The Analysis of 4-Vinyl-Cyclo-Hexene (VCH) in Butadiene with the DVLS LGI Injector

Introduction

In synthetic rubber manufacturing, 4-Vinylcyclohexene (VCH) can be found as a byproduct from the chemical processing of 1,3-Butadiene. VCH is a dimer of 1,3-Butadiene and is normally present in Butadiene. It is generally controlled below the 500-1000 ppmw level per product specifications. VCH is a very toxic and colorless liquid having a strong odor in normal conditions.

Application Note

Authors:

Lenny Kouwenhoven, Director R&D of Da Vinci Laboratory Solutions
Anita Ruissen, Application Specialist of Da Vinci Laboratory Solutions

VCH specification and test method

Control over VCH is important for Butadiene consumers. As indicated the product specification for VCH is between 500 and 1000 ppm.
At present there is no known inhibitor for the Butadiene dimer reaction. It is strictly a time/temperature phenomenon.
The lower the temperature, the slower the rate of dimer formation. Conversely, the higher the temperature, the faster the rate of dimer formation. To minimize dimer formation the transit and residence/storage times should be strongly shortened. Also storing Butadiene at low temperatures will minimize the amount of dimer formed. Dimer removal is currently done via distillation.

To accurately determine the VCH content in Butadiene Da Vinci Laboratory Solutions developed the Liquefied Gas Injector (LGI).

Application Description

The method uses the Liquefied Gas Injector. The sample is injected under pressure directly onto the column.
The Butadiene sample remains in liquid phase, at room temperature and without contact with transfer lines, vaporizers or valves. As a result all limitations of the conventional sample introduction techniques are resolved.

Figure One: the DVLS Liquefied Gas Injector

The chromatography is based on boiling point separation. The total amount is reported in parts per million.

The system setup is based on the ASTM D7756-11: Standard Test Method for Residues in Liquefied Petroleum (LP) Gases by Gas Chromatography with Liquid, On-Column Injection.

The GC is equipped with the Liquefied Gas Injector as displayed in Figure One, an on-column injector and a solvent vapor exit.

Figure Two shows the configuration of retention gap and columns.
Sample is injected into a 5 meter Sulfinert® coated stainless steel capillary. The retention gap is connected to a 3 meter non polar retaining column, with an exit for flushing the Butadiene light ends. Subsequently, the exit is closed and the flow is switched to the non-polar analytical column for the elution of VCH. In the same analysis another important parameter can be determined: Tertiary Butyl Catechol.

Table One shows the LGI settings, Table Two shows typical settings of the gas chromatograph and column details.

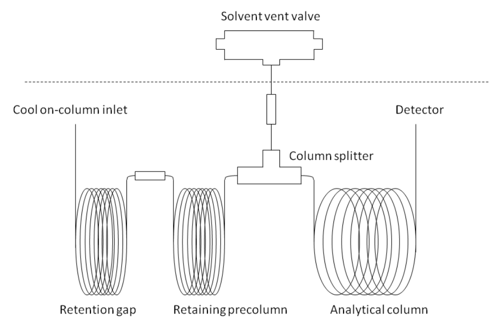

Figure Two: Column Configuration

Analytical Results

The VCH was dissolved in Toluene and four concentrations of VCH in Pentane were prepared; 24.7 ppm, 247 ppm, 494 ppm and 988 ppm. Figures Three, Four, Five show the chromatogram of 125 ppm VCH. Table Three lists the precision found.

Injection Time	50 ms
Pre Injection Delay	1 sec
Post Injection Delay	1 sec
Solvent Vent	10 sec
Stop Flow	0 sec

Table One: LGI Parameters

Equilibration Time	1 min
Oven Program	45 °C (2.0 min), 25 °C/min — 250 °C (0 min)
Run Time	12.2 min
Back COC Inlet He	55 °C (2.0 min), 25 °C/min — 250 °C (0 min)
Flow	4mL/min
Septum Purge Flow	12 mL/min

Table Two: GC Parameters

Concentration VCH	24.7 ppm	247 ppm	494 ppm	988 ppm
Average Counts	3543	34305	69821	143264
Standard Deviation	31	359	1039	1378
% RSD	0.9	1.0	1.5	1.0

