Quarterly Newsletter From Wasson-ECE Instrumentation:

Chromatography Corner

ISSUE 28 December 2012

this issue

upcoming events

- **March 17-21:** Pittcon 2013
  Where: Philadelphia, PA
  Booth:713

For more information visit:
www.wasson-ece.com
or call (970)221-9179

ASTM D3606 and D5599 in a World without Helium

Helium is the second most abundant element in the universe. Commercial helium is a byproduct of natural gas production and the U.S. is the world's largest supplier. Cutbacks in global production, shutdowns of helium processing plants, increased demand from health care and semi-conductor industries, and the U.S. government's attempts to privatize the Federal Helium Program have all contributed to the shortage of helium.

Due to the helium shortage, Wasson-ECE Instrumentation has configured an Agilent Technologies gas chromatograph (GC) using hydrogen and nitrogen carrier gases to continue to meet the requirements in ASTM D3606 and D5599.

The front train analyzes MTBE, ETBE, TAME, DIPE, methanol, ethanol, isopropanol, n-propanol, isobutanol, tert-butanol, sec-butanol, n-butanol, tert-pentanol, and dimethoxyethane to a lower detection limit of 0.3 vol% using an oxygenate flame ionization detector (O-FID) with nitrogen carrier gas.

The back train analyzes benzene and toluene to a 0.05 vol% lower detection limit using a thermal conductivity detector with hydrogen carrier gas. The application uses two column sets and a switching valve for column selection. The first column set retains C_9 and heavier components present in the gasoline matrix and backflushes the matrix to vent to avoid interferences and column contamination. The second column set separates benzene and toluene. The application is available either with packed columns that meet the requirements in ASTM D3606 or in a modified version using capillary columns. Hydrogen provides acceptable resolution, can reach the lower detection limits of the method, and meets all the requirements of ASTM D3606.

For laboratories encountering a helium shortage or just looking to cut costs on carrier gas, Wasson-ECE Instrumentation has helium-free guaranteed solutions for ASTM D3606 and ASTM D5599.

Figure 1. Oxygenate separation with helium carrier gas

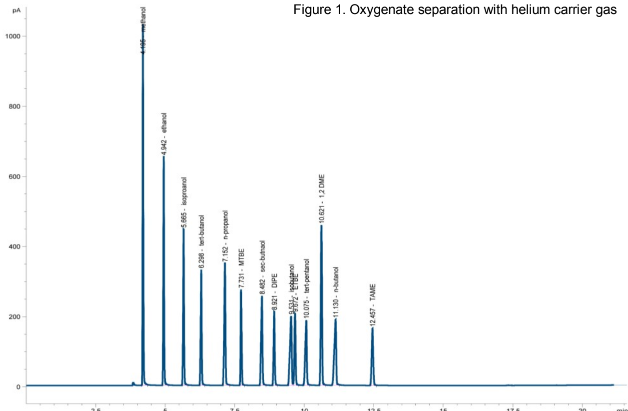
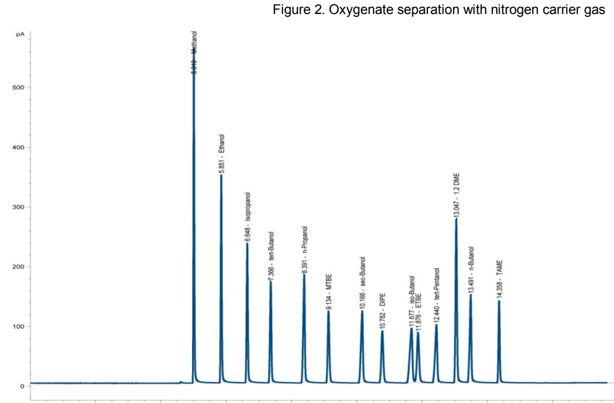


Figure 2. Oxygenate separation with nitrogen carrier gas



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Analysis of Oxygenates and Hydrocarbons in C_4 Streams Using Alternative Carrier Gas

Wasson-ECE Instrumentation has configured an Agilent Technologies gas chromatograph (GC) with dual flame ionization detectors (FID/FID) for the analysis of oxygenates and hydrocarbons in C_4 streams. The instrument is configured to perform a dual injection with the front train analyzing oxygenates and the back train simultaneously analyzing hydrocarbons. Both trains contain a deans switch to backflush the heavier components to vent, avoiding interferences and column contamination. Three different carrier gases, helium, hydrogen, and nitrogen, were used on the same instrument to verify the feasibility and quality of alternate carrier gases.

