Determination of Peroxide Traces in 1,3-Butadiene by the Fast Peroxide Analyzer (FPA) as an alternative to ASTM D5799

Introduction

Most 1,3-Butadiene is a by-product of Ethylene production from steam crackers. Butadiene is a colorless gas that is easily condensed to a liquid. It is widely used as a copolymer to produce synthetic rubbers. Butadiene is a reactive compound, therefore Peroxides may be formed upon exposure to air or during processing. Peroxides may initiate autopolymerisation to form popcorn polymers in storage tanks and vessels. Moreover, Butadiene Polyperoxides are known to cause violent explosions in storage vessels. As a result a fast and accurate analysis of Peroxide traces is required.
Current test method for determining Peroxides is ASTM D5799, an iodometric titration after the evaporation of Butadiene. Da Vinci Laboratory Solutions (DVLS) has developed a safe and accurate alternative based upon a flow injection system: the DVLS Fast Peroxide Analyzer (FPA). The application notes describes the analysis of Peroxides in 1,3-Butadiene using the FPA system equipped with a Pressure Station for a safe handling of liquid Butadiene in LPG contained in a cylinder.

Application Note

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Iodometric Titration

Since 1,3-Butadiene is a gas at atmospheric pressure and at room temperature, a traditional titration method cannot be used. ASTM test method D5799 describes the evaporation of a weighted quantity of 1,3-Butadiene after addition of dry ice. The residue is then refluxed with Sodium Iodide reagents. The Peroxides react to form Iodine, which is titrated with a standard Sodium Thiosulfate solution using visual end-point detection.

The method covers the range of 1 to 10 mg/kg as active Oxygen.
Repeatability of the ASTM D5799 method is 1.4 mg/kg and reproducibility is 3.4 mg/kg as active Oxygen.

Boosting laboratory efficiency

Figure One: The DVLS Fast Peroxide Analyzer configured with the DVLS Pressure Station

Flow Injection System

To eliminate the safety hazard and provide accurate results Da Vinci Laboratory Solutions has developed the Fast Peroxide Analyzer (FPA) based upon a flow injection system.

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The DVLS Fast Peroxide Analyzer uses an Agilent 1260 Infinity II HPLC system configured with a pump, an autosampler, a DVLS Reaction Module and a variable wavelength detector. Using a DVLS Pressure Station combined with a liquid sampling valve allows to inject the 1,3-Butadiene as a liquid into the reagent stream without the need for any sample preparation.

The pressure station allows a representative sample injection of a liquid hydrocarbon stream by keeping the pressure at a constant level.

Experimental

The sample is injected into the reagent stream of acidified Iodide and transferred to the Reaction Module. The Peroxides present in the sample will react with the Iodide to Iodine and form a brownish color. The DVLS Reaction Module is designed to optimize the conversion to Iodine. This is the same reaction that takes place in an iodometric titration as seen in Equation One.

$$ROOR + 2\,I^- + 2\,H^+ \rightarrow I_2 + 2\,ROH$$

Equation One: Redox reaction of Iodide with Peroxide

After the reaction, the formed Iodine is detected using UV-Vis spectroscopy at the optimal wavelength for Iodine.

The system is calibrated using Dibenzoyl Peroxide (DBP) standards in 1-Propanol (NPA). These standards have a concentration range of 0 to 50 mg/kg active Oxygen. All calibration levels are analyzed in triplicate. Figure Two displays the calibration curve.

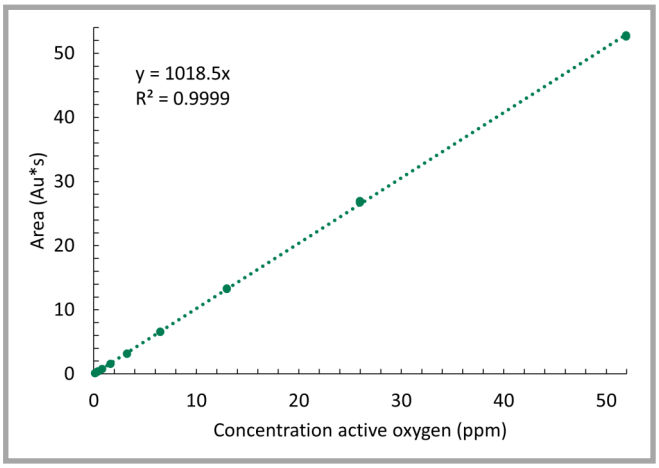

Figure Two: the calibration curve of DBP in 1-Propanol

To demonstrate the compatibility of the Pressure Station with the FPA, a pressurized Pentane sample is spiked with DBP equivalent to 0,750 mg/kg active Oxygen. Finally, two 1,3-Butadiene samples are analyzed. Both samples are analyzed in tenfold to measure the repeatability. The LOD and LOQ listed in Table One are estimated from the calibration curve of Figure Two.

Limits of Detection & Quantification	
LOQ	0.01 mg/kg active Oxygen
LOD	0.003 mg/kg active Oxygen

Table One: Lower Detection & Quantification limits of the FPA

Figure Four shows an example chromatogram of the second 1,3-Butadiene sample. Table Two displays the results of the samples injected by the Pressure Station.

