Improved Measurement of Sulfur and Nitrogen Compounds in Refinery Liquids Using Gas Chromatography–Atomic Emission Detection

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Abstract

The measurement of sulfur and nitrogen compounds in refinery liquids is an important analysis for the petroleum industry. Gas chromatography with atomic emission detection (GC–AED) provides a useful means of selectively detecting these compounds. This article presents a GC–AED method optimized for the analysis of sulfur and nitrogen compounds in gasoline through diesel-range materials. By optimizing such parameters as element wavelength, detector gas flow rates, and chromatographic conditions, the selectivity in the presence of hydrocarbons is increased 10-fold for sulfur and by more than 100-fold for nitrogen. These gains in selectivity result in the ability to measure sulfur and nitrogen at low parts-per-million levels.

Introduction

In recent years, the measurement of sulfur content in refinery liquids has increased in importance. Government regulations have reduced the allowable levels of sulfur in many fuel products. Meeting these requirements and product quality specifications in a cost-efficient manner requires the optimization of refinery processes. Characterization of the types and amounts of sulfur compounds in refinery streams is often a useful part of this optimization.

The analysis of nitrogen compounds is also gaining importance. The interest in these compounds is not driven as much by regulations as it is by product quality and process efficiency considerations. Nitrogen compounds are suspected of causing problems such as color and gum formation, engine deposits, and the poisoning of some catalysts.

The quantitation of sulfur and nitrogen compounds in petroleum materials is quite challenging. The sulfur and nitrogen compounds are usually present at low (parts-per-million) concentration levels, and the matrix is a very complex mixture of hydrocarbons. Gas chromatography (GC) is useful for resolving many of the individual components in fuels, but it is impractical to resolve all individual compounds at parts-per-million levels. For this

reason, GC with element-selective detection is often used (1–4). With a response to only those compounds containing the element of interest, the GC resolution problem is greatly simplified. For example, the sulfur compounds only need to be resolved from each other instead of from all matrix hydrocarbons when a sulfur-selective detector is used.

GC with atomic emission detection (GC–AED) (2–4) is a technique that provides element-selective detection for several elements of interest to the petroleum industry. In addition to sulfur and nitrogen, volatile compounds containing elements such as carbon, hydrogen, oxygen, lead, manganese, fluorine, silicon, nickel, vanadium, and iron can all be detected.

The technique of GC–AED has several characteristics important for the analysis of petroleum samples. Unlike the flame photometric detector (FPD), the AED sulfur response is linear, equimolar, and exhibits little or no quenching. These properties are important for determining the concentration of both total sulfur and individual sulfur species. Because of the large number of sulfur compounds present in petroleum samples, it is impractical to individually calibrate for each one. ASTM method 5623-94 (5) uses a single compound for calibration of all sulfur species, and the accuracy of the method relies on the detector possessing the three properties previously listed. For this reason, the method recommends the use of a detector such as the sulfur chemiluminescent detector (SCD) (6) or the AED, but not FPDs.

Since the introduction of a commercial GC–AED system in 1989, there have been several reports of the use of GC–AED for the measurement of sulfur compounds in petroleum (2–4). Although the technique has generally performed well for sulfur, the detection of nitrogen compounds was limited by selectivity. The original AED used the 174.53- and 174.27-nm atomic lines of nitrogen for detection. Because of severe carbon spectral interferences at these wavelengths, the selectivity of nitrogen over carbon was limited to about 5000. This resulted in the measurement of nitrogen being limited to only the samples with high nitrogen content.

In 1996, new versions of the GC–AED hardware and software became available. Changes in both the hardware and software resulted in noticeable performance improvements for the analysis of sulfur and nitrogen in petroleum matrices. This paper describes the nature of some of these changes and their effects on petroleum

analysis. The results of method optimization studies, which can further improve the technique's performance, are also described. The most significant gains are in selectivity, which are about 10-fold for sulfur and more than 100-fold for nitrogen. These improvements in selectivity allow measurement of both sulfur and nitrogen at low parts-per-million levels.

Experimental

Apparatus

Two similarly configured Hewlett-Packard (Wilmington, DE) HP 6890 GCs interfaced to Hewlett-Packard (Richmond, CA) G2350A AEDs were used. The inlets were split/splitless injection ports operated in split mode. All GC gas flows and pressures were controlled by electronic pneumatic control (EPC). An auxiliary EPC module on the GC was used to set the AED reagent gas pressures. Sample injections were made with an automatic liquid sampler and a 5-µL syringe.

The Hewlett-Packard AED ChemStation (using Microsoft Windows, Redmond, WA) was used to control the GC–AED system and to provide for data acquisition and peak integration. Carbon, sulfur, and nitrogen detection was performed in two separate runs. In the first injection, 179-nm carbon, 181-nm sulfur, and (if desired) 193-nm carbon chromatograms were collected using hydrogen and oxygen as the reagent gases. Nitrogen was measured at the 388-nm cyanogen band using hydrogen, oxygen, and methane as reagents. EPC allowed running both methods in an automated sequence, because the reagent gas pressures were dif-

ferent for the two analyses. The chromatographic conditions are presented in Table I.

It is important to use helium carrier and makeup gas that is free of nitrogen to obtain the best nitrogen detection. A helium purifier (heated getter type, model GC50, SAES Pure Gas, San Luis Obispo, CA) was used. This type of purifier removes N_2 and other impurities in helium to levels suitable for nitrogen analysis.

Chemicals

Sulfur and nitrogen optimization studies were carried out using the AED Checkout Sample (Hewlett-Packard), which is a mixture of 12 components used to measure detection limits and selectivities. Standards for linear range determinations were prepared by diluting *tert*-butyldisulfide and nitrobenzene (Aldrich Chemical, Milwaukee, WI) in iso-octane (Burdick and Jackson, Muskegon, MI). National Institute of Standards and Technology (NIST) standard reference materials (SRMs) were obtained from NIST (Gaithersburg, MD). California Air Resources Board low-sulfur reformulated and conventional gasoline quality control samples were obtained from AccuStandard (New Haven, CT). RFA gasoline with 14.9% methyltertiarybutylether was purchased from Scott Specialty Gases (Plumsteadville, PA). Samples of refinery liquids were obtained from various petroleum laboratories.

