# A Novel GC-ICP-MS Approach for Speciation of Sulphur in Reformulated Fuels

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Fuel combustion provides a significant source of sulphur to the atmosphere and there are on-going concerns with respect to the concentrations of atmospheric sulphates, sulphuric acid and the subsequent formation of acidic rain. Elevated atmospheric sulphur concentrations are also known to induce respiratory and cardiovascular illnesses in humans and there are significant risks associated with long term human exposure to sulphur pollution in the environment.

European Union (EU) and United Stated Environmental Protection Agency (USEPA) legislation is currently evolving to enforce lower total sulphur concentrations in petroleum and diesel fuels and to reduce subsequent sulphur emissions to the atmosphere. EU legislation currently requires all fuels to contain less than 10 ppm sulphur [1] and EPA legislation currently imposes a total sulphur limit of 30 ppm in gasoline with highway diesel fuels required to contain less that 15 ppm sulphur by 2006 [2].

Analytical techniques such as Gas Chromatography coupled with Atomic Emission Detection (GC-AED) and Sulphur Chemiluminescence Detection (GC-SCD) have been used extensively for analysis of sulphur species and total sulphur concentrations in various petrochemical fuels. However, the sensitivity of these techniques is considered insufficient for analysis of fuels containing reduced sulphur concentrations and a more sensitive analytical technique is required to satisfy future fuel analysis requirements. In accordance with the evolution of legislation, there is now an increasing requirement for the petrochemical industry to realize effective methodologies for sulphur removal in both raw and processed petrochemical samples, and specifically, to monitor and control total sulphur concentrations in petroleum and diesel fuels prior to supply. The majority of the sulphur content in gasoline results from incorporation of the fluid catalytically cracked naphtha (FCC naphtha) stream and the production of low-sulphur FCC naphtha will, in turn, enable the production of fuels with reduced sulphur content.

The hyphenated analytical technique of GC coupled with element specific Inductively Coupled Plasma-Mass Spectrometry detection (GC-ICP-MS) offers an elegant analytical solution for sensitive analyses of sulphur species in fuels and the merits of this technique are being recognized increasingly within the petrochemical industry. This Application Note describes use of the unique commercialized GC-ICP-MS instrument package from Thermo Electron Corporation to enable analysis of sulphur species in FCC naphtha and commercially available gasoline samples. The described GC-ICP-MS methodology facilitates quantification of intrinsic sulphur species using external calibration and a Species Independent Calibration (SIC) technique. Total sulphur concentrations are also inferred from the sum of the intrinsic sulphur species concentrations.

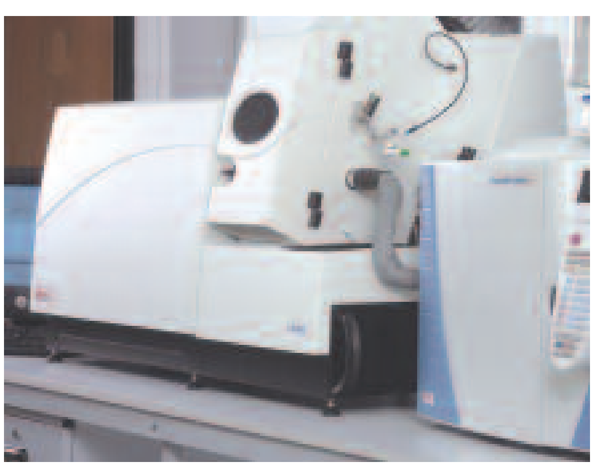

Figure 1: GC-ICP-MS instrumentation

## Experimental

A Thermo TRACE GC Ultra™ and AS3000 autosampler are coupled with the XSeries*II* ICP-MS detector via the commercialized GC Transfer Line unit as shown in Figure 1. The ICP-MS detector is configured with the dual mode sample introduction system as shown in Figures 2a-2b. This unique instrument component facilitates simultaneous introduction of both liquid and gaseous samples through the ICP-MS nebulizer/spray chamber arrangement and GC sample introduction systems respectively. The ICP-MS detector is initially 'Performance Tested' and 'Auto tuned' when required using the integral software tools. GC-ICP-MS analysis is then performed during continuous aspiration of an aqueous blank solution through the nebulizer/spray chamber arrangement, maintaining wet plasma conditions throughout.

