Determination of Stack and Flare Gas Emissions Using the Agilent GC-AED System

Application

Gas Chromatography

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Authors

Charles M. Dean
Agilent Technologies, Inc.
2125 East Katella Suite 300
Anaheim, California 92806
USA

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

Abstract

A single-column technique was developed to analyze carbon, sulfur, and nitrogen compounds in a gaseous matrix. The analysis is performed with an Agilent 6890 gas chromatograph (GC) and an Agilent G2350A atomic emission detector (AED). An Agilent 30 m × 0.53 mm × 5 µm J&W DB-1 capillary column is used for separation.

Introduction

Waste-gas emissions from processes at refineries, landfills, and wastewater treatment plants are under constant scrutiny from regulatory agencies. Pollutants from these sources can include many harmful hydrocarbons and sulfur compounds. Smog precursors including sulfur oxides (SOx) and nitrogen oxides (NOx) are also released into the atmosphere. The dynamics of these processes produce a variety of compounds with a wide range of concentrations. This is the analytical challenge. For instance, hydrogen sulfide can range from less than 1 ppm to as much as 10 to 20%. Additionally, compounds such as ammonia and water can be present in significant amounts, but until now there has been sparse reliable data. In order to evaluate compliance issues and to isolate process variations quickly, there is a need for timely, accurate analytical techniques.

Historically, multiple instruments have been used to analyze waste gas emissions: one for carbon compound speciation and fixed gases (nitrogen, carbon monoxide, carbon dioxide), one for sulfur speciation and others for moisture or total nitrogen content. These analyses would then have to be normalized into one final report. Each of these instruments experienced some analytical difficulties. The instrument used for carbon speciation was usually a multi-valve instrument that required constant monitoring of the valve switch times so that no compound would be lost out of the vent. The sulfur instrumentation was susceptible to sample carryover and sample overloading. Samples had to be diluted many times to reduce the effect of residual sulfur compounds on instrumentation and to give responses within the linear range. This sequential dilution of the gaseous samples is susceptible to huge amounts of operator induced error. Because the GC-AED is not prone to such contamination, the samples can be run undiluted with a minimal carryover and the GC-AED is linear from sub-ppm to percent levels. Additionally, many instruments used for sulfur analysis demonstrate unstable responses over just a few hours. This causes the analyst to recalibrate or to run quality control samples more than is practical, producing needless delays in results. The GC-AED is stable for extended periods of time—days, even months.

A method has been developed to perform these analyses by sequential injections on one instrument (the Agilent GC-AED) and produce one final report. The GC-AED is a multi-element detector that can be used to measure over 20 elements in a gaseous or liquid matrix. Selective wavelength emissions accurately quantitate calibrated components, and the compound independent calibration (CIC) feature of the Agilent GC-AED ChemStation can be used to identify and estimate unknown compounds.

Experimental

The setup and plumbing of the tubing for the gases is critical to this type of application.

The tubing was all electropolished stainless steel, and all of the regulators were assembled in a clean room. A minimum number of connections are recommended to keep the system as leak free as possible. For this reason there are no filters recommended, only a “getter” for the helium (used for carrier and AED plasma gas) to remove any low-level contaminants. All fittings are double ferrule stainless Swagelock fittings. Orbital welding of the tubing connections is not required.

An Agilent 6890 coupled to a G2350A AED was used for this analysis. The instrument conditions are shown in Table 1. The instrument was equipped with a six-port gas-sampling valve connected to a volatiles inlet (VI), as shown in Figure 1. The sample vent was connected to a low volume vacuum pump, which draws the sample from ambient pressure Tedlar sample bags. The samples can also be taken in Silcosteel lined pressurized sample bombs, so the exit line was fitted with a low pressure sample relief valve to ensure that all samples and standards are injected under identical conditions. The samples were run in the split mode under cryogenic conditions.

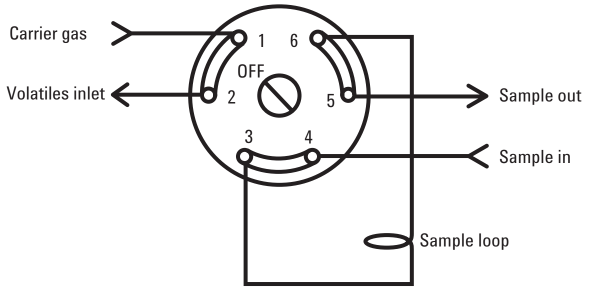

Figure 1. Plumbing diagram for sample introduction into GC.