Results and Discussion

Detector optimization: sulfur

In applying GC–AED to the analysis of sulfur compounds in

Table I. Chromatographic Conditions

		Optimization		Linear Range		Analysis	
		Sulfur	Nitrogen	Sulfur	Nitrogen	Sulfur	Nitrogen
GC							
Inlet	Volume (µL)	1	1	1	1	1	1
	Mode	split	split	split	split	split	split
	Temperature (°C)	250	250	280	280	280	280
	Inlet press (psi)	20	20	11.8	11.8	11.8	11.8
	Split ratio	17	17	100	10	50	10
Oven	Initial temperature (°C)	60	40	200	180	40	40
	Initial time (min)	0	1	4.5	4.8	0	0
	Ramp (°C/min)	30	30	isothermal	isothermal	10	10
	Final temperature (°C)	180	180			300	300
	Final time (min)	0	0			10	10
Column	Phase	HP-1	HP-1	HP-1MS	HP-1MS	HP-1MS	HP-1MS
	Film thickness (µm)	0.17	0.17	1	1	1	1
	Inside diameter (mm)	0.32	0.32	0.32	0.32	0.32	0.32
	Length (m)	25	25	30	30	30	30
AED							
Temperatures (°C)	Transfer line	250	250	350	250	310	310
	Cavity block	250	250	350	250	310	310
Reagent gases	H_2 reagent (psi)	14	40	43	40	43	40
	O_2 reagent (psi)	25	80	55	80	55	80
	CH_4 reagent (psi)		50		50		50
He makeup gas (mL/min)		30	230	100	230	100	230
Data rate (Hz)		5	5	2.5	2.5	2.5	2.5

petroleum samples, the most important figure of merit is usually the selectivity. In most cases, it is the selectivity that determines the method detection limit. The sample concentration (if diluted) and/or the split ratio is adjusted to give the best response to sulfur while not exceeding the selectivity of the sulfur channel. Higher

Table II. Optimization of Makeup and Reagent Gas Flows for Sulfur Detection

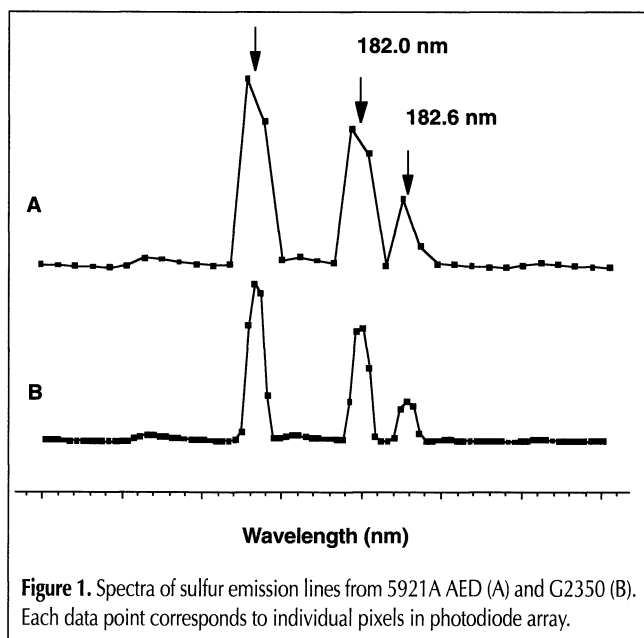| Makeup flow (mL/min)	Oxygen (psi)	Hydrogen (psi)	Sulfur MDL (pg/sec)	Selectivity (× 1000)
10	21	19	0.5	33
10	21	34	0.7	32
10	21	48	1.0	39
10	35	19	0.6	36
10	35	34	0.9	38
10	35	48	1.0	27
10	60	19	1.0	52
10	60	34	1.1	51
10	60	48	1.4	38
30	13	12	0.8	48
30	13	20	0.7	81
30	13	30	0.8	57
30	21	12	0.7	41
30	21	20	0.8	46
30	21	30	1.0	65
30	40	12	0.8	49
30	40	20	1.0	163
30	40	30	1.4	125
100	18	17	2.0	64
100	18	29	1.9	67
100	18	43	2.4	64
100	29	17	1.9	168
100	29	29	2.5	101
100	29	43	2.3	119
100	55	17	2.3	154
100	55	29	2.6	260
100	55	43	3.1	224

Figure 1. Spectra of sulfur emission lines from 5921A AED (A) and G2350 (B). Each data point corresponds to individual pixels in photodiode array.

selectivity allows a larger sample to be injected, thereby resulting in lower method detection limits.

One of the important parameters affecting the selectivity of sulfur in the AED technique is the optical resolution of the spectrometer. Figure 1 shows the spectrum of sulfur emission in the original AED (model 5921A) and in the new version (G2350A). Each datapoint corresponds to the signal from an individual pixel in the photodiode array (7). The resolution in the original AED was approximately 0.4 nm (full width at half the maximum) and that of the newer version was 0.25 nm. The wavelength per diode in the new spectrometer was 0.08 nm/pixel versus 0.22 nm/pixel in the original. The higher optical resolution and increased number of diode signals available to the software allowed for more effective background correction of the CO molecular emissions that interefere with sulfur detection. This resulted in increased selectivity for sulfur. Under typical operating conditions, the selectivity of the newer instrument was approximately 35,000 versus approximately 20,000 for the 5921A.

The hydrogen reagent gas restrictor in the G2350 was about five times less restrictive than in the original AED. This allowed the use of higher hydrogen reagent gas flows while still operating at acceptable pressures. This is useful when optimizing the instrument gas flows for sulfur detection. By optimizing the makeup and reagent gases, the selectivity for sulfur detection can be increased significantly.

Table II contains the results of a study of the effects of reagent and makeup gas on the detection limit (signal-to-noise ratio = 2) and selectivity for sulfur detection. The detection limit for sulfur became worse as either the makeup or reagent gases were increased. The overall trend in the selectivity was the opposite; as the makeup gas and reagent flows were increased, the selectivity was improved. These effects are seen in Figure 2, which shows the sulfur chromatograms obtained from running the AED Checkout Sample with low, typical, and high makeup and reagent gas flows. Note that the size of the response to large hydrocarbons in the sample relative to that of the sulfur peak was significantly reduced with higher flows.

Although the absolute detection limit for sulfur was worse with high flow rates, for petroleum applications, the higher selectivity allowed more sample to be injected without interference from hydrocarbons. This indicates that the actual method detection limit was improved with higher flow rates. Therefore, the higher flow rates listed at the bottom of Table II were used for the remainder of this work.

Detector optmization: nitrogen

Nitrogen can be detected simultaneously with carbon and sulfur using the 174.53- and 174.27-nm atomic lines. The makeup and gas flows which optimize the response for sulfur, however, degrade the N 174 performance. The detection limit and selectivity for N 174 were optimimum with typical flow conditions. With the gases optimized for sulfur, the nitrogen detection limit was degraded eight-fold and the selectivity by a factor of 2.5. Even at optimum conditions, the selectivity of N 174 was insufficient for most petroleum applications.

