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LABORATORY SOLUTIONS

The Analysis of Inhibitor, Extraction Agent and Dimer in Butadiene by On-column Chromatography with the DVLS LGI Injector

Introduction

1,3-Butadiene is a major petrochemical product and an important feedstock in the production of rubbers and plastics, such as Styrene Butadiene rubber and latex. It is contained in C4 mixtures, which are a by-product from naphtha crackers. The C4 mixtures cannot be fractionated into each component using conventional distillation since many of the C4 components have relative volatilities to Butadiene. Butadiene can be separated by extractive distillation using solvents such as dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP).

Application Note

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Storage of Butadiene as a compressed, liquefied gas presents a specific and unusual hazard. Over time, polymerization can begin, creating a crust of solidified material inside the vapor space of cylinder. If the cylinder is then disturbed, the crust can contact the liquid and initiate an auto-catalytic polymerization. The heat released accelerates the reaction, possibly leading to cylinder rupture. Inhibitors such as p-TBC are typically added to reduce this hazard.

Analysis of inhibitors and extraction agents in Butadiene is required for both producers and users of butadiene. Accurate reporting of the Butadiene specification is important to establish product pricing and to assure product quality. Butadiene testing is frequently carried out at production plants, as well as at testing labs before cargo (un) loading for vessels.
Dimer, styrene and other hydrocarbons are often present as impurities in commercial butadiene, depending on temperature conditions and storage time.
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 liquid sample.

Da Vinci Laboratory Solutions developed the Liquefied Gas Injector (LGI); an on-column chromatographic solution to accurately determine the impurities in liquefied gases such as Butadiene.

Figure One: Agilent GC & DVLS Liquefied Gas Injector

Application Description

The test method uses the Liquefied Gas Injector; a dedicated sampler that transfers a sample aliquot to an analytical column. The sample is injected under a constant pressure.
The chromatography after this representative sample introduction is based on an individual separation of the Butadiene impurities. The amount of each component is reported in parts per million mass.

The hardware setup is based on the ASTM D7756 & EN 16423 standards for determination of dissolved residue in LPG. The GC is configured with the Liquefied Gas Injector as displayed in Figure One, an on-column injection port, a solvent vapor exit and Flame Ionization (FID) detection.

Figure Two shows the configuration of retention gap and columns. The sample is injected into a Sulfinert® coated stainless steel retention gap. The retention gap is connected to a non-polar retaining pre-column, with an exit for flushing the Butadiene matrix.

After matrix venting, the valve is closed and the flow is directed to an analytical column for the separation of the various impurities present in the Butadiene.

Table One shows the typical instrument parameters.

Oven initial	40°C (3 min)
Rate	15°C/min
Oven final	250°C (8 min)
Inlet initial	55°C/min
Rate	15°C/min
Inlet final	250°C
Column flow	4 mL/min
Runtime	21 min
Solvent vent time	10 sec
LGI Injection pulse	50 ms

