Quantification and Characterization of Sulfur in Low-Sulfur Reformulated Gasolines by GC-ICP-MS

Application

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Abstract

Reducing total sulfur in motor fuels has become a critical air pollution control goal worldwide. As countries mandate ever lower permissible levels of total sulfur in fuels, the environmental monitoring and fuel manufacturing industries have been forced to find more sensitive techniques for analysis. Gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICP-MS) has the capability to meet current and projected detection limits for both total sulfur in reformulated gasolines and individual sulfur species. Additionally, GC-ICP-MS can identify and quantify other volatile organometallic species in fuels. This application note examines the quantification of total sulfur levels (using compound independent calibration) and sulfur speciation in reformulated gasoline.

Introduction

Sulfur in motor fuels has been implicated as a contributing factor to global warming and acid rain. It is also a catalyst poison for automobile catalytic converters [1] and refinery catalytic crackers [2]. As a result, the trend in Europe and the US has been to reduce the acceptable level of total sulfur in motor fuels. The US Environmental Protection Agency (EPA) tier-2 guidelines (to take effect in 2004) will create an average sulfur standard of 30 parts per million (ppm) and a cap of 80 ppm total sulfur by 2007 [3]. The California Air Resources Board (CARB) has established similar standards that are currently in effect [4]. Both New York and Massachusetts have adopted these requirements. The European Union announced, in December of 2002, that new regulations will require full market availability of sulfur-free fuels, defined as containing less than 10 ppm sulfur content, by January 1, 2005 [5]. The phase-in is to be complete by January 1, 2009. The EU committed under the U.N. Kyoto protocol of 1997, that it would reduce emissions 8 percent from 1990 levels by 2010.

To achieve these goals, it is necessary to be able to measure total sulfur in motor fuels at ever lower levels. It is also necessary to be able to determine the form and distribution of sulfur species to help facilitate their removal. The predominant sulfur containing compounds in gasoline consist of various substituted thiophenes ranging from thiophene to dimethylbenzothiophenes. Typically, total sulfur has been measured by x-ray fluorescence and sulfur species by gas chromatography using a sulfur-specific detector such as sulfur chemiluminescence detector (SCD), flame photometric detector (FPD), or atomic emission detector (AED). However, as the requirement for lower detection limits (DL) increases, there is need for a more sensitive sulfur-specific detector. Inductively coupled plasma mass spectrometry (ICP-MS) is known to be a very sensitive element-specific detector. When coupled to a gas chromatograph, ICP-MS has the potential to quantify very low concentrations of sulfur species in hydrocarbon fuels. Additionally, since ICP-MS is not limited to detecting only sulfur, it can be used for the simultaneous detection of other elements and volatile organometallics in fuels which may also contribute to air pollution or catalyst poisoning.

Experimental

In this study, the applicability of GC-ICP-MS to quantify and characterize total sulfur and sulfur species in low-sulfur reformulated gasoline (RFG) is examined. An Agilent 6890 gas chromatograph with split/splitless injector was coupled to an Agilent 7500a ICP-MS using the Agilent GC-ICP-MS interface (Figure 1). GC and ICP-MS conditions are summarized in Table 1. Calibration was based on a multilevel analysis of thiophene and 2-methyl-thiophene spiked into 3:1 isooctane:toluene obtained from Ultra Scientific [http://www.ultrasci.com]. Calibration levels ranged from 2.5 ppm per compound to 500 ppm per compound. Because GC-ICP-MS is capable of compound-independent calibration (Wilbur et. al. 2002 [6]), it was not necessary to calibrate every possible sulfur compound separately. The sulfur response factor for any compound(s) can be determined from a single compound. In this case, the response factors from thiophene were used and confirmed by those from 2-methylthiophene.

Figure 2 depicts calibration curves for thiophene from 2.5–150 ppm sulfur and 2-methylthiophene from 2.5–50 ppm sulfur. Figures 3, 4, and 5 depict three different gasoline samples, a low level RFG with approximately 55 ppm total sulfur, a conventional gasoline with approximately 330 ppm total sulfur and an ASTM gasoline sample which is not certified for total sulfur. Note the very different profile of sulfur compounds in each sample, especially with respect to the relative abundance of the higher boiling methyl and dimethylbenzothiophenes.