Nitrogen can also be detected using the cyanogen (CN) molecular emission bands at 388 nm. While there are interfering carbon molecular emissions in the same spectral region, the resolution of

the spectrometer is sufficient to permit their removal. Figure 3 shows the spectra of CN and the interfering CH emissions.

The makeup gas flow was automatically increased by the software when N 388 was analyzed. With the makeup flow controller set to deliver 100 mL/min for sulfur detection, the corresponding makeup gas flow when N 388 is present was about 230 mL/min. With this makeup flow and using the manufacturer's recommended reagent gas pressures of 80 psi oxygen, 40 psi hydrogen, and 50 psi methane, N 388 detection was found to perform satisfactorily.

Figure 4 compares N 174 detection (gases set for optimal sulfur detection) with N 388 detection. The nitrogen detection limit was improved from 55 pg nitrogen for N 174 to 15 pg nitrogen for N 388. The selectivity was improved from 1500 at N 174 to about 800,000 at N 388. This 500-fold improvement in selectivity is crucial for detecting low parts-per-million quantities of nitrogen in petroleum products; therefore, all further investigations used only N 388 detection.

GC Method

The method described here is to be used for general carbon, sulfur, and nitrogen analysis of gasoline through diesel-range

refinery liquids. The column chosen was a 30 m × 0.32-mm i.d. (1.0-μm film thickness) Hewlett-Packard HP-1MS. This column was selected as having the best compromise of speed, resolution, and capacity for the samples to be analyzed. Methyl silicone was chosen as the phase so that compounds would elute in approximate boiling point order. The MS designation indicates that the column is specified to have lower bleed, which is desirable when programming to 300°C or higher.

With this column, split ratios between 50:1 and 100:1 provided optimum results for sulfur analysis. Split ratios in this range provided the best signal-to-noise ratio for sulfur while avoiding interferences in sulfur detection from hydrocarbons. Because nitrogen detection at N 388 is so selective, the split ratio for the nitrogen analysis was reduced to 10:1.

One important parameter in developing a method to measure samples with a broad boiling range is selection of the injection port liner. The type of liner can influence the precision and accuracy of the analysis. This is particularly true of the current analysis, where the polar sulfur and nitrogen compounds can be adsorbed by the liner. Molecular weight discrimination in split injections can also lead to inaccuracies. For these reasons, the liner shown in Figure 5 was used.
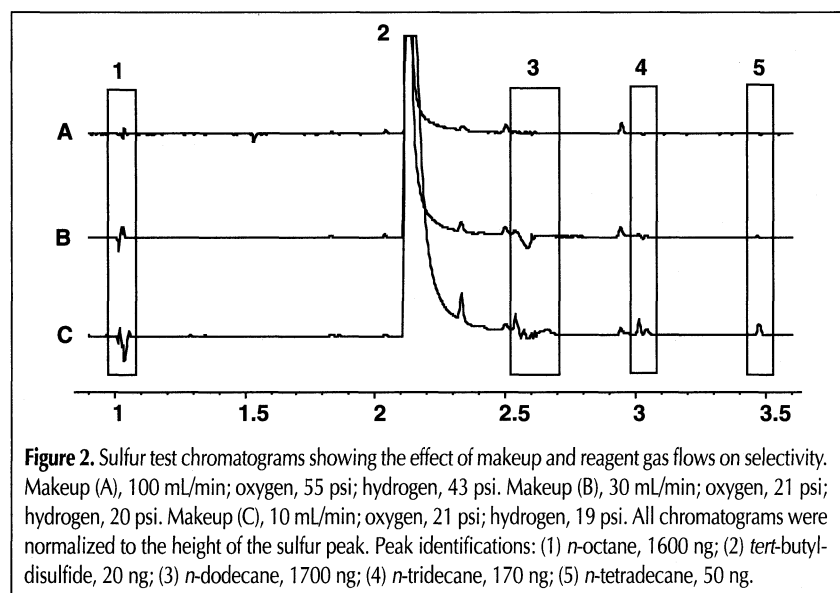
The liner (Hewlett-Packard, no. 5183-4647) is assembled by taking a deactivated, single-taper splitless liner and placing a tightly packed piece of pesticide-grade glass wool at the position indicated in Figure 5. By placing the glass wool at the indicated position, the end of the syringe needle is "wiped" during injection. This dramatically improves the precision, especially when injecting viscous samples like diesel fuels. Without the wiping effect, the raw area precision for diesels can be as bad as 10% relative standard deviation (RSD). With the liner shown here, the precision is usually 2% or better on replicate runs. Note that the column is inserted so that the end is near the center of the small diameter section of the liner.

Once the chromatographic conditions have been determined, it is useful to measure the width of the narrowest peaks of interest. The rate at which chromatographic data is acquired with the AED should be set at the lowest data rate that samples at least six points across a peak (baseline to baseline). The photodidode array is a continuously integrating detector, and using higher data rates than six points per peak only wastes disc space, adds processing time, and degrades the signal-to-noise ratio. For example, the basline noise is 2-fold greater at 10 Hz than at 2.5 Hz. For this work, 2.5 Hz was determined to be optimal.

The choice of chromatographic and detection parameters was based largely on detection limit and selectivity. It is important to determine the linear dynamic range of the analysis after all other parameters have determined to establish correct sample loading limits. This is especially important after changing detector gas flows, as was done here. Since the response of a single sulfur com-

Figure 2. Sulfur test chromatograms showing the effect of makeup and reagent gas flows on selectivity. Makeup (A), 100 mL/min; oxygen, 55 psi; hydrogen, 43 psi. Makeup (B), 30 mL/min; oxygen, 21 psi; hydrogen, 20 psi. Makeup (C), 10 mL/min; oxygen, 21 psi; hydrogen, 19 psi. All chromatograms were normalized to the height of the sulfur peak. Peak identifications: (1) n-octane, 1600 ng; (2) tert-butyl-disulfide, 20 ng; (3) n-dodecane, 1700 ng; (4) n-tridecane, 170 ng; (5) n-tetradecane, 50 ng.
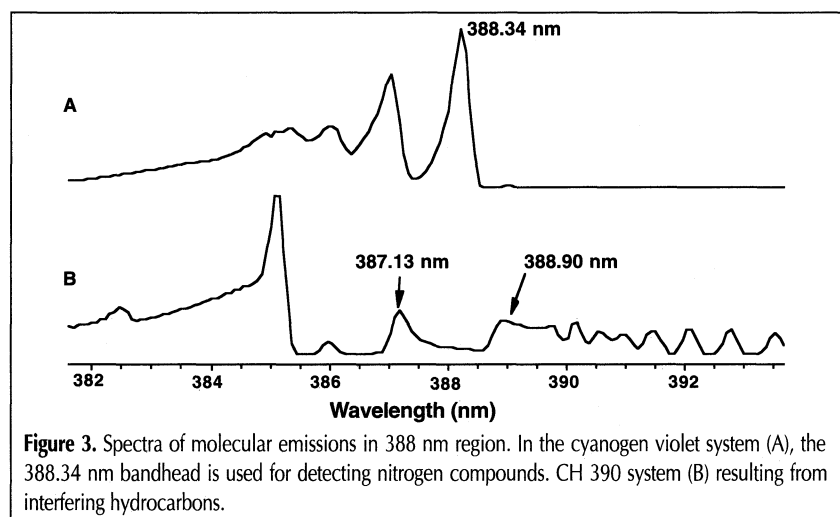

