Monthly Newsletter From Wasson-ECE Instrumentation:

Chromatography Corner

ISSUE 07 JULY 2009

this issue

upcoming events

- **July 29 or 30:** Basic GC One Day Course
  Where: Hilton-NASA, Houston, TX
  Cost: $500
- August 26: Free PNA 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 Impurities in Butadiene and Isoprene

Butadiene and isoprene are byproducts of the ethylene cracking process. These byproducts are usually isolated by extraction with a polar solvent, from which it is then stripped by distillation.

Most butadiene and isoprene are polymerized to produce synthetic rubber commonly used for automobile tires. During the production process government regulations require the addition of dibutylated hydroxytoluene (BHT) and 4-tert-butylcatechol (TBC). Both BHT and TBC are added as stabilizers and inhibitors to prevent the product from spontaneously polymerizing and reacting with oxygen.

An Agilent Technologies 7890A Series Gas Chromatograph with dual flame ionization detectors (FID/FID) was customized for the analysis of BHT in isoprene and TBC in butadiene.

Two methods were developed for this analysis. Method 1 was designed for the analysis of BHT in isoprene by FID1. The range of detection was 5 parts per million (ppm) to 150 ppm. Method 2 was for the analysis of TBC in butadiene by FID2. The range of detection was 5 ppm to 300 ppm. Samples were introduced to the GC as a liquid by syringe injection or by pressurized vessel.

This quantitative analysis was particularly difficult because BHT and TBC are highly reactive with atmospheric oxygen. Reactions with O_2 were avoided by rinsing sample lines with solvent after each run and thoroughly flushing lines with carrier gas before sampling. Extra precautions during the analysis were taken to ensure an accurate, qualitative analysis, so that the end user was confident they were within government guidelines.

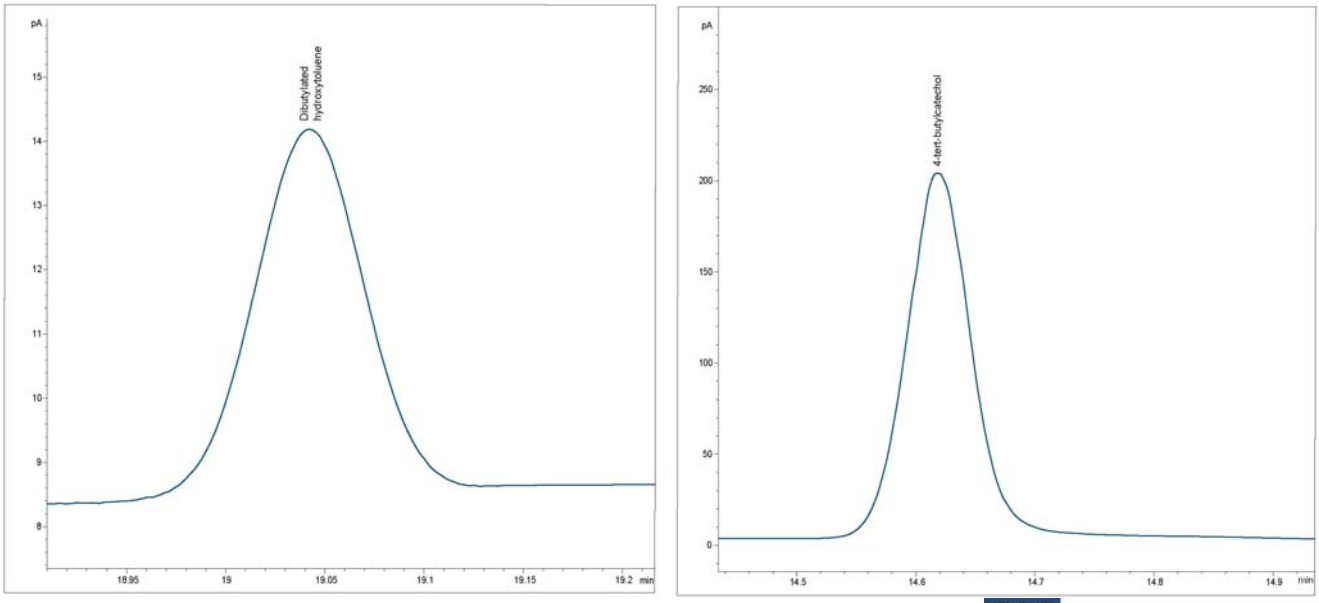

Figure 1 and 2: Chromatograms of BHT (13 ppm blend) in isoprene and TBC (156 ppm blend) in toluene made with a 1.0 µL liquid sample injection.

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Trace Polychlorinated Biphenyls in Transformer Wash Fluid Using GC/FID

Polychlorinated biphenyls (PCBs) have historically been used as insulating fluids in transformers because they have very high thermal conductivity, high flash points (from 170°C to 380°C) and are fairly inert. However, PCBs are extremely toxic. PCBs are removed from transformer fluid by adding a solvent made up primarily of decane (C_{10}) and undecane (C_{11}).

For the analysis of trace PCB oils in transformer wash fluid, Wasson-ECE Instrumentation customized an Agilent Technologies gas chromatograph (GC) with a flame ionization detector (FID) for liquid samples. The wash fluid consists of primarily C_{10} and C_{11}. The residual PCB oil to be quantified was between C_{12} and C_{34}, with a final boiling point of less than 485°C.

The inlet and sampling valve were modified to deliver a liquid slug and vaporize quickly as not to leave the heavier components behind. The detection range for the residual PCB oil was 5,000 parts-per-million volume (ppmv) to a minimum of 30 ppmv.