Table 1. Instrumental Conditions, GC and ICP-MS

Instrumentation	
Chromatographic system	Agilent 6890 GC
Inlet	Split/Splitless
Detector	Agilent 7500a ICP-MS
Liner	Splitless liner (part number 5062-3587)
Column	30 M × 0.25 mm id × 0.25 µ HP-5
GC Conditions	
Inlet temperature	250 °C
Injection volume	1 µL
Injection mode	Split 1:50
Carrier gas	Helium
Carrier gas flow	2.5 mL/min (constant flow mode)
Transfer line temperature	250 °C
Oven temperature program	40 °C/4 minutes, 20 °C/min to 250 °C, hold for 1 min
ICP-MS Conditions	
ShieldTorch	Long-life shield installed
Forward power	700 W
Sample depth	13 mm
Carrier gas flow	1.1 L/min
Extract 1	–150 V
Extract 2	–75 V
Auxiliary gas	He, 10 mL/min added to Ar carrier
Injector temperature	260 °C

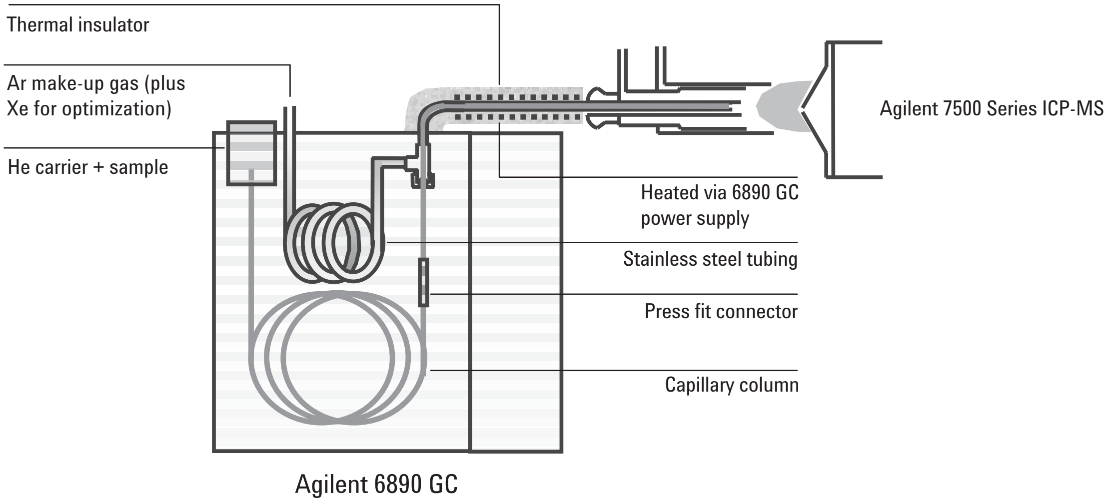
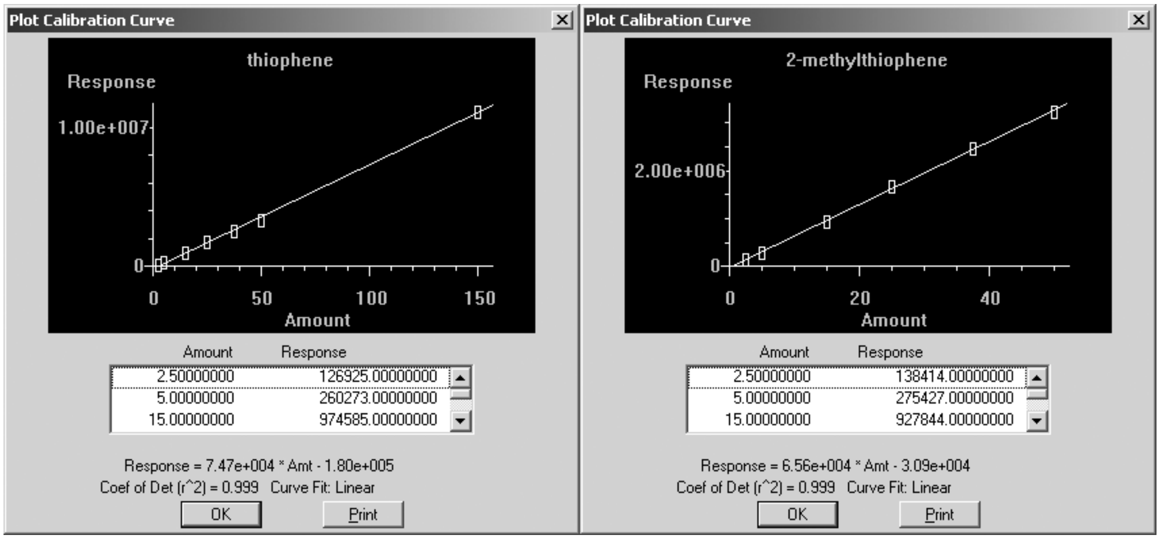


