Monthly Newsletter From Wasson-ECE Instrumentation:

Chromatography Corner

ISSUE 06 JUNE 2009

this issue

upcoming events

- **June 24:** Free Automator Webinar
  Time: 9:00am MT
- **July 29 or 30:** Basic GC One Day Course
  Where: Hilton-NASA, Houston, TX
  Cost: $500

To register for one of Wasson-ECE's events visit: **www.wasson-ece.com/events** or call (970)221-9179

Extended Refinery Gas Analysis Plus Trace Sulfur Compounds

During crude petroleum processing, by-products including ethane, propane, butanes, high molecular weight hydrocarbons, and elemental sulfur are produced. After distilling the crude petroleum into fractions sulfurs are removed by absorbers such as a caustic solution or amine. The burning of petroleum containing sulfurs generates sulfur dioxide (SO_2), which reacts with atmospheric water and oxygen to produce sulfuric acid (H_2SO_4). This sulfuric acid is a component of acid rain, which lowers the pH of soil and freshwater bodies. Fuel standards increasingly require sulfur to be extracted to prevent the formation of acid rain. Because of the significant impact sulfurs can have on the environment, sulfurs must be quantified to low parts-per-million (ppm) levels.

For this analysis streams containing a mixture of components including CH_4, CH_2H_6, C_3 + C_4, C_5+, CO/CO_2, O_2, N_2 and various sulfurs were analyzed. Wasson-ECE developed a system using an Agilent Technologies 7890A gas chromatograph with four detectors: a flame ionization detector (FID), dual thermal conductivity detectors (TCD/TCD), and a sulfur chemiluminescense detector (SCD).

Four different injections were made and a series of valves introduced samples to the separation columns. This instrument was configured for the injection of gases and pressurized liquids only.

Components analyzed on the FID included C_1 through C_5 paraffins and olefins with an initial C_6^+ backflush to the detector. The dual Wasson-ECE TCDs analyzed carbon dioxide, ethylene, ethane, acetylene, an argon/oxygen composite, nitrogen, methane, carbon monoxide, helium, and hydrogen. Components analyzed on the SCD included hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and ethyl mercaptan. The system could also quantify total sulfurs through peak summing. The total analysis time was approximately 15 minutes.

By adding an SCD to the system, sulfurs and standard refinery gas impurities can be analyzed with a single system. This ensures a pure product that has very little environmental impact on soil and freshwater.

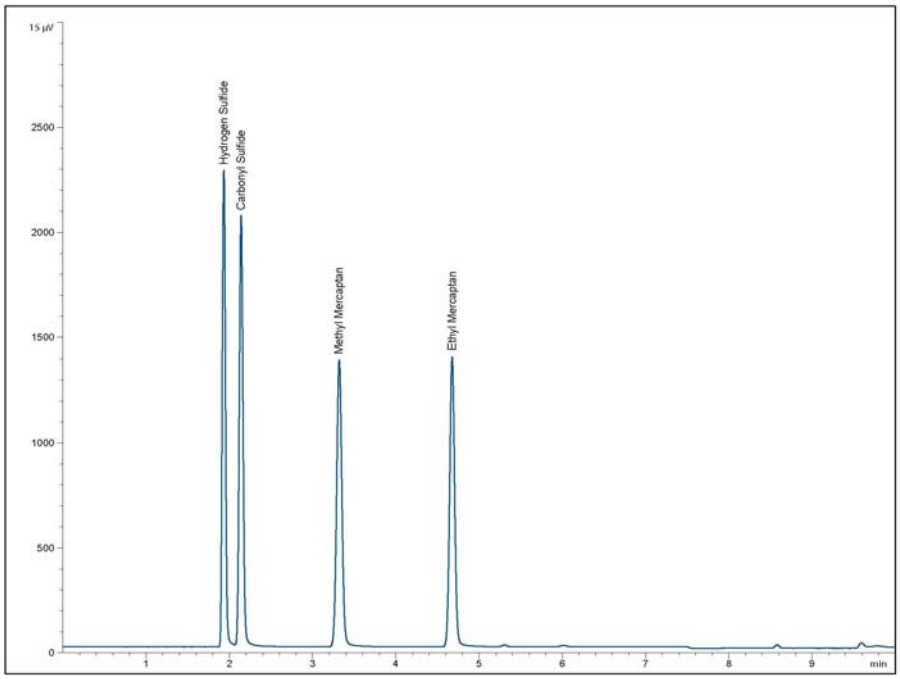

Figure 1: Chromatogram showing sulfurs speciated on the SCD

WASSON·ECE INSTRUMENTATION
Engineered Solutions, Guaranteed Results.

