The Analysis of 4-Tertiair Butyl Catechol (TBC) in Butadiene with the DVLS LGI Injector

Introduction

4-tert-Butylcatechol (TBC) is an organic chemical compound which is a derivative of catechol and a tertiary alcohol, it is a colorless to white, crystalline or waxy solid. TBC is used as a polymerization inhibitor and stabilizer for polymerizable monomers such butadiene and is added during the manufacturing process or to products that require transportation and storage. It is commonly added to commercial Butadiene as an oxidation inhibitor in amounts of 50 to 250 mg/kg.

Application Note

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TBC specification and test method

The test method ASTM D1157 – 91, Standard Test Method for Total Inhibitor Content (TBC) of Light Hydrocarbons, determines TBC in Butadiene. However the test method has a poor precision: at a level of 50 ppmw the repeatability is 20%!
Main disadvantage of this method is that the first step is to evaporate the Butadiene. Since Butadiene is carcinogenic this analysis presents a health risk in a lab environment.

To safely and accurately determine TBC in Butadiene Da Vinci Laboratory Solutions (DVLS) developed a test method with the use of the Liquefied Gas Injector (LGI).

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

The chromatography after this representative sample introduction is based on boiling point separation of the Butadiene and the TBC and the total amount is reported in parts per million mass.

Figure One: the DVLS Liquefied Gas Injector

Application Description

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. The 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 TBC. In the same analysis Vinyl-Cyclo-Hexene can be determined.

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

Analytical Results

The TBC was dissolved in Toluene and six concentrations of TBC in Pentane were prepared, 36 ppm, 120 ppm, 241 ppm, 361 ppm, 482 ppm and 602 ppm.
See Figure Three for the linearity and Figure Four for the chromatogram.

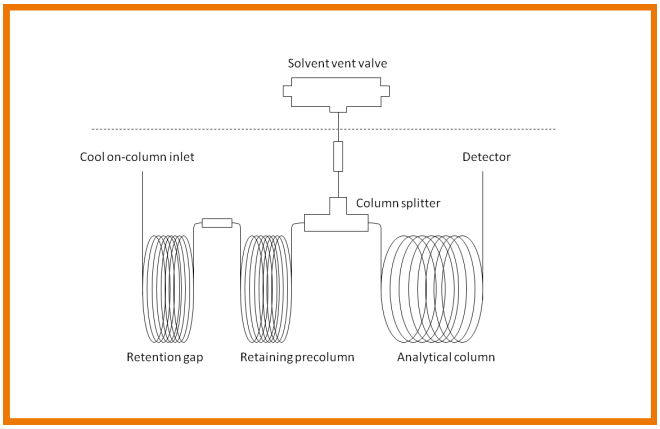

Figure Two: Column Configuration

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

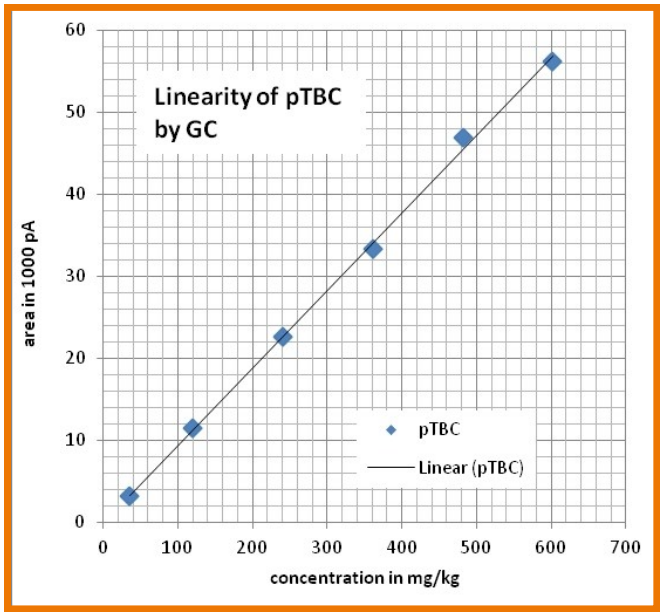

Figure Three: Lineariity of TBC analysis

Concentration pTBC	36 ppm	120 ppm	241 ppm	361 ppm	482 ppm	602 ppm
% RSD	2.4	3.3	3.0	1.6	3.3	4.0