Because of the nature of the samples, all tubing from the sample inlet to the VI was Silcosteel tubing from Restek (Bellefonte,PA). The distance inside the VI from the top of the ferrule to the tip of the tubing (coming from the sampling valve) is 15 mm. The inlet was additionally insulated to minimize condensation of heavier sulfur compounds on the tubing and the VI.

The nitrogen spectrometer purge was taken from the “boil-off” of the liquid-nitrogen Dewar (450 L) used for the cryogenic cooling of the gas chromatograph.

To give the instrument added functionality; the auxiliary reagent gas was configured for both oxygen analysis (10% methane in nitrogen), and for low level nitrogen (388 nm) analysis (research grade methane). The instrument was fitted with a manual-switching valve to select the correct auxiliary reagent gas.

The AED ChemStation controlled the GC-AED and automated the reagent gas flows. Three injections were required to quantitate all of the components. The first injection established the hydrogen content. The second injection determined carbon, sulfur, and nitrogen. The third injection determined oxygen-containing components.

The samples were quantified using an external calibration. The refinery gas standard and sulfur standards were obtained from Scott Specialty Gases. Because the response for sulfur is equimolar, a NIST H_2S sulfur standard was used to check responses for sulfur components in the standard and to provide a daily sulfur response quality control check. Additional sulfur components were added to the calibration table for identification purposes and the response factor of H_2S was used to quantitate all sulfur compounds. The refinery gas standard (containing C, H, O, N compounds) was used in a similar manner, in that the oxygen in the carbon monoxide provided the response for any other oxygen compound that was identified, and nitrogen provided the response for other nitrogen-containing compounds. NOx compounds were identified by the presence of an oxygen peak and a nitrogen peak for the same compound in the same sample (SOx compounds were identified using the same principal). The final report was generated using the Corex custom report generator. The final report links the sample data based on the ChemStation standard report and all of the physical constants compiled by the Gas Processors Association (GPA) to a modified Microsoft® Excel spreadsheet that performs calculations and prints the report.

Table 1 GC Conditions

Gas Chromatograph and Detector	
G1530A	6890 Series GC
G2350A	Atomic emission detector
G1530A Option 142	Volatiles interface
Column	30 m × 0.53 mm × 5.0 µm J&W DB-1 (Part no.19095Z-623)
Data acquisition	AED ChemStation
Operating Parameters, GC	
Volatiles interface temperature	250 °C
AED transfer line/cavity temperature	350 °C/350 °C
Oven temperature program	-45 °C for 9 min 8 °C/min to 50 °C, hold for 2 min 40 °C/min to 295 °C, hold for 2 min
Column pressure (ramped pressure)	3 psi for 9 min (0.5 psi/min to 5 psi)

Results and Discussion

The linearity of the instrument for sulfur was determined by performing a single level calibration using a NIST 20 ppm H_2S standard and running a second standard made by a third party as a sample. Figure 1 shows the undiluted standard run as a sample. Using the ChemStation to calculate the amounts shows a theoretical value for the standard as 2.07%. The actual value is 1.99%, a relative difference of 4%.

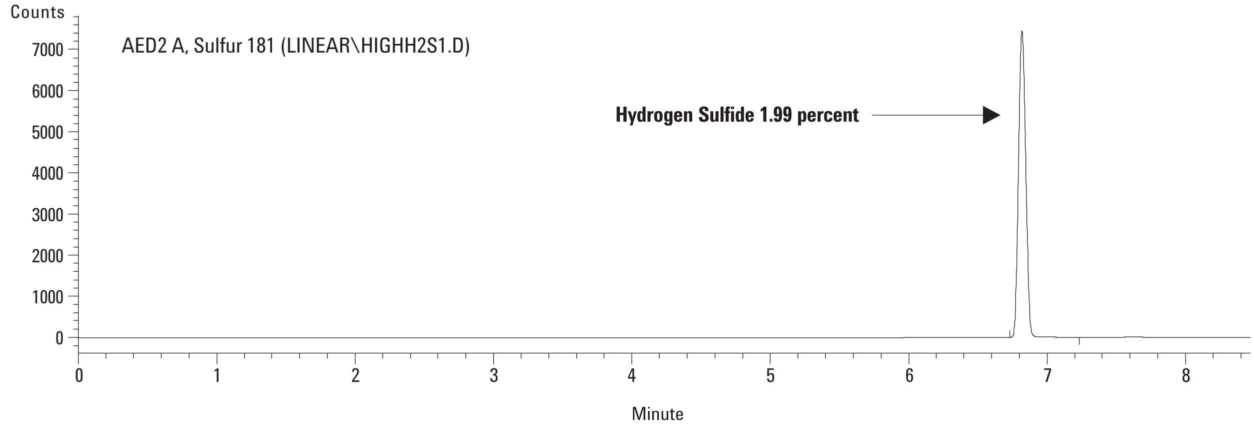

Figure 2. Chromatogram of 1.99 % hydrogen sulfide standard.