Figure 2a : Dual Mode ICP-MS

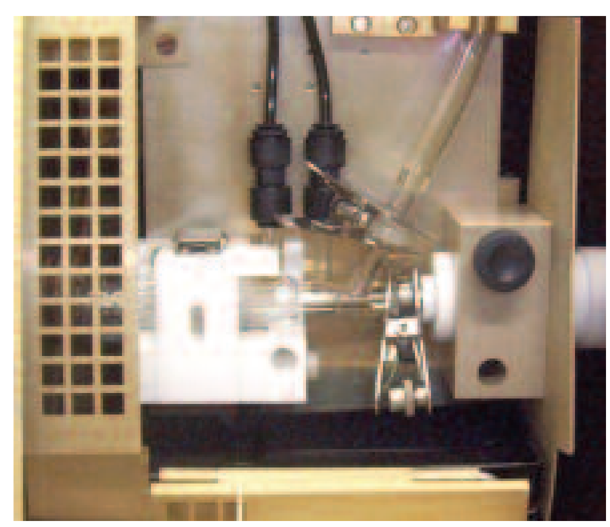

Figure 2b: Dual Mode Interface Torch

Ions derived from the processed chromatographic eluent are extracted from the plasma and focused into the collision/reaction cell of the XSeries*II* ICP-MS. The collision/reaction cell is pressurized with oxygen throughout the analysis and operated under non-Kinetic Energy Discrimination (KED) conditions to promote conversion of sulphur ($^{32}S^+$) to sulphur oxide ($^{48}SO^+$) species and subsequent transfer of the $^{48}SO^+$ species to the quadrupole for detection and quantitation. This analytical approach shifts the $^{32}S$ analyte away from common gas based polyatomic interferences and also converts any $^{48}Ti^+$ ions (which would otherwise form an isobaric interference with $^{48}SO^+$) to the $^{64}TiO^+$ species to facilitate interference-free analysis. Optimal GC-ICP-MS operating conditions are shown below in Table 1 for reference.

Table 1: GC-ICP-MS parameters

| | |
|---|---|
| **GC CONDITIONS** | |
| Column | Thermo Tr-5, 30 m x 0.25 mm i.d., $d_f$ 0.25 µm |
| Injection mode | Split (ratio 10:1) |
| Injection port temperature | 280 °C |
| Injection volume | 1 µL |
| Carrier gas flow | He @ 3 mL $min^{-1}$ |
| Make up gas flow* | Ar @ 600 mL $min^{-1}$ |
| Transfer line temperature | 320°C isothermal |
| Initial temperature | 40 °C |
| Ramp rate | 12 °C $min^{-1}$ |
| ICP-MS CONDITIONS | |
| Forward Power | 1350 W |
| Nebulizer Gas Flow | 0.35 L $min^{-1}$ |
| Auxilliary Gas Flow | 0.8 L $min^{-1}$ |
| Cool Gas Flow | 13 L $min^{-1}$ |
| Isotopes and dwell times, ms | $^{48}$M (200 ms) |
| Channels per AMU | 1 |
| Timeslice duration | 201 ms |
| Transient acquisition time | 1800 s |
| Interface Cones | XS |

## Results

The major sulphur containing species encountered in fuel are mercaptans, thiophenes, benzothiophenes, sulphides and disulphides. Standards of thiophene, 1-methyl thiophene, 1-ethyl thiophene, benzothiophene and 1-methyl benzothiophene were used to optimize the GC separation methodology and to generate fully quantitative external calibration curves. Examples of the resultant calibration standard chromatography are shown below in Figure 3a and chromatographs derived from selected commercial gasoline and FCC naphtha samples are shown in Figures 3b and 3c respectively. A noticeable broadening of the thiophene peak is observed in the commercial gasoline sample and this is attributed to coelution with benzene.

