The analysis of pTBC, Acetonitril and Butadiene Dimer by Gas Chromatography with the DVLS Liquefied Gas Injector

Introduction

1,3-Butadiene is an important industrial chemical used as a monomer in the production of synthetic rubbers and plastics such as Styrene, Butadiene Rubber and Latex. It is contained in C4 mixtures, a byproduct of the naphtha cracking. Butadiene is typically isolated from the other C4 hydrocarbons by extractive distillation using a polar solvent such as Acetonitrile (ACN), which is removed afterwards by distillation. This application note describes the gas chromatographic analysis of inhibitors and extraction agents in Butadiene using the DVLS Liquefied Gas Injector.

Application Note

Authors:

Anita Ruissen PhD, Application Specialist, and Cees Oudijn, Product Manager, of Da Vinci Laboratory Solutions

Use of Butadiene

Storage of Butadiene as a compressed, liquefied gas represents a specific and unusual hazard. Over time polymerization may start, possibly leading to a cylinder rupture. Inhibitors such as para-tert-Butylcatechol (pTBC) are typically added to reduce this hazard.

Analysis of inhibitors and extraction agents in Butadiene is required for both producers and users of Butadiene. Butadiene dimer 4-Vinylcyclohexene-1 (VCH) and other hydrocarbons are often present as impurities in commercial Butadiene.
ASTM D1157 is the current standard test method for determining Total Inhibitor Content (TBC) of Light Hydrocarbons. This method is considered labor intensive and requires evaporation of the sample matrix.

Da Vinci Laboratory Solutions developed the Liquefied Gas Injector (LGI), a closed system for direct injection of liquid gas samples into a GC inlet system. The LGI system eliminates the evaporation of the sample matrix prior to the analysis.
It was introduced in 2010 originally for the analysis of oily residue in Liquefied Petroleum Gases (LPG). LGI includes the proven fuel direct injection technique used by the automotive industry to inject fuel into the automotive engine combustion chamber. The LGI consists of an Injector (on top of the GC), a Pressure Station and a Controller box. The LGI pressure station keeps the sample under constant pressure. This allows to inject a representative and repeatable amount of the liquid sample.

Figure One: the DVLS Liquefied Gas Injector

Application Description

The LGI injector is applied for the analysis of inhibitor pTBC, ACN and VCH. To mimic the Butadiene matrix the compounds are dissolved in a mixture of C3 & C4 (automotive LPG: mixture of Propane & Butane) and in C5 (n-Pentane). The GC is configured with the LGI, an on-column injection port, a solvent vapor exit and Flame Ionization (FID) detection.

The light ends of the matrix are vented via a solvent vent valve. The compounds with higher boiling points are retained on a precolumn. After closing the vapor exit valve the retained compounds are separated on the analytical column.

Boosting Laboratory Efficiency

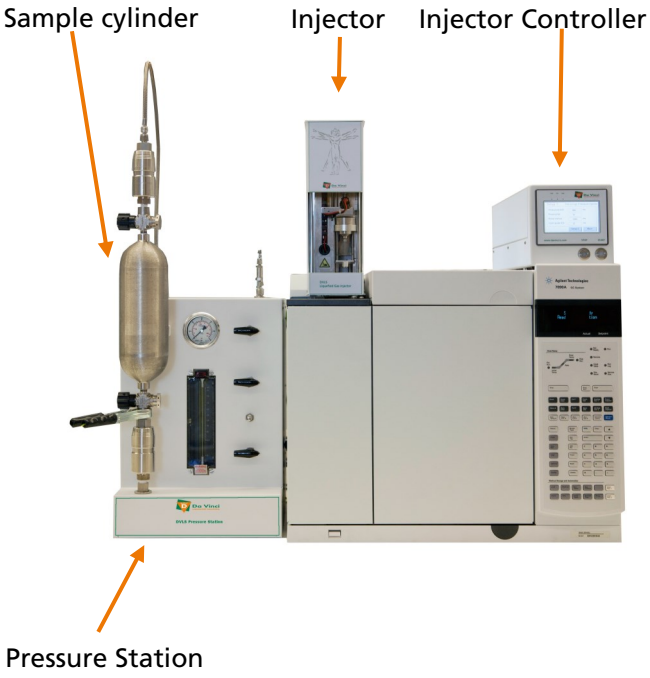

Figure Two: DVLS Liquefied Gas Injector installed on the GC

Analytical Results

In first instance all compounds are tested on the non polar column commonly used for residue analysis. The results show that pTBC can be very well separated from the C3/C4 matrix of LPG.
The LOQ is 0.078 mg/kg, which is far lower than the range for which the ASTM D1157 is applicable (50-500 mg/kg).

