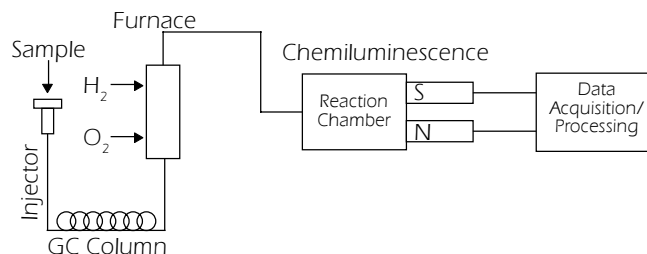


Theory and Applications of Nitrogen and Sulfur Chemiluminescence Detection via GC

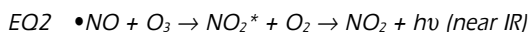
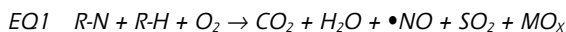
- Jeffrey Werner
Chromatography
Product Manager

Overview

Sulfur and nitrogen compounds are important to many aspects of analytical chemistry. The problem with their analysis is that the matrix in which they are found can be very complex and the compounds are usually at very low concentration. Chemiluminescence provides detection for these compounds that is selective, sensitive, linear, and equimolar. The following provides examples of this as well as a brief description of chemiluminescence.

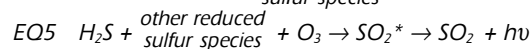
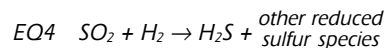
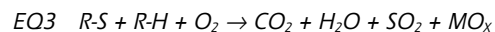


Nitrogen Chemiluminescence Reaction



Nitrogen chemiluminescence begins with the complete, high temperature oxidation of the entire sample matrix, as illustrated in EQ1, where R-N is any chemically bound nitrogen compound and R-H is any non-nitrogenous organic compound. As each component elutes from the GC column, the component is combined with oxygen at a temperature in excess of 1000°C. Oxidation products include CO₂, H₂O, •NO, SO₂, and various other oxides (designated in equation as MO_x). The conversion of all chemically bound nitrogen to •NO (nitric oxide) is quantitative. The combustion gases are routed to the detector module for quantitation. As shown in EQ2, the •NO is reacted with O₃ (ozone), produced by an on-board ozone generator, to form NO₂* (nitrogen dioxide in the excited state). As the excited species decays to the ground state, a quantum of light is emitted and detected, at specific wavelengths, by a photomultiplier tube. This chemiluminescent emission is specific for nitrogen and is proportional to the amount of nitrogen in the original sample. Only chemically bound nitrogen is detected; atmospheric, diatomic nitrogen (N₂) is not sensed.

Sulfur Chemiluminescence Reaction



Sulfur chemiluminescence detection also begins with complete, high temperature oxidation of the entire sample matrix, as illustrated in EQ3, where R-S is any organic sulfur compound and R-H is any non-sulfur containing organic compound. As each component elutes from the GC column, the component is reacted with oxygen at a temperature in excess of 1000°C. Oxidation products include CO₂, H₂O, SO₂, and various other oxides (designated MOX). The conversion of chemically bound sulfur to SO₂ (sulfur dioxide) is quantitative. The oxidized gases are then reacted with hydrogen in the reductive zone of the furnace, generating H₂S and other reduced sulfur species as illustrated in equation 4. These reduced sulfur species are then passed through the reaction chamber where they react with ozone. According to EQ5, the H₂S and other reduced sulfur species are reacted with O₃ (ozone), produced by an on-board ozone generator, to form SO₂* (sulfur dioxide in the excited state). As the excited species decays to the ground state, a quantum of light is emitted and detected, at specific wavelengths, by a photomultiplier tube. This chemiluminescent emission is specific for sulfur and is proportional to the amount of sulfur in the original sample.



Performance

Antek's SCD employs a 14" furnace, which has virtually eliminated SCD coking problems. This dual zone furnace provides optimal oxidation and reduction temperatures and larger surface area for the reduction reaction to take place. Today, SCD is stable for much longer periods of time, eliminating need for overnight reconditioning or decoking valves. This, in turn, has reduced overall maintenance required for the instrument. Ceramics last 6–12 months at a time and in many cases even longer. Add to this the use of an oil-less vacuum pump, and the system can be operated virtually maintenance-free for much longer. Electronic mass flow controllers replace mechanical controllers previously used, providing precise gas flow regulation and allowing analysts to check or change gas flows without opening the system to atmosphere. This enhances the instrument's overall stability and eliminates risk of burning your hands or breaking ceramic tubes while trying to properly adjust flows for different applications.

