

Application of ICP–MS as a Multi-Element Detector for Sulfur and Metal Hydride Impurities in Hydrocarbon Matrices

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Abstract

Maturation of inductively coupled plasma–mass spectrometry (ICP–MS) in terms of size, reliability, and cost has had a significant impact on its consideration as a viable detector for gas chromatography. Its generally excellent sensitivity for those elements it can measure has been a contributing factor. A method for sulfur speciation in various hydrocarbon products is investigated, as well as sulfur and metal hydride contaminants in high purity hydrocarbon feed stocks. Detection limits for sulfur species in hydrocarbon liquids and gases are approximately 5 and 10 ppb, respectively, as sulfur. Lower detection limits on the order of 100 parts per trillion are achieved for arsine. The use of collision cell technology (CCT) is exploited to remove interferences. CCT has been described elsewhere (1) using helium or helium–hydrogen mixtures for suppression of $^{16}\text{O}^{16}\text{O}^+$ interference with ^{32}S . In this work, a novel approach is investigated which uses oxygen to remove this interference by shifting it in a comprehensive fashion. The advantage of operating the system at full power with a tandem gas and liquid interface is also discussed.

Introduction

Combustion of hydrocarbon-based fuels provides a significant source of sulfur contamination to the atmosphere and is a concern with respect to the formation of acid rain. High concentrations of sulfur combustion products also pose significant risks to human respiratory and cardiovascular systems. European Union and United States Environmental Protection Agency legislation is currently evolving to enforce lower total sulfur concentrations in petroleum-based fuels to reduce subsequent atmospheric emissions. EU legislation currently requires all fuels to contain less than 10 ppm sulfur (2). EPA legislation requires a total sulfur limit of 30 ppm gasoline, with highway diesel fuels requiring less than 15 ppm sulfur by 2006 (3). Sulfur is also a critical contaminant in a number of polymer grade feedstocks such as ethylene and propylene, because they have a deleterious effect on the poly-

merization catalyst as well as the final product. Not only are hydrogen sulfide and carbonyl sulfide problematic, but other impurities such as arsine are also considered significant contaminants even at part per billion levels.

Analytical techniques such as gas chromatography (GC) coupled with atomic emission detection (AED), flame photometric detection, or chemiluminescence detection have been used

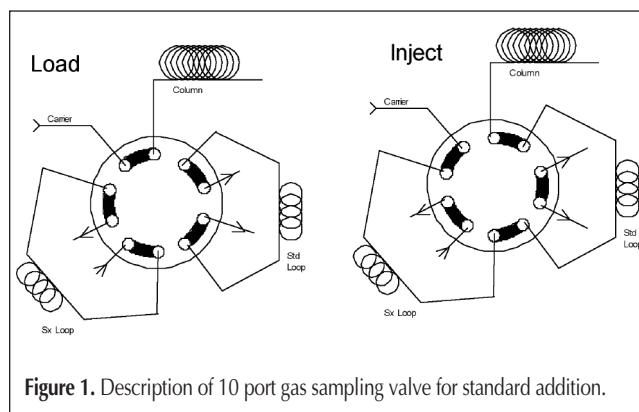


Figure 1. Description of 10 port gas sampling valve for standard addition.

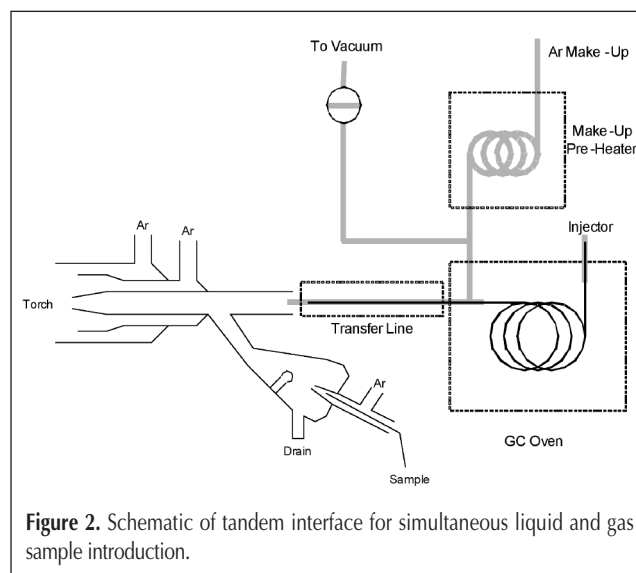


Figure 2. Schematic of tandem interface for simultaneous liquid and gas sample introduction.

