

DVLS Fast Peroxide Analyzer (FPA)

Automates the Analysis of Peroxides in Hydrocarbon Streams

Diluted solutions of peroxides are used as catalysts or reaction initiators in petrochemical processes. Hydrocarbon streams such as Styrene, Isoprene and Butadiene may form thermally unstable peroxides upon exposure to air, but Peroxides can also be formed through autoxidation in certain classes of compounds including ethers, acetals, dienes, and alkyl aromatic hydrocarbons. As Peroxides present a potential safety hazard during production and storage an accurate monitoring is required to determine trace amounts of peroxides. Most traditional analysis methods, such as ASTM D2340 and ASTM E299, are affected by oxygen (air) interference. Da Vinci Laboratory Solutions (DVLS) has developed a safe and fast alternative based upon a flow injection analysis: the DVLS Fast Peroxide Analyzer.

Automated Analysis

Next to the safety hazard Peroxides also have a negative effect on fuels and fuel systems by reducing the octane rating in gasoline and deleting elastomers in fuel systems.

The DVLS Fast Peroxide Analyzer (FPA) is based upon an Agilent HPLC stack configured with a dedicated reaction



The DVLS Fast Peroxide Analyzer

oven module to automate the safe, fast and precise analysis of active oxygen originated from hydrogen peroxides and other organic peroxides.

The Fast Peroxide Analyzer was initially developed to monitor peroxides in alphaolefinic streams, it can also be used to determine peroxides in different matrices such as:

- 1,3-Butadiene
- Aqueous process streams
- Glycols
- Styrene

Application Range

The Fast Peroxide Analyzer is based on a customized method as an alternative to:

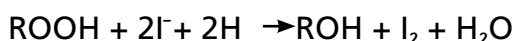
- ASTM D2340, E299
- ASTM D3703, D6447
- ASTM D5799

The FPA determines both hydrogen peroxides & organic peroxides in:

- 1,3-Butadiene
- Aqueous matrices in process streams
- Aviation turbine fuels
- Glycols
- Isoprene
- Olefinic hydrocarbon streams
- Styrene monomer

Flow Injection Analysis

The analysis of Peroxide, as active Oxygen, is based on the oxidation of Iodide by Peroxide:



Two reagents: Acetic Acid in n-Propanol and Sodium Iodide in n-Propanol are mixed, resulting in a stream of acidified Iodine solution in n-Propanol. The sample is injected into this stream.

Subsequently, the liquid stream is lead through a heated inert reaction coil. Iodine is formed under temperature controlled conditions inside the dedicated reaction oven developed by Da Vinci. After passing the reaction coil the HPLC UV detector spectrophotometrically determines the formed Iodine, which is proportional to the level of peroxide.



Configuration

The DVLS Fast Peroxide Analyzer is based upon the Agilent 1260 Infinity II Liquid Chromatograph (LC) configured with:

- A Quaternary Pump with integrated degassing functionality;
- An Automatic Liquid Sampler for an automated sample introduction;
- An UV Detector for a single wavelength detection;
- An DVLS Reaction Oven module to hold and heat the inert reaction coil.

The Agilent OpenLab instrument software not only controls the optimal instrument conditions, but also automates the data analysis and reporting.



The DVLS FPA configured with the Reaction Oven Module

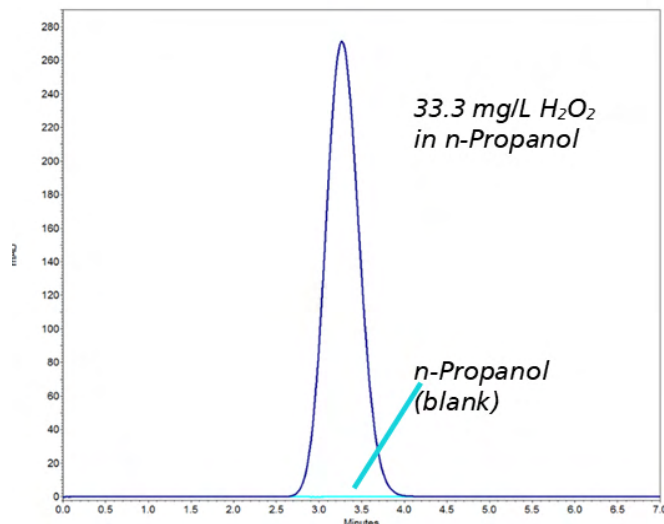
Dedicated Reaction Oven

The reaction oven developed by Da Vinci enables an optimal heat distribution to the reaction coil. The oven design matches the HPLC modules thus allowing stacking of the oven between the autosampler and the detector.



