Monthly Newsletter From Wasson-ECE Instrumentation:

Chromatography Corner

ISSUE 10 October 2009

this issue

Isobutylene and 1-Butene P.1
H_2S Analysis by Headspace P.2
Chromatography Tips & Tricks P.3
Question of the Month P.3
Events Calendar P.4

upcoming events

- **Oct. 14-15:** Basic GC Course
  Where: Wasson-ECE in Fort Collins, CO
  Cost: $2,000 per person
- **Oct. 28:** Free TO-Clean Webinar
  Time: 9:00am MT

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

Analysis of Hydrocarbons and Oxygenates in High Purity Isobutylene and 1-Butene Streams

Isobutylene is used as an intermediate in two refining processes. When reacted with methanol and ethanol, it is used to make methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) and as a monomer in the polymerization process to produce butyl rubber. Isobutylene is isolated from refinery streams by reaction with sulfuric acid, but most commonly by catalytic dehydrogenation of isobutane. Another gas present in crude oil is butene. It is obtained by catalytic cracking of long chain hydrocarbons left during refining and extracted by fractional distillation. Butene is used as the monomer for the polymer polybutene. Since isobutylene and 1-butene are used in polymerization processes it is important to quantify impurities to part per million (ppm) levels to avoid catalyst poisoning.

Wasson-ECE configured an Agilent Technologies 7890A Gas Chromatograph (GC) with dual flame ionization detectors (FID/FID) for the analysis of hydrocarbons and oxygenates in high purity isobutylene and 1-butene.

FID 1 detected oxygenates including: acetaldehyde, isobutyraldehyde, butyraldehyde, isovaleraldehyde, valeraldehyde, dimethyl ether, ethyl tert-butyl ether, methyl tert-butyl ether/diisopropyl ether composite, isobutyl tert-butyl ether, diisobutyl ether, acetone, acetonitrile, methanol, ethanol, isopropanol/n-propanol composite, isobutanol/sec-butanol composite, tert-butanol, and n-butanol.

FID 2 detected C_1 through C_8 paraffins and olefins including: methane, ethane, ethylene, propane, propylene, acetylene, isobutane, propadiene, n-butane, trans-2-butene, 1-butene, isobutylene, cis-2-butene, neopentane, isopentane, methyl acetylene, n-pentane, 1,3-butadiene, neohexane, isoamylene, n-hexane, diisobutylene, and vinylcyclohexane with a C_9^+ backflush to the vent.

The challenge of this application is due to some hydrocarbon components eluting on the tail of the matrix peak (isobutylene or 1-butene) making them non-quantifiable. These components (including c-2-butene, neopentane, isopentane, methyl acetylene, n-pentane, and 1,3-butadiene) were heart-cut and trapped. Components heavier than 1,3-butadiene were allowed to elute to the detector as normal, but the lighter components were captured on a proprietary trap. The compounds were then released from the trap by heating to a temperature necessary to achieve desorption. The freed components were then re-injected on a low temperature secondary column before eluting to the detector.

