# Fuel knowledge

## Analyze$^{IT}$ for low sulfur levels in fuel

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**A high sulfur level in fuel, especially gasoline, is a bad thing. Sulfur compounds dramatically diminish the performance of catalytic converters, leading to increased emissions of hydrocarbons, carbon monoxide, particulate matter and other air toxins.**

**To reduce the levels of this natural crude oil component in fuel, many regions around the world have already imposed tight legal limits. These are due to become even more stringent, with gasoline average sulfur limits of 5–50 ppm on the way. Eventually, all developed societies will adopt these standards.**

**Compliance with standards necessitates measurement, especially in refineries. Demand has consequently grown for an accurate, reliable and *on-line* analyzer. Enter the ABB PGC2007.**

The enactment of the US Clean Air Act Amendment (CAA) in 1990 set in motion changes the dimensions of which were unparalleled in the history of air quality control. What this legislation in effect did was place a duty on motor vehicle fuel manufacturers and resellers to reduce refueling, evaporative and exhaust emissions of ozone-forming compounds, carbon monoxide and other air toxins from motor vehicles. A principal target of the legislation was the sulfur level in fuel.

Sulfur compounds are natural components of the crude oil from which petroleum-based fuels are made. Studies have shown that sulfur compounds can diminish the efficiency and limit the oxygen storage capacity (the measure of catalyst performance) of an automobile's catalytic converter. This can lead to increased emissions of hydrocarbons, $NO_X$, carbon monoxide, other air toxins and particulate matter. The detrimental health effects of the poor air quality created by many of these pollutants is well documented.

### California shows the way

Most gasoline sold in the United States has a relatively high sulfur level. According to a recent petroleum industry survey, the national average of sulfur in conventional (non-reformulated) gasoline was approximately 350 ppm, with one quarter of samples containing levels greater than 500 ppm. Sulfur levels in diesel fuels are even higher. Typical levels in reformulated gasoline are 150 ppm.

To combat these high levels, some regions of the world have introduced limits. California has the strictest standards, with average sulfur levels of 30 ppm for gasoline (with a maximum cap of 80 ppm) and below 500 ppm for diesel fuels.

Refiners and automakers are in agreement that hydrocarbon-based fuels must become cleaner. The debate between these two industries is over what the specific sulfur limits should be. It is becoming clear that sulfur limits in the USA of 5–50 ppm in both gasoline and diesel fuel will become reality in the next few years.

A further aspect has focused interest on sulfur levels in fuel: 'sweet' crude oil (oil with a low sulfur content, which tastes sweet) is the refiner's raw material of choice. However, as sources of sweet crude become harder to find, more and more 'sour' crude finds its way onto the market. The higher sulfur levels found in this oil contribute to the increasing average sulfur levels in the crude oil reaching the refineries.

These factors, the higher sulfur level in the crude supply and the lower levels mandated for the refined products, have led to an increase in demand for reliable on-line measurement of low sulfur levels in fuel. Gasoline as well as diesel products are affected, and operations in North America, Europe, and Asia have similar requirements.

Until recently, it was usual for only off-line laboratory test methods to be used to determine low sulfur levels in fuel. This was because very few on-line process analyzers can measure the total sulfur accurately and reliably at the low levels now being proposed or enforced. The technology used in the ABB PGC2007 total sulfur analyzer changes that.

### A quarter century of US regulation

- Lead-free gasoline, early 1970s
- Low evaporation gasoline, 1989
- Winter oxygenated gasoline, 1992
- Diesel fuel, 85% less sulfur, 1993
- Reformulated gasoline, 1995
- Cleaner burning gasoline, ca. 1996

## Choosing the right technology

For many years, during which most parts of the world had mandated levels in the hundreds or even thousands of parts per million (ppm), many of the measurement methods in use were quite capable of quantifying sulfur in fuels. However, the new, much lower limits present a significantly greater challenge, and with environmental regulations continually evolving even more stringent limits for total sulfur in gasoline and diesel fuel may be expected in the future. In response, various technologies for gasoline and diesel fuel analysis have appeared on the market. These feature technical approaches as varied as X-ray energy dispersion, lead acetate tape, UV fluorescence (UVF) and gas chromatography, each with its specific advantages and limitations.

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Most of these measurement techniques are laboratory methodologies that have not been easily or reliably adapted to on-line measurement use.

In 2002, ASTM round-robin tests were performed on X-ray fluorescence, microcoulometry, UV fluorescence and the electrochemical methods of sample analysis. Seventy labs were involved and over 5600 data points were collected. What this very extensive test showed was that two of these methods were unable to meet the requirements and the other two were not as precise as hoped for. Obviously, another technique was required if refiners are to ensure low sulfur levels in their products.