Figure 3 is an air blank injection, which was run just after the sample in Figure 2 to demonstrate the extremely low carryover. The negative peak at 4.2 min is the interference from the nitrogen in the sample.

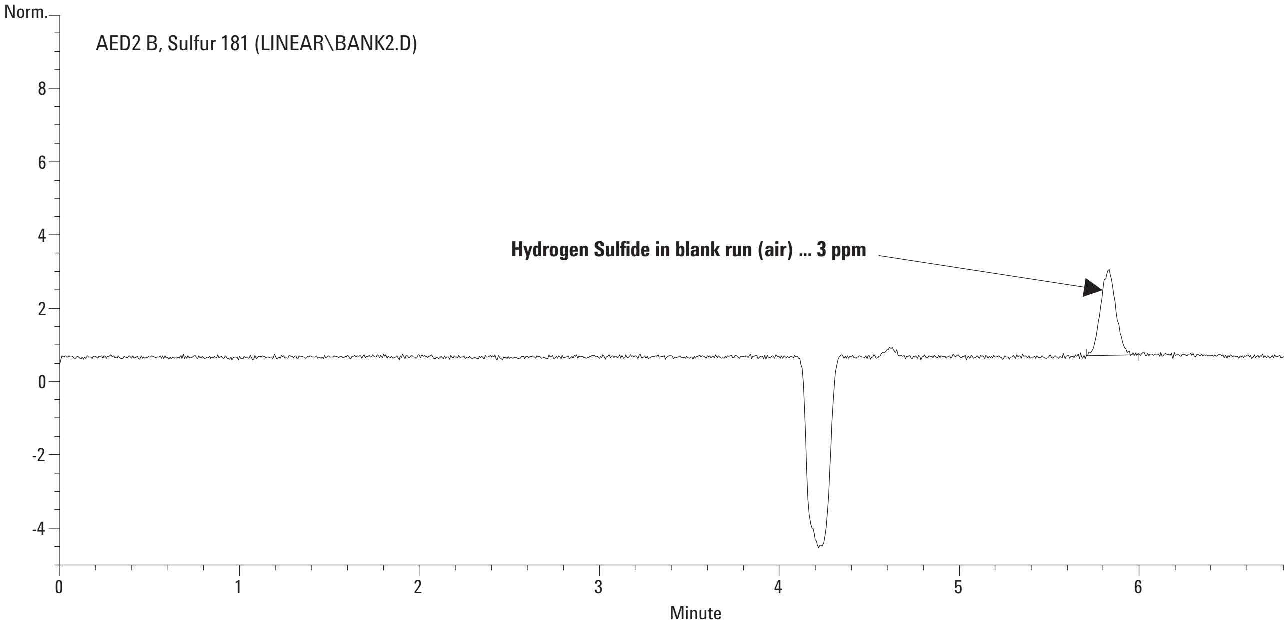

Figure 3. Blank run after high level standard showing low carryover of system.

Figure 4 shows a refinery stack gas sample. This sample was chosen for its unusually high H_2S content (4,000 ppm). The other interesting feature of the chromatography is the presence of ammonia. This peak co-elutes with a hydrocarbon, but can be distinguished by the presence of the nitrogen 174 peak at this same retention time.