Table Three: Precision of four concentrations VCH in Pentane

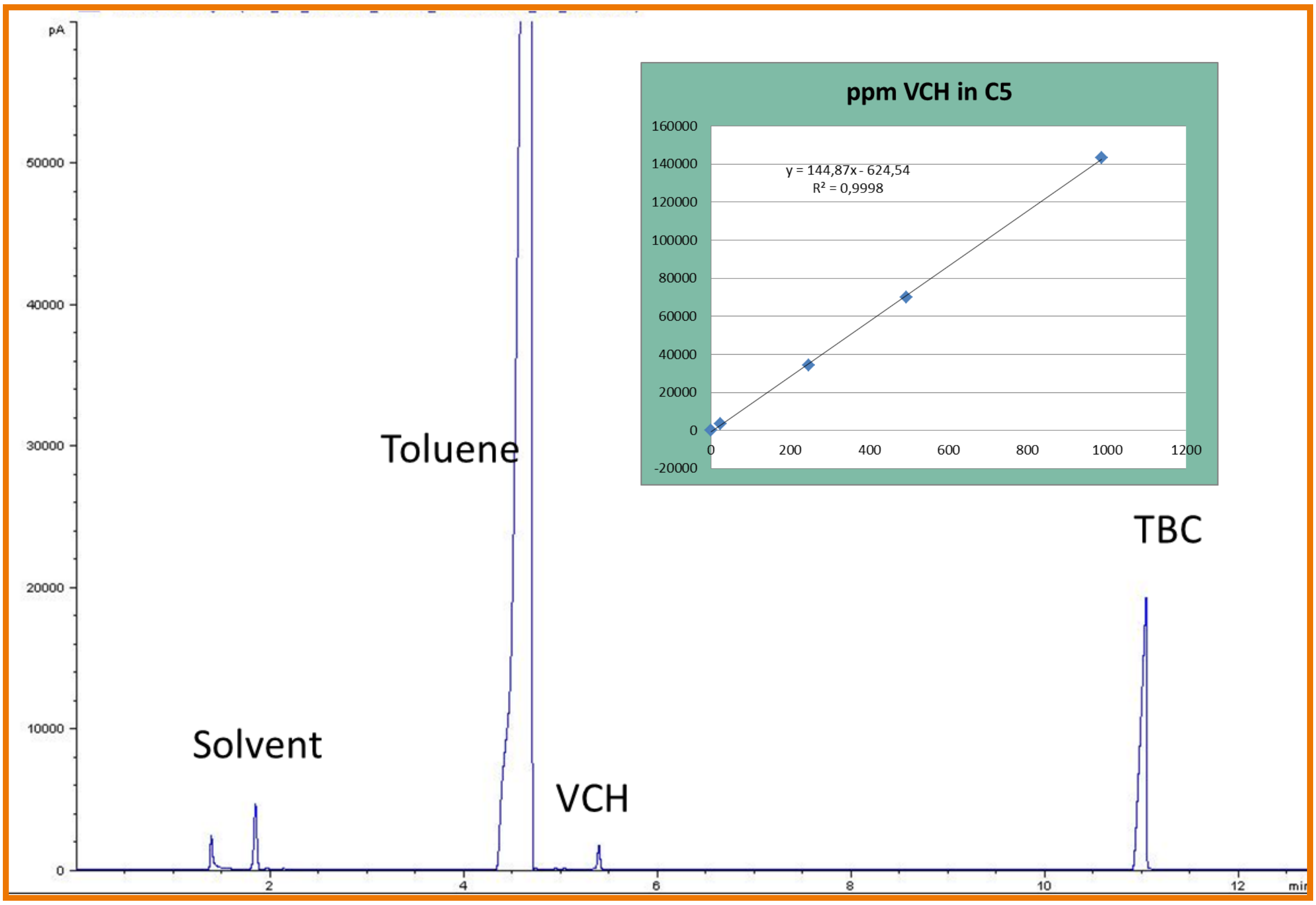

Figure Three: Chromatogram of 24.7 ppm VCH in Pentane

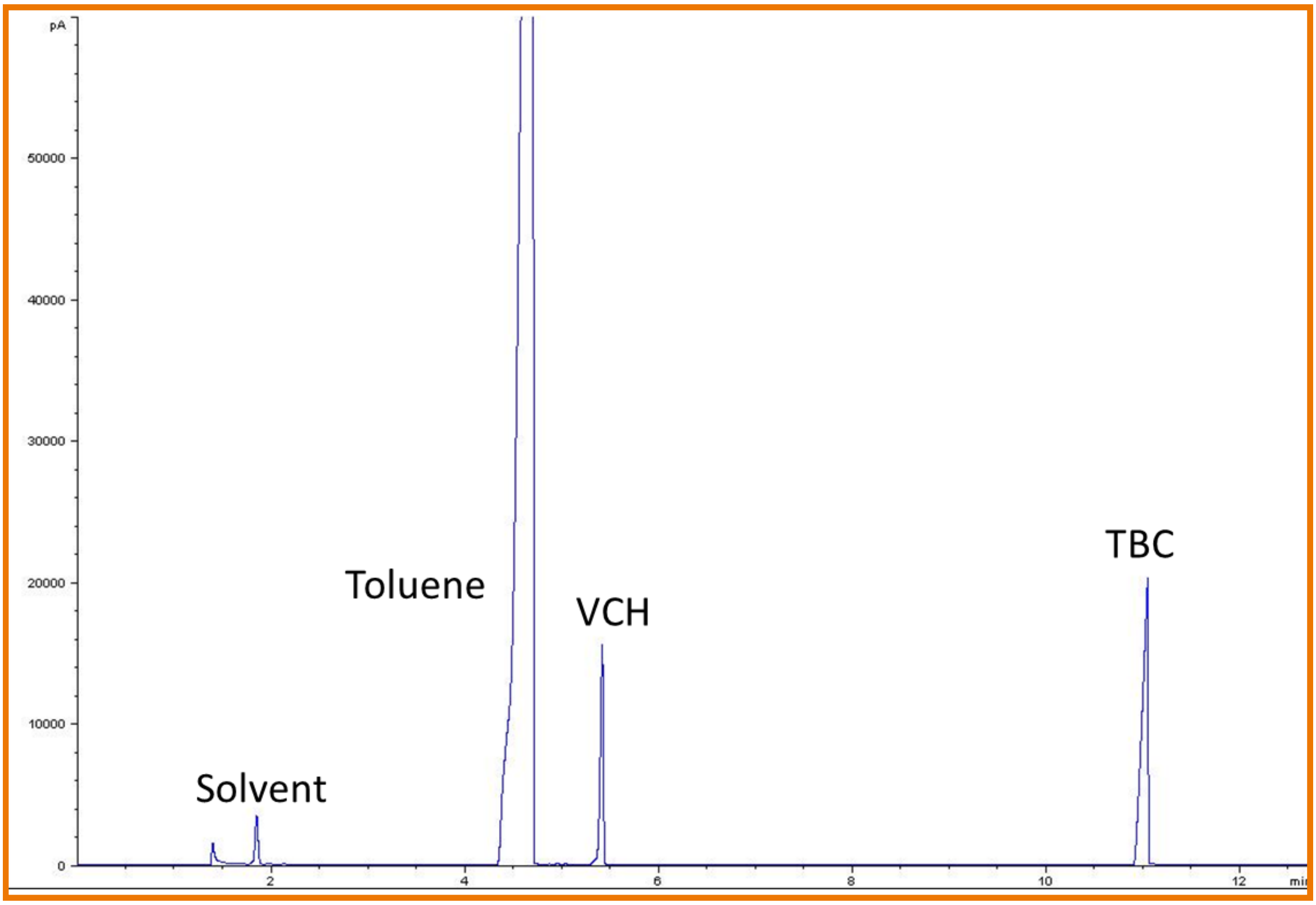

Figure Four: Chromatogram of 247 ppm VCH in Pentane

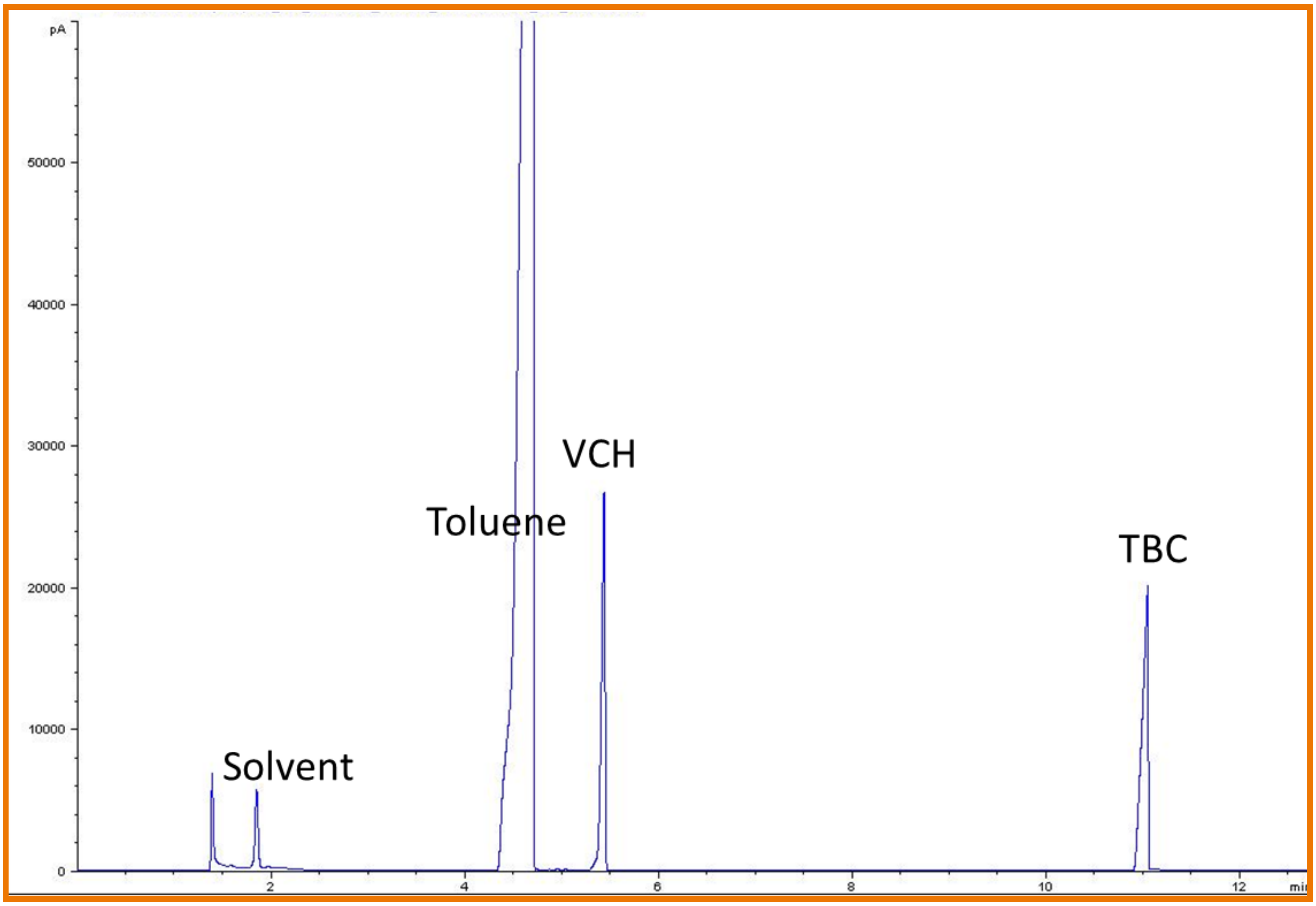

Figure Five: Chromatogram of 494 ppm VCH in Pentane

