

Improved Analysis of Sulfur, Nitrogen, and Other Heteroatomic Compounds in Gasolineand Diesel-Range Materials Using GC/Atomic Emission Detection

Application

Gas Chromatography January 1998

Authors

Bruce D. Quimby Agilent Technologies, Inc. 2850 Centerville Road Wilmington, DE 19808-1610 USA

Abstract

An optimized procedure was developed for the analysis of sulfur and nitrogen compounds in gasoline- and diesel range materials. The analysis is performed using an Agilent 6890 gas chromatograph (GC) configured with an Agilent G2350A atomic emission detection (AED) system. A $30 \text{-m} \times 0.32 \text{-mm}$, $1 \text{-} \mu \text{m}$ HP-1 MS capillary column is used for separation. The method is applicable to low-sulfur gasoline and diesel fuels. Nitrogen compounds can also be determined. The method can be applied to other light gas oil fractions with final boiling points of approximately C25 (402 °C, 756 °F). The configuration meets the requirements for determining sulfur in gasoline by ASTM method D 5623. The procedure can be extended to also measure

oxygenates, organolead, organomanganese, and fluorine compounds.

Introduction

Determination of the sulfur content in petroleum feed streams is useful for improving and optimizing refinery catalytic processes. With the trend toward manufacturing of low-sulfur fuel products, such as gasoline and diesel fuel, accurate and precise measurements are important for obtaining product quality and meeting regulatory requirements. Additionally, knowledge of the individual sulfur types gives valuable insight into processing characteristics.

The measurement of nitrogen compounds is also of interest as these compounds are suspected of causing problems such as color and gum formation, engine deposits, and poisoning of some catalysts. The quantitation of the nitrogen compounds in petroleum materials is quite challenging, however, because of the low levels of nitrogen present and the potential for interference from the petroleum matrix.

Gas chromatography-atomic emission detection (GC/AED) has been used to measure the sulfur and nitrogen content in many types of petroleum samples.^{1,2,3} The AED technique is well suited for these measurements because it has:

- High sensitivity required to measure low amounts of sulfur and nitrogen
- High selectivity required to reject hydrocarbon interferences
- No quenching
- Linear response
- Compound-independent element (equimolar) response factors

The ASTM method D 5623-94 (Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection)⁴ recommends the use of the sulfur chemiluminescence detector (SCD) or the AED.



Flame photometric detectors, both conventional and pulsed,⁵ are not recommended because of problems with quenching of the sulfur signal by coeluting hydrocarbons.

With the development of the G2350A GC/AED system and further improvements in spectrometer design and element detection algorithms, the AED is well suited for sulfur and nitrogen measurements in petroleum liquids.⁶

The AED is a multi-element detector that can be used to measure twentythree different elements. In addition to sulfur and nitrogen, elements such as carbon, hydrogen, oxygen, lead, manganese, fluorine, and silicon, can all be detected. A single instrument setup can then be used for a wide range of petroleum analyses.

This application note describes a procedure for the analysis of sulfur and nitrogen compounds in gasoline- and diesel-range materials. This method can also be extended to materials boiling just beyond the diesel fuel range (for example, light gas and cycle oils). The experimental conditions used in this study, including AED reagent gas flows, were adjusted to maximize the sulfur and nitrogen selectivity over carbon (hydrocarbons). Using these conditions, the GC/AED can be used to perform ASTM D 5623-94. Examples of detecting other elements such as oxygen, lead, manganese, and fluorine are also given.

Experimental

A 6890 GC coupled to a G2350A AED was used for this study. The GC was equipped with a split/splitless

injection port operated in split mode. All gas flows and pressures within the GC were controlled electronically. An auxiliary pressure control module on the 6890 GC was used to set the AED reagent gas pressures. Sample injections were made by a 6890 Series automatic liquid sampler and a 5-µL syringe.

The inlet was fitted with a singletapered liner (part no. 5181-3316) containing a 1-cm piece of glass wool. The glass wool plug was transferred directly from the standard split/splitless liner (part no. 19251-60540) to the single-tapered liner and positioned so that the top of the plug was 16 to 18 mm from the top of the liner. This liner acted to minimize discrimination across the boiling range and improve sample repeatability by "wiping" the sample droplet from the end of the syringe. The inlet end of the capillary column was positioned in the center of the small diameter section of the liner at about 4 mm above the tip of the column ferrule. A $30\text{-m} \times 0.32\text{-mm}$ id $\times 1\text{-}\mu\text{m}$ film thickness HP-1 MS capillary column was used for separation (part no. 19091S-713). This column was chosen because it has a lower specified rate of column bleed than conventional methyl silicone capillary columns. The inlet ferrule used is graphitized polyimide to reduce diffusion of air into the inlet. Note that the ferrule should be retightened after the first few runs to compensate for shrinkage.