Figure 3. Spectra of molecular emissions in 388 nm region. In the cyanogen violet system (A), the 388.34 nm bandhead is used for detecting nitrogen compounds. CH 390 system (B) resulting from interfering hydrocarbons.

pound is used for calibration in ASTM method 5623-94, it is important to run the samples and standards within the linear range of the detector, or significant bias can result.

The dynamic range of carbon (both the 179- and 193-nm wavelengths) and S 181 was measured using serial dilutions of *tert*-butyldisulfide in isooctane. Measurements were made with both typical and sulfur-optimized reagent and makeup gas flows. The results are shown in Figure 6. By operating at the optimized conditions for sulfur analysis, the detection limits for all three wavelengths were degraded by a factor of approximately five when compared to typical conditions. The linear range, however, was extended by a similar factor, resulting in no net change in the size of the linear region (about 10^4). Note that although C 193 and

C 179 have similar ranges, the 193-nm range covers much lower levels. This is useful for simultaneously measuring trace levels of carbon compounds when necessary. For accurately measuring the carbon profile simultaneously with sulfur, however, the C 179 signal is preferred because it extents to higher absolute carbon concentrations.

The dynamic range of N 388 was measured using serial dilutions of nitrobenzene in isooctane. The linear dynamic range was found to be the same as the other signals (about 10^4).

In practice, for a given instrument, the approximate signal height at which the linear range will be exceeded is recorded for each signal. All chromatograms were inspected to make sure the data was collected within the linear range.

It was noted that the N 388 baseline was somewhat flatter if a blank run preceded a group of analytical runs. For this reason, when analyzing large numbers of samples, the carbon and sulfur analyses were run as one group. The nitrogen analyses were then run as a second group, with a blank N 388 run inserted between the two groups. Both the carbon–sulfur and the nitrogen analyses can be done in a single automated sequence if EPC control of the reagent gases is used.

Figure 4. Nitrogen test chromatograms comparing N 174 and N 388 nm detection. N 174 (A) with 100 mL/min makeup gas, 55 psi oxygen, and 43 psi hydrogen. N 388 nm (B) with 230 mL/min makeup gas, 80 psi oxygen, 40 psi hydrogen, and 50 psi methane. Peak identifications: (1) *n*-octane, 1600 ng; (2) nitrobenzene, 28 ng; (3) *n*-dodecane, 1700 ng; (4) *n*-tridecane, 170 ng; (5) *n*-tetradecane, 50 ng.
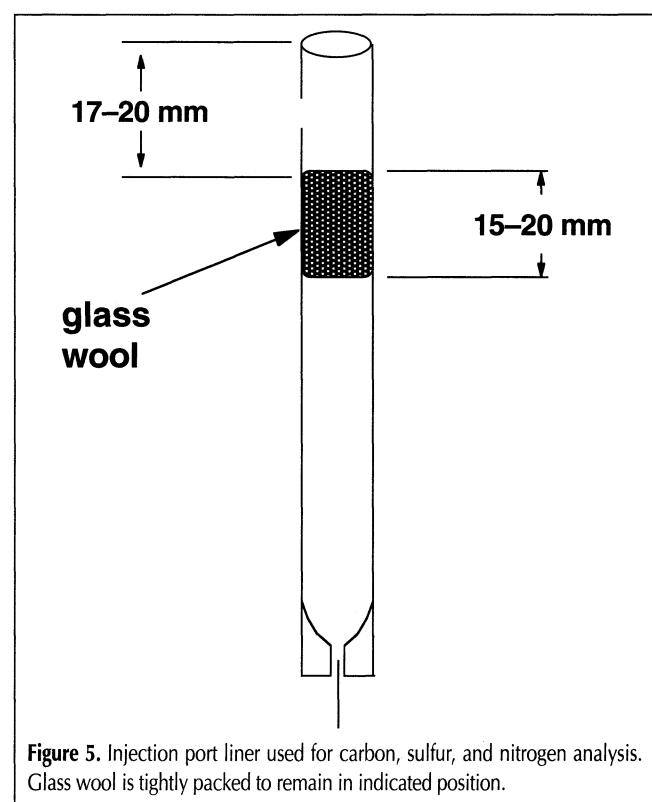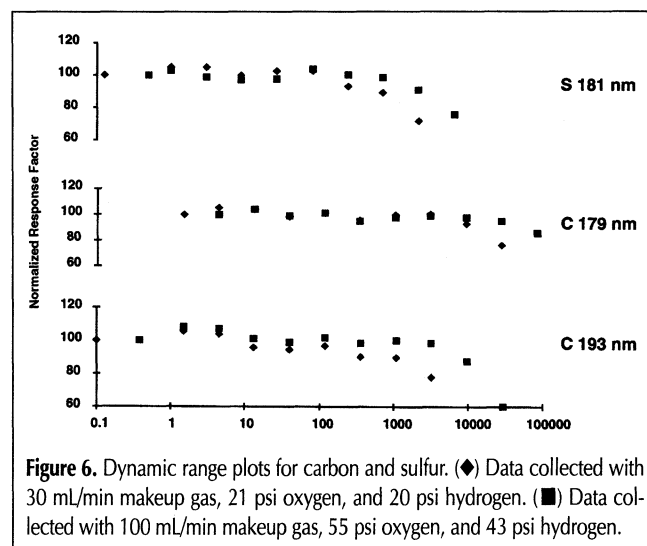