The Reaction Oven Module

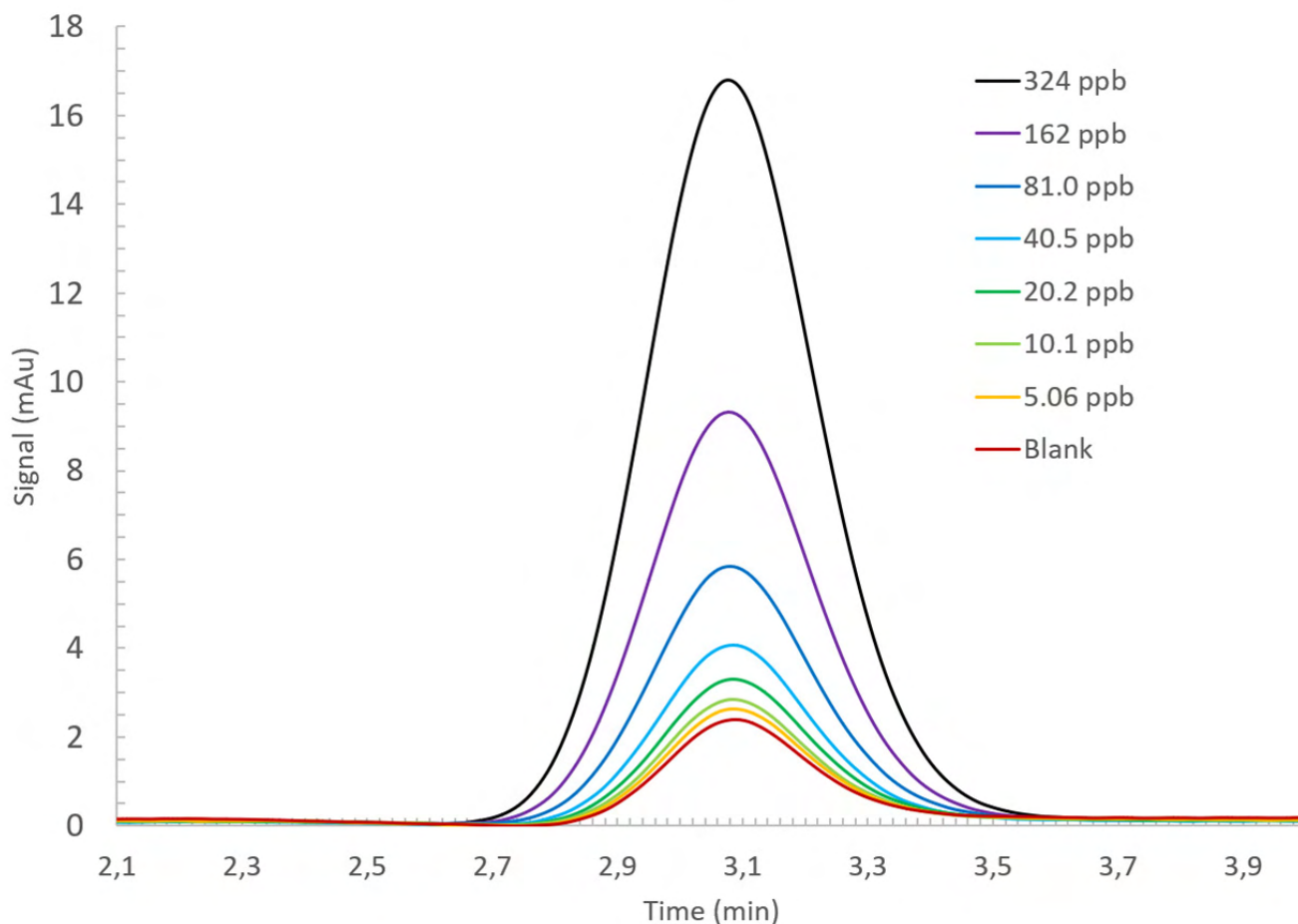
The DVLS Reaction Oven module holds and heats the reaction coils through a precise temperature control. To stabilize the heating cycle and to prevent a temperature overshoot an air fan is installed at the back of the module. The outlet of the reaction coil is placed in a cooling compartment to ensure a cooldown of the reagents and product before they enter the UV detector. The oven maximum temperature is 225 °C (437 °F).