The Agilent AED ChemStation was used to control the GC/AED system and to provide for data acquisition and peak integration. The ChemStation was operated using a Microsoft® Windows[™] environment, and the AED ChemStation automated the entire process. Two injections were made to determine carbon, sulfur, and nitrogen in the samples. Hydrogen and oxygen were used as reagent gases for both carbon (179 nm) and sulfur (181 nm). In the case of nitrogen (388 nm), methane was added as the third reagent gas.

To further improve sulfur and nitrogen selectivity over carbon, the AED gas flows (hydrogen, oxygen, and helium makeup) were optimized to minimize interferences from hydrocarbons. In addition to the reagent gases, the amount injected was optimum for each analysis. The AED ChemStation method automated this process for routine laboratory use. The makeup gas flow was set to 100 mL/min when the high makeup flow valve turned on for the nitrogen and metals analysis. With this setting, the makeup flow is raised to about 230 mL/min. With electronic pressure control (EPC) of the reagent gases, all methods shown here can be run in sequence without intervention except for the oxygen analysis. This requires the source of auxiliary gas to the AED to be changed from methane (used for nitrogen analysis) to 10% methane in nitrogen.

To obtain the best performance for nitrogen detection, it is important to use helium carrier and makeup gas that is nitrogen-free. A heated gettertype helium purifier (model GC50, SAES Pure Gas Inc.) was used in the present setup. This type of purifier removes N_2 and many other contaminants in helium down to ppb levels.

Quantitation of sulfur and nitrogen was based on ASTM D 5623-94 with

both internal and external standardization used. External standard quantitation was based on the response of a t-butyl disulfide (TBDS) solution. For internal standard calculations, a solution of TBDS in iso-octane was gravimetrically spiked into the gasoline. The samples used for internal standard calculations were determined to be free of TBDS. Nitrogen was quantitated externally based on the response of a nitrobenzene standard.

CARB Low Sulfur RFG and Conventional Gasoline quality control samples were obtained from AccuStandard. RFA gasoline with 14.9% methyltertiarybutylether was purchased from Scott Specialty Gases. Tertiary-butyldissulfide (TBDS), nitrobenzene, and methylcyclopentadienyl manganese tricarbonyl (MMT) were from Aldrich Chemical. The standard reference materials with certified sulfur content and the tetraethyl lead were obtained from National Institute of Standards Technology (NIST). The remainder of the samples were provided by various petroleum laboratories.

Table 1 lists the entire set of equipment and conditions used for this study.

Results and Discussion

Gasoline Range Analysis

Figure 1 shows the carbon, sulfur, and nitrogen chromatograms from

Table 1 Experimental Setup and Conditions

Gas Chromatograph and Detector	
Agilent G1530A Option 002 Option 112	6890 Series GC Power supply for fast oven ramps Split/splitless inlet
Option 207	GC-AED interface
Option 308	Aux EPC for AED reagent gas control
G2350A AED	Atomic emission detector
Column	30-m x 0.32-mm, 1.0 μm HP-1MS (part no. 19091S-713)
Automatic Liquid Sampler	
Agilent G1916A	6890 Series ALS with tray
Data Acquisition/Data Analysis	
Agilent G2371AA	AED ChemStation
Operating Parameters, GC	
Injection port temperature	280 °C
AED transfer line/cavity temperature	310 ℃
Oven temperature program	40 °C to 300 °C at 10 °C/min, hold 10 min
Column pressure (constant pressure mode)	12 psi
Carrier gas	Helium
Split ratio (Carbon, Sulfur)	50/1
Split ratio (Lead, Manganese, Oxygen)	100/1
Split ratio (Nitrogen)	10/1 (Gas Saver 200 mL/min at 0.3 min)
Split ratio (Fluorine)	20/1
Injection volume	1 μL (except as noted)
Operating Parameters, AED	
Data rate	2.5 Hz
Method 1, carbon 179 nm and sulfur 181 nm Reagent gases Makeup flow	Oxygen 55 psi, hydrogen 45 psi 100 mL/min
Method 2, nitrogen 388 nm Reagent gases Makeup flow	Oxygen 80 psi, hydrogen 40 psi, methane 50 psi 230 mL/min
Method 3, Oxygen 171 nm Reagent gases Makeup flow	Hydrogen 40 psi, 10% methane in nitrogen 25 psi 100 mL/min
Method 4, lead 261 nm and manganese 259 nm Reagent gases Makeup flow	Oxygen 55 psi, hydrogen 45 psi 230 mL/min
Method 4, fluorine 690 nm Reagent gases Makeup flow	Hydrogen 15 psi 100 mL/min

