

Determination of Elemental Sulfur in Gasoline by Gas Chromatography with On-Column Injection and Flame Ionization Detection Following Derivatization with Triphenylphosphine

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Abstract

Several years ago, the presence of elemental sulfur in gasoline became a significant issue for the automotive and fuel industries. In several incidents, elemental sulfur at trace levels led to the corrosion of silver alloy fuel sensing elements in automobile gasoline tanks. This report describes a derivatization method that allows the determination of trace levels of elemental sulfur using flame ionization detection. The sample is derivatized with triphenylphosphine to form triphenylphosphine sulfide. This component is readily detected with a flame ionization detector. In most analyses, on-column injection was employed to allow detection of trace levels of elemental sulfur. However some analyses with splitless injection were also performed. For some gasolines, detection limits on the order of less than 1 $\mu\text{g/g}$ elemental sulfur were possible with this approach. However, the detection limit can vary depending upon the concentration of trace higher boiling components. The precision of the analysis, as measured by the relative standard deviation of triplicate injections, for gasolines containing 1 to 10 $\mu\text{g/g}$ of elemental sulfur was in the 1 to 3% range. The recovery of a gasoline spiked with $\sim 4 \mu\text{g/g}$ elemental sulfur was 102%. The presence of ethanol did not appear to affect results.

Introduction

Several years ago, the corrosion of silver alloy level-sensor elements in fuel tanks arising from the presence of elemental sulfur in the gasoline emerged as a problem for the automotive and motor fuel industries. Corrosion of the fuel level sensing element can result in a fuel gauge providing false level readings. This prompted the addition of a maximum silver corrosion level to the ASTM gasoline specification, and the development of a corrosion test based on the discoloration of a silver coupon after a

4-hour exposure to the fuel at 50°C (1). The corrosion problem is thought to arise primarily from the presence of trace levels of elemental sulfur in the fuel. Other sulfur species (hydrogen sulfide or mercaptans) may also play a role in silver corrosion. Certain gasoline additive chemistries can help in reducing the corrosion extent.

An analytical method to determine trace levels of elemental sulfur is therefore desirable to confirm the presence of elemental sulfur in cases where corrosion has occurred or to predict the presence of silver corrosive species. The standard corrosion test requires 4 h for completion followed by a visual and subjective rating process. A rapid analytical technique to determine elemental sulfur would therefore be of value. It appears that elemental sulfur levels as low as 2–3 $\mu\text{g/g}$ may be sufficient to induce silver corrosion.

A number of analytical techniques have been applied to determine elemental sulfur in hydrocarbons. These include chemical methods (2), polarography (3–6), liquid chromatography (7), and gas chromatography (GC) (8–11). GC is particularly suited for the determination of elemental sulfur and a number of variants using selective detection have been described. Elemental sulfur may also be detected by GC or liquid chromatography after derivatization with triphenylphosphine (12–14). This results in the formation of the corresponding triphenylphosphine sulfide. This product has typically been determined by GC with element selective detection (S or P selective).

In this work, we describe the determination of low levels of elemental sulfur in gasoline with flame ionization detection (FID). This is advantageous to refinery laboratories that do not have access to GCs equipped with element selective detection. One of the advantages of the derivatization scheme is an almost 9-fold increase in the mass concentration of the sulfur species (i.e., one mole of sulfur produces 8 moles of TPS). This, coupled with on-column injection, allows the detection of sub- $\mu\text{g/g}$ (ppm) levels of elemental sulfur in gasoline without the need for element selective detection. On-column injection is well-suited

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for the trace level determination of high boiling components as it avoids discrimination effects typically found in the analysis of high boiling compounds with split or splitless injection, although some analyses reported here employed splitless injection. In this work, both internal and external calibration approaches were employed.

Experimental

Reagents

Triphenylphosphine (TPP), triphenylphosphine sulfide (TPS), and phenyl tridecane, the internal standard (IS), were obtained from Aldrich and used as received. Elemental sulfur was obtained from Acros and was 99.999% pure. In initial experiments, it was used as received; in some later experiments, it was heated for 1 h at 100°C (2). Gasoline samples were prepared in commercial fuels including both unleaded regular and premium grades.