Figure 1. **Schematic diagram of Agilent GC-ICP-MS system.**



Amount	Response
2.50000000	126925.00000000
5.00000000	260273.00000000
15.00000000	974585.00000000

Response = 7.47e+004 * Amt - 1.80e+005
Coef of Det (r^2) = 0.999 Curve Fit: Linear

Amount	Response
2.50000000	138414.00000000
5.00000000	275427.00000000
15.00000000	927844.00000000

Response = 6.56e+004 * Amt - 3.09e+004
Coef of Det (r^2) = 0.999 Curve Fit: Linear

Figure 2. **Calibration curves, thiophene and 2-methylthiophene in 3:1 isooctane:toluene.**

Analytical Conditions

All analysis were performed using an Agilent 6890 gas chromatograph with split/splitless injector coupled to an Agilent 7500a ICP-MS with Shield-Torch system. GC-ICP-MS coupling was via the Agilent GC interface (model G3158A).

Results and Discussion

Sensitivity

The method as tested exhibits excellent sensitivity compared with other sulfur specific GC detectors such as the FPD, SCD, and AED. Single compound DL based on peak-to-peak signal-to-noise measurements for thiophene and 2-methylthiophene are in the 3–10 ppb range based on peak-to-peak signal-to-noise of 2:1. When translated to total sulfur in gasoline, assuming approximately 40 significant sulfur-containing compounds as detected by the ChemStation integrator, the DL for total sulfur is approximately 0.1 ppm to 0.5 ppm (Figure 6). This is in good agreement with visual inspection of overall signal-to-noise for the 55 ppm gasoline standard (Figure 3). In fact, examining the peak-to-peak signal-to-noise for 2-methylthiophene in the 50-ppm RFG standard gives a signal-to-noise of about 300:1 which is in agreement with the estimated DL of about 1/100 of the 55-ppm standard or 0.5 ppm. The analysis of certified, lower sulfur natural gasoline standards is needed in order to verify these assumptions about the absolute DL for total sulfur.

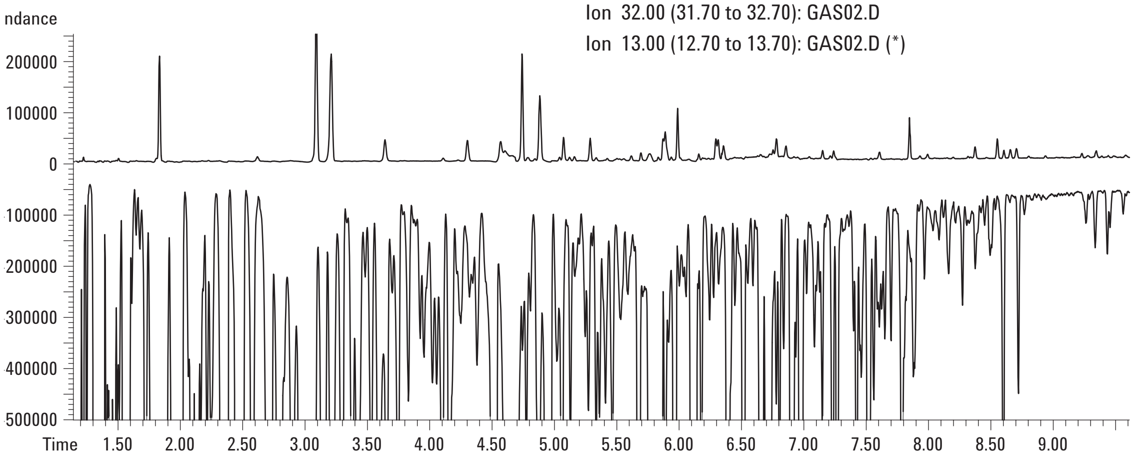


Figure 3. CARB low sulfur RFG with ~55 ppm total sulfur. Sulfur chromatogram (top), inverted carbon-13 chromatogram (below).