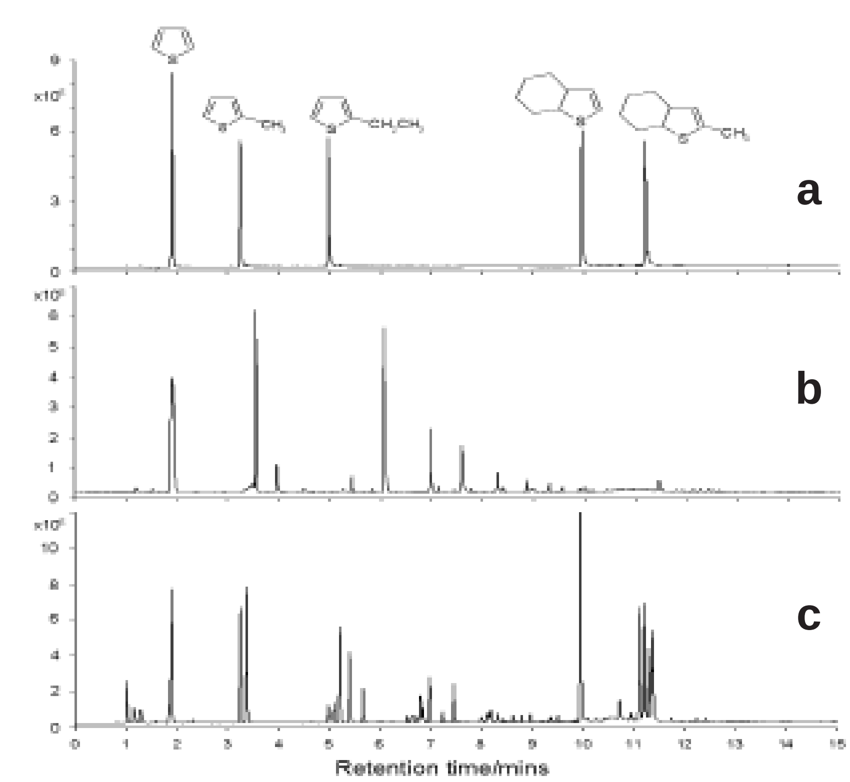


Figure 3: GC-ICP-MS chromatograms of (a) mixed sulphur species at 1 ppm, (b) commercially available gasoline (c) FCC naphtha sample diluted 1:4 in hexane.

Wherever possible, sulphur species are identified in the FCC naphtha and gasoline samples using spiking experiments with known standards. However, similar sensitivity responses are observed for each thiophene standard (i.e. as calculated from each fully quantitative external calibration curve). This observation is further illustrated in Figure 4, which shows a sulphur calibration in the region of 0.1 to 10 ppm using calibrant standards derived from 5 different sulphur species.

