Determination of Peroxides in Various Chemical Products by the Fast Peroxide Analyzer (FPA)

Introduction

Peroxides in various hydrocarbon products can be formed through autoxidation and present a potential safety risk due to their reactive nature. Even at low concentrations Peroxides may promote unwanted side reactions and impact product quality. A fast and accurate analysis of the Peroxides content is required to prevent dangerous conditions during transport and storage and to warrant product quality. The Fast Peroxide Analyzer (FPA) developed by Da Vinci Laboratory Solutions provides a fast and accurate alternative to the current titration and spectrophotometric methods. This application note describes the analysis of Peroxides in various chemical products, such as Aromatics, alpha-Olefins and Styrenes using the FPA system.

Application Note

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Current Test Methods

The existing methods to determine Peroxides in hydrocarbon products include iodometric titration and spectrophotometry. These methods are labor intensive and may lead to erroneous results due to air interference. Some examples of current titration methods are: ASTM D2340, E299, D3703, D6447 , D5799 and ISO 3960.

Flow Injection Analysis

To eliminate the safety hazard and solve the air interference issue Da Vinci Laboratory Solutions has developed the Fast Peroxide Analyzer (FPA) based upon a flow injection technique.

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 UV-VIS detector. The FPA system is shown in Figure One.

Figure One: The DVLS Fast Peroxide Analyzer

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 the iodometric titration, see 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 its optimal wavelength for Iodine.

The analyzer is calibrated using Dibenzoyl Peroxide standards in 1-Propanol (NPA). To test whether the detector response is not affected by the hydrocarbon matrix, additions of Dibenzoyl Peroxide to 1-Hexene and Toluene at the same concentration levels are prepared. These standards have a concentration range of 0 up to 40 ppm active Oxygen. All concentration levels are analyzed in triplicate.

Figure Two displays the curves resulting from the calibration and addition.

The intercept of the calibration curve of 1-Hexene represents the Peroxides present in the 1-Hexene sample.
The LOD is estimated as <10 ppb active Oxygen based on the uncertainty in the regression of the calibration curve.

A wide range of hydrocarbons are analyzed. All hydrocarbons analyzed are shown in Table Two & Three.
Solid samples are dissolved in NPA. Liquid samples are analyzed without any sample preparation. Using the calibration in NPA, the Peroxide content of the samples is calculated.

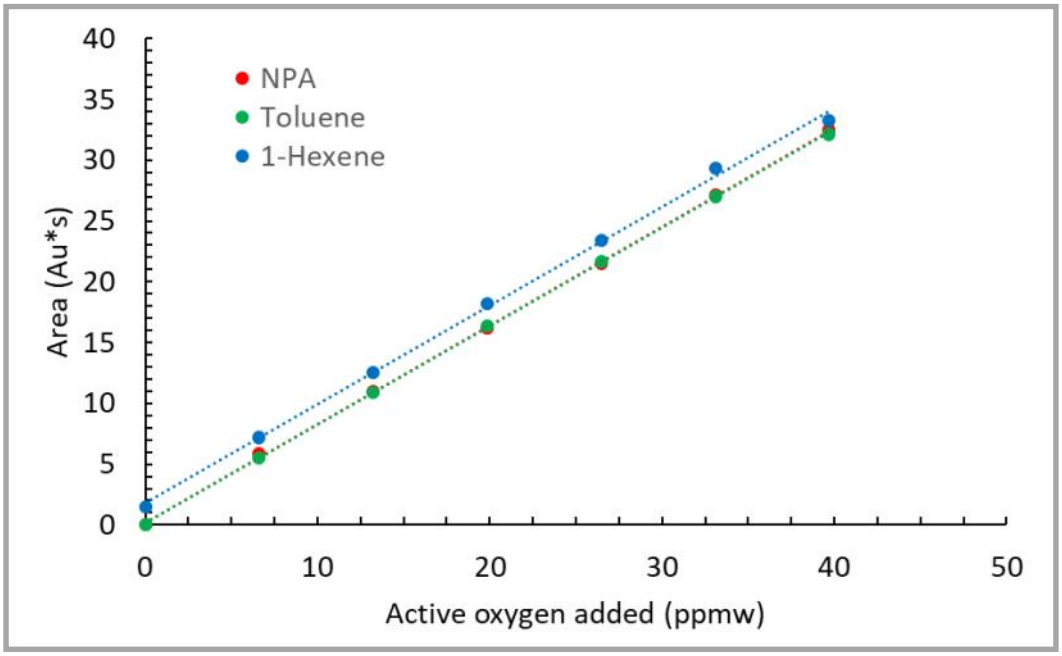

Figure Two: The calibration curves in 1-Propanol, 1-Hexene and Toluene

Table One shows that the uncertainty intervals overlap, this demonstrates that the Peroxide response is not affected by the hydrocarbon matrix.

Figure Three and Four display the stacked triplicate analysis of Styrene and 1-Hexene. Table Two and Three list the quantitative analysis results of the samples analyzed.