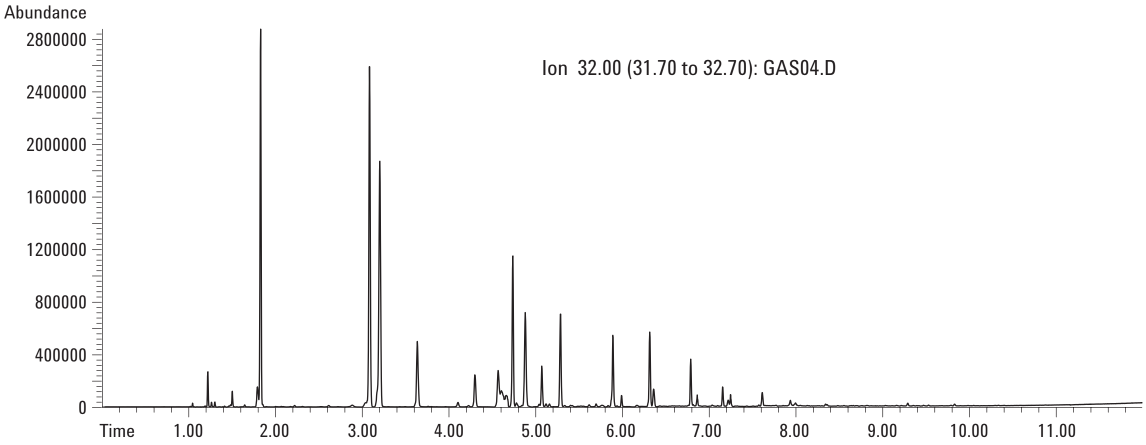


Figure 4. ASTM-Fuel-QCS-02, Conventional gasoline QC sample, ~330 ppm total sulfur.

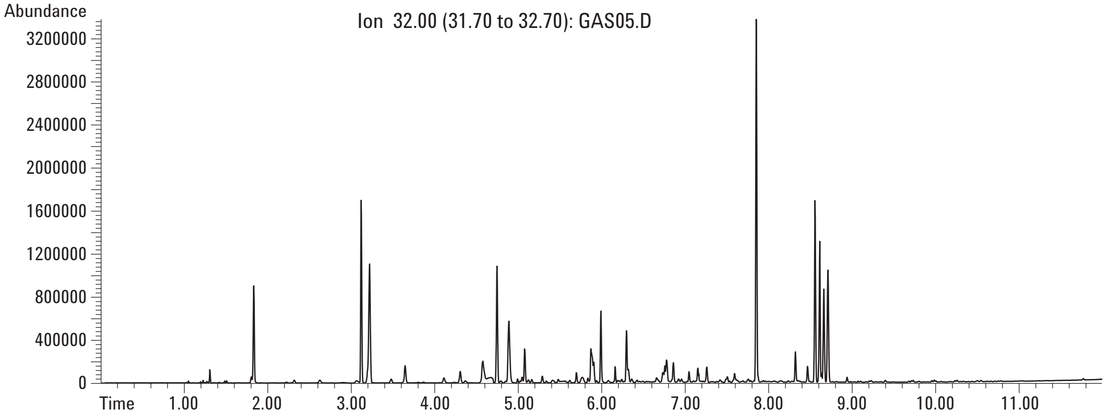


Figure 5. ASTM Round robin gasoline standard #2, not certified for sulfur.

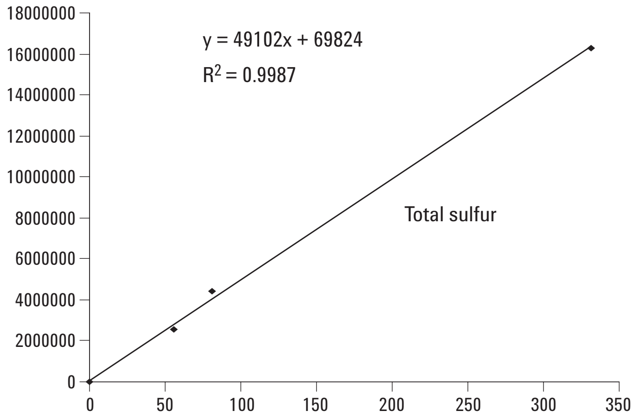


Figure 6. **Calibration, total sulfur in gasoline calculated as area sum of sulfur-32 peaks.**

Compound Independent Calibration

When calculated against thiophene using the area sum of all sulfur containing peaks ($m/z = 32$), the ASTM QCS02 conventional gasoline standard and CARB low sulfur RFG sample showed excellent recovery (see Table 2).