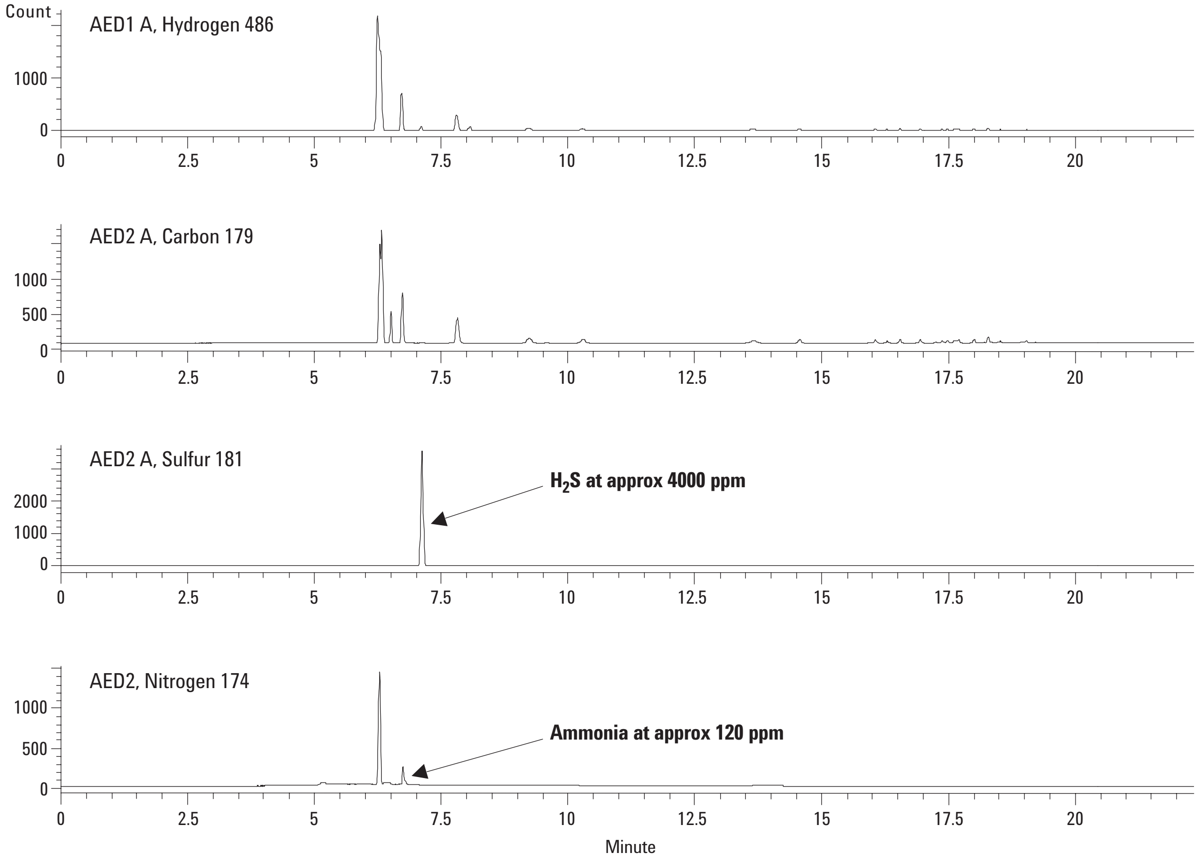

Figure 4. Refinery stack gas sample.

Figure 5 shows a drift study using a 20 ppm NIST standard. The raw area counts are plotted against time and the last point was taken 9 hours after the first point. The first run was used to passivate the active sites in the system. The overall drift was 3.7%.

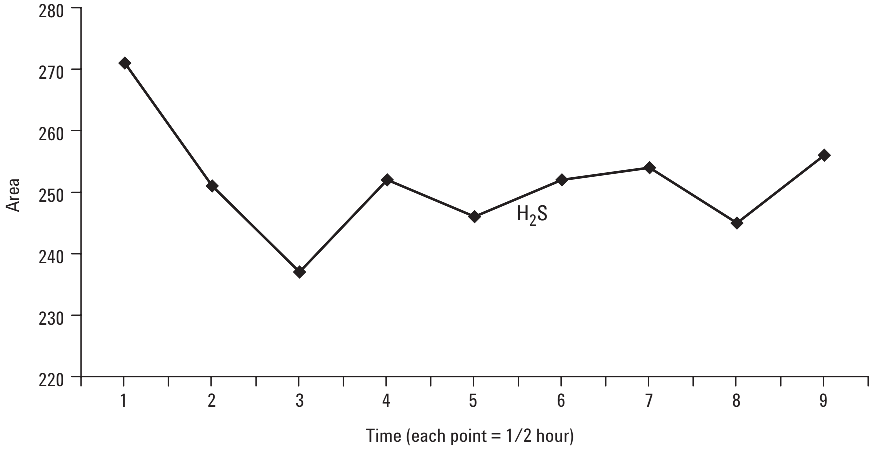

Figure 5. 3.7% Area repeatibility for 20 ppm NIST standard over 9 hours.

Conclusions

The Agilent GC-AED can combine analyses that were traditionally done on multiple instruments, and can give more reliable results. Combining these analytical techniques into one instrument can save time and money. In addition, the GC-AED is a robust, stable, versatile instrument that can offer many application possibilities.

References

South Coast Air Quality Management District Reference Method 307-91.

Bruce Quimby, Vince Giarrocco, Improved Analysis of Sulfur, Nitrogen, and Other Heteroatomic Compounds in Gasoline and Diesel Range Materials using GC/Atomic Emission Detection. Application Note 228-394, December 1997.

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