A calibration solution of IS and TPS was prepared in isooctane at concentrations of ~ 750 µg/mL each. This was diluted 1:10 with toluene prior to analysis. An internal standard solution of phenyl tridecane was prepared in isooctane. This contained ~ 750 µg/mL of the IS. Calibration check solutions were prepared by weighing 10 mL of unleaded regular grade gasoline into a vial followed by addition of 1 mL of IS solution and 1 mL of a solution of TPS in isooctane containing an appropriate concentration of TPS. External standard solutions were prepared by serial dilution of a 250 µg/mL solution of triphenylphosphine sulfide in xylene or toluene and typically spanned the range of 5 to 150 µg/mL.

Procedure

A solution of the reagent (TPP) was prepared in toluene at 4 mg/mL. It was prepared fresh daily to minimize degradation caused by exposure to air. Samples were prepared for analysis by weighing out 10 mL of sample followed by addition of 1 mL of IS solution and 2 mL of the TPP reagent solution. The reaction

appeared to be rapid, but it was not investigated in detail. Borchardt and Easty (11) report that the reaction was instantaneous in toluene and that the solutions were stable for at least 24 h. In this work, samples were typically allowed to react for 15 min before being loaded into autosampler vials. All samples were typically analyzed on the same day immediately after preparation, although some data presented later suggests that the solutions are stable for several days. Typically, 6 to 8 samples were analyzed at a time. In cases where the gasoline was spiked with known amounts of sulfur, 1 mL of a solution of the appropriate amount of elemental sulfur in toluene was added. These were prepared by serially diluting a stock solution containing ~ 175 µg/mL elemental sulfur in toluene.

The response factor (RF) for TPS and the concentration of elemental sulfur in samples by the internal standard method were calculated as below.

$$RF = (\text{wt. IS} / \text{wt. TPS}) \times (\text{Area TPS} / \text{Area IS})$$

$$\text{Elemental Sulfur } \mu\text{g/g} = (1 / (9.2 \times RF)) \times (\text{wt. IS} / \text{wt. Sample}) \times (\text{Area TPS} / \text{Area IS})$$

The factor 9.2 converts the weight of TPS into the corresponding value for elemental sulfur.

For external standardization, the area of the TPS peak was converted to a concentration using the slope and intercept of the calibration curve. This was multiplied by the total volume and divided by the sample weight and the 9.2 factor to obtain the elemental sulfur concentration (µg/g).

Instrumentation

Most analyses were performed on a Hewlett Packard 5890 GC equipped with an FID and an on-column injector. A Hewlett Packard Model 7673 was used to inject samples. The analytical column was a 30 m × 0.25 mm polydimethylsiloxane (DB-1, J&W Scientific, Santa Clara, CA) with a film thickness of 0.25 µm. This column was found to provide sufficient resolution for this analysis. The analytical column was preceded by a section of fused silica 1 m × 0.53 mm to facilitate use of automated on-column injection. A direct “press tight” connector was employed to couple the columns. The column oven was temperature programmed from 80°C to 325°C at 6°C/min after a 2 min initial hold. The column head pressure was 20 psig, and helium was employed as the carrier gas. Cool on-column injection was employed with an injection volume of 1 µL. The detector temperature was maintained at 350°C. Analyses with splitless injection were performed on an Agilent 6890 GC equipped with FID, split/splitless injector, and an autosampler. Chromatographic conditions were identical to those described.

GC-MS analyses were performed on a Hewlett Packard Model 5970 coupled to a 5890 GC. The column was a 30 m × 0.32 mm HP-1MS (Agilent) with a 0.25 µm film thickness. The column was temperature programmed from 80°C to 330°C at 8°C/min. The column head pressure was 4.5 psig,