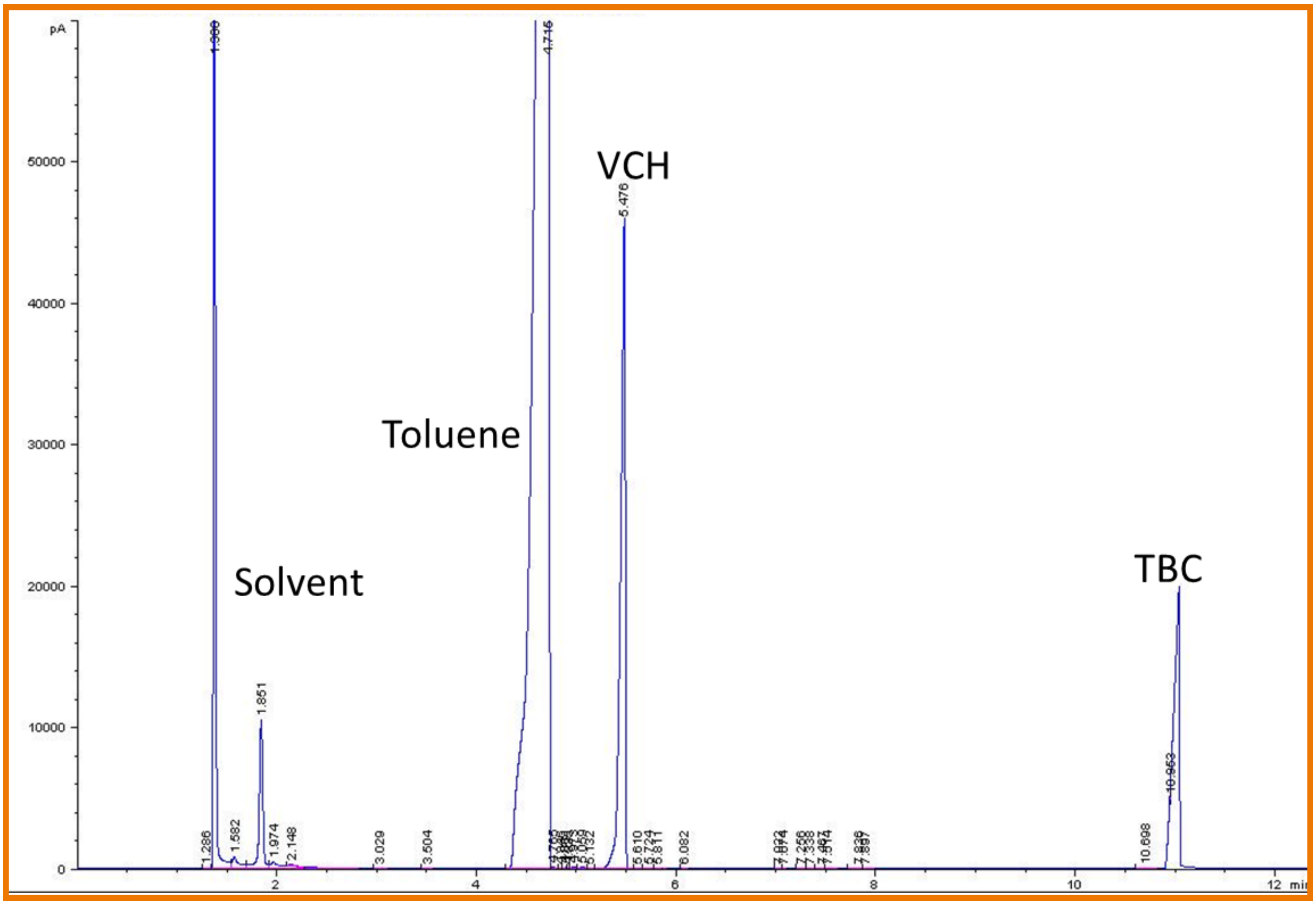

Figure Six: Chromatogram of 988 ppm VCH in Pentane

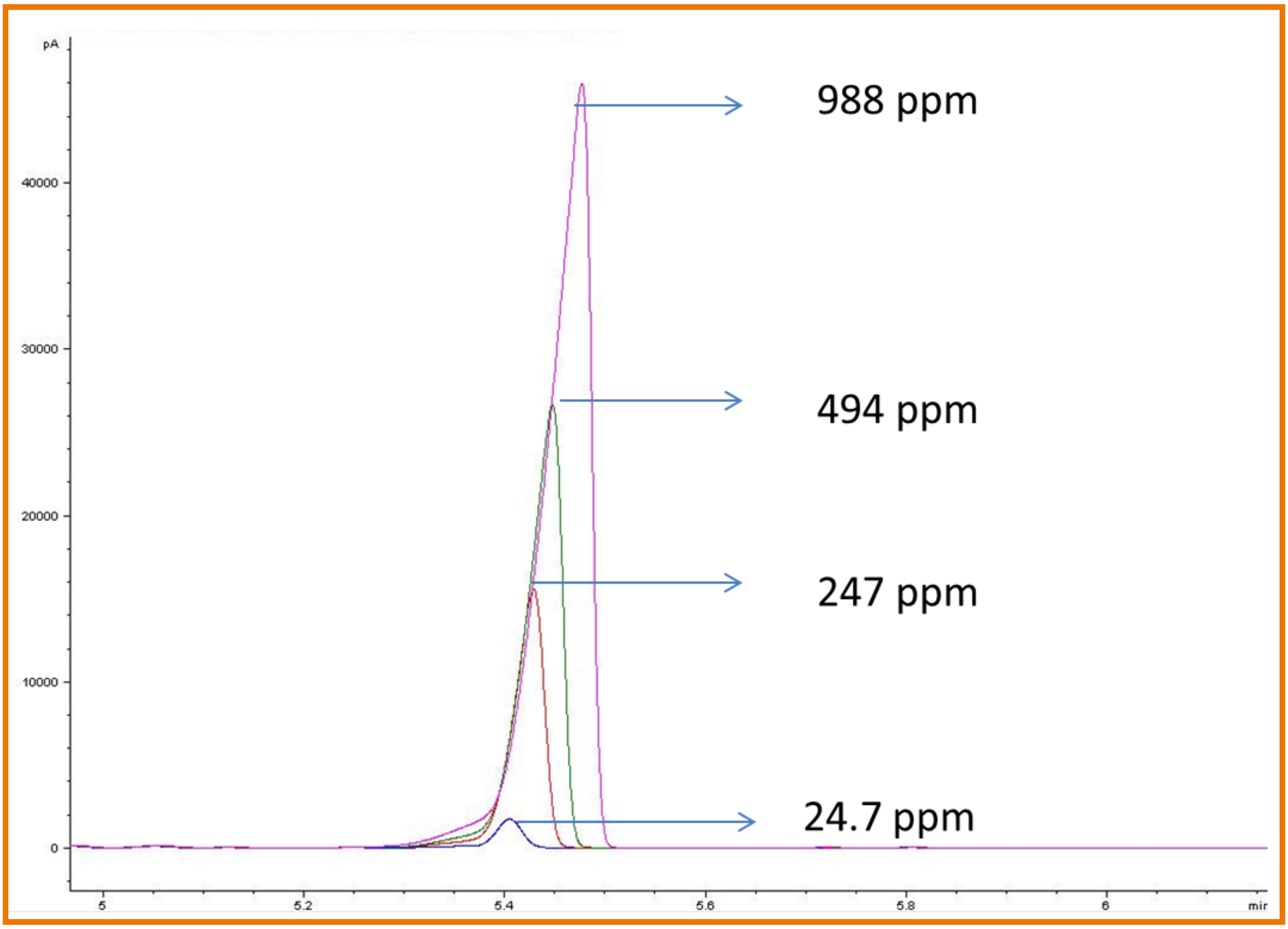

Figure Seven: Overlay of four concentrations of VCH in Pentane

Conclusion

A method developed by DVLS uses the new Liquefied Gas Injector (LGI) to inject Butadiene under pressure, in liquid phase directly on the analytical GC column. Analytical results have demonstrated that the LGI technique is a safe, fast and accurate method for the determination of VCH in Butadiene.
In the same analysis Tertiary Butyl Catechol can be determined. The repeatability is better than 2% relative and the lower detection limit is far below 1 ppm.

References:

1. ASTM D7756-11 :Standard Test Method for Residues in Liquefied Petroleum (LP) Gases by Gas Chromatography with Liquid, On-Column Injection
2. The analysis of Contaminants in Liquefied Gases by Gas Chromatography by Lenny Kouwenhoven and Anita Ruissen, Petro Industry News, October/November 2011
3. A Safe and Fast Solution for Accurate Quantification of Heavy Residues in LPG by Gas Chromatography, Representative Liquefied Gas Sample Introduction via High Pressure On-Column Injection into a Gas Chromatographic System, by Lenny Kouwenhoven and Anita Ruissen, Petro Industry News, August/September 2012

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