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extensively for total sulfur speciation (4–8). These detectors all have some attributes that make them less than ideal, such as matrix interferences from large amounts of hydrocarbons, non-linearity, incomplete sample combustion, or plasma tube coking. With the exception of AED, they do not have the capability for the measurement of other species, and none have the stand-alone capability of inductively coupled plasma (ICP)–mass spectrometry (MS) analysis.

The hyphenated analytical technique of GC coupled with specific ICP–MS detection (GC–ICP–MS) offers a powerful analytical solution for the sensitive analysis of total sulfur as well as sulfur

species in fuels. It also provides the capability to measure other non-sulfur contaminants in polymer-grade gases. The new torch design now facilitates both the introduction of gas and liquid analytes simultaneously. This allows specific tuning to target elements rather than generalized optimization on xenon or other carrier gas dopants for gas phase analysis. The GC–ICP–MS methodology described facilitates quantitation of indigenous sulfur species using species independent calibration. It also allows for inferred total sulfur measurement in fuels, gases, and liquid products, as well as the determination of critical non-sulfur contaminants in polymer grade feedstocks.

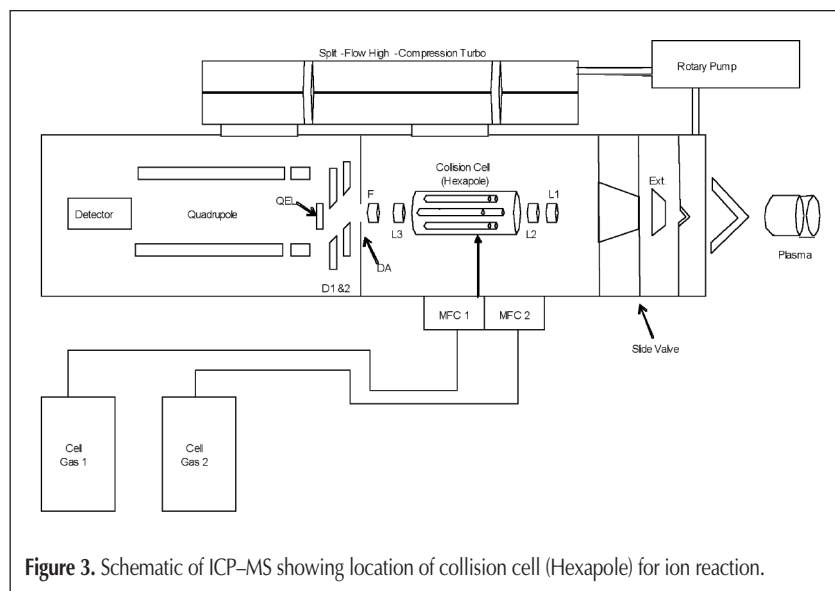


Figure 3. Schematic of ICP–MS showing location of collision cell (Hexapole) for ion reaction.

Experimental

Apparatus

A Thermo TRACE GC Ultra and AS3000 auto sampler were used for the speciation of liquid fuels (Thermo Fisher Scientific, Waltham, MA). A Thermo Focus GC equipped with a VICI Valco 10 port valve was used for gas analysis. The use of a 10 port sample injection valve facilitates the ability to make a standard addition or add an internal standard to gas samples by introducing a standard gas simultaneously with the sample in an additional loop. Figure 1 shows this arrangement.