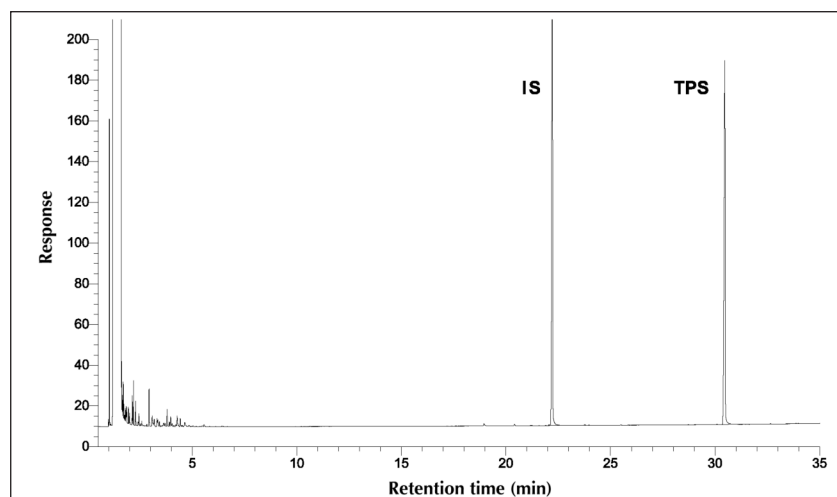


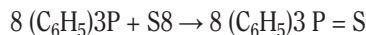
Figure 1. Chromatogram of TPS calibration standard containing phenyl tridecane internal standard (IS). Concentration of each component is approximately 75 µg/mL. See text for chromatographic conditions.

and helium was employed as the carrier gas. Cool on-column injection was employed. The transfer line to the MS was held at 300°C. The injection volume was 1 μ L.

Results and Discussion

Elemental sulfur appears to be present in gasoline primarily in the form of S8 rings with smaller amounts of S6 and S7 (2). The method described in this report is based on the rapid reaction of

TPP with elemental sulfur to form TPS (13) as shown:



Thus one mole of elemental sulfur is converted into 8 moles of product. There are several interesting consequences arising from this reaction. First, the elemental sulfur is converted into a form suitable for detection with an FID. Second, as a result of this reaction, a 9.2-fold increase in the mass of the sulfur-containing molecule occurs. Thus a sample containing 1 $\mu\text{g/g}$ of elemental sulfur will contain 9 $\mu\text{g/g}$ of the derivative. In addition, all cyclic sulfur species (S6, S7, S8, etc.) react to form a single product. The derivative has a high boiling point and elutes in a region in the chromatogram where few major gasoline components elute. As a result of these factors, it is possible to detect elemental sulfur without the use of an element-selective detector. On-column or splitless injection was employed to improve the detection limit. On-column injection also minimizes injector discrimination effects; however, in this case, similar results were obtained with either injection approach.

This approach also incorporates phosphorous into the sulfur containing species allowing use of phosphorous selective detectors if desired. This approach may be particularly useful for the determination of elemental sulfur in diesel fuel where it is not possible to separate TPS from the diesel components or for gasolines that contain high boiling components that interfere with TPS.

Calibration

Where possible, an IS approach to calibration was adopted. In cases where gasoline components interfered with the IS peak, an external standardization method was employed. Figure 1 contains a chromatogram of a calibration solution of triphenylphosphine sulfide and the IS (phenyl tridecane) prepared in isooctane and diluted in toluene. The response factor for TPS was ~ 0.85 . The relative standard deviation of the response factor from triplicate runs of this solution was less than 1%. The triphenylphosphine sulfide (TPS) had a retention time of 30.5 min, while the IS (phenyl tridecane) had a retention time of 22.5 min.

Figure 2 contains a typical calibration curve for TPS that was obtained using the external standard approach. The curve is linear through the range and had a correlation coefficient exceeding 0.999. The lowest point on this particular calibration curve corresponds to 0.8 $\mu\text{g/mL}$ of elemental sulfur.

A series of solutions of TPS in unleaded regular grade gasoline were prepared and analyzed via the IS approach. These contained TPS at concentrations ranging from 15 to 300 $\mu\text{g/g}$. These are equivalent to 1.7 to 33 $\mu\text{g/g}$ of elemental sulfur in gasoline. Results of these experiments are provided in Table I. In all cases, we were able to determine the spiked TPS with good recovery even at the lowest level. The average recovery was 99.6% (recovery defined as the ratio of the found to prepared values times 100%).