Table One: Instrument Parameters

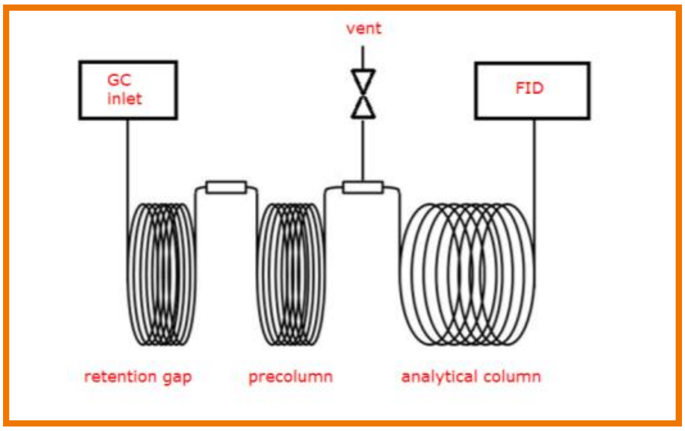
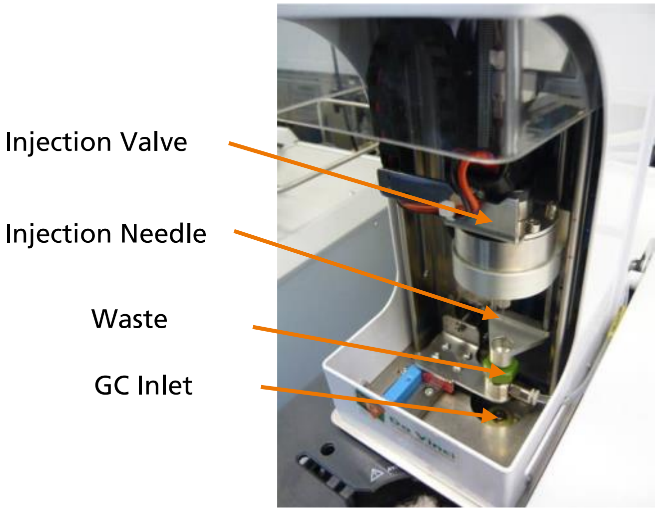
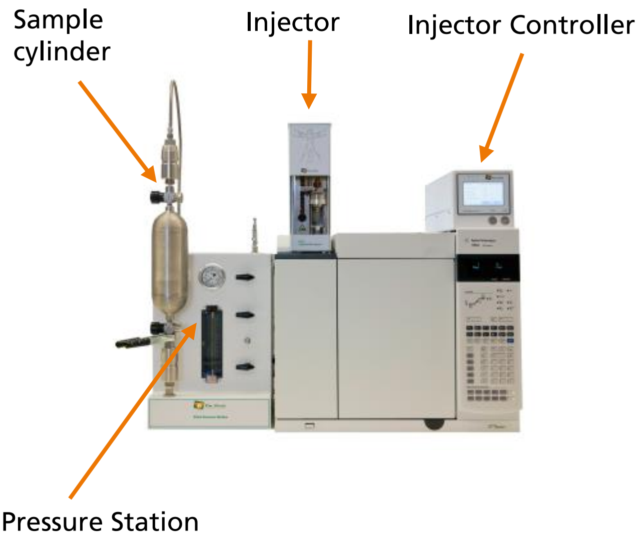


Figure Two: Column Configuration





Analytical Results

Butadiene samples were transported and analyzed using metal sample cylinders. A constant pressure of 15 bar was applied during the GC injection cyle. Figure Three, Four and Five show the LGI analyses of various impurities in Butadiene.

Table Two lists the precision data. Due to the limited availability of the samples the repeatability data were calculated based on single sample and duplicate analyses. The precision data demonstrates that the LGI repeatability is similar to ASTM D 1157.

The detector linearity for individual components has been published in the application notes on VCH, NMP and p-TBC in Butadiene analysis.