Figure 6. Dynamic range plots for carbon and sulfur. (◆) Data collected with 30 mL/min makeup gas, 21 psi oxygen, and 20 psi hydrogen. (■) Data collected with 100 mL/min makeup gas, 55 psi oxygen, and 43 psi hydrogen.
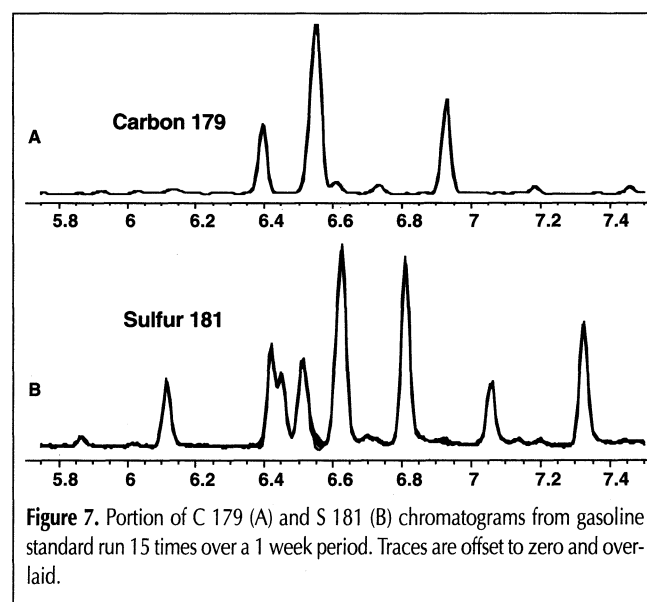

Figure 5. Injection port liner used for carbon, sulfur, and nitrogen analysis. Glass wool is tightly packed to remain in indicated position.

Figure 7. Portion of C 179 (A) and S 181 (B) chromatograms from gasoline standard run 15 times over a 1 week period. Traces are offset to zero and overlaid.

Precision, accuracy, and detection limits

The precision of both the retention times and peak areas observed with the method were quite good. Figure 7 shows an expanded portion of the carbon and sulfur chromatograms from the "conventional gasoline" quality control standard (Accustandard, New Haven, CT). The sample was run 15 times over a 1-week period. The signals shown in Figure 7 are the traces from all 15 runs overlaid. The y-axis of the chromatograms were offset to zero, but not scaled. The precision of the total peak areas was 1.1% RSD for C 179 and was 1.8% RSD for S 181. This degree of precision was observed for all samples, with the RSD approximately 2% or less for signals with sufficient signal-to-noise ratio.

To assess the accuracy of the sulfur analyses, four NIST SRMs were used. NIST offers two kerosenes and two diesel fuels with certified sulfur levels. The chromatograms of these standards are shown in Figures 8 and 9. The sulfur distributions appear typical of refinery samples of kerosenes and diesel fuels with the exception of the 2-K kerosene standard, SRM 1617. This high-sulfur standard appears to have been assembled from a low-sulfur kerosene
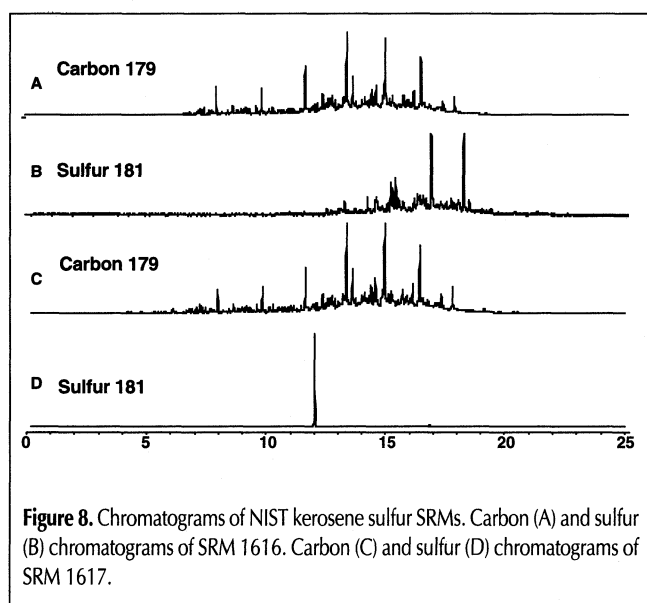

Figure 8. Chromatograms of NIST kerosene sulfur SRMs. Carbon (A) and sulfur (B) chromatograms of SRM 1616. Carbon (C) and sulfur (D) chromatograms of SRM 1617.
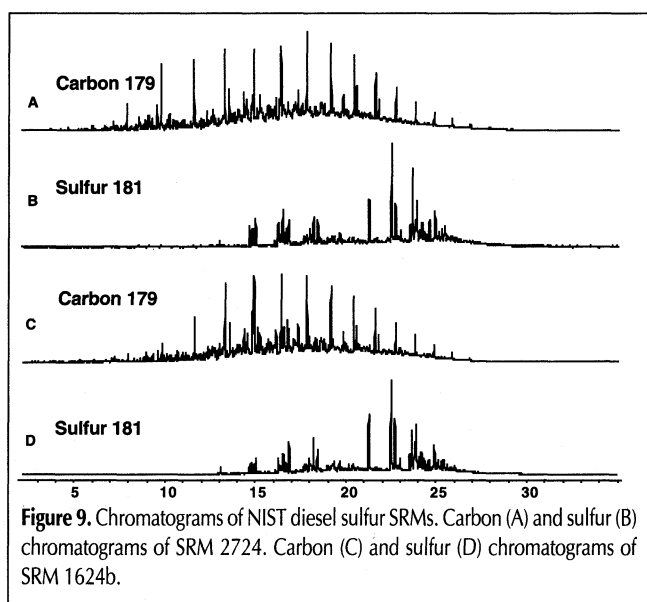

Figure 9. Chromatograms of NIST diesel sulfur SRMs. Carbon (A) and sulfur (B) chromatograms of SRM 2724. Carbon (C) and sulfur (D) chromatograms of SRM 1624b.

and *tert*-butyldisulfide.

Table III contains the results of the total sulfur analysis of these standards using the current method and the ASTM method 5623-94 calculation scheme. All but one of the samples were analyzed using *tert*-butyldisulfide as the internal standard. Because SRM 1617 already contained *tert*-butyldisulfide, this sample was analyzed using the external standard approach. The agreement between the certified and measured values was quite acceptable.

Figure 10 illustrates the detections limits of the current method. The sample contains 42 ppm total sulfur. Peak 3 in the sulfur chromatogram represents approximately 4.4 ppm sulfur. The detection limit for a single sulfur compound was 0.7 ppm sulfur.