A Thermo X-Series ICP–MS was used as the detector. The ICP–MS was configured with a tandem mode sample introduction system as

Table I. Analytical Parameters

GC Conditions			
Analyte	Gasoline, naphtha	Sulfur in Propane/Propylene	Arsine in Propane/Propylene
Column	Thermo Tr-5 30 m × 0.25 mm × df 0.25 μm	J&W Scientific GS-GASPRO 60 m × 0.32 mm × df 5.0 μm	J&W Scientific DB-1 100 m × 0.53 mm × df 5.0 μm
Injection mode	Split (10:1)	Split 12 mL/min	Splitless
Injection port temperature	280°C	Valve ambient	Valve ambient
Sample size	1 μL	1000 μL	500 μL
Carrier flow	He @ 3 mL/min	He @ 14 psig	He @ 10 psig
Make up flow	Ar @ 600 mL/min	Ar @ 120 mL/min	Ar @ 90 mL/min
Transfer line temperature	320°C	100°C	50°C
Initial temperature	40°C	70°C Isothermal	35°C Isothermal
Initial time	1.5 min	NA	NA
Ramp rate	12°C/min	NA	NA
Final temperature	280°C	NA	NA
ICP–MS Conditions			
Forward Power	1350 W	1400 W	1400 W
Nebulizer Gas Flow	0.35 L/min	0.72 L/min	0.68 L/min
Auxiliary Gas Flow	0.8 L/min	0.8 L/min	0.8 L/min
Cool Gas Flow	13 L/min	13 L/min	13 L/min
Collision Gas Flow	0.4 mL/min	0.25 mL/min	NA
Isotopes and dwell time	⁴⁸ M (200 ms)	⁴⁸ M (400 ms)	⁷⁵ M (400 ms)
Acquisition time	1800 s	900 s	1100 s
Interface Cones	XS	Xi	Xi

shown in Figure 2. This configuration allows for simultaneous introduction of both liquid and gas samples through the Nebulizer/spray chamber and the GC sample interface (9) simultaneously.

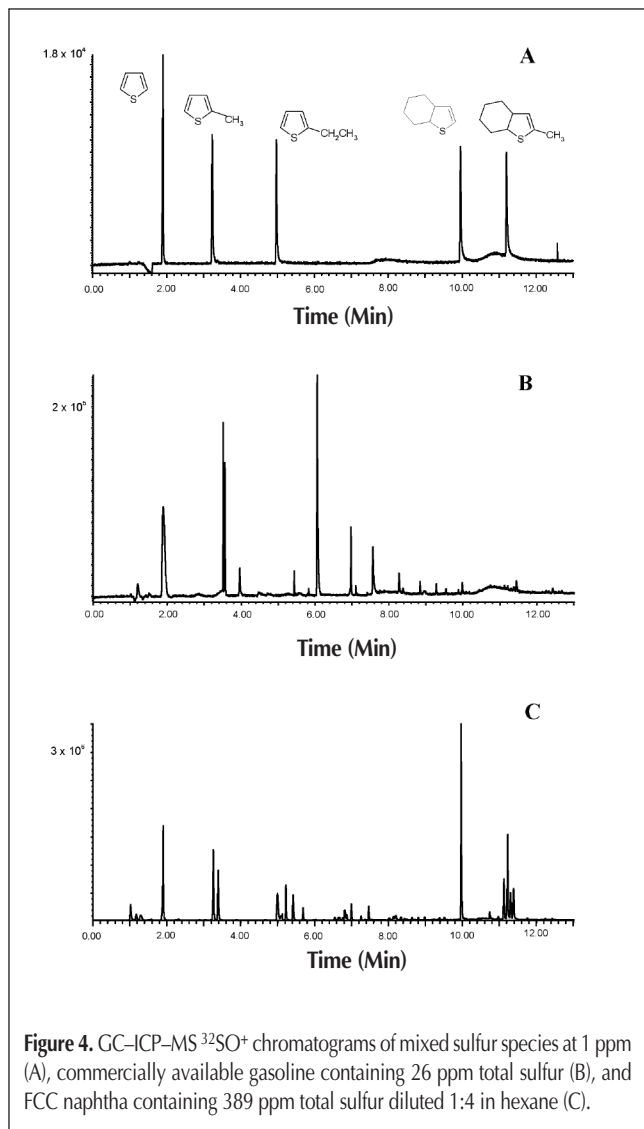


Figure 4. GC-ICP-MS $^{32}\text{SO}^+$ chromatograms of mixed sulfur species at 1 ppm (A), commercially available gasoline containing 26 ppm total sulfur (B), and FCC naphtha containing 389 ppm total sulfur diluted 1:4 in hexane (C).