Advantages of ICP-MS

No Signal Suppression: In addition to excellent sensitivity and selectivity for sulfur, ICP-MS offers significant additional advantages over other detectors for the analysis of fuels. Because of the size and robustness of the ICP plasma, signal suppression of the analyte signal, in this case sulfur, by coeluting hydrocarbon compounds is virtually eliminated in gasoline samples. Figure 3 shows the sulfur peaks in the CARB low-sulfur RFG standard contrasted with the hydrocarbon peaks. The hydrocarbons are displayed as the C13 elemental chromatogram for scaling and dynamic range purposes. In this figure, the C13 chromatogram has been displayed inverted for ease of viewing. Note that while the C13 trace shows only 1% of the actual carbon abundance (C13/C12 ratio is 0.01), there is no apparent suppression of the sulfur signal. Very slight suppression was observed in the sulfur baseline when analyzing standards made up in a non-natural hydrocarbon solvent such as 3:1 isooctane:toluene. In this case, the entire carbon signal is concentrated into two very large peaks unlike natural fuels where each hydrocarbon peak is a much smaller fraction of the total carbon concentration. The slight depressions in baseline in Figure 7 immediately after thiophene and before 2-methylthiophene are due to suppression from isooctane and toluene respectively.

Faster Run Times: Since GC-ICP-MS does not suffer from significant analyte signal suppression due to coeluting hydrocarbons, the GC separation does not need to be compromised to separate analyte and hydrocarbon peaks. As a result, much faster run times can be achieved. Typical run times for sulfur species in gasoline by GC using conventional detectors are 25 to 30 minutes. In this work, the total run time was 12 minutes, with good separation of all compounds of interest (see Figure 8).

Table 2. **Calculated Recovery of Total Sulfur in ASTM and CARB Gasoline Samples by Compound Independent Calibration Against Thiophene Standard**

Sample	Area sum	Thiophene RF	Certified concentration	Measured concentration	% Recovery
ASTM QCS 02 gasoline	16299680	50958 cts/ppm	330 ppm	319 ppm	96.7
ASTM #2 Round robin gasoline	20050794	50958 cts/ppm	NA	393 ppm	NA
CARB low sulfur RFG	2755986	50958 cts/ppm	55	54.08 ppm	98.3

NA Not applicable

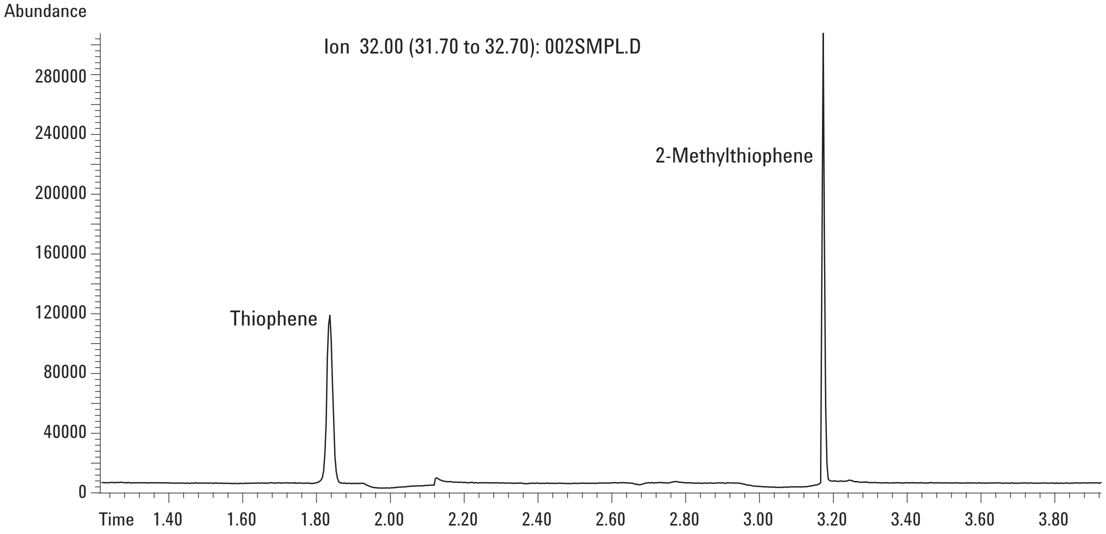


Figure 7. Calibration standard, 2.5 ppm each thiophene and 2-methylthiophene.