TPS prepared ($\mu\text{g/g}$)	TPS found ($\mu\text{g/g}$)	Equivalent S prepared ($\mu\text{g/g}$)	Equivalent S found ($\mu\text{g/g}$)	Recovery (%)
15.6	15.6	1.69	1.69	100
31.2	31.5	3.40	3.43	101
77.9	77.0	8.45	8.35	99
156	154	16.9	16.7	99
312	307	33.8	33.3	98

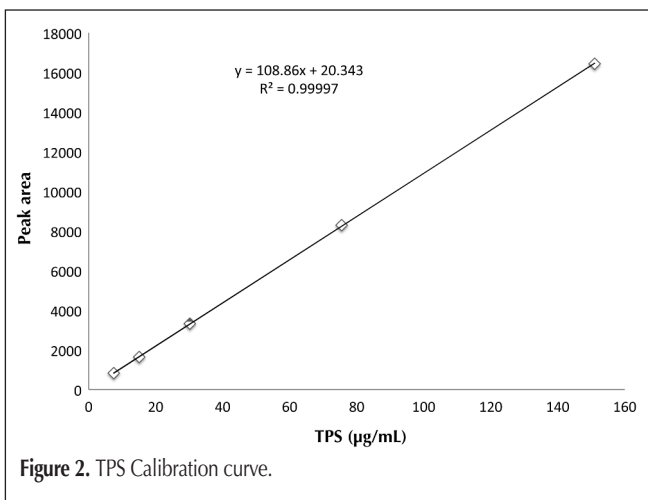


Figure 2. TPS Calibration curve.

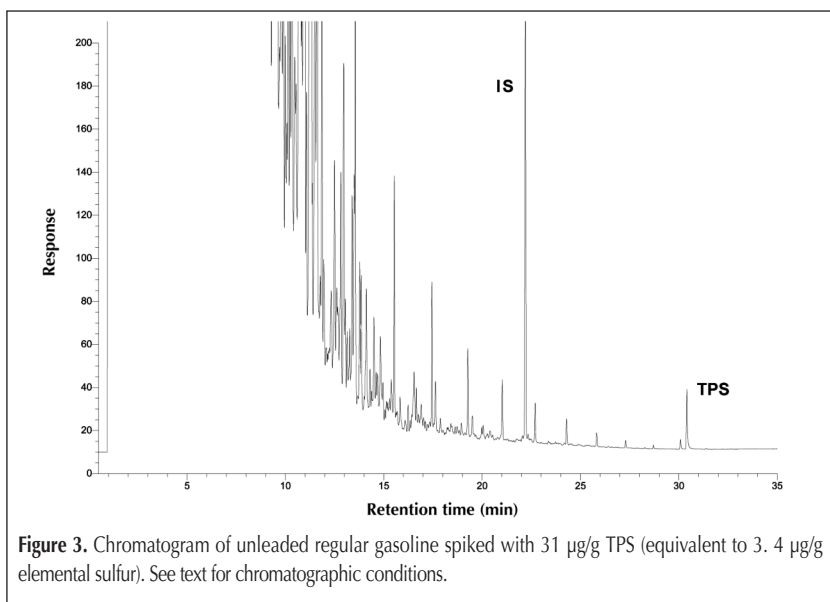


Figure 3. Chromatogram of unleaded regular gasoline spiked with 31 $\mu\text{g/g}$ TPS (equivalent to 3.4 $\mu\text{g/g}$ elemental sulfur). See text for chromatographic conditions.