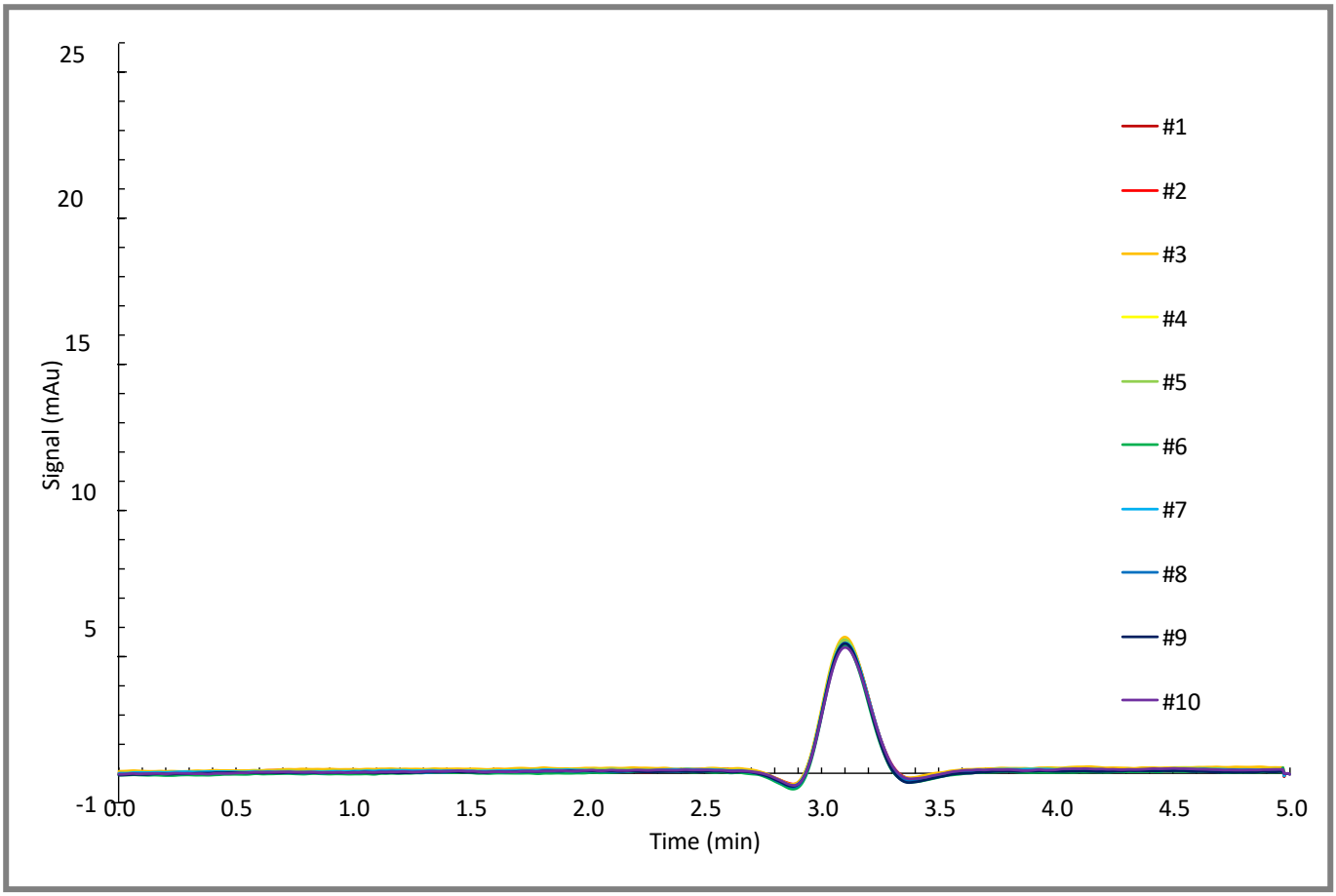

Figure Four: An example chromatogram of the second 1,3-Butadiene sample containing 0.0629 mg/kg active Oxygen

Analysis #	Pentane Standard (mg/kg)	1,3-Butadiene #1 (mg/kg)	1,3-Butadiene #2 (mg/kg)
1	0.751	0.0445	0.0640
2	0.742	0.0431	0.0627
3	0.761	0.0421	0.0638
4	0.752	0.0405	0.0636
5	0.753	0.0405	0.0632
6	0.707	0.0406	0.0621
7	0.750	0.0394	0.0633
8	0.745	0.0405	0.0630
9	0.736	0.0430	0.0628
10	0.745	0.0427	0.0608
Average	0.745	0.0417	0.0629
RSD (%)	2.00	3.89	1.46
Repeatability	0.04	0.004	0.003
Estimated Reproducibility	0.1	0.01	0.007

Table Two: Analysis results of the samples injected by the DVLS Pressure Station

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Conclusion

The iodometric titration method suffers from poor repeatability and reproducibility for the intended range; it also depends on the addition of dry ice to maintain an Oxygen free atmosphere.
The analysis results demonstrate that the DVLS Fast Peroxide Analyzer is a safe and accurate alternative for the analysis of Peroxide traces in 1,3-Butadiene.

	ASTM D5799	DVLS FPA
Range	1 – 10 mg/kg	0.01 – 50 mg/kg
Repeatability	1.4 mg/kg	0.004 mg/kg
Estimated Reproducibility	3.4 mg/kg	0.01 mg/kg
Analysis Time	75 min	5 min

Table Three: Comparison of ASTM D5799, an iodometric titration method, with the FPA, flow injection system

Table Three shows that compared to the iodometric titration ASTM D5799 method the FPA greatly improves the repeatability and reproducibility and it also significantly reduces the analysis time.

More information

- Application Note: Determination of Peroxides in Various Chemical Products by the Fast Peroxide Analyzer: Publication number: DVE.36.01

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