Measuring ACN in the C3/C4 matrix on the same non polar column does not result in the separation of ACN from the matrix. Therefore this compound is analyzed on a WAX type column.
The test results demonstrate that this polar column is able to separate ACN and VCH very well, even from a C5 matrix.
LOQs are 0.045 and 0.011 mg/kg respectively. This is far less than what is usually required by the industry: 1-5mg/kg. For all compounds the relative standard deviation is < 1% for 3 analyses, showing a good repeatability for all compounds.

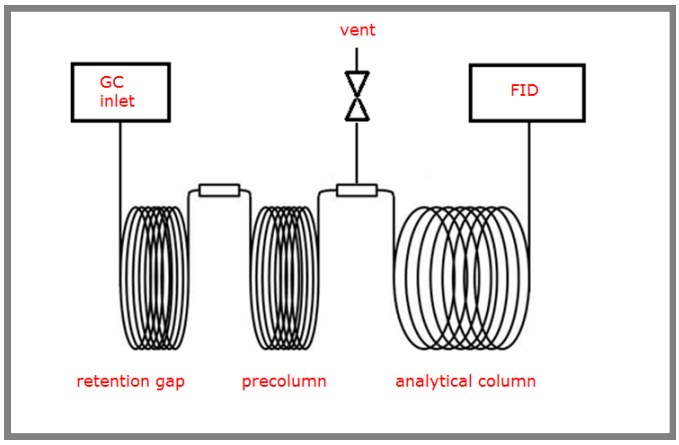

Figure Three: The column configuration of the Liquefied Gas Injector

Instrument Configuration and Settings	
LGI	
Inject pulse	50 ms
Vent open	8 s
Nitrogen sample pressure	25 bar
GC	
Inlet	COC
Inlet temperature	pTBC: 55°C (3 min) → 325°C, 25°C/min ACN & VCH: 55°C (3 min) → 240°C, 25°C/min
Oven	pTBC: 35°C (3 min) → 325°C, 25°C/min ACN & VCH: 35°C (3 min) → 240°C, 25°C/min
Columns	• Sulfinert retention gap • Non polar pre-column • Non polar analytical column • pTBC: non polar analytical column • ACN & VCH: Wax column
Carrier	Nitrogen
Detector	FID