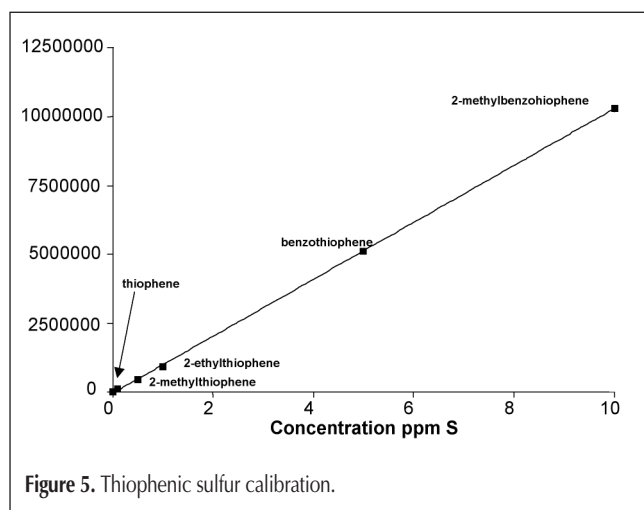


Figure 5. Thiophenic sulfur calibration.

The ICP-MS was initially tuned with the integral “Autotune” software. Following this tune, the instrument was re-tuned using oxygen in the collision cell operating under non-kinetic energy conditions. This promotes the conversion of sulfur ($^{32}\text{S}^+$) to sulfur oxide ($^{48}\text{SO}^+$) species and subsequent transfer of the $^{48}\text{SO}^+$ to the quadrupole for detection and quantitation. This analytical strategy shifts the $^{32}\text{S}^+$ analyte away from OO^+ interference and also converts any traces of $^{48}\text{Ti}^+$ ions that might be an isobaric interference to $^{64}\text{TiO}^+$. Figure 3 describes the collision cell as it integrated with the rest of the ICP-MS.

For gas analysis, a VICI Metronics precision gas dilution system with flow controllers (VICI Metronics, Poulsbo, WA) was used to make ppb level standards from ppm standards (accuracy $\pm 1\%$). The dynamic range of this device was approximately 10,000. Thus, a 100 ppm standard can be diluted accurately to 10 ppb.

GC and ICP conditions

Several analytical conditions were used for the determination of sulfur species in commercially available gasoline, determination of carbonyl sulfide in polymer grade propane-propylene mixtures, and determination of arsine in polymer grade propane-propylene mixtures. Both GC and ICP-MS conditions are shown in Table I for reference. A common technique for GC-ICP-MS tuning makes use of Xenon doping in either carrier or an auxiliary gas stream (10). This strategy is somewhat problematic because there is no direct tuning or optimization for the analyte of interest. The unique advantage of the tandem liquid-gas interface allows for direct tuning to optimize for the element of interest by direct liquid aspiration of a standard containing that element. Additionally, it allows for operation of the ICP-MS in “wet” plasma mode at full power, a state that is more stable and robust than “dry” and/or “cool” plasma conditions. This becomes an important consideration when there is significant sample matrix loading on the plasma.

Table II. Quantitative Data For Sulfur Species Used to Prepare Calibrations and Semi-Quantitative Data For Other Species in Gasoline and FCC Naphtha

Species	Gasoline ppm S	FCC Naphtha ppm S	Recovery (%)
Thiophene + s-Butyl Mercaptan	7.73	22.26	98
2-Methyl Thiophene	3.85	44.93	88
3-Methyl Thiophene	–	50.83	
2-Ethyl Thiophene	–	6.89	89
C ² -Thiophenes	–	56.02	
Benzothiophene	0.14	39.33	103
Methylbenzothiophenes	0.42	76.01	97
C ² -Benzothiophenes	0.46	2.72	
Unidentified as S	13.45	89.68	
Total S concentration	26.05	388.67	

Reagents

ICP-MS argon, diluent argon (99.999%), and oxygen (99.9995%) collision cell gases were obtained from Air Liquide America (Houston, TX). Helium carrier gas was obtained from AirGas (99.9995%) (Bay City, MI). High purity deionized ASTM type II water from Aqua Solutions (Deer Park, TX) was used for nebulizer/spray chamber. Standards of thiophene (99%), 2-methylthiophene (98%), 2-ethyl thiophene (97%), benzothiophene, and 2-methyl benzothiophene (97%) were obtained from Sigma-Aldrich Chemical Co (St. Louis, MO). Standards were prepared in pesticide-grade hexane mix from Thermo Fisher Scientific. A 100 ppm carbonyl sulfide balance nitrogen gas standard from AirGas was used for carbonyl sulfide calibration. An 11 ppm arsine balance hydrogen gas standard from Praxair Electronics (Orangeburg, NY) was used for arsine calibration.