the analysis of the conventional gasoline sample. The carbon and sulfur data are collected simultaneously in the first method and the nitrogen in a second. For comparison The sulfur chromatogram of the sample after addition of internal standard tertiarybutyldisulfide, is also shown. This sample was analyzed according to ASTM D 5623 using both internal and external standard quantitation. The total sulfur content was measured to be 330 ppm (weight) by both methods. Two trace level nitrogen peaks were also detected, each containing about 0.30 ppm of nitrogen. The lack of any significant response on the sulfur and nitrogen chromatograms from the large hydrocarbons in the gasoline demonstrates the high selectivity afforded by the AED.

A gasoline range product from a catalytic cracking unit is shown in figure 2. Most of the sulfur compounds observed in figure 1 are also present in this sample. Unlike the gasoline in figure 1, the sulfur content of this material is made up mostly of benzothiophene and alkyl-substituted benzothiophenes and the level of nitrogen is much higher (about 560 ppm). The nitrogen profile in figure 2 is typical of that observed in gasolines. The tentative identifications of the nitrogen compounds are taken from the literature.7 We have observed that for most gasolines having measurable nitrogen content, the pattern of nitrogens is very similar to that in figure 2, with only the total amount varying significantly. The AED responds uniformly to nitrogen in all forms, including N2. The large peak at the beginning of the nitrogen chromatogram results from small amounts of air injected with the sample. This peak is excluded from the total nitrogen measurement.







The analysis of a low sulfur (California Phase II) gasoline sample is presented in figure 3. The detection limit for any one component was found to be approximately 0.7 ppm S. This sample contains about 42 ppm of sulfur by ASTM D 5623. The first two peaks in the sulfur chromatograph are not sulfur compounds, but are slight interferences from the largest hydrocarbons in the gasoline. These responses should not be included in the total sulfur calculation. If they are included, the error introduced is minimal because their total area corresponds to only approximately 3 ppm sulfur.

The nitrogen chromatogram in figure 3 was made with a 2-mL injection to increase sensitivity. The largest hydrocarbons at the front of the chromatogram produce small negative responses, but the actual nitrogen peaks are easily identified, even at the relatively low level of 25 ppm total nitrogen.

Figure 4 represents the analysis of a reference gasoline, RFA, containing methyl tertiary-butyl ether (MTBE). The large amount, 14.9 volume %, of MTBE does not cause an interference in the sulfur channel. As in the previous sample, the nitrogen chromatogram was collected with a 2-mL injection. The nitrogen peaks are still visible at 13 ppm total nitrogen. Peak 9 contains approximately 2.5 ppm N.

Figure 5 shows the oxygen chromatogram for RFA. Measuring additive oxygenates in gasoline is simplified greatly by using oxygen selective detection.³⁸ With the



Figure 3. CARB Low-sulfur RFG quality control sample



conditions used here, the AED can detect individual oxygenates down to approximately 0.05%. The detection limit (signal-to-noise ratio = 2) for MTBE in figure 5 is 0.02%, and its performance is comparable to, or exceeds that of, the oxygen flame ionization detector (OFID).

Atomic emission with a helium plasma is a very sensitive and selective means of detecting volatile organometalic compounds. Also shown in figure 5 are the lead and manganese chromatograms from tetraethyl lead (TEL) and methylcyclopentadienyl manganese tricarbonyl (MMT) spiked into RFA. Lead compounds have been used worldwide as antiknock additives for gasoline but are currently being phased out of use in most countries. MMT has been used in the past in the U.S. and Canada.