Components analyzed on the FID included all of the heavy isomers in the C_{12} to C_{34} carbon number range. This mixture was known to the customer as being an accurate surrogate for the actual PCBs that are the contamination in the wash fluid. As this system was required to be used on-line, a short run-time was needed. This time requirement pushes the heavy components to elute with little, or no, resolution. Therefore, heavy components were detected in much the same way as a simulated distillation sample, in that individual hydrocarbon species are rarely resolved.

Due to the toxic nature of PCBs, these components had to be measured to trace levels. Wasson-ECE was able to achieve this difficult analysis using a modified injection technique and simulated distillation-like separation to deliver a quick analysis with a reliable quantification of PCBs in transformer wash fluid.

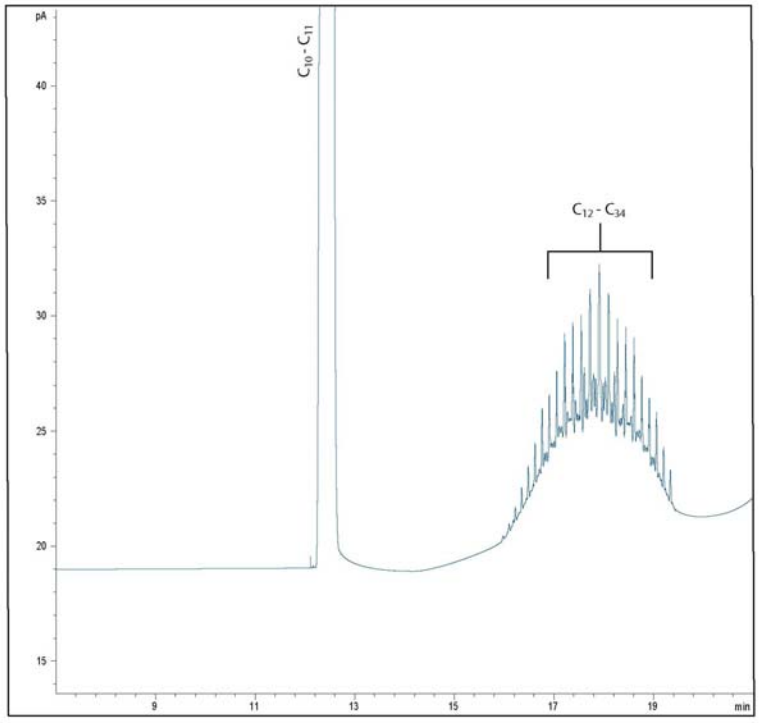


Figure 3: Chromatogram showing liquid sample injection of C_{10}-C_{11} matrix peak with C_{12}-C_{34} PCB impurities at 1500 ppm total.

Chromatography Tips and Tricks

Like all laboratory instrumentation, gas chromatographs occasionally run into problems. The key to fixing those problems is having a knowledge of the GC subsystems and a systematic approach for troubleshooting problems.

First, asses the situation; did the problem come on suddenly or slowly. Has anything on the GC been changed lately (new column, liner, routine maintenance, etc.)? Next, begin to isolate the problem. There are five main areas where problems arise, but it can also be a combination of any of these areas:

- Injector
- Flow (carrier gas)
- Column
- Detector
- Electronics

This article will focus on four common GC problems including tailing peaks, missing or no peaks, ghost peaks, and change in peak response. The following problems show a systematic approach to diagnosing the problem, but in no way list all possible causes or fixes.

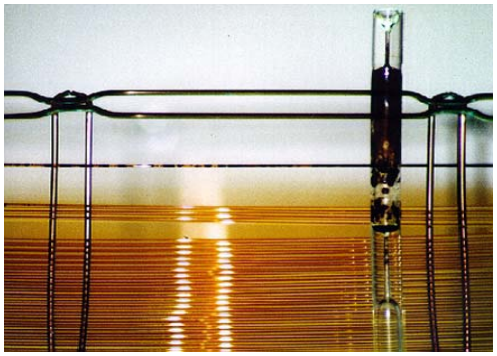
Peak tailing is often a sign of an active injector or column, but can also signal a flow problem such as dead volume, a plug, poor column installation or column contamination. A peak tailing problem can be narrowed down to a cause by injecting a light hydrocarbon sample. The sample should not tail unless there is a problem with the flow path.

Missing or no peaks can be a sign of a detector that is not operational or an injector that is not working properly. A problem with the column can be eliminated unless the baseline is completely flat. If this is the case the column may be broken or there maybe a substantial leak in the system.

Ghost peaks are usually caused by a contamination in the injector, column, carrier gas, or septum bleed, or can signal carry-over from a previous sample. Clean the liner, replace the septum and check gas traps. Then test for further contamination by shooting a blank and evaluate the chromatogram. If the problem persists try baking out or solvent rinsing the column.

There are two types of peak resolution problems; either all peaks decrease or only certain peaks decrease. If all peaks have decreased it can be a sign of a leaky injector, incorrect split ratio, an injector temperature that is too low or a detector response problem. If only some peaks have decreased the injector or column may be active or contaminated. First make sure your column is appropriate for your sample; refer to the Tips and Tricks section of *Chromatography Corner* Issue 03. If the column is appropriate and the problem still persists, clean the liner and bake out the column.

By isolating the problem, changing only one variable at a time, and comparing before and after chromatograms, GC problems can be diagnosed quickly with little down time. If the suggestions in this article do not help your specific GC problem, contact our service department at (970) 221-9179 or service@wasson-ece.com.



Question of the Month

Your sample contains impurities of naphthalene (boiling point = 218°C), phenol (boiling point = 181.7°C), and toluene (boiling point = 110.6°C). Which compound will elute first on a nonpolar column?

a) naphthalene
b) phenol
c) toluene

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

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

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

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