Determination of sulfur species in gasoline and FCC naphtha

The major sulfur species in fuels are mercaptans, thiophenes and benzothiophenes, and sulfides and disulfides. Standards of

thiophene, 2-methylthiophene, 2-ethyl thiophene, benzothiophene, and 2-methyl benzothiophene were used to optimize the GC separation over the boiling range of the sample and to generate fully quantitative external calibration curves. Examples of the 1 ppm standard used in the calibration curve and chromatograms from commercial gasoline and FCC naphtha are shown in Figures 4A, 4B, and 4C, respectively. Wherever possible, sulfur species were identified in the gasoline and FCC samples by either spiking with other known qualitative standards or comparison to documented references (7,8). Similar sensitivity responses were observed for each thiophenic species as calculated from the calibration curve. This is shown in Figure 5, which illustrates a sulfur calibration in the range of 0.1 to 10 ppm using the five different thiophenic species.

Table II presents fully quantitative data for the five sulfur species used to prepare calibrations and semi-quantitative data for the other species in the gasoline and FCC naphtha using the species independent calibration strategy. The gasoline and FCC naphtha samples (Figure 4B and 4C) were found to contain 26 and 389 ppm, respectively. The analytical strategy was validated by calculating the recoveries of standard additions in the FCC naphtha sample. Five thiophenic homologs also used in the standard calibration were added to the FCC naphtha. This allowed the calculation of recovery based on the concentration of addition for each of the homologs. The limits of detection (based on signal-to-noise of 3 sigma) were in the 5–10 ppb range.

Determination of carbonyl sulfide and arsine in polymer grade propylene

Under routine operating conditions, a thick-film megabore boiling point column is used for speciation of sulfur compounds in natural gases, fuel gases, and LPGs as described in Figure 6. It has been determined empirically that the sulfur to carbon specificity ratio is between 250,000:1 to 500,000:1. When specifications or required detection limits are 0.5 to 1.0 ppm or higher, there is little need to be concerned about this small interference. However, when measuring impurities at single or double digit ppb levels, a chromatographic separation is warranted. This situation applies to the analyses of impurities in polymer grade propane–propylene mixtures. Standards for this analysis were prepared at ppb levels using the previously described dilution apparatus. These concentrations were then virtually reduced further by introduction in the smaller loop fixed to the gas sampling valve. Linearity of response has been documented (11), however at double digit ppb levels, single point standards and standard additions within a factor of ten of the target concentration are the normally all that are required.

Figures 7A and 7B represent analyses of carbonyl sulfide and arsine in a propane–propylene