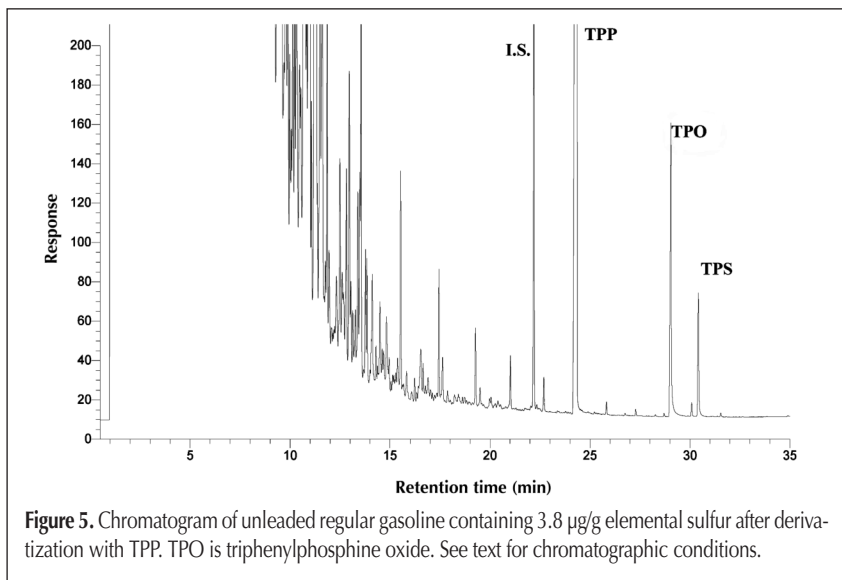
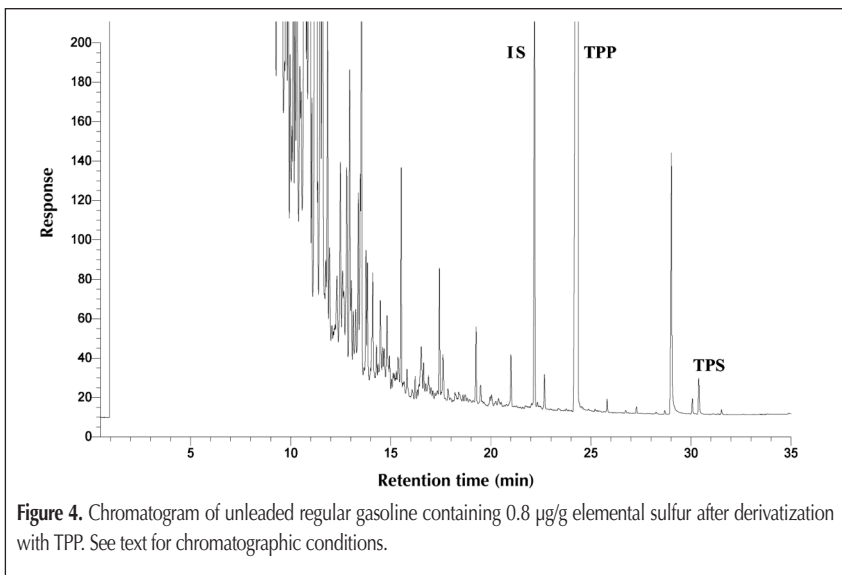
Figure 3 contains a chromatogram of one of these TPS in gasoline standards. The TPS concentration is equivalent to 3.4 $\mu\text{g/g}$ of elemental sulfur in an unleaded regular gasoline. Elemental sulfur in gasoline at these concentrations appears sufficient to cause silver corrosion (15).

Blank

A small peak was noted at the same retention time as TPS (30.5 min) in solutions of triphenylphosphine diluted into

Spiked Conc. ($\mu\text{g/g}$ elemental S)	Average determined Conc. ($\mu\text{g/g}$ elemental S)	RSD (%)	Recovery (%)
0.8	1.1	2.7	130
2.1	2.3	1.3	110
3.8	3.9	1.3	102
10.4	10.1	1.1	97

*Results of triplicate analyses.



toluene or xylene at the same concentrations as in gasoline samples. Given the sample size of gasoline employed in this analysis (7–8 g), the blank contribution from the reagent would be equivalent to approximately 0.1 $\mu\text{g/g}$ elemental sulfur in gasoline.

Analysis of spiked gasolines

Table II contains results from the triplicate analysis of unleaded regular gasoline spiked with known amounts of elemental sulfur after derivatization with TPP. Once again the IS approach was employed in these analyses. Spiked levels ranged from 0.8 to 10 $\mu\text{g/g}$ elemental sulfur. Precision, as measured by the relative standard deviation, of triplicate injections ranged from 1% to 3%. Recovery of the lowest spike (0.8 $\mu\text{g/g}$) was slightly high, but the absolute error in the determined value was only 0.3 $\mu\text{g/g}$. Average recovery for the four spikes was 110%. Excluding the lowest concentration solution, average recovery of the spiked elemental sulfur was 103%. These were not corrected for any blank effects.