Table One: Instrument Configuration and Settings

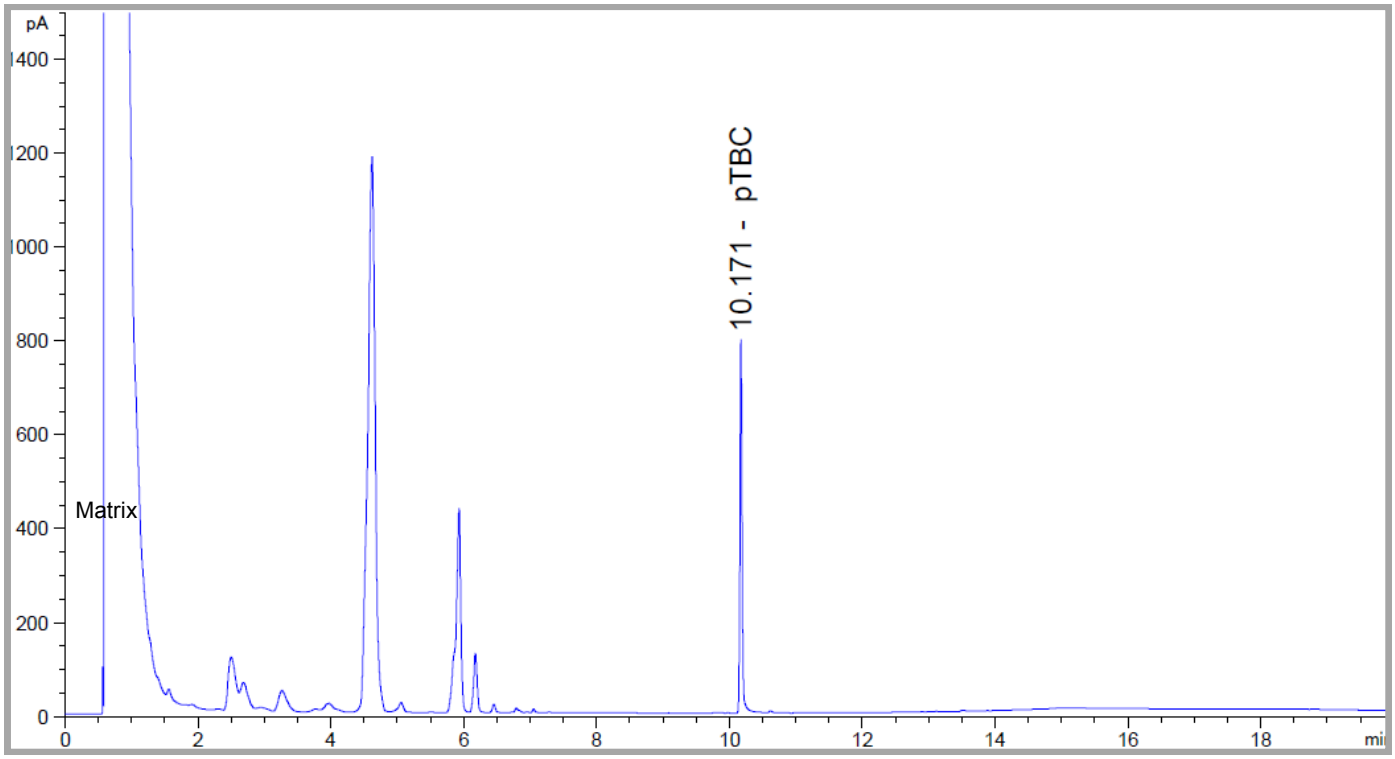

Figure Four: Chromatogram of the LGI analysis of 35.6 mg/kg pTBC in C3/C4 matrix (automotive LPG) on a non polar analytical column

	Analysis #1	Analysis #2	Analysis #3	Average	St Dev	%RSD	LOQ*	LOD*
	Area	Area	Area	Area	Area		mg/kg	mg/kg
TBC	1820.7	1825.5	1840.9	1829	10.6	0.6	0.078	0.023

Table Two: Results of the LGI analysis of 35.6 mg/kg pTBC in C3/C4 matrix (automotive LPG) on a non polar analytical column