Isobutylene was spiked with methane, ethane, ethylene, propane, propylene, acetylene, isobutane, propadiene, n-butane, trans-2-butene, 1-butene, cis-2-butene, neopentane, cyclopentane, isopentane, n-pentane, 1,3-butadiene, 3-methyl-1-butane, and trans-2-pentene. The spiked isobutylene was analyzed using the industry standard carrier gas, helium, to establish a chromatogram for the comparison of alternatives.

The spiked isobutylene was then analyzed using hydrogen as a carrier gas. Mystery peaks could be observed when compared to the helium carrier analysis. The hydrogen carrier gas reacted with isobutylene to create isobutane. Additional transitional species peaks could also be observed on the chromatogram. The reduction reaction appeared to increase in magnitude during multiple runs. Hydrogen carrier gas interference has only been observed in high concentrations of olefins on certain types of columns.

The spiked isobutylene was then analyzed using nitrogen as a carrier gas. Comparable chromatograms to those generated using helium were produced. Nitrogen was selected as a suitable alternative to helium for a carrier gas for the analysis of oxygenates and hydrocarbons in C_4 streams. When using nitrogen as a carrier gas the inlet is limited to 200 mL/min total flow (versus 1250 mL/min when configured with He or H_2). This limitation is easily overcome by configuring the instrument to inject with a low column flow and a high split flow and then programming a flow ramp after the injection is complete.

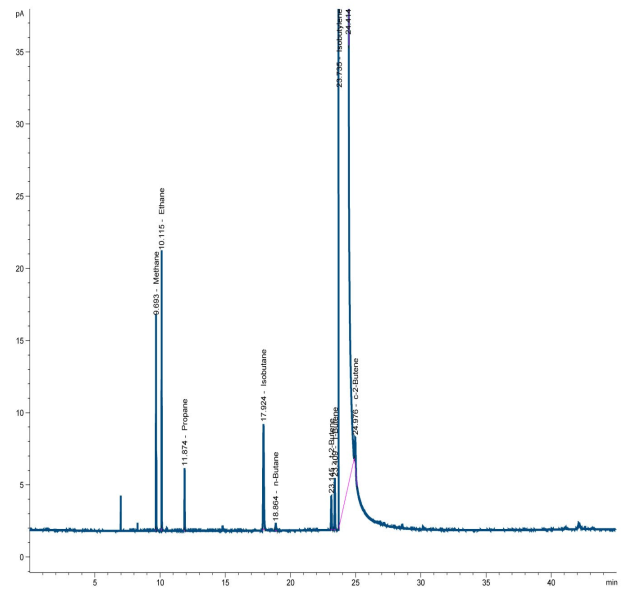


Figure 3. Isobutylene separation with helium carrier gas

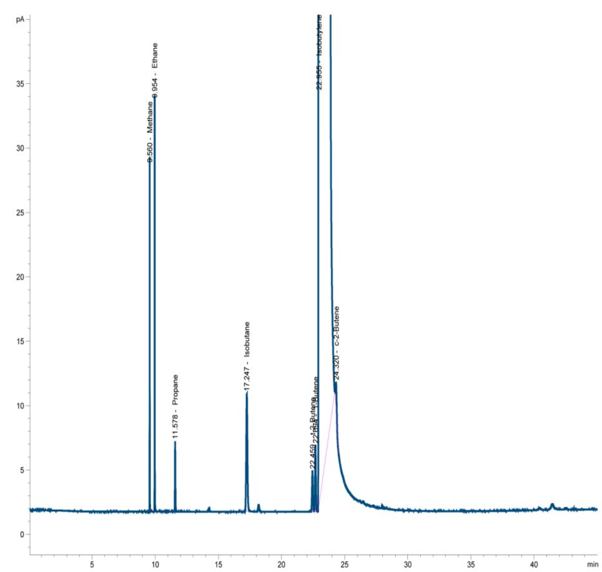
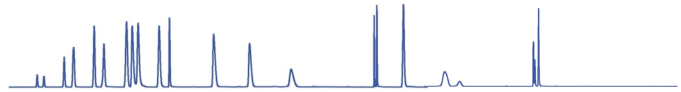


