

# Chromatography Corner

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## upcoming events

- **August 26:** Free Simulated Distillation Webinar  
Time: 9:00am MT

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

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## Trace Sulfur Compounds in Light Petroleum Liquids by GC and Sulfur Selective Detection per ASTM D5623

In petroleum processing, most feed-stocks contain sulfur species. After distilling the crude petroleum into fractions, sulfurs are removed by absorbers such as a caustic solution or amine. Sulfurs must be removed from light petroleum liquids because of their corrosive nature, ability to destroy catalysts used downstream in chemical feed-stocks and environmental impact. Because of the significant impact on chemical feed-stocks, fuel standards require sulfurs to be quantified to low parts-per-million (ppm) levels.

For the analysis of trace sulfur compounds in light petroleum liquids per ASTM D5623, Wasson-ECE Instrumentation configured an Agilent Technologies gas chromatograph (GC) with a sulfur chemiluminescence detector (SCD).

The GC test method is applicable to distillates, gasoline motor fuels (including those containing oxygenates) and other petroleum liquids with a final boiling point of approximately 230°C (450°F) or lower at atmospheric pressure.

Based on ASTM method D5623, the SCD identifies the following compounds in light petroleum liquids to a lower-detection-limit (LDL) of 0.1 ppm:

- Methanethiol
- Ethanethiol
- Dimethyl sulfide
- Carbon disulfide
- 2-Propanethiol
- 2-Methyl-2-propanethiol
- 1-Propanethiol
- Ethylmethyl sulfide
- Thiophene/2-Methyl-1-propanethiol
- Dimethyl disulfide
- 2-Methylthiophene/3-Methylthiophene
- C<sub>2</sub>-thiophenes
- Diethyl disulfide
- Benzothiophene
- C<sub>1</sub> and C<sub>2</sub>-benzothiophenes
- Diphenyl sulfide

Heavier sulfur compounds can be detected, but may co-elute or result as composite peaks.

By using an SCD and an Agilent GC, sulfurs in light petroleum products can be quantified to ppm levels per ASTM D5623. This analysis ensures a pure product that has very little negative impact.

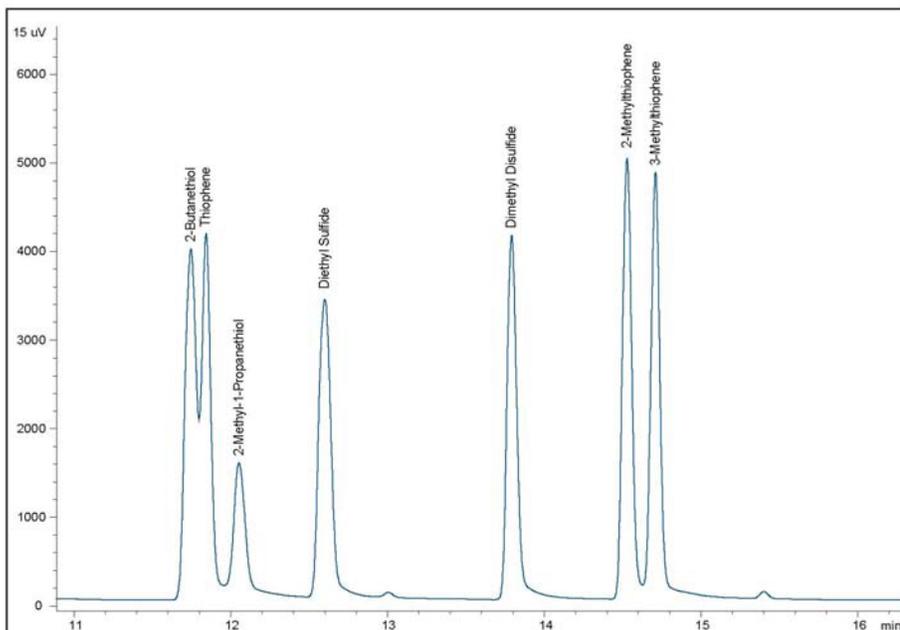


Figure 1: Wason-ECE in-house sulfur blend; each component is approximately 0.20-0.25 ppm as sulfur.



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## Analysis of Benzene in 1-Hexene, and Xylenes in 1-Octene

Linear low density polyethylene (LLDPE) is commonly produced at low temperatures by the co-polymerization of ethylene with short chain alpha-olefins, such as 1-hexene and 1-octene. The production of LLDPE is initiated by a transition metal catalyst. The actual polymerization process can be done in either a liquid or gas phase reactor. Usually, 1-octene is the co-polymer in the liquid phase while 1-hexene is co-polymerized with ethylene in a gas phase reactor. LLDPE is widely used in packaging material, such as plastic bags, food storage containers, and plastic wrap.

Benzene is formed as an impurity in the production of 1-hexene, and xylenes are used to wash the polymers out of the reactor in the alpha-olefins units. It is important to quantify benzene and xylenes to ppb levels because not only can they poison the catalyst used in the polyethylene reactor, but aromatics are also toxic.

Wasson-ECE configured an Agilent Technologies 6890N Series Gas Chromatograph (GC) with a pulsed discharge helium ionization detector (PDHID) for the analysis of benzene in 1-hexene, and xylenes in 1-octene. Benzene and xylenes are first separated using two columns. The first column separates by boiling point and the second separates by polarity. The lower quantifiable limit (LQL) on the PDHID was 100 parts-per-billion (ppb) for benzene, and 150 ppb for xylenes. The PDHID requires helium and argon of very high purity to maintain a stable, low noise discharge arc. To help insure that the helium and argon are free of atmospheric gases, two helium gas purifiers, or "getters", were used with the instrument. This GC was configured for syringe injection using an Agilent Technologies 7683B auto-injector.