Figure 1 shows SCD sensitivity of 7 ppb sulfur as dimethyldisulfide with a signal to noise ratio of approximately 10 to 1. Sensitivity alone is not enough to prove the instrument's viability, however, so the data in **Figures 2–3** show % deviation for 10 sulfur components run during a six month stability study at Valero Oil. The data was collected by running the control sample with samples in the lab's normal work load. This instrument was not run by a single dedicated operator, but rather, by everyone in the lab. Also, no maintenance was carried out during this study. This shows a technique finally stable enough for routine operation by a lab. For the first month of the study, most % deviations are at or near 10%; but for the sixth month, all % deviations improved with the exception of H₂S, which has its own difficulties with analysis. The only change made to the analysis was the actual sample used. It was changed as necessary due to stability of the sulfur compounds in the mixture. **Table 1** outlines the Antek SCD's equimolarity—the ability to

Figure 1 7 ppb S with 10:1 signal to noise ratio

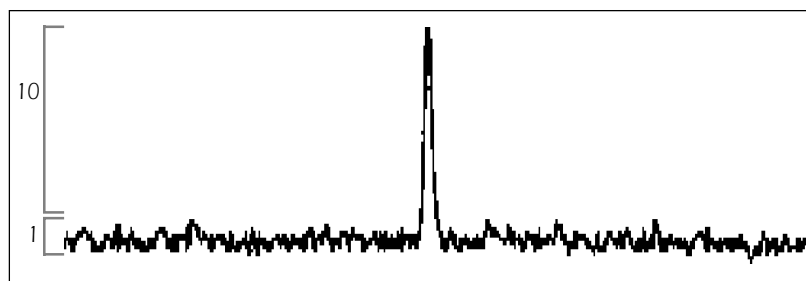


Figure 2 1st month of SCD stability study

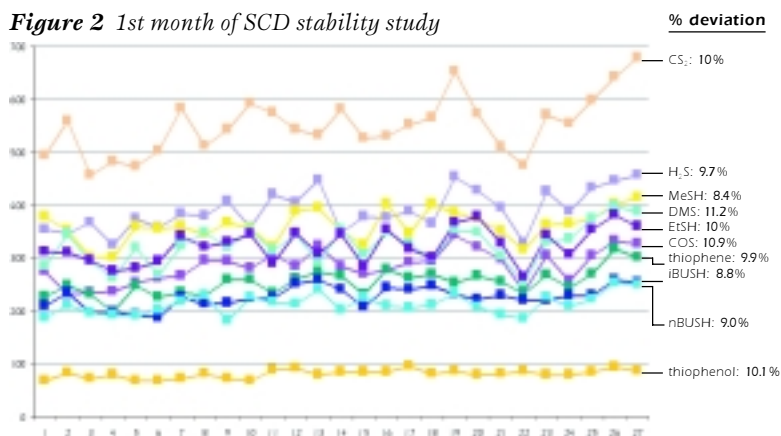
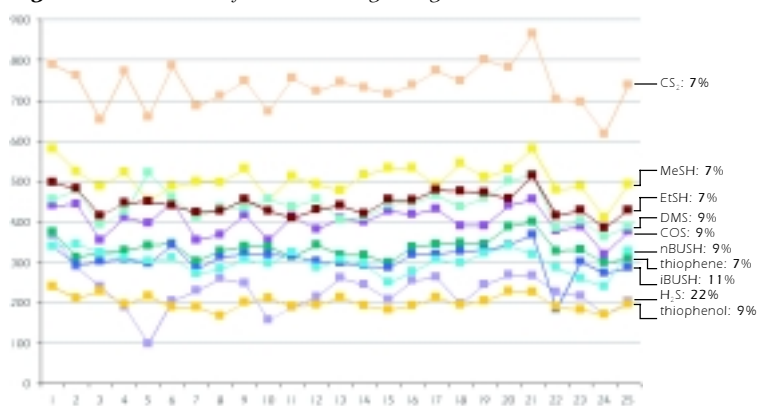


Figure 3 6th month of SCD stability study



calibrate with one compound and quantify another. In general, there is less than 10% deviation of response factors across all classes of compounds for both the sulfur and nitrogen detectors.