Note that both the lead and manganese chromatograms exhibit little or no peak tailing and no hydrocarbon interference. Under the chromatographic conditions used here, the detection limit for TEL is approximately 1 ppm. Manganese detection is also very sensitive, allowing measurement of MMT well below 1 ppm. The small peaks before and after the MMT peak are not interferences, but are manganese containing impurities in the MMT.

An important capability of the AED is the ability to confirm the presence of an element in an unknown peak. Figure 6 shows the emission spectra obtained on the MMT peak and on the impurity peak (cymantrene) in figure 5. The three emission lines are







Figure 6. AED Emission spectra used to confirm presence of manganese in peaks 3 (cymantrene) and 4 (MMT) from figure 5

a fingerprint for the element manganese. If the spectrum of a peak contains these three emission lines in the relative intensities shown, then the presence of manganese is confirmed. The cymantrene peak only contains 40 ppb manganese. At this low level, the spectrum clearly shows the three manganese emission lines as seen in figure 6.

Figure 7 shows the chromatogram of a product from an alkylation unit. In this process, a C4 stream undergoes alkylation using hydrofluoric acid as the catalyst. In this example, the process is out of specification, with the level of organofluorides in the product at about 1000 ppm total fluorine. The AED fluorine chromatogram clearly shows the organofluoride impurities elute as compared to the hydrocarbons. From the relative patterns of the carbon and fluorine chromatograms, it appears that the fluorinated compounds are analogues of each of the main hydrocarbons in the sample. The detection limit (signal-to-noise ratio = 2) for a single fluorinated compound is about 0.6 ppm F under the conditions used here.

Kerosine Analysis

The analysis of NIST sulfur in kerosine Standard Reference Materials (SRMs) is shown in figures 8 and 9. The SRM 1616 is a 1-k low-sulfur kerosine with a certified value of 152 ppm total sulfur. The retention time region where TBDS elutes is free from sulfur peaks, so the internal standard technique could be used.

The SRM 1617 is a high-sulfur kerosine standard, with a certified value of 1690 ppm total sulfur. It is interesting to note that the standard appears to have been constructed from a lowsulfur, 1-k kerosine with TBDS added



Figure 7. Off-specification product of HF alkylation unit



Figure 8. NIST SRM 1616 Sulfur in 1-k kerosine standard



Figure 9. NIST SRM 1617 Sulfur in kerosine standard

to increase the sulfur content. Because TBDS is already in the standard, it could not be used as the internal standard for analysis.

There were no detectable nitrogen compounds observed in either kerosine.

Diesel Analysis

Figures 10 and 11 show the sulfur and nitrogen analysis of NIST sulfur in diesel fuel SRM 2724 and SRM 1624b.The SRM 2724 is a commercial no. 2-D distillate fuel oil as defined by ASTM. The certified total sulfur content is 425 ppm. The SRM 1624b is a similar fuel with a certified total sulfur content of 3320 ppm. These standards are very useful for diesel analysis because they bracket the range of sulfur normally encountered in these fuels.

The distribution and relative concentrations of sulfur compounds are similar in both SRMs, with only the total sulfur concentration being significantly different. The reverse is observed in the nitrogen chromatograms—the total nitrogen level is similar, but the profiles are noticeably different, especially in the earlier sections of the chromatograms.

A high-sulfur, high-nitrogen Light Cycle Oil (LCO) is shown in figure 12. Here the sulfur and nitrogen profiles are similar to the other diesels, but the carbon profile is clearly different. This sample contains higher-boiling material and requires an extra 10 minutes of hold time at the end of the chromatographic run to elute the sample completely.

Two samples of commercial lowsulfur diesel fuels from California are



Figure 10. NIST SRM 2724 Sulfur in distillate fuel (diesel) standard



Figure 11. NIST SRM 1624b Sulfur in distillate fuel (diesel) standard

shown in figures 13 and 14. Comparison of the chromatograms illustrates how different the composition of sulfur and nitrogen can be at similar total concentrations. In the first sample, the total nitrogen is contained in a broad, unresolved distribution. In the second sample, the total nitrogen content arises from a few discrete peaks. It was thought that some of the nitrogen peaks in sample 2 could be nitro compounds added as cetane improvers. Both samples were then analyzed for oxygen to see if any of the nitrogen peaks were also oxygenated (i.e., nitro

compounds). While there were no oxygenates found in sample 2, an oxygen-containing peak that did not contain nitrogen was observed in sample 1. The oxygenate was identified as MTBE, and the concentration was measured to be at 0.26%.