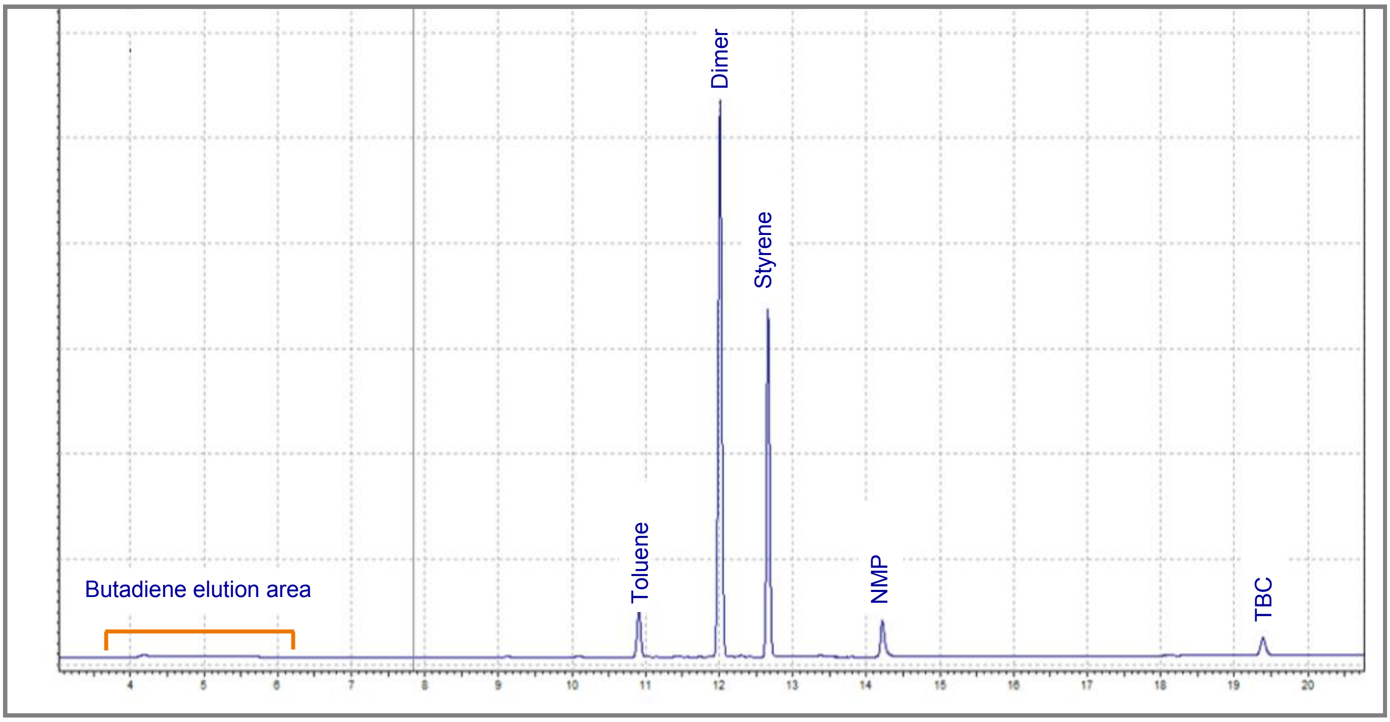


Figure Three: Chromatogram of the analysis of a liquid calibration standard

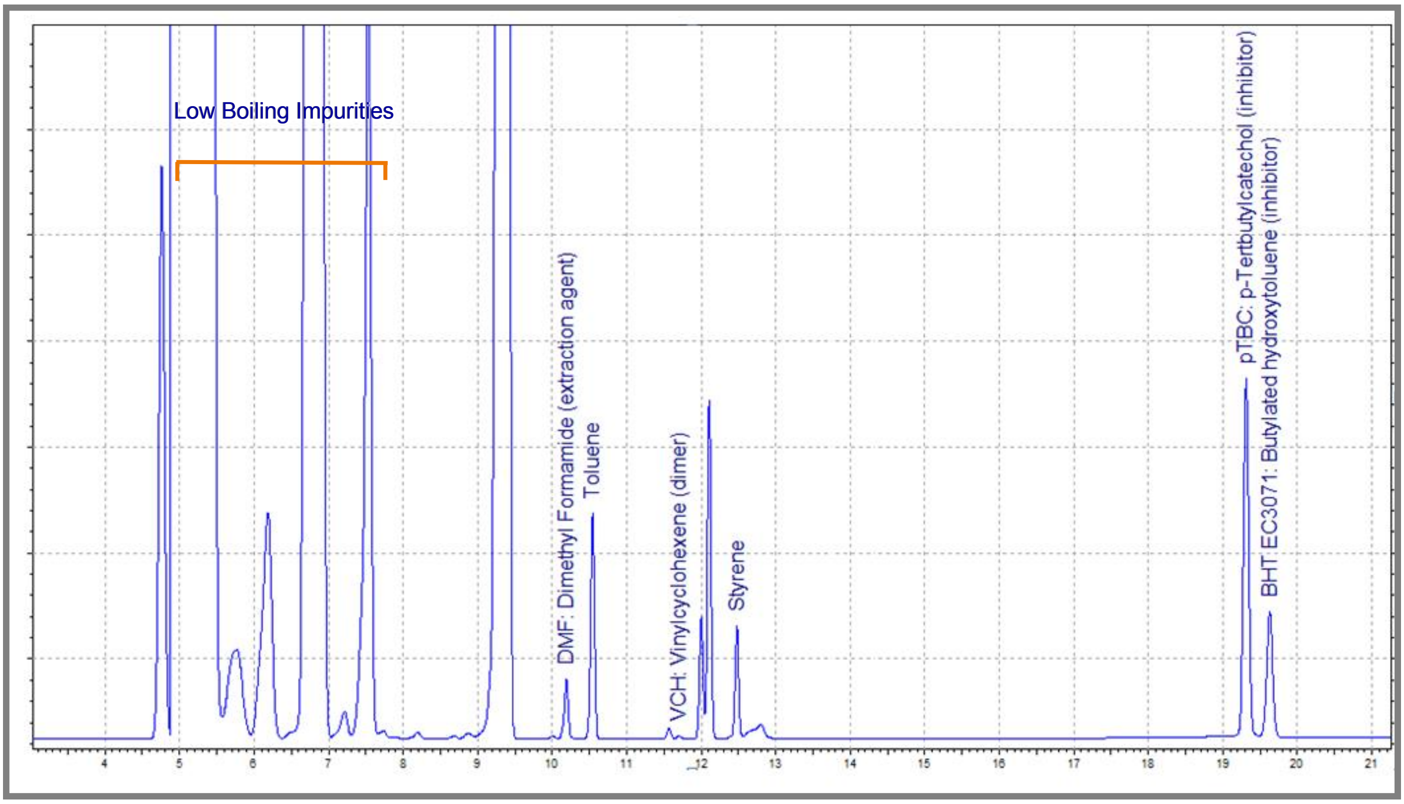


Figure Four: Chromatogram of Inhibitor and other impurities in Butadiene analysis

Repeatabilities at concentration levels	Multiple analyses Single sample	Duplicate analyses Various samples	ASTM r/R
Dimer	55 (416 mg/kg)	48 (200—3500 mg/kg)	50/180 (1500 mg/kg)
pTBC	11 (86 mg/kg)	17 (85-330 mg/kg)	10/20 (50-500 mg/kg)
Toluene	0.5 (3.6 mg/kg)	0.4 (1-4 mg/kg)	Not available