Figure 4 contains a chromatogram of the 0.8 $\mu\text{g/g}$ elemental sulfur spike, while Figure 5 contains that of the 3.8 $\mu\text{g/g}$ spike. In this gasoline sample the elemental sulfur derivative is well resolved from any gasoline components. The peak immediately in front of TPS at 29 min in these chromatograms is due to triphenylphosphine oxide (TPO) (Figure 5). The TPO forms from reaction of elemental oxygen as well as hydroperoxides with TPP (16). Some authors (11,14) who have employed the triphenylphosphine reaction with elemental sulfur have taken care to exclude oxygen to minimize this reaction. This was typically necessary for cases where the TPP to elemental sulfur ratio was small to minimize other side reactions (11) or when the reaction was carried out in solvents which limited the reaction rate (non-hydrocarbon solvents). In our case, a large excess of TPP was added and a significant excess remained after the reaction was complete (see TPP peak in Figure 5). This coupled with the results in Table II indicate that oxygen exclusion was not necessary for our analyses.

Several additional samples of gasolines were spiked with elemental sulfur and subjected to IS analysis. These included additional analyses of the same unleaded regular gasoline (Fuel A) as before both with and without 10% ethanol, two premium gasolines (Fuels B and C), and another unleaded regular (Fuel D) both with and without 10% ethanol. These data are summarized in Table III. Recovery values were similar to those reported in Table II. The overall average recovery was 105%. The analyses of Fuel D were performed with splitless injection rather than on-column. This did not appear to appreciably alter results.

The presence of ethanol did not appear to have any substantial impact on the results. Fuel C contained high levels of impurity peaks, and

there were peaks due to gasoline components in the vicinity of the IS and TPS. It was necessary to carefully integrate these peaks. In such cases, the use of an element selective detector such as an atomic emission detector, selective sulfur or phosphorus detector, or ICP-MS could prove useful. However, despite this

Matrix	Spiked Conc. ($\mu\text{g/g}$ S)	Found Conc. ($\mu\text{g/g}$ S)	Recovery (%)
Fuel A	5.1	5.2	102
Fuel A*	5.0	4.6	92
Fuel A	5.1	5.3	104
Fuel B	5.3	4.8	90
Fuel C	5.5	6.0	110
Fuel D	5.1	5.7	111
Fuel D*	2.5	3.1	124
Fuel D*	5.1	5.5	108
Fuel D*	7.6	8.0	105

* With 10% ethanol.

Fuel	Spiked Conc. ($\mu\text{g/g}$ S)	Average Conc. Found ($\mu\text{g/g}$ S)	Recovery (%)	Std. Dev. ($\mu\text{g/g}$ S)	No. of Measurements
Fuel E	1.9	2.1	110	0.16	5
Fuel E*	2.0	1.8	90	0.23	5
Fuel F	2.6	2.7	104		2
Fuel F	0	0.2			1
Fuel G	2.6	2.7	104		1

* With 10% ethanol.

fact, reasonable recovery of the spiked elemental sulfur was achieved for Fuel C.

We also explored use of external calibration for this determination in order to address situations like that described earlier. This approach eliminates the need for clean separation of the IS from gasoline components. Fuels E through G, spiked with known amounts of elemental sulfur, were employed in this study. Figure 6 shows a chromatogram of Fuel E, a premium gasoline spiked with 1.9 $\mu\text{g/g}$ elemental sulfur. For this sample, note the presence of interfering peaks in the time window where the IS would normally elute (~ 22 min). Table IV contains data from the external calibration analysis of Fuel E as well as that from the analysis of two additional premium gasolines (both from different refiners) that were spiked with low levels of elemental sulfur. Fuel F was also analyzed without the addition of elemental sulfur. Recovery values were in line with those noted earlier. The relative standard deviation for replicate analysis of Fuel E was on the order of 10%, slightly higher than those noted in Table II. The recovery for Fuel E containing ethanol was slightly lower than that of the fuel without ethanol, but the variation was not significant. The five replicate analyses of Fuel E, both with and without ethanol, were performed over a 4-day period on the same solutions. No differences were noted in the results over this time, indicating the derivative was stable in these solutions. The analysis of Fuel F without addition of elemental sulfur gave a value of 0.2 $\mu\text{g/g}$, a value similar to that noted earlier for a toluene blank.