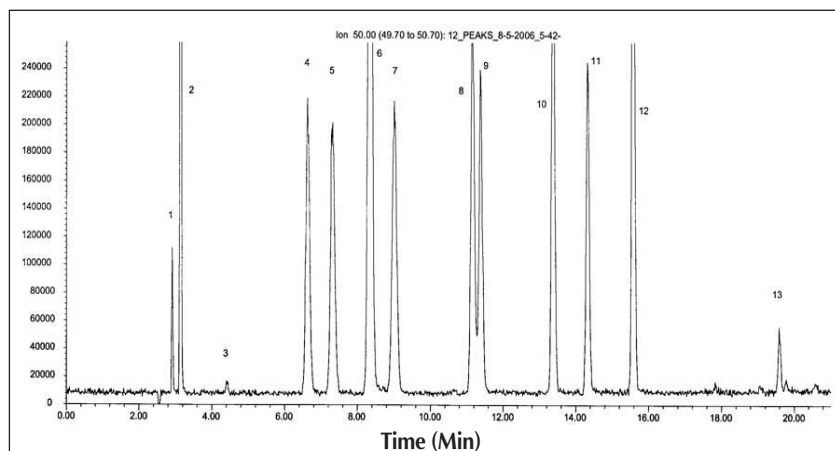


Figure 6. Chromatogram of qualitative sulfur species for gas analysis. Hydrogen sulfide, 1; carbonyl sulfide, 2; methyl mercaptans, 3; ethyl mercaptan, 4; dimethyl sulfide, 5; carbon disulfide, 6; isopropyl mercaptan, 7; *n*-propyl mercaptan, 8; methyl ethyl sulfide, 9; thiophene, 10; diethyl sulfide, 11; dimethyl disulfide, 12; diethyldisulfide, 13. Note use of mass 50 ($^{34}\text{S}^{16}\text{O}^+$ isotope). Column 100-m \times 0.53-mm \times 5- μm film DB-1. Initial temperature 35°C. Initial hold 8 minutes. Ramp rate 15°C min $^{-1}$. Final temperature 220°C.

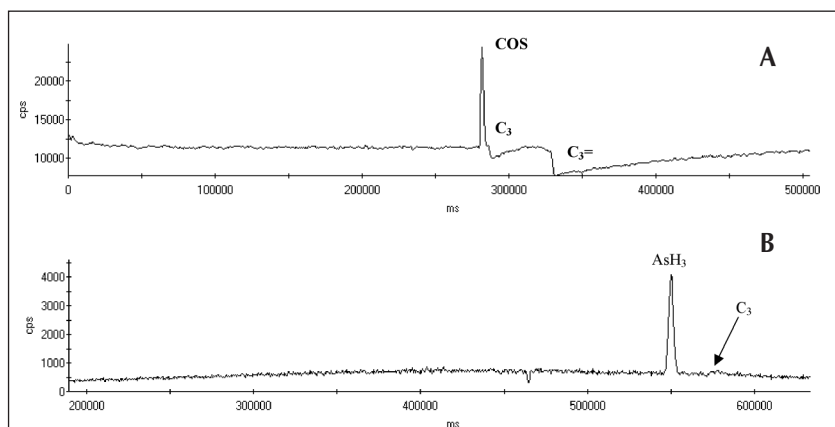


Figure 7. 40 ppb carbonyl sulfide, balance propane and propylene (A). 2.5 ppb arsine in Propane–Propylene mix. Detection limit \sim 200 parts per trillion (B).

mix, respectively. A concentration of 40 ppb of carbonyl sulfide was found in the sample, and it is evident that at low ppb levels there is some small amount of signal suppression from the matrix peak. What is notable is that there is no lasting effect on the torch or ICP-MS system, and subsequent analyses yielded consistent results. In Figure 7B, the matrix interference is negligible when measuring arsine at single digit ppb levels.

Conclusion

Commercial GC-ICP-MS instrumentation has evolved to become a proven academic research tool as well as a routine tool for the commercial laboratory environment.

In the case of sulfur analysis, the GC-ICP-MS instrumentation facilitates similar calibration sensitivities for different sulfur compounds because the inductively coupled plasma processes the eluting sulfur compounds in the same fashion regardless of their functionality, just as it does in direct aspiration of aqueous samples for various elements.

Normally oxygen in the form of OO^+ presents a serious interference for the measurement of S^+ at low concentration. Use of oxygen as a collision cell technology (CCT) gas, albeit counterintuitive, is an excellent choice for the measurement of sulfur by ICP-MS because it shifts the OO^+ interference away from the S^+ comprehensively. This latest generation of collision/reaction cell technology exploits the ability to remove or shift otherwise isobaric interferences to the point where they virtually disappear. Other products that have successfully been analyzed in this laboratory are trace amounts of thiophene in benzene (Figure 8) and characterization of sulfur content in kerosene (Figure 9). The sulfur chromatogram in Figure 9A displays a broad unresolved envelope beginning near 700 s. This is due to unresolved sulfur compounds because, as discussed earlier, the carbon interference is quite negligible, indeed generally a slightly negative signal. Attempts have not been made to determine the reliability of these measurements for total sulfur in anything other than gas samples.