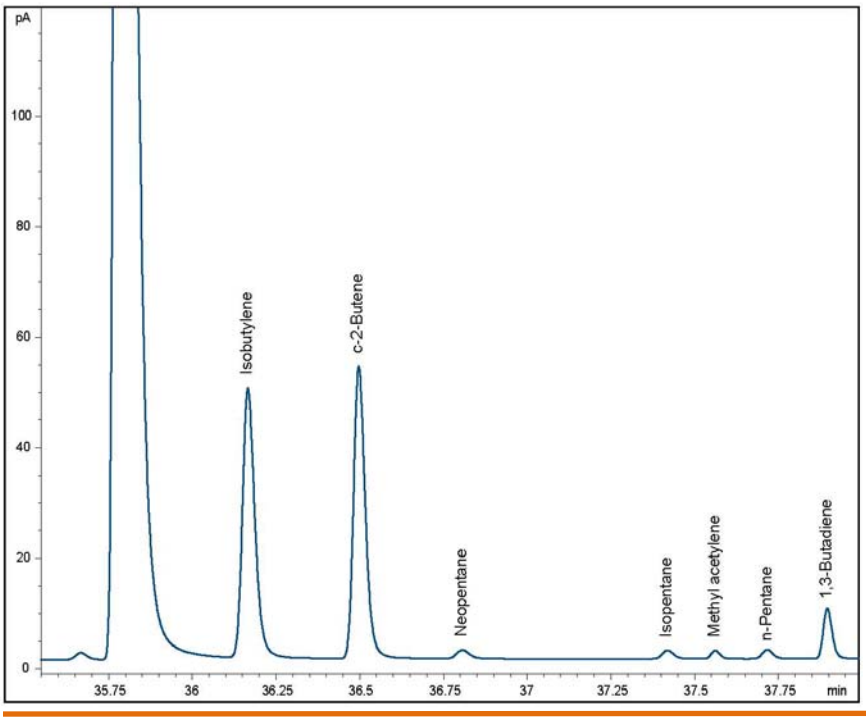


Figure 1: 2.0 µL liquid injection of customer supplied 1-butene sample showing heart-cutting and trapped components separated from matrix peak by FID.

WASSON·ECE INSTRUMENTATION
Engineered Solutions, Guaranteed Results.

Measurement of Total Hydrogen Sulfide in Natural Gas by Multiple Headspace Extraction and Sulfur Specific Detection

Natural gas sources often contain sulfur compounds that are odorants with low thresholds, highly corrosive, and poisonous to catalysts in downstream refining processes. For these reasons, volatile sulfur compounds must be quantified to low parts per million (ppm) levels.

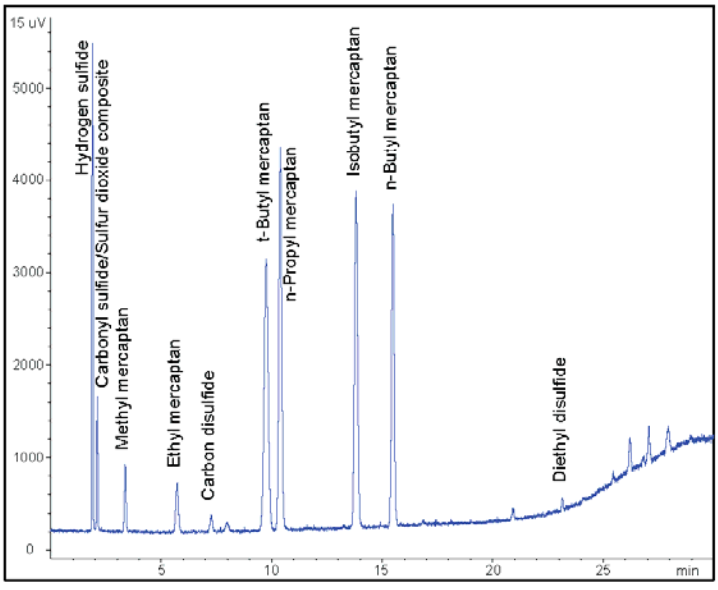
Wasson-ECE configured an Agilent Technologies Gas Chromatograph (GC) with a sulfur chemiluminescence detector (SCD) and headspace sampler for the analysis of total hydrogen sulfide in residual fuels by multiple headspace extractions. The SCD provides a sensitive and selective response to sulfur compounds. System performance was guaranteed to ASTM D6021 and ASTM D5504 with two separate methods for the analysis.