## ABB and sulfur analysis

In 1975, ABB Analytical introduced the first process gas chromatograph incorporating flame photometric detection. In the meantime, hundreds of sulfur applications (targeting both species and total sulfur) in complex stream

## Gas chromatography

Gas chromatography is a technique used to separate or analyze mixtures of gases. The apparatus consists of a fine tube containing a stationary phase that may be an adsorbing solid or a non-volatile liquid coating on a solid support (gas-liquid chromatography). For some analyses, the wall of a very fine column itself can act as the support medium. This is the packed column referred to in the text.

In our case, the sample is swept through the column by an air stream, with appropriate pressure regulation. The sample components have different affinities for the immobilized stationary phase and so they are adsorbed to different extents and, therefore, pass through the column at different rates. The various peaks of the components are detected as they exit the column, for example by a flame photometric detector. Under known conditions, the components can be identified by the time it takes them to pass through the column. This detector signal, when recorded as a function of time, produces the familiar chromatogram.

matrices have used this basic hardware design.

Less than two years after the US Clean Air Act set the limit for total sulfur in reformulated gasoline, ABB introduced the Vista Model 3107 Fuel Sulfur Analyzer for on-line analysis of total sulfur in gasoline. In 1997, the Model 2007 replaced the Model 3107.

Given all this experience, designing an apparatus to take care of these new low-level measurements might be considered a relatively simple affair. However, this is not so. ABB has also had to invest substantially in the refinement of its hardware and measurement methods in order to achieve the required performance at these low-levels. The investment has nevertheless paid dividends, having produced an updated analyzer and method capable of measurement ranges as low as 0–10 ppm.

### Where's the problem?

Measuring such a straightforward substance, even at these low levels, hardly seems difficult. But it is.

For a start, sulfur compounds seem to be everywhere and in everything, so minimizing carry-over or cross-contamination in samples is no easy matter. Special attention must be paid to the selection of construction materials. Not only in those parts of the analyzer that are exposed to the sample, but even in the sample transport tubing and sample conditioning hardware. Care must be taken during the design phase to minimize dead spots or tiny spaces that may hold up even the smallest amounts of sample. These small pockets of 'old' sample might contain higher levels of sulfur, thus contaminating the current measurement and producing wildly inaccurate results.

As for the analyzer itself, extra diligence is necessary when handling parts, like the components of the injection valve, columns and detector, during assembly. Some metal surfaces are specially treated in a process known as silco-treating in order to make the surfaces that come into contact with the sample more inert or passive.

Analyzers must be calibrated with a known standard. To measure 10 ppm of sulfur in diesel fuel, a calibration standard for a hydrocarbon of similar density to diesel containing about 8–10 ppm sulfur, guaranteed, is needed. That means that a sulfur-free hydrocarbon which can be dosed with the appropriate amount of sulfur to produce the guaranteed standard is required. There is just one small problem: as mentioned above, there is not much in this world that does not contain sulfur. Finding these sulfur-free bases from which to make standards is a difficult task.

| 1 | Features such as proven FPD technology and a simple furnace converter ensure analytical stability. |
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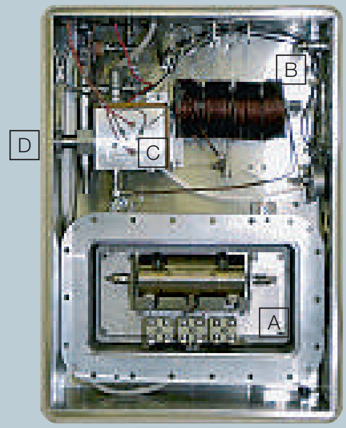



A = Furnace
B = Column
C = FPD burner block
D = Photomultiplier tube

The finished product has to be tough, too: often, a process analyzer will have to operate continuously and unattended close to the sample point in hazardous and variable environments, and meet strict safety regulations (NEC, CSA, ATEX, etc). And there has to be full communication with the plant's process control system.

### Simplicity: injection, oxidation, separation, measurement

The PGC2007 1 from ABB utilizes gas chromatography and an oxidation furnace for total sulfur measurement. Unlike some of the other more hardware-intensive methods mentioned, the ABB device utilizes the field-proven flame photometric detector (FPD), well known for its reliability and simplicity. The features and performance of the complete analyzer system make ABB Analytical the leader in process chromatography for total sulfur.

The platform is familiar to refinery technicians; in addition, its simple furnace converter and proven FPD technology provide excellent analytical stability. An electronic pressure control (EPC) module helps the device meet the exacting demands made on it.