GC/MS/FID Analysis of Impurities in Polymer Grade Ethylene, Isopentane, 1-Hexene, 1-Butene, and Hexane

Ethylene, isopentane, 1-hexene, 1-butene, and n-hexane are all components for the production of polyethylene and polypropylene plastics. Polyethylene and polypropylene are used in a variety of products including packaging, textiles, laboratory equipment, and automotive components.

An Agilent Technologies 7890A series gas chromatograph was configured for use with the Agilent 5975 mass spectroscopy detector and a flame ionization detector (MSD/FID) for the analysis of impurities in polymer grade ethylene, isopentane, 1-hexene, 1-butene, and hexane.

Isopentane, hexane, 1-butene, and 1-hexene samples were vaporized with an on-board vaporizer above 63°C prior to injection to the GC. Ethylene was injected in the gas phase using a gas sample valve.

Four methods were created for each matrix to complete the analysis on the MSD/FID. Method A used silica lined sample lines and separated oxygenates and sulfurs at trace levels on the MSD. Methods B and C separated carbonyl sulfide and hydrogen sulfide as well as hydrocarbons on the MSD. Method D used an FID and separated C_1-C_4 hydrocarbons. One set of methods (one for each matrix) was analyzed and had a run time of approximately 20 minutes. A total of 58 individual components were analyzed by wet needle injection to the MSD to identify their specific retention times. The MSD was run in both SCAN and SIM mode to identify the components.

By using the MSD, low level impurities in polymer grade ethylene, 1-butene, isopentane, n-hexane and 1-hexene could be analyzed between 0.1-100 parts-per-million (ppm).