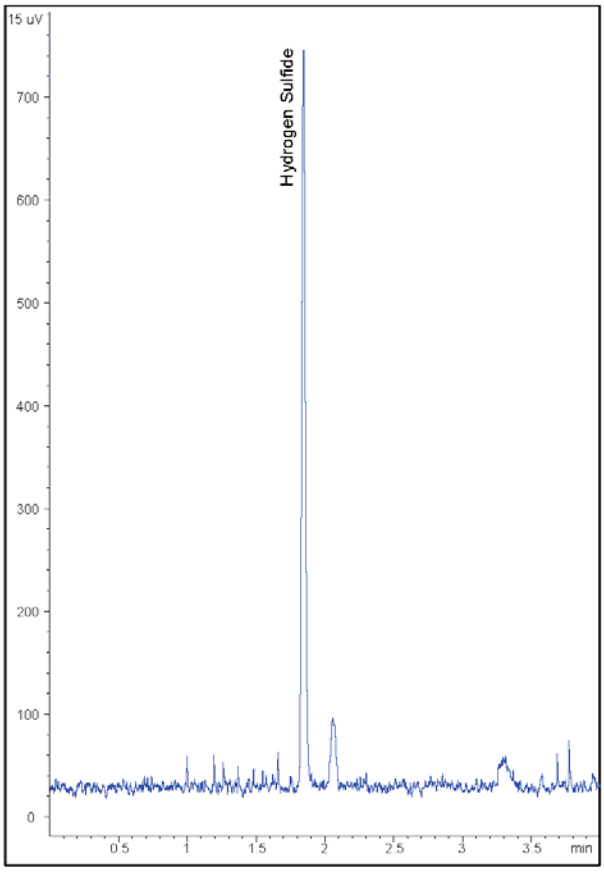
Method one was based on ASTM D5504 and quantified hydrogen sulfide, a carbonyl sulfide/sulfur dioxide composite, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, carbon disulfide, isopropyl mercaptan, t-butyl mercaptan, n-propyl mercaptan, ethyl methyl sulfide, 2-butyl mercaptan, thiophene, isobutyl mercaptan, diethyl sulfide, n-butyl mercaptan, dimethyl disulfide, and diethyl disulfide to 0.01 ppm by SCD.

Method two used three separate extractions of the oil using multiple headspace extraction procedure (MHE) per ASTM D6021.

MHE is a technique used to determine the total concentration of gas trapped in a liquid and involves heating the sample in a 60°C oven, making a headspace or vapor phase injection, allowing the sample to cool, and repeating this process a total of three consecutive times. Hydrogen sulfide was quantified to a lower detection limit of 0.015 parts per million by volume (ppmv) by SCD. This method allowed heavier sulfur compounds to be detected, but with some co-elutions.

This analysis was particularly difficult due to the reactivity of gaseous sulfur compounds. All sample wetted lines were Silcosteel® lined and purged after each run. Using an Agilent Technologies GC configured with an SCD, Wasson-ECE was able to detect and quantify low ppm levels of volatile sulfur compounds in residual fuels, ensuring the integrity and safety of the final product.





Figures 2 and 3: Sulfur standard by 3.0 mL gas sample injection and hydrogen sulfide analysis using the headspace sampler by SCD.

Chromatography Tips and Tricks

With any type of analytical instrumentation, a periodic maintenance and inspection schedule can lead to increased up-time, reliable results, and longer instrument lifetime. The following table assists in determining when to inspect, replace and clean key components of the gas chromatograph.

Injection	Item	Symptoms	Recommended
If doing a syringe injection	Septa	Retention times increase; peak areas change; ghost peaks; tailing peaks; noisy baseline.	Replace every 50 to 100 injections.
If doing a syringe injection	Syringes	Poor repeatability; low peak areas; excessive bubbles in syringe barrel; stiff plunger motion.	Inspect when adding sample; clean or replace every 200 injections.
If doing a syringe injection	Inlet liners	Tailing peaks; loss of polar peak areas; ghost peaks; mass discrimination; poor repeatability.	Replace with every other septa change or when dry.
All injection methods	Ferrules	Poor retention time repeatability; tailing peaks; excessive gas consumption; noisy baseline.	Replace when making new connection or check old connections for leaks.
All injection methods	Columns	Broad peaks; tailing peaks; high bleed (significant baseline rise); shorter retention times.	Replace when performance does not improve with other column fixes such as baking overnight.

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

Question of the Month

Your sample primarily contains low boiling compounds. You notice that your early eluting peaks are broad and distorted. Would you increase or decrease the film thickness of the column to alleviate the problem?

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.

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

October 14-15: Basic GC Course at Wasson-ECE in Fort Collins, CO

October 28: Free TO-Clean Webinar

November 11: Free Automator Webinar

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
Engineered Solutions, Guaranteed Results

101 Rome Court
Fort Collins CO, 80524
www.wasson-ece.com