The Analysis of Di-Iso-Propanol-Amine (DIPA) in Liquified Petroleum Gas (LPG) with the DVLS LGI Injector

Introduction

Historically, the main potential residue contaminant in LPG was lubricating oil, picked up from compressors during manufacturing. The boiling range of this lubricant contamination is high enough to be detected by the gravimetric testing techniques.

However, with the introduction of amine based treating processes, treating products, such as DIPA, are also potential residue contaminants. These are more volatile than lubricants and consequently, very significant amounts are lost during the evaporation and drying processes in the gravimetric test methods. This can and has led to products being released to the market containing small but significant amounts of residue. The reported values pass the residue specification requirement but their true concentration is in fact much greater than the analytical test indicates. As a result LPG customers encountered significant problems.

Application Note

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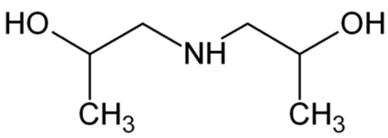
DIPA Effect on Car Engines

DIPA in LPG has the same effect on car engines as oily residue. It deposits on membranes and filters and results in unexpected high maintenance or stalled vehicles. There is a need to quantify DIPA and also to provide an alternative to the gravimetric methods for residues testing, to improve both efficiency (they are labour intensive) and HSE due to the relatively large sample volumes used for some of the gravimetric methods.



$HN(CH_2CHOHCH_3)_2$

In order to solve residue effect Da Vinci Laboratory Solutions developed a test method for the determination of DIPA in LPG with the use of the Liquefied Gas Injector.
The LPG sample is injected under pressure directly onto the column. The 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.

Boosting Laboratory Efficiency

Figure One: the DVLS Liquefied Gas Injector

Application Description

The test method uses the Liquefied Gas Injector. The sample is injected under pressure directly onto the column.
The chromatography after this representative sample introduction is based on boiling point separation of the LPG and the DIPA and 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 LPG light ends.
Subsequently, the exit is closed and the flow is switched to the non-polar analytical column for the elution of DIPA.

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

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

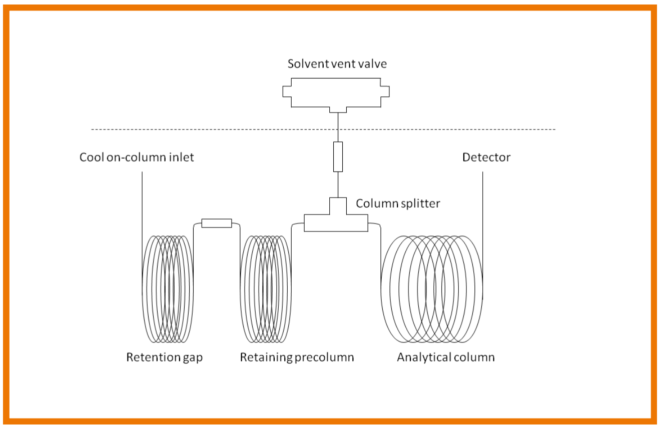


Figure Two: Column Configuration

Analytical Results

The DIPA was dissolved in MTBE and four concentrations of DIPA in Pentane were prepared, 5 ppm, 50 ppm, 125 ppm and 250 ppm. The samples for this test are prepared in Pentane. Since the solvent is vented it does not affect the detection of the DIPA. This feature allows users to easily prepare standards.

See Figure Three for the chromatogram of 125 ppm DIPA. Dodecane was added as a marker.