** Calculated based on analysis #1*

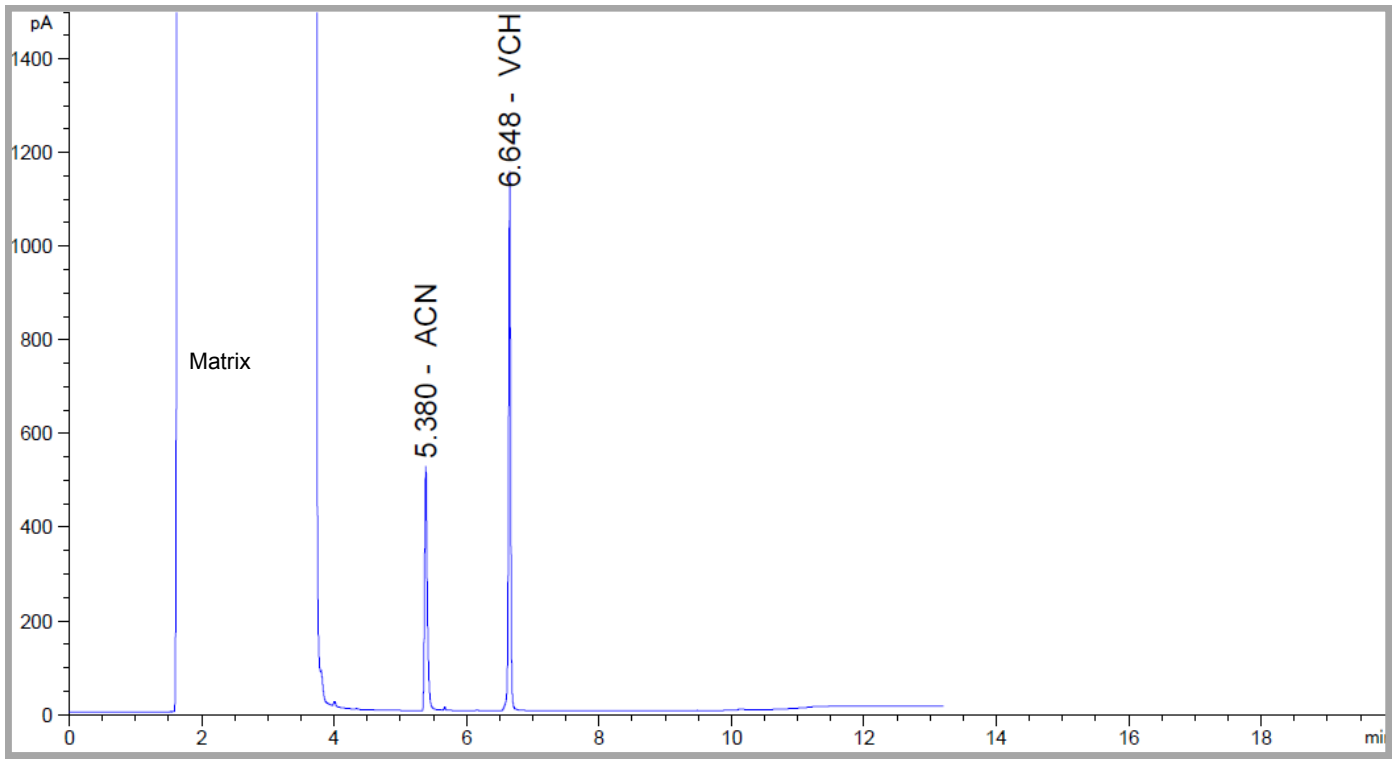

Figure Five: Chromatogram of LGI analyis of 49.8 mg/kg ACN and 26.3 mg/kg VCH in n-Pentane using a WAX type column

	Analysis #1	Analysis #2	Analysis #3	Average	St Dev	%RSD	LOQ*	LOD*
	Area	Area	Area	Area	Area		mg/kg	mg/kg
ACN	1462.9	1466.8	1475.2	1468.3	6.3	0.4	0.045	0.013
VCH	2482.3	2466.8	2478.1	2475.7	8	0.3	0.011	0.003

Table Three: Results of the LGI analyis of 49.8 mg/kg ACN and 26.3 mg/kg VCH in n-Pentane using a WAX type column

** Calculated based on analysis #1*

Conclusion

Using the LGI-GC technique it is possible to measure low levels of the Butadiene inhibitor pTBC, the rather polar extraction agent ACN and the Butadiene dimer VCH with a good repeatability. The LGI-GC technique is a safe and accurate alternative to the existing Butadiene test method ASTM D1157. Controlled handling of Butadiene cylinders, in combination with on-column GC injection, reduces health and safety risks for analysts involved in Butadiene quality control.

References:

1. ASTM D7756-13 :Standard Test Method for Residues in Liquefied Petroleum (LP) Gases by Gas Chromatography with Liquid, On-Column Injection
2. Application note: The Analysis of Inhibitor, Extraction Agent and Dimer in Butadiene by On-column Chromatography with the DVLS LGI Injector

DA VINCI LABORATORY SOLUTIONS B.V.
P.O. Box 12103, 3004 GC Rotterdam - The Netherlands
T: +31 (0)10 258 1870 - F: +31 (0)10 258 1879 - E-mail: solutions@davinci-ls.com

www.davinci-ls.com