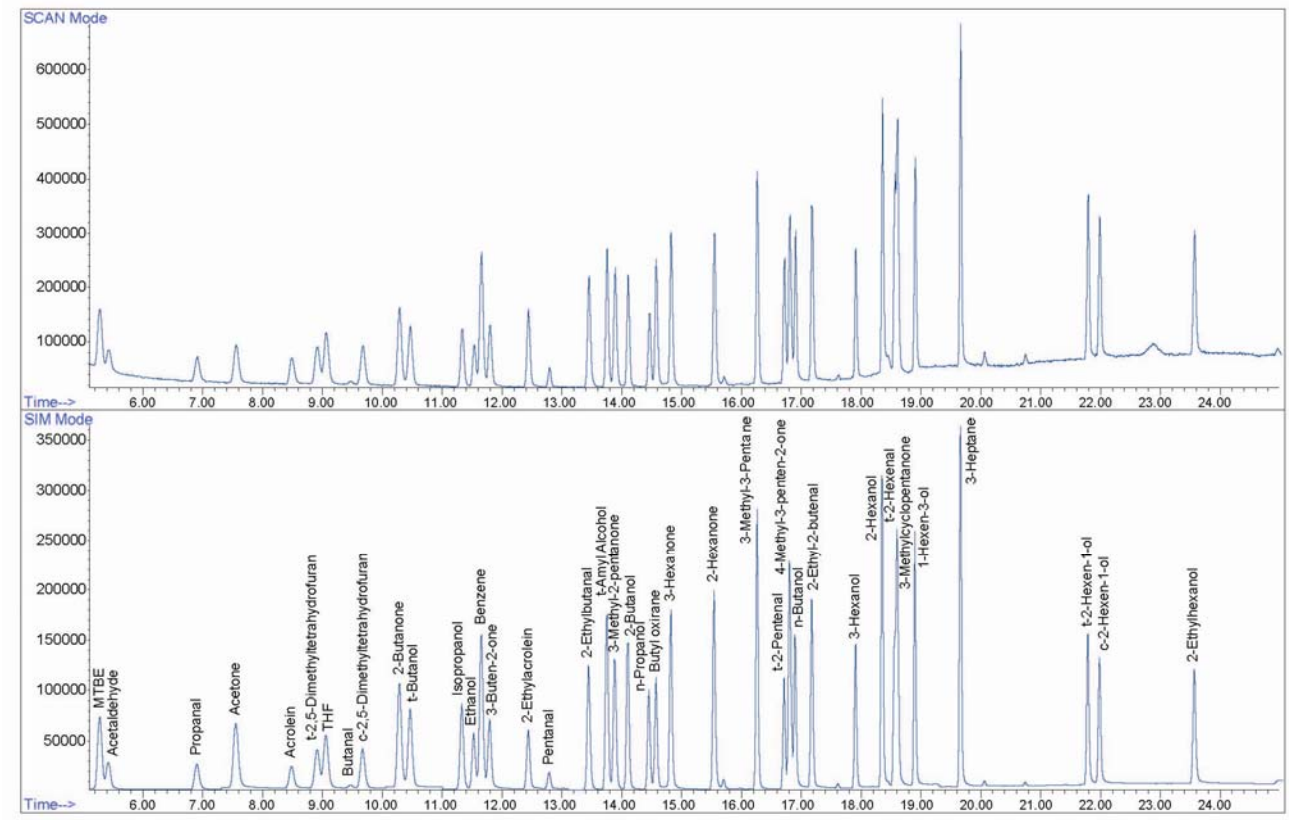

Figure 2: Method A chromatogram using ethylene as the matrix on the MSD. The top chromatogram shows the sample run in SCAN mode, which identifies components in a chosen ion range. The bottom chromatogram was run in SIM mode and shows specific ions selected for the analysis.

Chromatography Tips and Tricks

The main purpose of a GC inlet is to deliver the sample to the column while preserving the components in a way that is highly reproducible and accurate. GC inlets can be divided into two categories: capillary and packed. However, since most complex gas chromatography today uses capillary columns this article will focus on capillary inlets. The three main types of capillary inlets include: split/splitless, cool on-column, and programmed temperature vaporization (PTV).

Split/splitless inlets are most commonly used in gas chromatography. They are vaporizing inlets and have two modes of operation. The split mode allows the user to introduce a selected fraction of the injected sample onto the capillary column while the other portion is sent to the split vent. Because a large portion of the sample is sent to vent, split mode can cause sample discrimination and is best suited for analyses of ppm and higher. Splitless mode allows the entire sample to evaporate and mix uniformly with the carrier gas. Operating an inlet in splitless mode is a way of improving sensitivity because virtually the entire sample is injected onto the capillary column. Injections using the splitless mode are most useful for analyses with lower detection limits of single ppm to ppb concentrations.

A cool on-column inlet is designed to introduce the entire sample onto the capillary column without vaporization. The sample is later vaporized in the column using temperature programming. Injecting a sample directly onto the column without vaporizing can be used for samples with wide boiling-point ranges, samples that are heat sensitive or that require trace level analysis. Cool on-column inlets provide the best quantitative representation of the sample but can cause problems if dirty samples are introduced because nearly all sample material is allowed to reach the column.

Finally, the PTV inlet provides the cool injection of the cool on-column inlet and the rapid heating and vaporization of the split/splitless inlet while accommodating up to a few hundred microliters of sample. The sample is injected cold into a chamber and is rapidly heated to vaporize the sample onto the capillary column. A large difference between the PTV inlet and other inlets is that it is extremely flexible and versatile because of its wide variety of injection possibilities.

When choosing the appropriate inlet for your GC it is important to examine the sample makeup and analysis. Factors affecting the inlet include, but are not limited to, lower detection limits, sample stability, boiling point ranges, and injection volume.

Additional questions? Contact our service department at (970)221-9179 or service@wasson-ece.com.

Question of the Month

Many times repeatability issues in gas chromatography come down to the operator. What would be the effect of an operator making a slow injection at a large sample volume?

a) Increased resolution
b) Decreased resolution
c) Non-linear detector response

Enter for a chance to win a digital camera for your lab. One winner will be chosen quarterly from a random drawing from the correct answers received. Answers to the monthly question can be faxed to 970-221-9364, emailed to QOM@wasson-ece.com or mailed to 101 Rome Court, Fort Collins, CO, 80524, Attention: Marketing.

Events Calendar

June 24: Free Automator Webinar

July 29-30: Basic GC One Day Course at Hilton-NASA in Houston, TX

August 26: Free PNA Webinar

September 16-17: Lab Managers Training at Wasson-ECE in Fort Collins, CO

September 23: Free Oxy RGA Webinar

October 21-22: Basic GC Course at Wasson-ECE in Fort Collins, CO

October 28: Free Webinar TBD

Want a custom training course for your company? Need training at your site? Contact Wasson-ECE for your quote today at training@wasson-ece.com or call (970)221-9179.

Wasson-ECE Instrumentation

specializes in configuring and modifying new or existing Agilent Technologies gas chromatographs. Our systems are guaranteed, turn-key analytical solutions, with the installation, warranty and service plan on us. Contact us for your custom GC analysis needs and find out what a difference over 20 years of experience can make.

Wasson-ECE brings GC Training to Houston, TX July 29 and 30.

Register at www.wasson-ece.com or call (970)221-9179 today!

WASSON·ECE INSTRUMENTATION
Engineered Solutions, Guaranteed Results
101 Rome Court
Fort Collins CO, 80524
www.wasson-ece.com