Table Three: Precision of six concentrations of TBC in Pentane

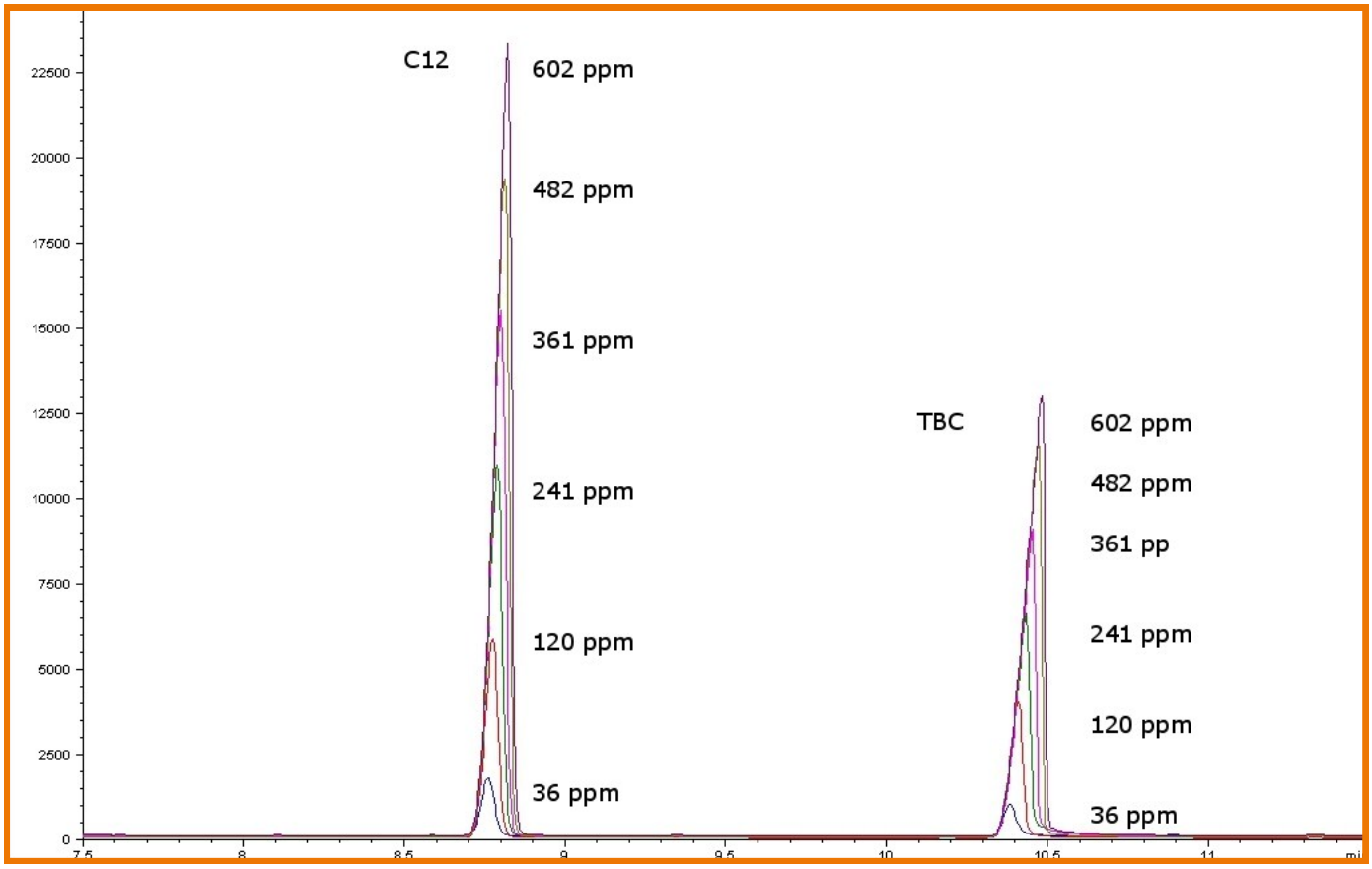

Figure Four: Overlay of six concentrations of TBC in Pentane

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 TBC in Butadiene compared to the ASTM D1157 method. In the same analysis Vinyl-Cyclo-Hexene can be determined. The repeatability is better than 3% 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