The Analysis of n-Methyl-2-pyrrolidone (NMP) in Butadiene with the DVLS LGI Injector

Introduction

A well-established application for NMP is the large-scale recovery of hydrocarbons by extractive distillation. This technique utilizes the high solubility of hydrocarbons in NMP and the fact that differences in volatility are sometimes considerably increased in the presence of NMP. Compared to other commercial solvents and extraction media, NMP offers the following advantages: no azeotropes are formed with hydrocarbons; NMP is very resistant to heat and chemicals; and NMP has a favorable toxicological and environmental profile.

An important application is the recovery of 1,3-butadiene using NMP as an extractive distillation solvent. The specification of NMP in the final Butadiene product lies between 3 and 10 ppm.

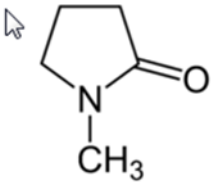
Application Note

Authors:

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

NMP specification and test method

Although the amount of NMP has a specification for both Butadiene product and Raffinate there is no standardized test method.
Commonly the ASTM method D2593 (Standard Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography) is used for the impurity analysis of Butadiene, but this method does not contain guidance or a precision statement for NMP.



Methylpyrrolidone

In-house test methods are based on the analysis of evaporation residues of Butadiene. As the evaporation of Butadiene is regarded as unsafe, the common practice is to calculate the theoretical amount of NMP in Butadiene, which is prone to error. Reducing the amount of NMP in the product or Raffinate results in a higher value for the Butadiene batches.

Figure One: the DVLS Liquefied Gas Injector

An accurate analysis based on Gas Chromatography is now available. The Liquefied Gas Injector developed by Da Vinci Laboratory Solutions injects the Butadiene under pressure, in liquid phase directly on the analytical column, and a GC analysis of NMP is benefiting from all advantages of GC analysis.

Next to NMP, it is also possible to analyze VCH and p-TBC in the same analytical run, with a better precision as stated in ASTM D2593.

Boosting Laboratory Efficiency

Application Description

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

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

Analytical Results

The NMP was dissolved in Toluene and four concentrations of NMP in Pentane were prepared, 4 ppm, 8 ppm, 10 ppm, 15 ppm and 20 ppm.
See Figure Three and Four for the chromatograms of 4 and 20 ppm NMP.