Matrix	Slope	Uncertainty	Intercept	R^2
NPA	812	3	207	0.9998
Toluene	810	2	157	0.9999
1-Hexene	812	9	1821	0.9985

Table One: Slope and Intercept of 1-Propanol, 1-Hexene and Toluene

Compound	Active Oxygen content (ppbw)	Standard Deviation	Relative Standard Deviation (%)
1-Methylnaphtalene	799	4	0.47
Benzene	Not detected	-	-
Toluene	66	1	2.0
p-Xylene	Not detected	-	-
1,2,4-Trimethylbenzene	270	7	2.7
Mesitylene	47	1	2.8
o-Xylene	Not detected	-	-
1-Decene	28	2	5.9
1-Tetradecene	340	20	4.7
1-Octadecene	101	2	1.6
Styrene	366	4	1.2
Diisopropyl ether	102	4	4.7
THF	Not detected	-	-
Diethyl ether	Not detected	-	-
1,4-Dioxane	Not detected	-	-

Table Two: Analysis results of samples containing Peroxides in ppb range

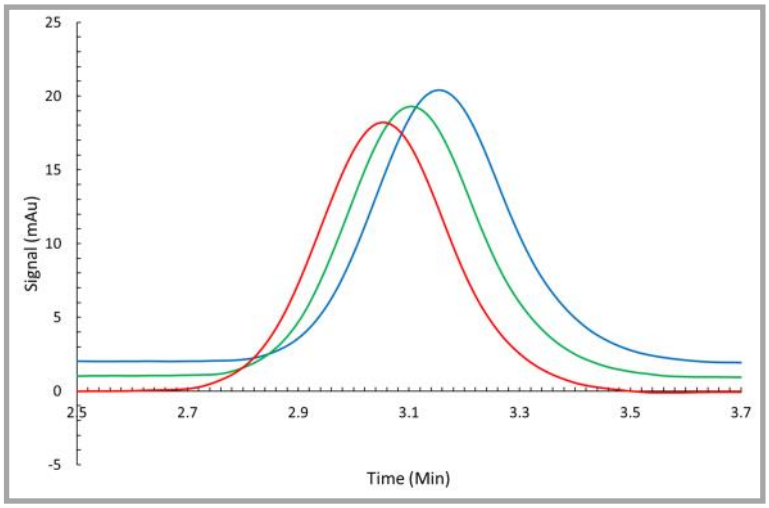

Figure Three: The overlay of 366 ppb Active Oxygen in Styrene

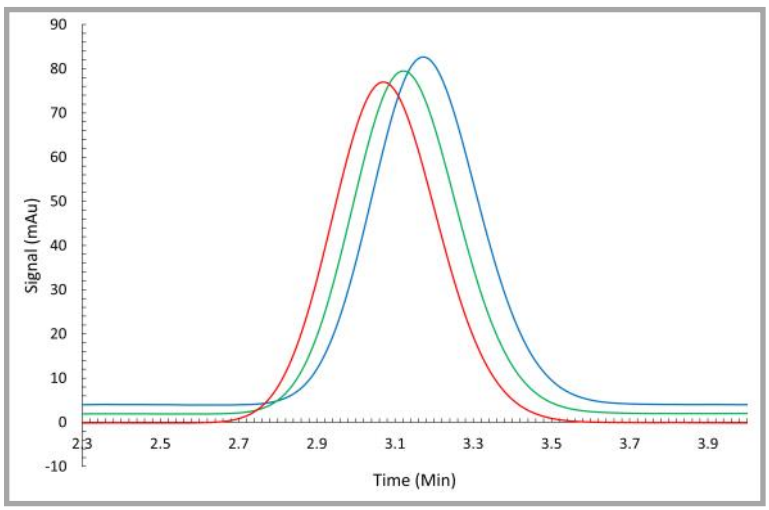

Figure Four: The overlay of 1.73 ppm Active Oxygen in 1-Hexene

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Compound	Active Oxygen content (ppmw)	Standard Deviation	Relative Standard Deviation (%)
m-Xylene	2.83	0.02	0.66
Ethylbenzene	4.23	0.03	0.64
1-Hexene, bulk #1	2.11	0.02	0.92
1-Hexene, bulk #2	1.73	0.03	2.0
1-Hexene, bulk #3	8.07	0.05	0.62
1-Octene	23.16	0.09	0.40
1-Dodecene	5.19	0.02	0.34
1-Hexadecene*	131.1	0.7	0.52
DCPD, BHT stabilized (aged)	8.177	0.006	0.07
DCPD, unstabilised	20	1	5.4
Styrene (spiked)	7.193	0.008	0.11
2-Vinyl pyridine	8.51	0.01	0.12
4-Vinyl pyridine	23.19	0.01	0.05
MTBE	10.02	0.02	0.16
1,2-Dimethoxyethanne	73.74	0.02	0.03

Table Three: Analysis results of samples containing Peroxides in ppm range

*1 µL of 1-Hexadecene was injected instead of 10 µL due to the high peroxide concentration

Conclusion

The results show that the Fast Peroxide Analyzer is a fast and accurate alternative to current titration and spectrophotometric test methods. Examples of the chemical samples that can be analyzed with the FPA are Alcohols & Ethers, Aromatics, Dicyclopentadiene, Styrenes and Vinyl Pyridines.
The calibration curves in different sample matrices show that the sample matrix does not affect the response. Depending on the product detection limits at ppb level are achieved.

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