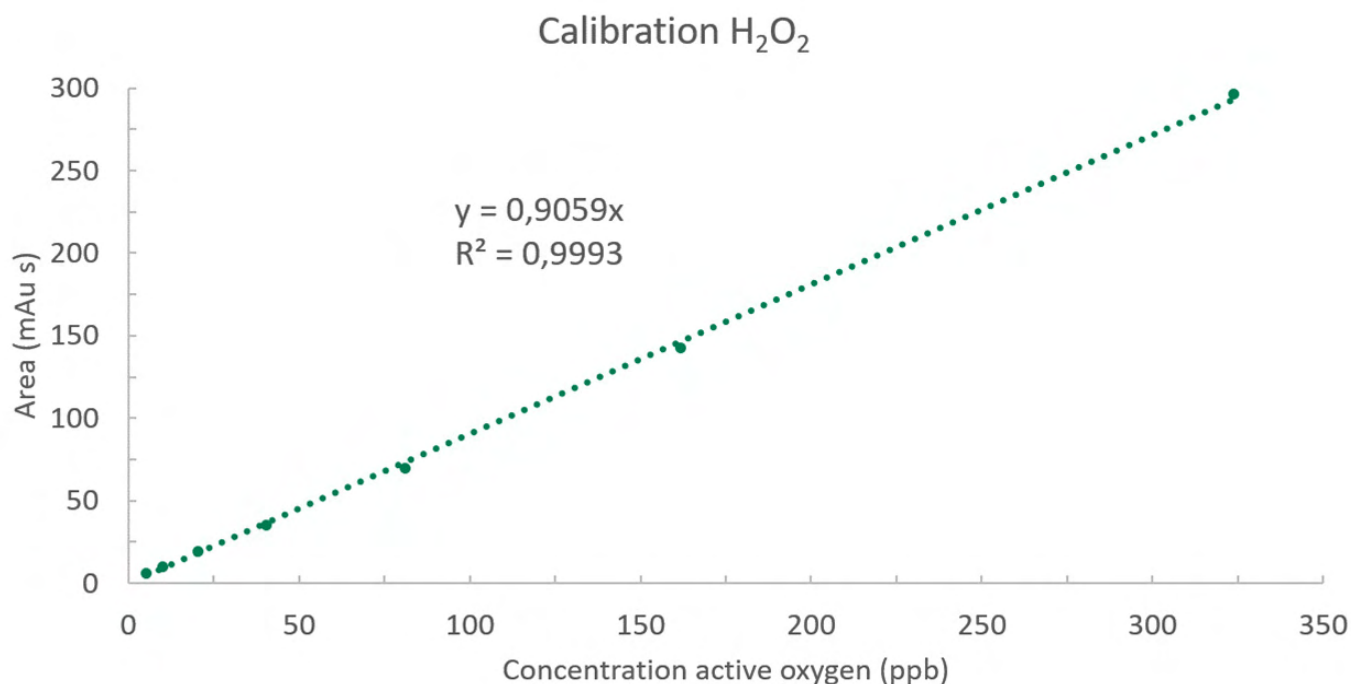
Chromatogram of 33.3 mg/L H₂O₂ solution n-Propanol

Features of the Reaction Oven Module

- Variable temperature control
- Flexible coil length
- Inert coil material
- Cooldown of effluent before detector
- Matching design of the HPLC stack



Overlay of several H₂O₂ in 1-Propanol calibration standards tested



The calibration curve of H₂O₂ in 1-Propanol

Performance Specifications

Linearity, detection limits and repeatability were determined by analyzing a series of Hydrogen Peroxide dissolved in 1-Propanol at a concentration range of 5 up to 324 µg/L active Oxygen. Each concentration level was analyzed in tenfold.

The LOD was estimated based on the residual error of the linear regression of the calibration curve. By multiplying the residual error with a factor of 3.3 and dividing by the slope of the curve, the LOD was obtained. By using a factor of 10 instead of 3.3, the LOQ was calculated.

Parameter	Value
S_y	2.622
LOD	9.52 ppb w
LOQ	28.8 ppb w

Performance Specifications of the FPA

Concentration	Average area (mAu*s)	RSD (%)
0.000	40.084	1.67
5.060	45.821	2.58
10.119	49.842	2.11
20.239	59.128	1.57
40.477	75.479	1.21
80.954	109.767	1.18
161.908	182.614	0.47
323.817	336.506	0.33

Results of FPA Analysis of H₂O₂ in 1-Propanol

Key Benefits

- ✓ Safe and automated alternative to traditional wet chemistry analysis methods;
- ✓ Wide application range: from alpha-olefinic streams to 1,3-Butadiene, Aqueous process streams, Glycols and Styrene;
- ✓ Excellent performance down to ppb level;
- ✓ Configuration based on the standard Agilent HPLC modules saves benchspace;
- ✓ Fast analysis in less than 5 minutes.

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