Figure 10 also contains the nitrogen chromatogram of a gasoline with a total nitrogen content of 13 ppm. The chromatogram was made with a 2-μL injection volume. The detection limit for an individual nitrogen compound is about 2 ppm (nitrogen) as seen in peak 10, which corresponds to 2.5 ppm nitrogen. Peak 9 is the air peak, and it is excluded from total nitrogen calculations.

Example analyses

Increasing economic requirements to better utilize refining feedstock components, coupled with more stringent product specifications to maintain fuel quality, are demanding a greater understanding of the composition of transportation fuels and their chemical conversions. The concentration of sulfur and nitrogen is often a critical parameter in the assessment of product quality and refinery process performance. Many reports in the literature use

Table III. Analysis of NIST Sulfur Reference Materials

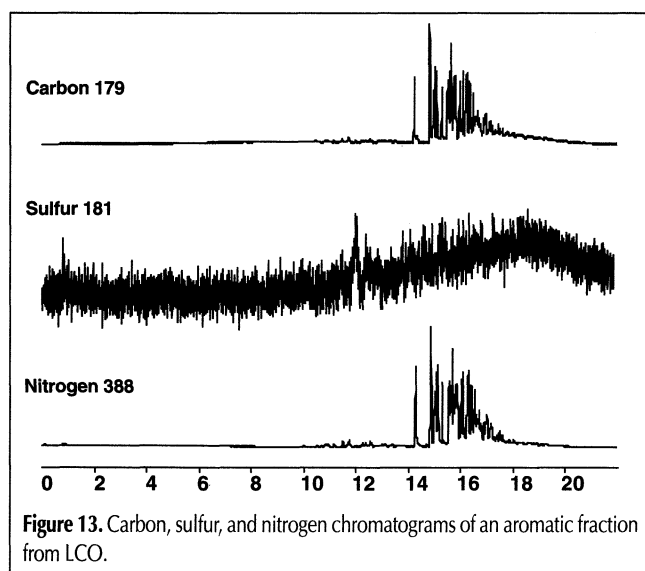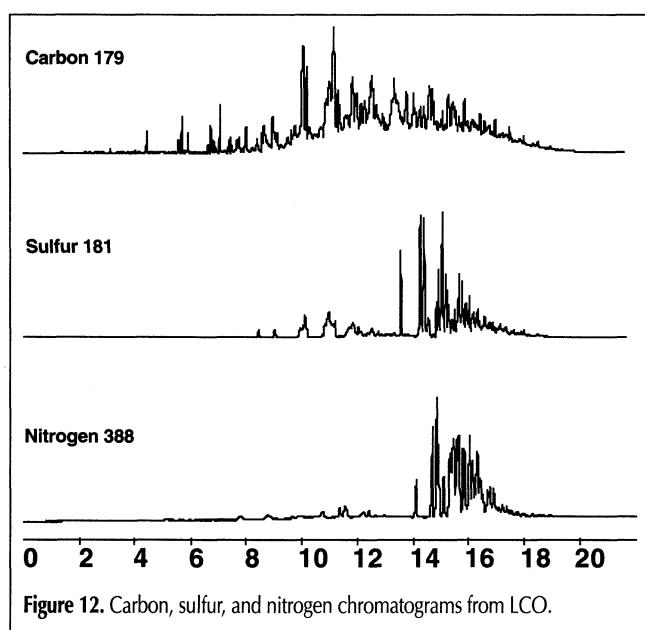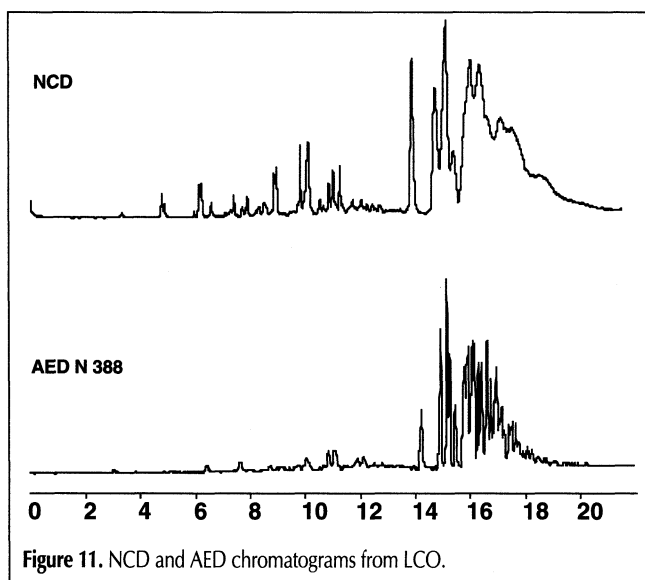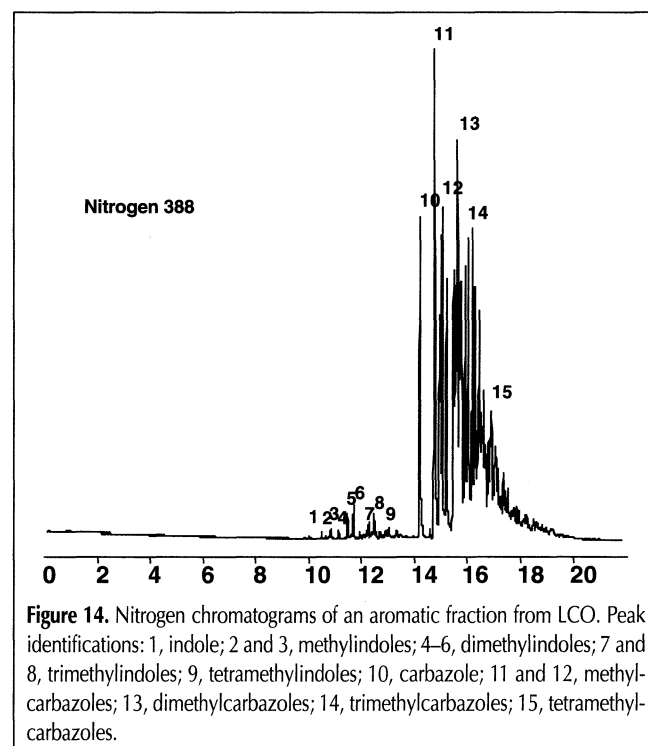|	Certified value (ppm S)	Measured value (ppm S)	% Difference
NIST SRM 1616 (kerosene)	152	155	2.0
NIST SRM 1617 (kerosene)	1690	1720	1.8
NIST SRM 2724 (diesel)	425	420	−1.2
NIST SRM 1624b (diesel)	3320	3340	0.6
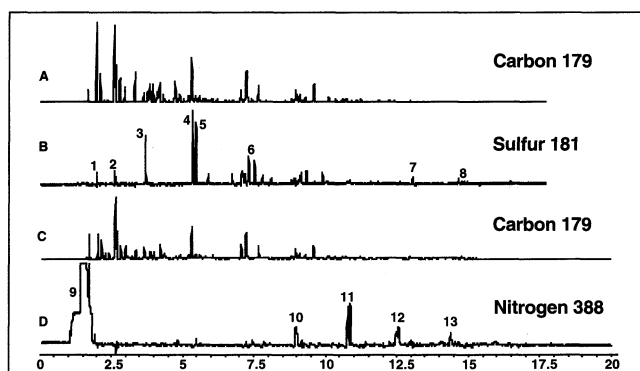
Figure 10. Detection limits for sulfur and nitrogen analysis. Carbon (A) and sulfur (B) chromatograms of CARB low-sulfur RFG quality contol sample (42 ppm total sulfur). Carbon (C) and nitrogen (D) chromatograms of RFA gasoline with 14.9% MTBE (13 ppm total nitrogen). Peak identifications: 1 and 2, hydrocarbon interferences; 3, thiophene and/or 2-methyl-1-propanethiol; 4, 2-methylthiophene; 5, 3-methylthiophene; 6, C_2-thiophenes; 7, benzothiophene; 8, C_1-benzothiophenes; 9, air; 10, aniline; 11, toluidines; 12, C_2-anilines; 13, indoles.