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

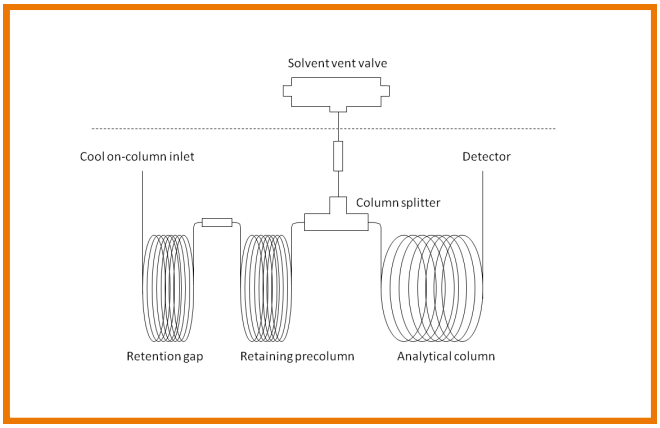


Figure Two: Column Configuration

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

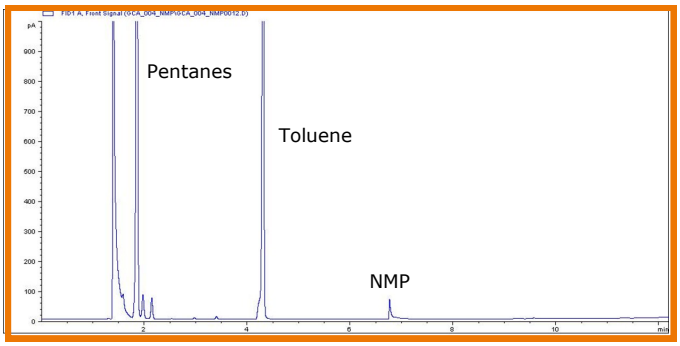


Figure Three: Chromatogram of 4 ppm NMP in Pentane

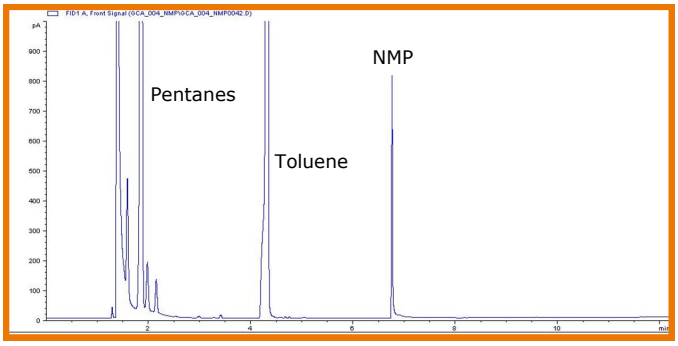


Figure Four: Chromatogram of 20 ppm NMP in Pentane

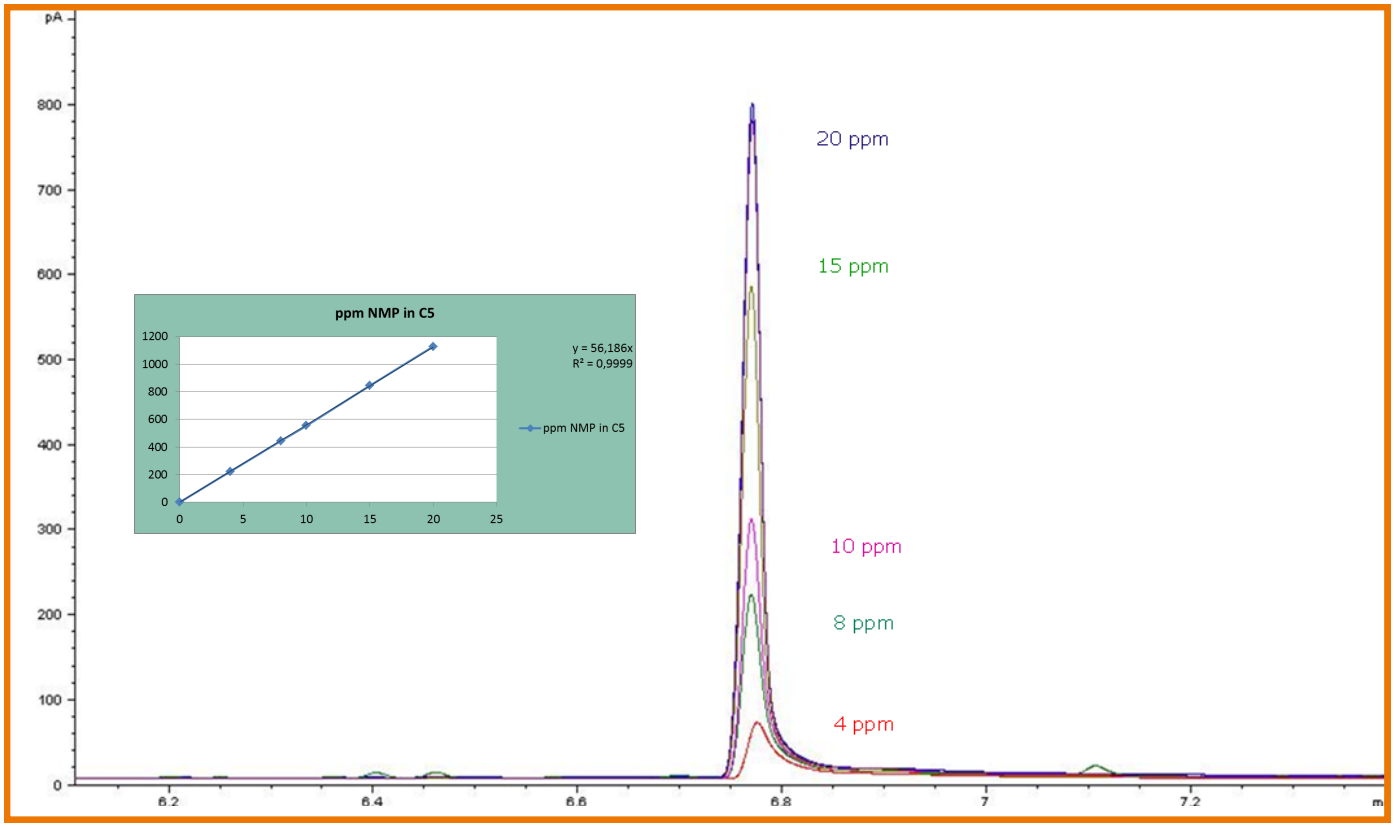


Figure Three: Overlay of five concentrations of NMP in Pentane

Concentration NMP	4 ppm	8 ppm	10 ppm	15 ppm	20 ppm
Average Counts	223.4	445.6	554.7	844.3	1128.0
Standard Deviation	4.5	2.6	5.5	7.9	11.1
% RSD	2.0	0.6	1.0	0.9	1.0

Table Three: Precision of five concentrations of NMP 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 NMP in Butadiene. 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