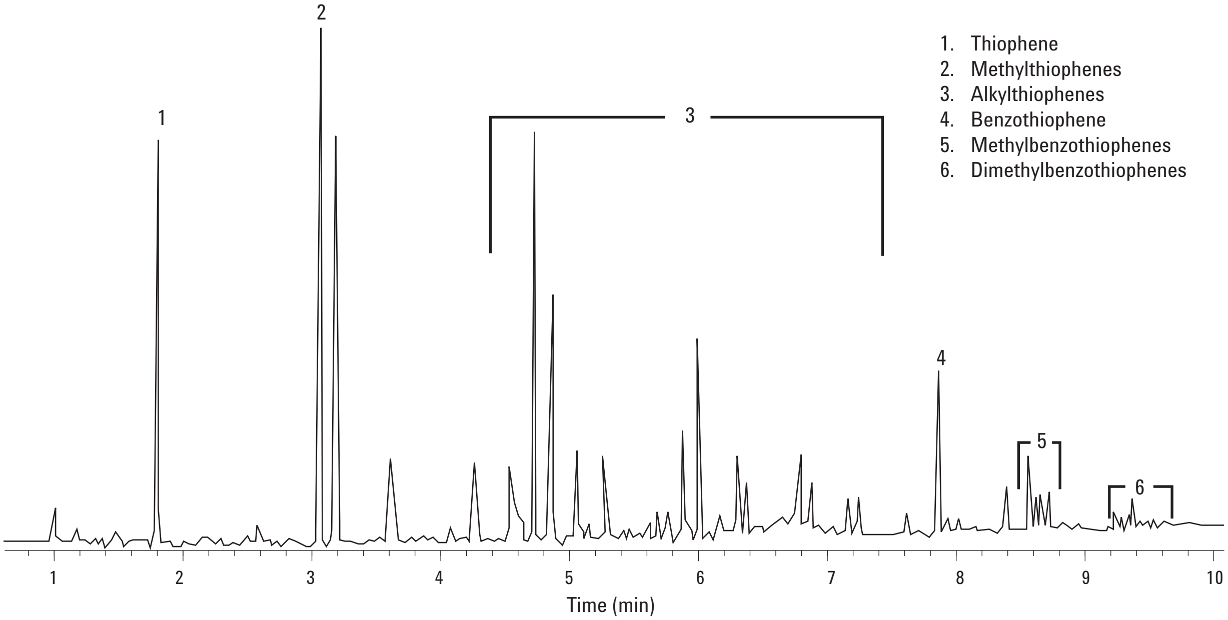


Figure 8. Typical distribution of sulfur containing compounds in low-sulfur RFG.

Additional Elements: Since ICP-MS is a scanning, elemental detector, the detection of additional elements such as vanadium, manganese, lead, mercury, or others can be performed simultaneously with DL similar to those for sulfur. This can give important additional information about fuel quality and process control without additional investment in time or equipment.

Ease of Use

Since the ICP-MS is actually designed to handle much higher matrix loads of aqueous liquid samples, it exhibits exceptional stability and robustness when used as a GC detector. As a result, the need for frequent tuning, cleaning and calibration is minimized and the use of internal standards is not necessary. The large dynamic range of the detector means that accurate quantification can be achieved over several orders of magnitude without the need for dilution or preconcentration of samples.

Conclusions

GC-ICP-MS offers a simple, sensitive, selective technique for the characterization of sulfur in fuels at the levels needed to meet new US and EU regulations. With DL for individual sulfur species in the low ppb range and total sulfur at less than 1 ppm, it is the only technique currently available which can measure both individual sulfur species and total sulfur at newly regulated levels. With the ability to do both, GC-ICP-MS can offer the hydrocarbon processor both regulatory compliance information and process control information simultaneously.

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