Figure 11. NCD and AED chromatograms from LCO.

Figure 12. Carbon, sulfur, and nitrogen chromatograms from LCO.

Figure 13. Carbon, sulfur, and nitrogen chromatograms of an aromatic fraction from LCO.
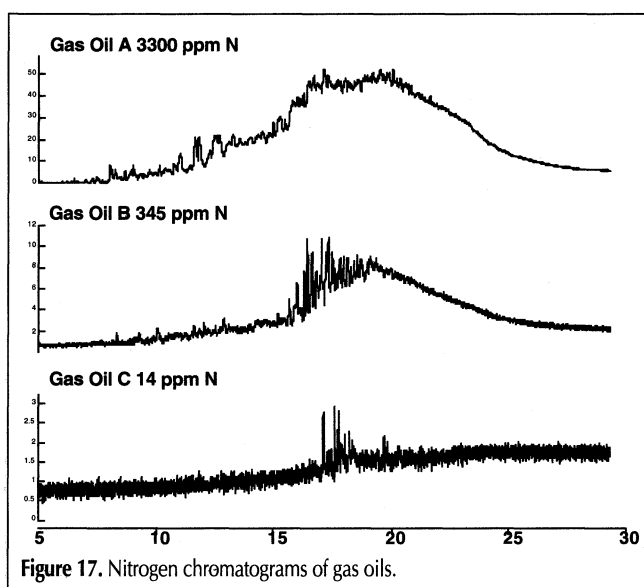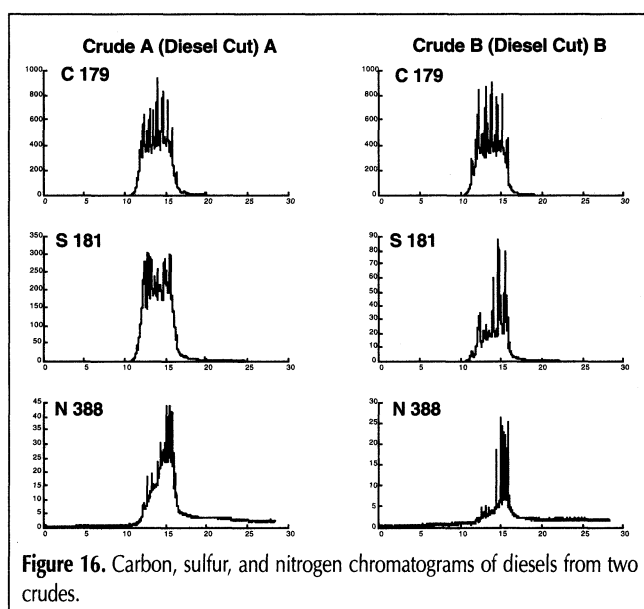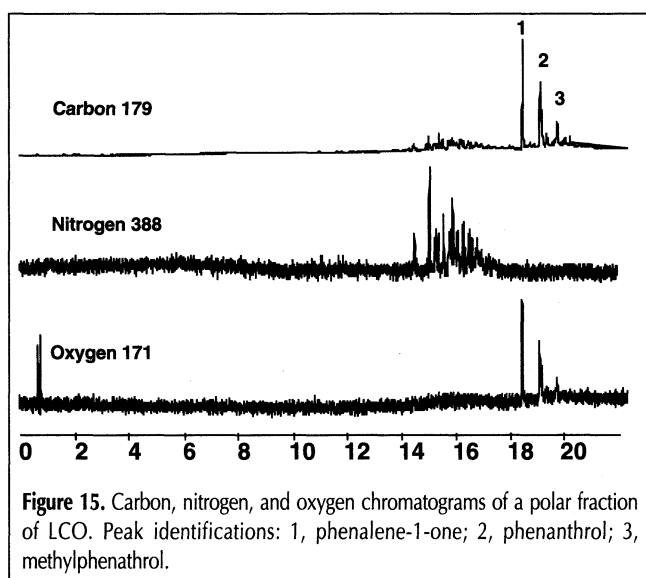
multidimensional techniques for the separation and speciation of sulfur and nitrogen content, and some reports attempt to explore the challenge of hetero-element distributions in petroleum streams (8–11).

Light cycle oil (LCO) is an interesting petroleum stream, both because of its economic importance as a blending component and its unique composition (8). LCOs are a product of fluid catalytic cracking processes and contain some of the highest sulfur and nitrogen concentrations in the mid-distillate fuel components. They also contain some of the most refractory compounds in refining processes. Recent reports have identified many of the components in LCO using single-channel detectors. These results can provide meaningful information to refiners when they are correctly applied and the complexity of the sample matrix is considered (1,11). Figure 11 presents the chromatographic profiles for an LCO analyzed by a nitrogen chemiluminesence detector and by an AED with similarly configured chromatographic conditions. Both profiles clearly show the compound-class clusters of the nitrogen species present. Figure 12 presents the chromatograms for carbon, sulfur and nitrogen as detected by AED, and it shows the complexity of chromatographic overlap of the heteroelement sulfur and nitrogen species. Accurate identification of these compounds cannot be achieved without significant improvements in chromatographic resolution or preseparation of heteroelement classes.