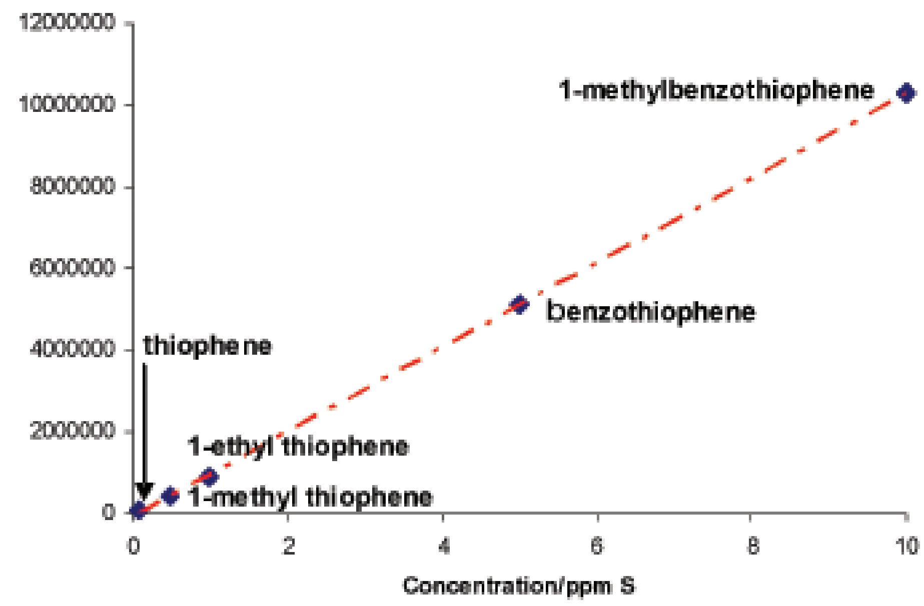


Figure 4: 0.1-10 ppm sulphur calibration derived from 5 individual species

The GC-ICP-MS instrumentation facilitates similar calibration sensitivities for different sulphur species because the inductively coupled plasma processes the eluting sulphur species similarly regardless of the organic/inorganic functionality. This 'Species Independent' process can be exploited to enable semi-quantification of uncharacterized sulphur species and, as such, avoids the necessity for multiple species-specific fully quantitative calibrations.

Table 2 presents fully quantitative data for the 5 sulphur species used to prepare fully quantitative calibrations and semi-quantitative data is provided for the other unidentified species using the Species Independent Calibration approach. The gasoline and FCC naphtha samples are found to contain total sulphur concentrations of 26 and 389 ppm respectively. The approach was validated by calculating the recovery (89 – 103%) of standards spiked into the FCC naphtha sample. Limits of detection ($3\sigma$) for the 5 thiophene analogues were calculated in the range 5 – 10 ppb.

Table 2: Fully and semi-quantitative data and figures of merit

| **Species** | **S Concentration (ppm)** | | **Recovery (%)** | **LOD** |
|---|---|---|---|---|
| | **Gasoline** | **FCC Naphtha** | | |
| Thiophene | 7.73 | 22.26 | 98 | 4.96 |
| 2-methyl thiophene | 3.85 | 44.93 | 88 | 9.39 |
| 2-ethyl thiophene | - | 6.89 | 89 | 5.26 |
| Benzothiophene | 0.14 | 39.33 | 103 | 8.32 |
| 1-methyl benzothiophene | 0.05 | 18.69 | 97 | 7.26 |
| Unidentified species* | 14.28 | 256.56 | | |
| **Total S concentration** | **26.05** | **388.67** | | |

*Sum of species quantified by SIC

## Summary

Commercial GC-ICP-MS instrumentation has evolved to advance a proven academic research tool into the routine and commercial research laboratory environment. The unique Dual Mode sample introduction system provides a simple and automated approach for performance testing and optimization of the chromatographic detector and the resultant wet plasma GC-ICP-MS operating conditions facilitate robust plasma processing and high analyte sensitivity. Capabilities of 3rd generation collision/reaction cell technology are exploited within the XSeries*II* ICP-MS detector and a powerful reactive chemistry approach attenuates the required isobaric and gas-based polyatomic species to achieve interference-free analysis.

The above GC-ICP-MS methodology provides a highly sensitive and selective approach for quantitative sulfur speciation analyses, offering a complete analytical solution to the petrochemical industry for the characterization and quantification of sulphur species in reformulated fuels.

[1] European Union, Commission Directive 2003/17/EC
[2] Environmental Protection Agency Code of Federal Regulations Title 40: Protection of the Environment, Part 80: Regulation of Fuels and Fuel Additives