Figure 4. Isobutylene separation with nitrogen carrier gas

Wasson-ECE Instrumentation's research and development provided the customer with a turn-key solution that provided the required separation and detection limits without using helium. With over 25 years of chromatography experience, Wasson-ECE has the knowledge to reconfigure methods and replumb instruments to use alternative carrier gases.

Chromatography Tips and Tricks



The oxygenate flame ionization detector (O-FID) is a selective and useful tool for the analysis of oxygenates in hydrocarbon matrices. The O-FID consists of a cracking reactor, methanizer, and flame ionization detector (FID). The analysis begins when the effluent from the capillary column reaches the cracking reactor. The cracking reactor thermally pyrolizes the organic compounds present in the sample. The oxygenated compounds are converted to carbon monoxide and non-oxygenated compounds to elemental carbon. The carbon is deposited on the walls of the catalyst tubing in the cracking reactor and helps in maintaining the reaction kinetics in the cracking reactor. The carbon monoxide elutes to the methanizer where it is converted to methane and is detected by the flame ionization detector.

Oxygen introduced into the cracking reactor through atmospheric leaks can reduce the lifetime of the catalyst. It is crucial that the O-FID is properly leak checked. The nitrogen purge surrounding the O-FID protects the catalyst from accidental oxygen introduction. The nitrogen purge should flow at 15-20 mL/min to protect the cracking reactor. The OMI filters should be monitored daily for changes from black to light brown indicating the catalyst is spent. The trap should be changed when 80% of the material has changed. To extend the life of the cracking reactor, the reactor should be cooled to 700–800ºC overnight or turned off when not in use.

The cracking reactor requires maintenance when there are ghost peaks, tailing peaks, no peaks, or an extremely noisy baseline. To maintain the cracking reactor inject hydrocarbon samples to “build-up coke” on the cracking reactor walls. If no peaks are visible, the fuse for the cracking reactor should be checked to verify operational condition. The cracking reactor is a consumable part and may need to be replaced if coking does not improve performance.

The efficiency of the methanizer can decrease with use due to trace carbon elution from the cracking reactor. Carbon contamination of the methanizer will result in lower responses, poor peak shape, broad peaks, tailing peaks, and lower sensitivity. To maintain the methanizer turn off the temperature of the cracking reactor, turn off the FID gases, and switch the air/hydrogen select valve to the air position. For maximum methanizer cleanup, a twelve hour bake out period is recommended. It is important that the temperature of the cracking reactor is cool during the methanizer cleanup process. The flow of helium through the cracking reactor should prevent the back flow of air from the methanizer but even trace amounts of oxygen at high temperatures can reduce the life of the cracking reactor.

The FID is a standard Agilent Technologies detector and should be maintained following the Agilent manual. With proper maintenance, the O-FID detector will provide a high level of sensitivity and performance for the detection of oxygen containing compounds. Additional questions? Contact our service department at (970)221-9179 or service@wasson-ece.com.

Wasson-ECE Instrumentation News

Wasson-ECE Expands Virtual Application Notes

Wasson-ECE has recently updated our website to include new application notes that highlight analyzer descriptions, chromatography examples, key features and benefits, and additional literature references.

Some of the most recent application notes include:

- ASTM D7754
- Trace Helium in Hydrogen or Deuterium
- Vinyl Chloride Monomer in PVC Powder
- LPG in Seawater

Is there an application you would like to learn more about or see on the website? Email sales@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.

Events Calendar

March 17th-21st: Pittcon 2013 in Philadelphia, PA, Booth 713

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.

Happy Holidays and Thank You for Choosing Wasson-ECE Instrumentation for Your Chromatography Needs in 2012!

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