A sulfur analysis with the PGC2007 comprises three simple steps 2 and takes about 5–6 minutes to complete:

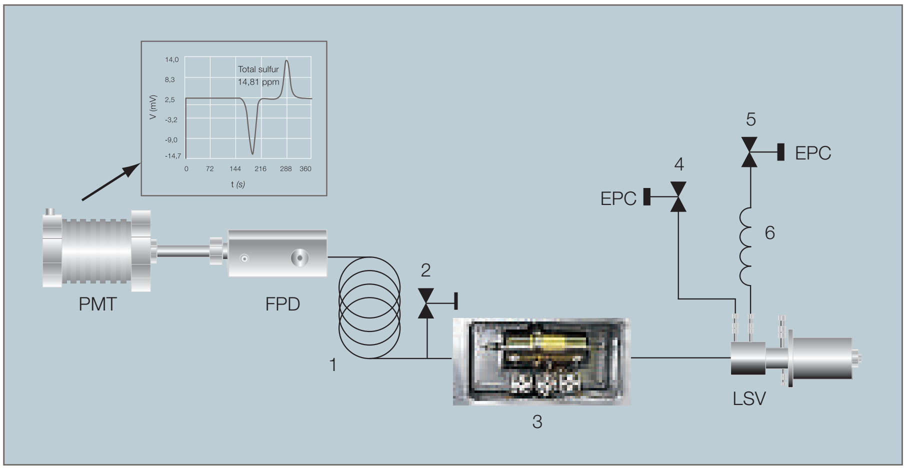
1. ABB's liquid sample valve (LSV) is used to inject a fixed volume of liquid fuel stream.
2. An air carrier transports the sample to the furnace, where it oxidizes to carbon dioxide, water and sulfur dioxide.
3. Specially packed columns separate these components, which then pass into the FPD for measurement.

### Flame photometric detection

Different detectors are used in gas chromatography to achieve selective and/or highly sensitive detection of specific compounds. Invented over 30 years ago, the flame photometric detector (FPD) is the detector of choice for sulfur-containing compounds.

In an FPD, the sample is burned in a hydrogen-rich flame (this is a different combustion from that occurring in the PGC2007 furnace). The optical emission from the excited chemical species, which emit in the region of 320–460 nm upon decay to the ground state, in the flame (chemiluminescence) are picked up and amplified by a PMT (thermoelectrically cooled to reduce thermal noise from heat or the dark current) and passed on to a computer for processing. The output signal is the familiar chromatograph curve, and reveals how much sulfur was in the original sample. The low-level sensitivity and linearity are enhanced by standard addition of sulfur.

**2** The PGC2007 combines a very simple operating principle with tried and tested components.




EPC = Electronic pressure controller
FPD = Flame photometric detector
LSV = Liquid sample valve
PMT = Photomultiplier tube

1 = Column, 2 = Split vent
3 = Furnace, 4 = Air carrier
5 = Sample sweep, 6 = Capillary

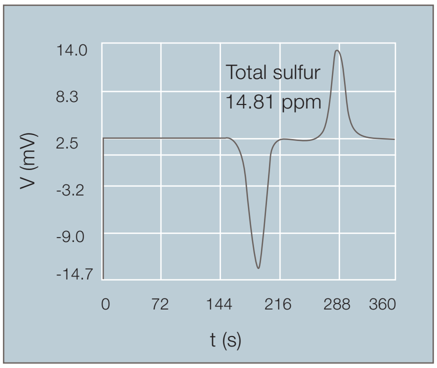
The flow rate through the LSV is varied, being at first low and then increasing over time to minimize tailing. Use of hydrogen or helium as the valve sweep gas improves the vaporization of heavy samples. The PGC2007 features a new method of flow control: The flow through the sample valve can now be controlled separately from the column, which improves response time, stability, detectability and linearity. Besides increasing sensitivity by optimizing the hydrocarbon flow rates, the PGC2007 also eliminates the mixing chamber used to reduce peak sample delivery rate, and the separator valve used to compensate for poor separation of $CO_2$ and $SO_2$. Cross interference due to variation in sample composition is also reduced.

LSV features include a one-piece vaporizer assembly and low-tension load adjustments that allow for months of operation without additional adjustments In a chromatograph, proper separation of the components in the sample prior to measurement is critical. An example of a chromatogram from the PGC2007 showing the separation of $CO_2$ and $SO_2$ is shown in 3.