The use of the tandem gas-liquid interface simplifies tuning for gas phase analysis while introduction of small amounts of water through the nebulizer/spray chamber allows for near normal operation of the plasma in its most robust operational state. This analytical strategy also facilitates changeover from gas to liquid analysis to occur with virtually no changes in instrument tuning. Indeed this feature is used to calibrate gas phase analytes for which standards are not readily available such as iron and nickel carbonyls. Using the species independent calibration and cross-calibration two different elements can be measured and their relative responses characterized in the aqueous phase so one can be used to calibrate the other in a gas phase sample.

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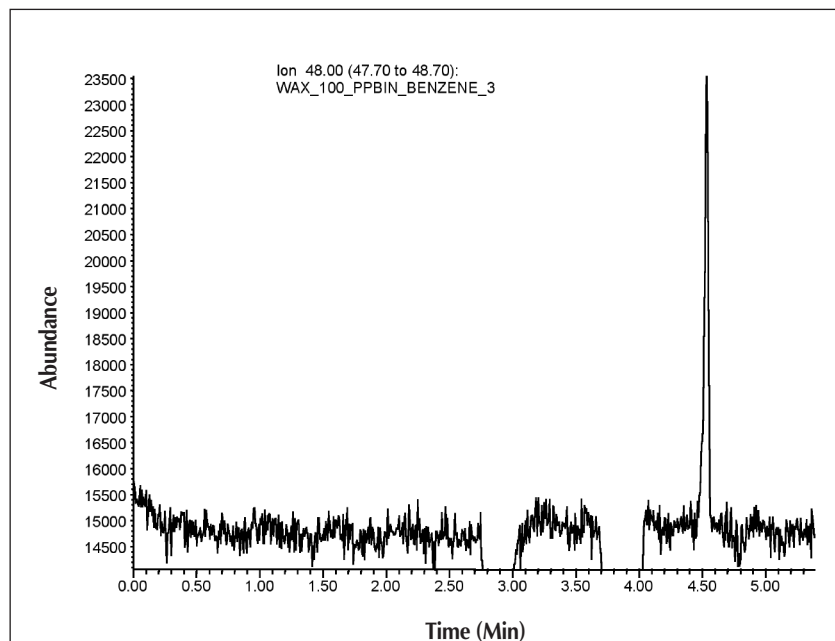


Figure 8. 100 ppb thiophene in reagent grade benzene. Column 60-m \times 0.32-mm \times 1.0- μ m film Stabilwax. 60°C isothermal. Argon carrier @ 15 psig. Split 10 mL/min.

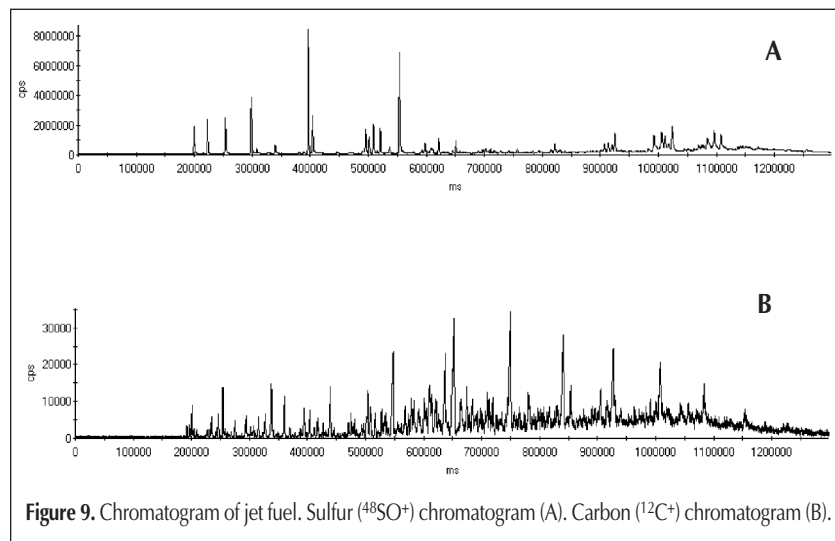


Figure 9. Chromatogram of jet fuel. Sulfur ($^{48}SO^+$) chromatogram (A). Carbon ($^{12}C^+$) chromatogram (B).

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