Table 1 Relative response factors demonstrate SCD's equimolar response

	Sulfur		Nitrogen	
	2-Ethylthiophene	Thianaphthene	Indole	3-Methylindole
High	1.08	1.00*	1.00	1.00*
Medium	1.09	1.05	0.99	1.00
Low	0.98	0.94	1.00	0.98

* normalized to 1.00

Figure 4 demonstrates simultaneous nitrogen and sulfur detection of a regular unleaded gasoline sample run on the Model 7090NS. **Figure 5** shows similar detection of diesel fuel. In both figures, a post column split provides an additional FID trace.

Figure 4 Regular unleaded gasoline

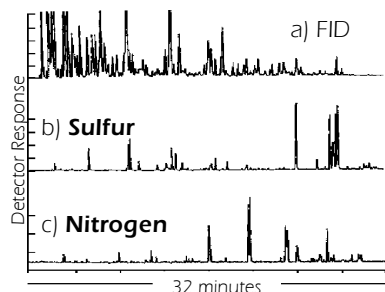
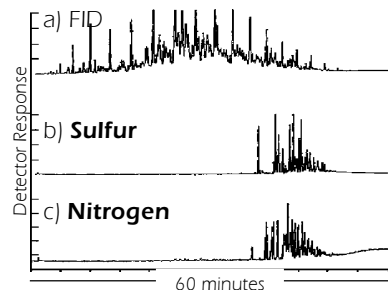


Figure 5 Middle distillate



In **Figure 6**, chromatogram *6a* presents an FID trace of peach flavor adulterated with the compound 2-isopropyl-4-methylthiazole. Chromatograms *6b* and *6c* compare adulterated and unadulterated peach flavor determined by CLND. Only one adulterant is seen on the CLND, and its retention time makes it virtually invisible on the FID.

Figure 6 Peach flavor

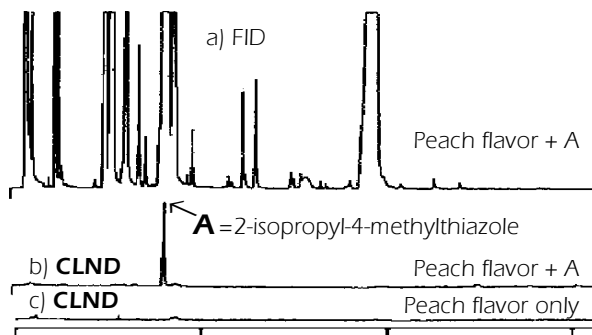
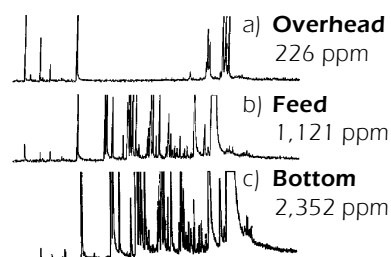


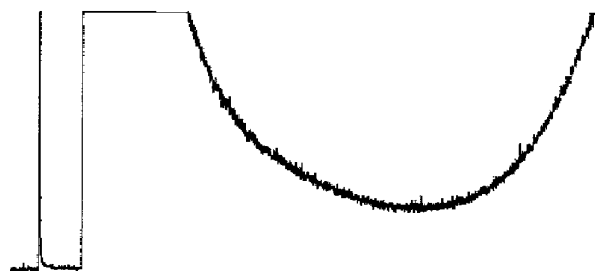
Figure 7 presents SCD results of hydrodesulfurization treatment. *7b* shows feedstock to the HDS unit measuring 1121 ppmS, which is determined by adding area counts. Overhead and bottoms are shown in *7a* and *7c* respectively. Using the 7090, engineers can now determine the sulfur amount present in the samples (*7a* = 226 ppmS, *7b* = 2,352 ppmS) in addition to the type of sulfur compounds present, enabling a better understanding of the process.

Figure 7 Hydrodesulfurization process



As long as the compound of interest can be chromatographically separated, the solvent is not a problem even if it is a sulfur-containing solvent such as CS₂. This is demonstrated by **Figure 8**, a sample of 4 ppm carbonyl sulfide (COS) in carbon disulfide (CS₂).

Figure 8 99.9% carbon disulfide



Large volume injectors coupled with Antek's 7090 Series detectors can significantly lower the detection limit and save sample preparation time. **Figure 9**, shot on a normal split/splitless inlet, demonstrates a limit of quantitation at 22 ppbN as indole. Adding an APEX ProSep inlet in **Figure 10**, a 10µl injection of 2.2 ppbN as indole yields an order of magnitude increase in limit of quantitation.