Table Two Repeatability of Butadiene analyses

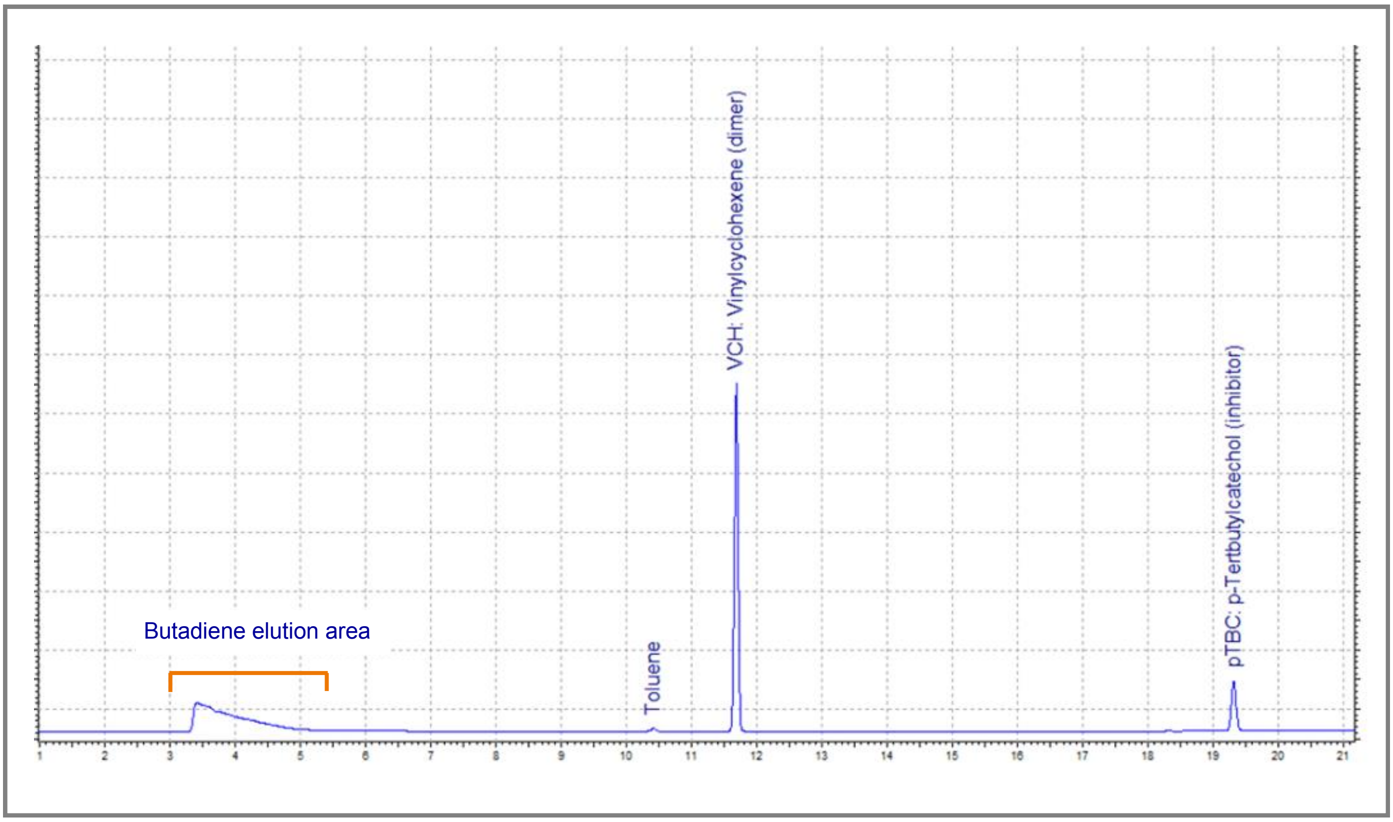


Figure Five: Chromatogram of the analysis of a Butadiene production sample

Conclusion

The analysis of Inhibitor content and other impurities by the Liquefied Gas Injector offers a safe and accurate alternative to existing Butadiene test methods. Although there is limited publication on repeatability data for heavier traces in Butadiene, the reported results for the production of Butadiene samples indicate similar repeatabilities to methods such as 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. The LGI technique also provides excellent detection limits due to the large volume injection.

References:

1. ASTM D7756-13 :Standard Test Method for Residues in Liquefied Petroleum (LP) Gases by Gas Chromatography with Liquid, On-Column Injection
2. ASTM D5274 Standard guide for analysis of 1,3-butadiene product
3. ASTM D2593 Standard test method for butadiene purity and hydrocarbon impurities by gas chromatography
4. ASTM D1157 Standard test method for Total Inhibitor Content (TBC) of Light Hydrocarbons
5. Dow Product Safety Assessment Butadiene
6. ASTM D2426 Standard test method for Butadiene Dimer and Styrene in Butadiene concentrates by Gas Chromatography
7. ASTM D1025 Standard test method for Nonvolatile Residue of Polymerization-Grade butadiene

Acknowledgements:

- Harm Moes, SGS Vlissingen, The Netherlands