Many procedures have been reported for the fractionation of nitrogen compounds in petroleum into basic, neutral, polar, and other classes, as determined by the separation scheme that was used (12–15). Figure 13 presents the carbon, sulfur, and nitrogen AED chromatogram for a fraction we have designated as aromatic. The AED clearly shows the similarity in the carbon and nitrogen profiles and the absence sulfur compounds, indicating the effectiveness of the separation. Figure 14 presents the nitrogen chromatogram and the identification of the peaks in this fraction

Figure 14. Nitrogen chromatograms of an aromatic fraction from LCO. Peak identifications: 1, indole; 2 and 3, methylindoles; 4–6, dimethylindoles; 7 and 8, trimethylindoles; 9, tetramethylindoles; 10, carbazole; 11 and 12, methylcarbazoles; 13, dimethylcarbazoles; 14, trimethylcarbazoles; 15, tetramethylcarbazoles.

Figure 15. Carbon, nitrogen, and oxygen chromatograms of a polar fraction of LCO. Peak identifications: 1, phenalene-1-one; 2, phenanthrol; 3, methylphenathrol.

Figure 16. Carbon, sulfur, and nitrogen chromatograms of diesels from two crudes.

Figure 17. Nitrogen chromatograms of gas oils.

as determined by GC–mass spectrometry (MS) in conjunction with the AED results.

When examining a polar fraction by GC–MS, we found three major peaks in the total ion chromatogram which could not be assigned. The fragmentation patterns from these peaks represented a homologous carbon series of benzocinnolines with two nitrogen atoms in the aromatic ring core or phenaleneones and phenanthrols which contain oxygen. Analysis by GC–AED (Figure 15) clearly resolved the ambiguity and allowed the assignment of the compounds to the oxygen-containing species.

Routine analysis of sulfur and nitrogen is required for the assessment of product variation and feed processability. Figure 16 presents a comparison of sulfur and nitrogen distributions in two diesels from different crude sources. Both crude A and B have similar carbon distributions and carbon concentrations; however, the sulfur and nitrogen contents are very different and suggest that different processing conditions would be required by these diesel cuts for optimal use as fuels.

The measurement of nitrogen in gas oils has always been a challenge because of the difficulties in the sample matrix. Figure 17 presents three AED nitrogen chromatograms covering three orders of magnitude in a concentration range for total nitrogen, as determined by a combustion-chemiluminesence method. Quantitation challenges for gas oil analysis still remain. The AED provides a unique measurement capability in gas oil and heavy oil hetero-element analysis.

Conclusion

The results presented in this article show that by optimizing several experimental parameters in the GC–AED system, the selectivities of sulfur and nitrogen versus hydrocarbons can be substantially improved. These improvements in selectivity come at the cost of some degradation of the absolute detection limits. The selectivity gains, however, are large enough to allow the amount of sample injected to be increased, resulting in a net improvement in the method detection limits. The suggested parameter changes are shown to provide acceptable linearity, accuracy, and precision.

Acknowledgments

References

1. B. Chawla. Speciation of nitrogen compounds in gasoline and diesel range process streams by capillary column gas chromatography with chemilumenescence detection. *J. Chromatogr. Sci.* **35:** 97–104 (1997).
2. T.G. Albro, P.A. Dreifuss, and R.F. Wormsbecher. Quantitative determination of sulfur compounds in FCC gasoline by GC–AED. *J. High*

Resol. Chromatogr. Chromatogr. Commun. **16:** 13–17 (1993).

3. A. Amorelli, Y.D. Amos, C.P. Halsig, J.J. Kosman, R.J. Jonker, M. de Wind, and J. Vrieling. Estimate feedstock processability—characterize sulfur compounds in middle distillates and deeply hydrotreated products. *Hydrocarbon Process.* **June:** 93–100 (1992).

4. B.D. Quimby, V. Giarrocco, J.J. Sullivan, and K.A. McCleary. Fast analysis of oxygen and sulfur compounds in gasoline by GC–AED. *J. High Resol. Chromatogr. Chromatogr. Commun.* **15:** 705–709 (1993).

5. ASTM D 5623-94: Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection. *Annual Book of Standards*, Vol. 5. ASTM, West Conshohoken, PA, 1994, pp 791–95.

6. S.E. Eckert-Tilotta, S.B. Hawthorne, and D.J. Miller. Comparison of comercially available atomic emission and chemiluminescence detectors for sulfur-selective gas chromatographic detection. *J. Chromatogr.* **591:** 313–23 (1992).

7. J.J. Sullivan and B.D. Quimby. Characterization of a computerized photodiode array spectrometer for gas chromatography–atomic emission spectrometry. *Anal. Chem.* **62:** 1034–43 (1990).

8. M. Dorbon and C. Bernasconi. Nitrogen compounds in light cycle oils: identification and consequences of ageing. *Fuel* **68:** 1067–74 (1989).

9. C. Lewis, S.A. Askey, K.M. Holden, K.D. Bartle, and M.J. Pilling. On-line LC–GC–AED and LC–GC–MS—multidimensional methods for the analysis of PAC in fuels, combustion emissions and atmospheric samples. *J. High Resol. Chromatogr. Chromatogr. Commun.*. **20:** 109–114 (1997).

10. I. Dzidic, M.D. Baldicki, H.A. Peterson, J.G. Nowlin, W.E. Evans, H. Siegel, and H.V. Hart. A study of catalytic hydrodenitrification by the use of chemical ionization GC/MS and GC/MS/MS. *Energy and Fuels* **5:** 382–86 (1991).

11. R.J. Young and E.M. Fujinari. Nitrogen detection for simulated distillation of refinery streams. *Am. Lab.* **45:** 39–40 (1994).

12. M.M. Boduszynski. Composition of heavy petroleums. Molecular characterization. *Energy and Fuels* **2:** 597–613 (1988).

13. M. Dorbon, I. Ignatiadis, J. Schmitter, P. Arpino, G. Guiochon, H. Toulat, and A. Huc. Identification of carbazoles and benzocarbazoles in a coker gasoil and influence of catalytic hydrotreatment on their distribution. *Fuel* **63:** 565–72 (1984).

14. J. Mao, C.R. Pancheco, D.D. Traficante, and W. Rosen. Identification and characterization of nitrogen compounds in Brazilian diesel oil by particle beam LC–MS. *Fuel* **74:** 880–87 (1995).

15. C.S. Hsu, K. Kian, and W.K. Robbins. Nitrogen speciation of polar petroleum compounds by compound class separation and on-line liquid chromatography–mass spectrometry (LC–MS). *J. High Resol. Chromatogr. Chromatogr. Commun.* **17:** 271–76 (1994).