### Repeatability

The measure of a process analyzer's performance is its demonstrated repeatability. To obtain this a known sample is injected and measured repeatedly for several hours. The standard deviation of the measured value is an accurate representation of analyzer performance and gives a good idea of how it will perform on process samples, in other words how close the analyzer reading will be to the actual, correct value when used to monitor the level of sulfur in blended gasoline or diesel. It

**3** Chromatogram from the PGC2007 showing the separation of $CO_2$ (negative peak) and $SO_2$



also tells us how confident an operator can be that the analyzer will repeatedly give the same answer for the same actual level in the sample, whether the next day or the next week.

The lower the measuring range (ie, 0–10 or 0–100 ppm), the more difficult it is to analyze with good repeatability. For example, a very good analyzer should be able to exhibit a repeatability of ± 1–2 % of the full-scale range. On a 0–100 ppm range, the expectation would be 1–2 ppm. 4 shows repeatability data for both gasoline and diesel with the PGC2007.

The ABB PGC2007 performs with superior repeatability and reproducibility. In fact, work is currently under way to obtain ASTM designation of the application method used in the device. This would assure refiners of the capabilities required of low-level, reliable measurement and of a recognized measurement method.

## Industrial IT Enabled

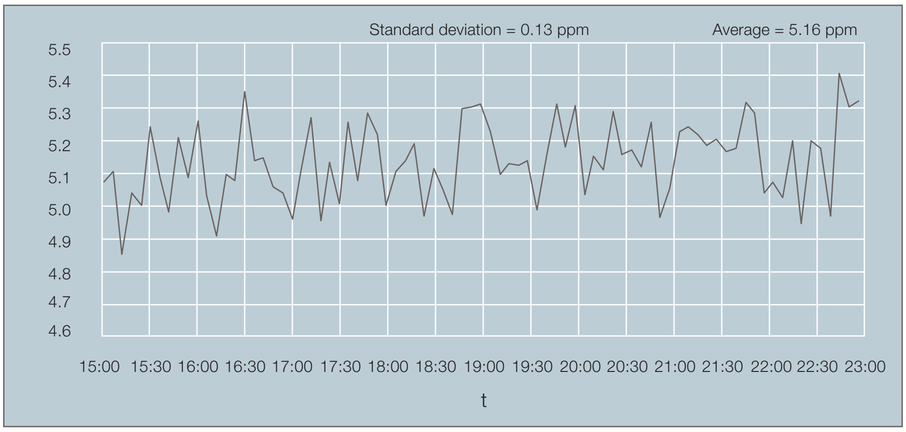
Currently installed at over 100 locations in 18 different countries around the world, the PGC2007 is gaining widespread acceptance as an accurate and reliable process analyzer for total sulfur measurements.

ABB's Industrial$^{IT}$ architecture is being used increasingly in process plants around the world. This means that the PGC2007, being Industrial IT Enabled, can be easily integrated into any process plant where this architecture is used.

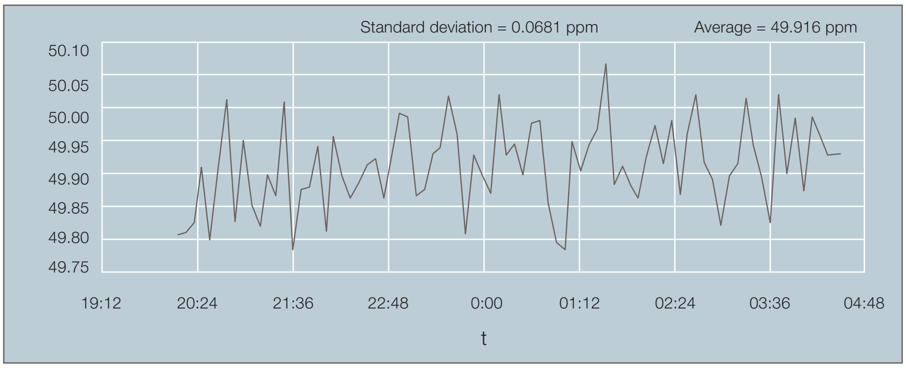
Mandated low-sulfur specifications in hydrocarbon-based fuels have presented many technical challenges to both the refining industry and instrument manufacturers. The process gas chromatographic technique with flame photometric detection has not only met these challenges but also proved to be a reliable solution for the measurement of low total sulfur levels in fuels. The distinct advantage of this approach is its simplicity of operation, its reliability and repeatability, and its demonstrated capability to meet even today's low-level sulfur measurement requirements.

> Since the PGC2007 is Industrial IT Enabled it can be easily integrated into any process plant where this architecture is used.

**4a** PGC2007 repeatability data for diesel




**4b** PGC2007 repeatability data for gasoline





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