Due to the sensitivity of the PDHID, ppb aromatic impurities could be separated and quantified in 1-hexene and 1-octene and ensure a pure product that is safe for consumers.

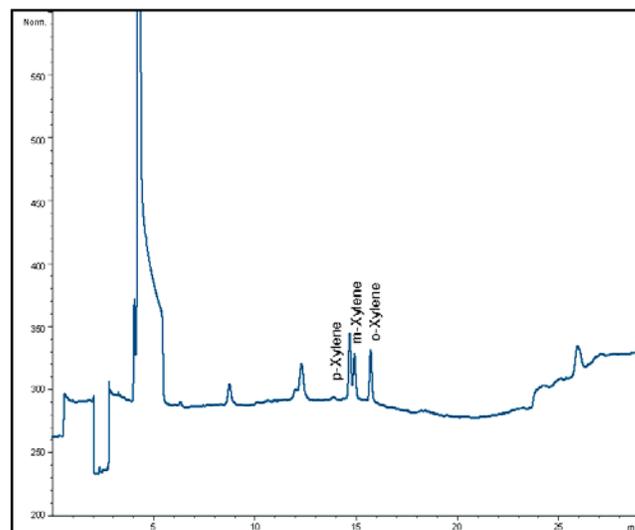
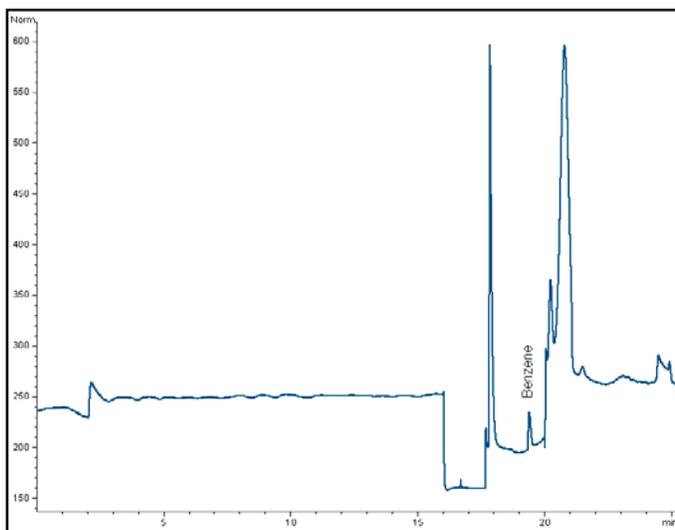


Figure 2 and 3: Syringe injection of 1-hexene spiked with 100 ppb benzene and 1-octene spiked with 100 ppb xylenes by PDHID.

## Chromatography Tips and Tricks

Air switches actuate air actuators for valves by alternating the gas supplies to either side of the rotating pistons inside the actuators. Air switches can develop leaks during use. A small leak at the vent of a switch is often heard as a small hiss from the top side of the GC. This leak will not affect the chromatography unless it affects the operation of the valve. Sometimes actuating a valve rapidly several times will solve the problem. When a leak is encountered, a simple test is required to determine whether an air switch or air actuator is leaking. Use the following steps for this determination:

1. To test which part is responsible for the leak, use needle nose pliers to pinch off one of the two air hoses leading to the air actuator at the bottom of the air switch.
2. If the leak stops, the valve air actuator is responsible. Replacing the valve actuator will be covered in the Sept. 2009 issue of *Chromatography Corner*. If the leak continues, the air switch is responsible.

### Air Switch Replacement:

1. Turn off the GC and air actuator gas supply. Remove the power cord from the power supply.
2. Remove the top rear cover of the GC.
3. Carefully cut the tie wraps from the air switch wires, until the wires reach a socket, butt connector, or terminal strip.
4. Cut the wire leading to the connector on the other side of the air actuator wire and/or remove the wire or pin from the appropriate connector or terminal strip.
5. Loosen the two nuts or hex screws holding the air switch to the GC and remove.
6. Disconnect the 1/16" tubing leading from the air switch to the valve.
7. Cut the wires for the replacement air switch to the appropriate length and strip approximately 3/16" of insulation from each wire.



8. Crimp the appropriate pin (if necessary) to one wire or connect directly to the appropriate terminal strip connector.
9. Place the pin into the appropriate hole of the connector if necessary.
10. Take the other wire and crimp one end of the appropriate connector to the wire.
11. Crimp the other previously cut wire, expose approximately 3/16" of wire, and crimp the connector to the wire. Note: Check all crimps and wires to ensure that all are tight and no exposed wire is visible.
12. Fasten the air switch to the gas chromatograph chassis with two nuts or hex screws.
13. Reconnect the 1/16" stainless steel tubing to the air switch.
14. Plug the power cord into the power supply and turn on the gas chromatograph.
15. Turn on the air actuator gas supply.
16. Rotate the appropriate valve to test the new air switch.
17. Replace the top rear cover of the gas chromatograph.



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

## Question of the Month

What component of gas chromatography has the most influence over the separation of compounds in a sample?

- A. Mobile phase
- B. Injection method
- C. Stationary phase



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](mailto:QOM@wasson-ece.com) or mailed to 101 Rome Court, Fort Collins, CO, 80524, Attention: Marketing.

## Events Calendar



### 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.

**August 26:** Free Simulated Distillation 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](mailto:training@wasson-ece.com) or call (970)221-9179.**



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