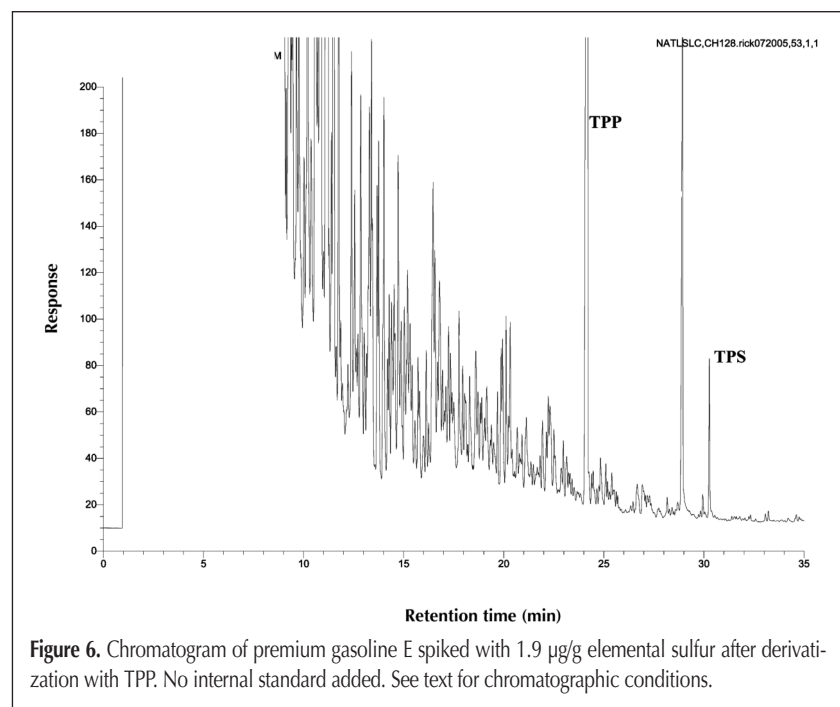
GC-MS Confirmation of TPS as Reaction Product

To confirm that the peak formed from the reaction of TPP with elemental sulfur was TPS, a sample of gasoline containing ~ 8 $\mu\text{g/g}$ of elemental sulfur was derivatized and examined by GC-MS. The spectrum shows a large molecular ion at 294 Da, as well as large peaks at 183, 262, and 293 Da and the spectrum closely matched that reported in the literature for triphenylphosphine sulfide (17). We also confirmed the identity of the triphenylphosphine oxide peak.

Summary

Derivatization with triphenylphosphine to form triphenylphosphine sulfide is an effective approach to determine trace levels of elemental sulfur in gasolines with standard flame ionization detection. The reaction is rapid and quantitative.

On-column injection allows detection of low levels of elemental sulfur although comparable results were obtained with splitless injection. It was possible to reproducibly determine elemental sulfur at concentrations of less than 1 $\mu\text{g/g}$ with this approach. The precision of the analysis, as measured by the relative standard deviation of triplicate injections, of a gasoline containing 1 to 10 $\mu\text{g/g}$ of elemental sulfur was



typically in the 1 to 3% range. Relative standard deviations for gasolines containing higher levels of high boiling impurities were on the order of 10%. The recovery of a gasoline spiked with approximately 4 µg/g elemental sulfur was 102%. The presence of ethanol does not appear to present problems. Gasoline samples with higher levels of higher boiling components may contain interferences requiring use of selective detectors. Either internal or external calibration were found to be suitable, although most results reported in this report were based on internal standardization.

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Manuscript received April 6, 2009
revision received June 2, 2009.