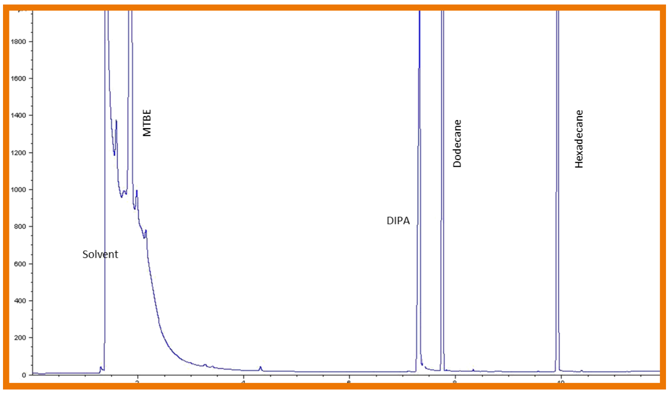


Figure Three: Chromatogram of 125 ppm DIPA in Pentane

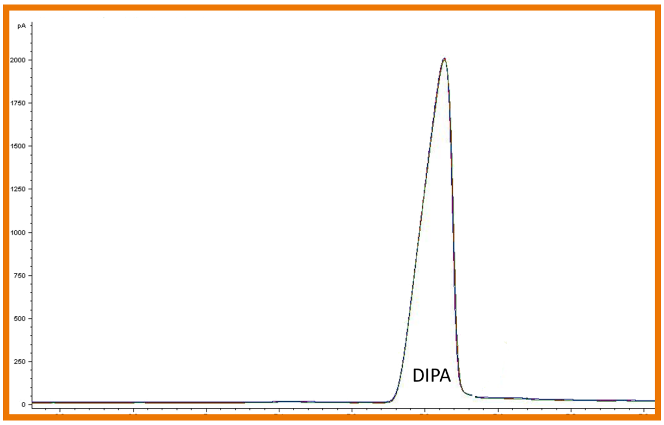


Figure Four: Overlay of three chromatograms of 125 ppm DIPA

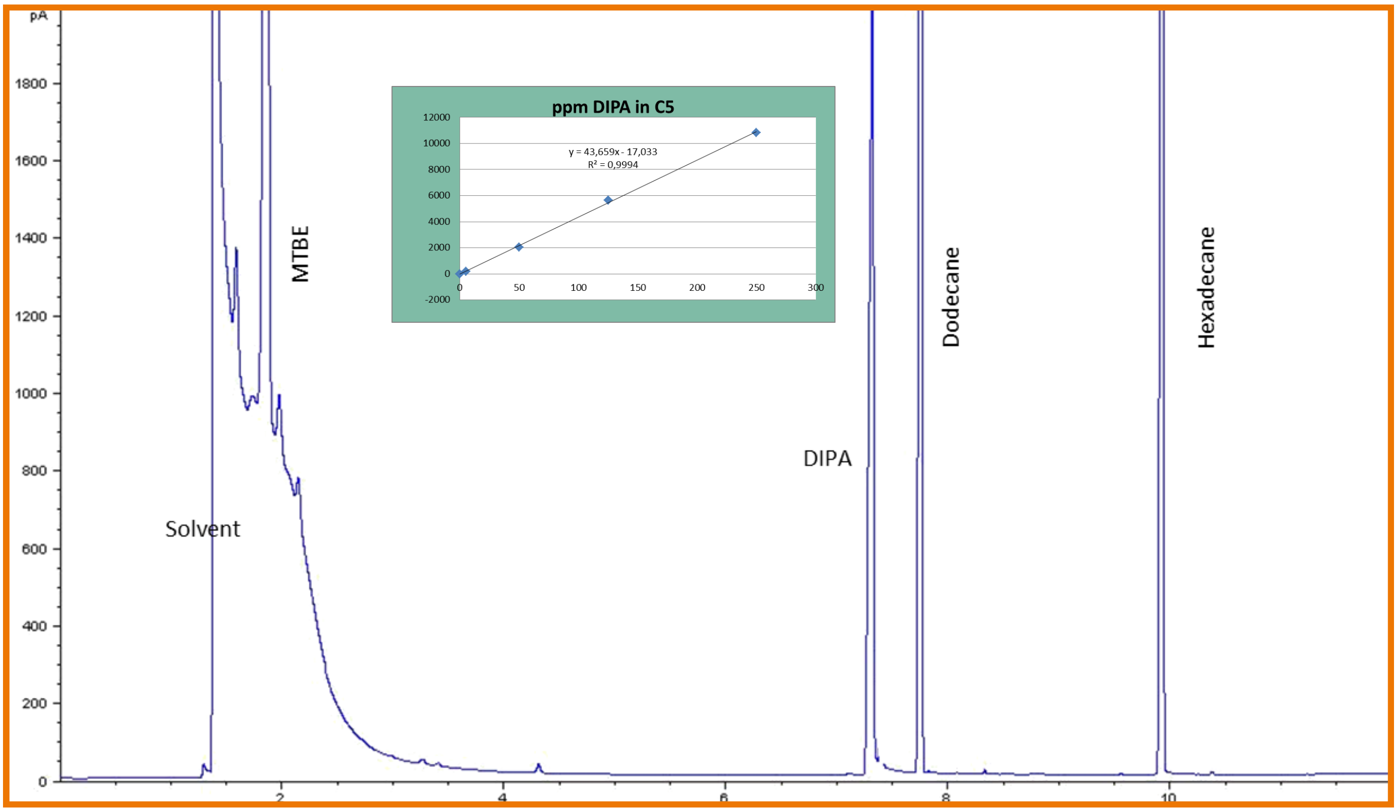


Figure Three: Chromatogram of 125 ppm DIPA in Pentane

Concentration DIPA	5 ppm	50 ppm	125 ppm	250 ppm
Area Counts	181.3	2053.7	5625.0	10828.3
Standard Deviation	1.53	23.71	44.54	185.06
% RSD	0.8	1.2	0.8	1.7

Table Three: Precision of four concentrations of DIPA in Pentane

Conclusion

A method developed by DVLS uses the new Liquefied Gas Injector (LGI) to inject LPG 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 DIPA in LPG. 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

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