Figure 9 1µl splitless injection on standard split/splitless port; 22 ppbN limit of quantification

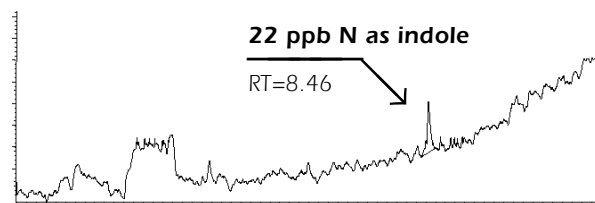
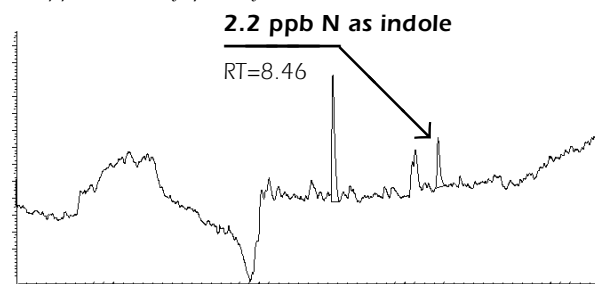
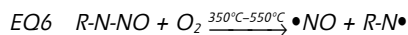


Figure 10 10µl injection on ProSep 800 XT™; 2.2 ppbN limit of quantification



Modified Detection for Nitrosamines

Nitrosamine Reaction



The Model 7090N can also be used to selectively study nitrosamine compounds, as illustrated in Figures 11 and 12. The reaction is carried out at a lowered furnace temperature (350–550°C) and a lowered O₂ flow (~1.5 mL/min). This allows cleavage of the N-NO bond (EQ6) and detection of the NO (EQ7). **Figure 11** is a 5 compound nitrosamine standard at approximately 1 ppm compound for all 5 nitrosamines. **Figure 12** is a 2 compound 20 ppb NO standard, which shows sensitivity and equimolarity for NO.

Figure 11 Nitrosamine standard

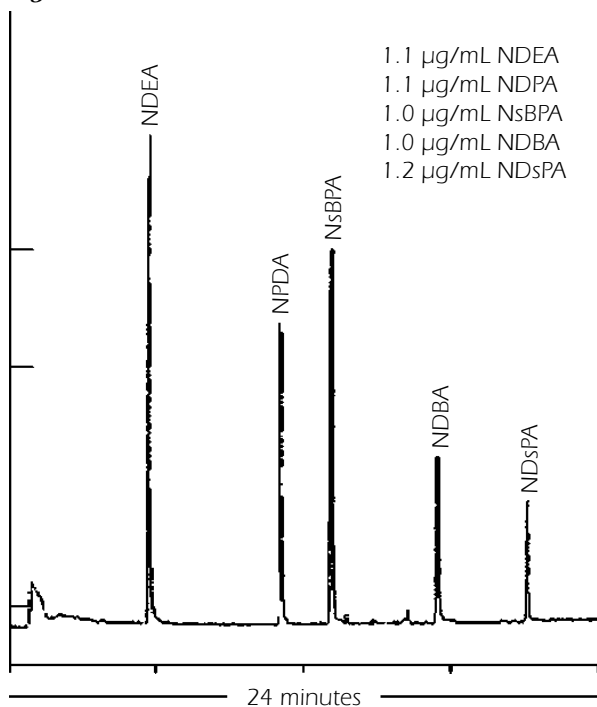
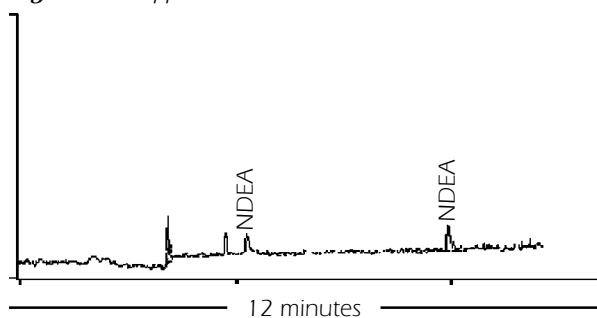


Figure 12 20ppb standard



ANTEK Advantages:

- Oxygen as oxidation gas, rather than air
- 14" dual zone furnace
 - optimum oxidation: 1050°C
 - optimum reduction: 950°C
 - large surface area for complete combustion
- Electronic mass flow controllers for precise gas flow regulation
- Low maintenance
 - ceramic tubes: 6–12 months
 - oil-less vacuum pump: several years
- Enhanced sensitivity
- Long term stability
 - day-to-day reproducibility
 - months on same calibration



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