In all the diesel-range samples analyzed, the time range where TBDS elutes had little or no sulfur signal, allowing its use as an internal standard.

Precision and Accuracy

The precision of the GC/AED system was evaluated by analyzing the "conventional" gasoline sample, discussed above, fifteen times over a 5-day period. A section of the chromatogram is shown in figure 15. The chromatograms are all offset to zero and are drawn overlaid. The precision of the retention time and sulfur response for the system is clearly evident. The percent relative standard deviation (%RSD) of the total sulfur area is 1.8%. The %RSD of the total carbon area measured simultaneously was 1.1%. The standard deviation of the retention time was 0.001 min for the peak at 8.6 min in the carbon chromatogram of figure 1.

The long-term precision observed here is significantly improved over that of 5890/5921 AED systems. Improvements in the 6890 EPC, such as atmospheric pressure correction, provides more precise control of column flow and split ratio. When used with the split liner described here, the amount injected into the column is very repeatable. The G2350 AED uses the 6890 Aux EPC module to control the reagent gases. The more precise control of reagents, combined with spectrometer and detection algorithm improvements, greatly increases the precision of the AED detector. The sum of the



Figure 12. Refinery Light Cycle Oil (LCO) sample



Figure 13. Commercial California low-sulfur diesel fuel, sample 1

improvements in both the GC and the AED using the conditions described here result in a measured response factor drift for sulfur and carbon of less then 3% in a week.

Seven of the samples shown here were analyzed for total sulfur using both the external and internal standard calculations from ASTM D 5623. The results agreed within 2%, indicating that with the precision observed

with the AED, acceptable results can be obtained with the simpler external standard method. The external standard analysis is simpler to perform because there is less sample preparation required, and the problem of finding a suitable internal standard compound for each sample is eliminated. The internal standard approach is most useful with sulfur detectors or GC systems that have response factor drift problems. The

system described here does not exhibit these problems, thus, simplifying the analysis.

The NIST kerosine and diesel fuel SRMs were used to assess the accuracy (bias) of the method. Using the method as described here, the measured values for total sulfur agreed within 2% of the certified value.

Conclusions

The technique of GC/AED has many valuable uses in petroleum analyses. The ability to speciate of sulfur, nitrogen, oxygen, fluorine, lead, and manganese compounds in one instrument provides a very cost-effective solution to a broad range of analytical needs.





Figure 15. Chromatograms from 15 analyses of conventional gasoline sample run over a 1-week period. Chromatograms are offset to zero and drawn overlaid.

References

- 1. T. Albro, P. Dreifuss, and R. Wormsbecher, "Quantitative Determination of Sulfur Compounds in FCC Gasoline by GC-AED," *J High Resolution Chromatography*, Volume 16 (1), January 1993.
- 2. A. Amorelli, et al, "Estimating Feedstock Processability—Characterize Sulfur Compounds in Middle Distillates and Deeply Hydrotreated Products," *Hydrocarbon Processing*, June 1992.
- B. Quimby, V. Giarrocco, and J. Sullivan, "Fast Analysis of Oxygen and Sulfur Compounds in Gasoline by GC-AED," *J High Resolution Chromatography*, Volume 15, November 1992.
- ASTM D 5623, "Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection," *Annual Book of Standards*, Volume 5, ASTM 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
- J. Robinson, "Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and PFPD," Varian GC Application Note No. 56.
- B. Quimby, P. Larson, and
 P. Dryden, "A Comparison of the G2350A AED vs. 5921A AED for Average Values of MDL and Selectivity for Selected Elements," Agilent Technologies, Inc., Application Note 228-363, Publication (23) 5965-4720E, August 1996.

- D. Tourres, C. Langellier, and D. Leborgne, "Analysis of Nitrogen Compounds in Petroleum Cuts by Gas Chromatography with Chemiluminesce Specific Detection," *Analusis*, Volume 23, Number 4, 1995 (in French).
- J. Diehl, J. Finkbeiner, and F. DiSanzo, "Determination of Ethers and Alcohols in Reformulated Gasolines by GC-AED," *J High Resolution Chromatography*, Volume 18, February 1995.

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

 $\operatorname{Microsoft}{}^{\circledast}{}^{is}$ a registered trademark of Microsoft Corporation.

Copyright©2000 Agilent Technologies, Inc.

Printed in the USA 3/2000 5966-3089E



Agilent Technologies Innovating the HP Way