**FIG. 7.** Raw data collected at a 10-second measurement for a batch transition from low to high sulfur levels.



**FIG. 8.** Gasoline batch tracking for high sulfur concentration—repeatability of the results; measurement time is 300 seconds.

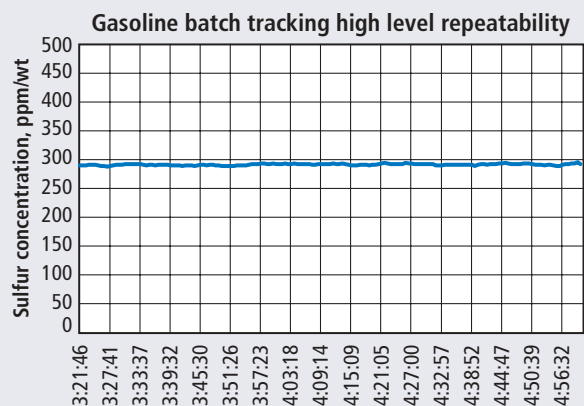
x-ray photons obtained. The relationship between the sulfur concentration in fuel and the total number of sulfur x-ray photons for a given measurement time is linear for sulfur content below 3,000 ppm. The slope and the intercept of the linear relationship is determined by a calibration curve that is obtained by using up to five sulfur-based standards with sulfur concentrations in a defined region of interest. Typically, these would cover the range of 0 to 500 ppm. The sulfur concentration in the fuel stream is determined from the number of photons counted using the slope and the intercept. The value of the sulfur concentration is converted to a 4–20mA signal as an output for the analyzer.

**Field test data.** Several units have been installed in the field for testing. The reported data are obtained from pipeline terminals. Terminals present a particularly interesting test environment as measurement precision and speed are critical. Besides monitoring product quality, terminals require fast response times to ensure that interface cuts between fuel batches are precisely executed; this avoids cross contamination or excessive downgrading. Likewise, the analyzer can continuously and nondestructively measure a sample stream. This allows

continuous flow, instantly representative of pipeline material.

Short measurement times enable fast response to sulfur concentration changes. Product pipelines routinely transport various grades of motor gasoline, diesel and jet fuel in the same physical pipeline. Batches of various fuels are butted against each other. Terminals separate batches, redirect fuel batches and organize fuel tanks. Off-spec transmix (fuel mixture between two different fuel batches) is downgraded or reprocessed. Manual sampling takes too long and results in deep interface cuts and significant downgrading. Interface cuts (to separate fuel batches) should be done based on real-time monitoring of sulfur content—measurement times of 30 seconds or less—to avoid wasting material.

**30-second measurement data.** Fig. 3 illustrates the raw data collected on a 30-second measurement time for a 20-hour period, running on a gasoline batch pipeline system. This data shows eight batch transitions during the monitoring period. From the data, the MWD XRF can quickly measure a wide dynamic concentration range without rescaling. All transitions are clean and the proprietary window system eliminates “memory effects”



**FIG. 9.** Gasoline-batch tracking for low sulfur concentration—repeatability of the results; measurement time is 300 seconds.

from earlier high concentration batches.

Fig. 4 shows data from a typical transition from high to low S levels. Ninety percent of the transition is covered by five data points. Thus, the transition timings are on the order of 2.5 minutes. No tailing or other holdup is observed, indicating an absence of sulfur retention in the sample system and window module. In comparison, if more than one data point is required to register change (a statistical requirement of many online control systems), then, with a measurement time of 5 minutes, registration of a cut of 2.5 minutes duration would occur as late as 7.5 minutes after the transition.

**Repeatability at 30 seconds.** Two stable sulfur response regions from the 20-hour period were selected for repeatability analysis, one at a high level (290 ppm/wt average) and at a low level (27 ppm/wt average). These are shown in Figs. 5 and 6 respectively.

For 290 ppm over one hour and 29 minutes, the analyzer produced a 2 sigma standard deviation of 9.74 ppm/wt, or 3.39% of the average reading. For 27 ppm in the low level period, over 2 hours and 10 minutes, the analyzer produced a 2 sigma standard deviation of 1.73 ppm/wt, or 6.29% of the average reading.

**10-second data.** Fig. 7 shows the raw data collected at a 10-second measurement time for a batch transition from low to high S concentration. This figure illustrates that the transition takes about 2 minutes. The statistical detail of the start of the transition is enough to locate it within 20 seconds. This is an improvement of one and a half orders of magnitude over other techniques.

**300-second data.** The nature of the continuous flow and continuous measurement technique provides a simple relationship between measurement precision and measurement time. Averaging a number of measurements gives exactly the same result as measuring for a longer period. At levels above the limit of detection, measurement precision improves in proportion to the square root of the measurement time.

**Repeatability.** Two segments known to be level values were selected for repeatability analysis, one at a high level (290 ppm/wt average) and one at a low level (28 ppm/wt average). These are shown in Figs. 8 and 9.

In Fig. 8 (over 1 hour and 24 minutes), the analyzer produced a 2 sigma standard deviation of 3.39 ppm/wt, or 1.17% of the average reading. Total deviation was from a low of 277 ppm/wt to a high of 294 ppm/wt, or a total of  $\pm 2.9\%$ .

In the low level period, over 2 hours and 10 minutes, the analyzer produced a 2 sigma standard deviation of 0.72 ppm/wt, or 2.62% of the average reading (Fig. 9). Total deviation was from a low of 25.9 ppm/wt to a high of 29.7 ppm/wt, or a total of  $\pm 6.9\%$ . Expressed as a percent of full scale, using 300 ppm/wt as full scale for this test, this equates to  $\pm 0.6\%$  of full scale.

MWD XRF has been demonstrated as an effective method to detect sulfur concentration from 0 ppm to 3,000 ppm for online applications. The technique allows high sample-cell pressure and improved measurement sensitivity over conventional XRF techniques. Excellent repeatability and limit of detection have been achieved for measurement times from 10 seconds up to 300 seconds. Short measurement times allow users to identify changes in sulfur concentration on a real-time basis. This, in turn, enables accurate interface cuts at pipeline terminals and the secure handling of low sulfur fuels. **HP**

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