



## Determination of Peroxide Traces in Styrene by the Fast Peroxide Analyzer as an alternative to ASTM D2340

### Introduction

Peroxides are reactive compounds that may impact product quality and promote unwanted side effects such as autopolymerisation. A traditional method for quantifying Peroxides is ASTM D2340: an iodometric titration method for determining the Peroxide content in Styrene monomer. Da Vinci Laboratory Solutions has developed an automated alternative to the current titration method based on a flow injection analysis: the Fast Peroxide Analyzer (FPA). This application note describes the analysis of Peroxides in Styrene monomer using the FPA system compared with the iodometric titration method ASTM D2340.

### Application Note

Authors:

*Bas de Jonge, Harm Moes & Larissa Ram,  
Da Vinci Laboratory Solutions*

### Iodometric Titration ASTM D2340

Peroxides in Styrene are usually analyzed with the ASTM D2340 method. In this method 50 ml of sample is refluxed for 10 min with an excess of Sodium Iodide. After cooling down, the liberated Iodine is visually titrated with Sodium Thiosulfate until a light yellow color just disappears.

A blank analysis is performed to compensate for Oxygen (air) interference. The scope of the method is 1 to 60 mg/kg H<sub>2</sub>O<sub>2</sub> with a repeatability of 6 mg/kg H<sub>2</sub>O<sub>2</sub> and a reproducibility of 13 mg/kg H<sub>2</sub>O<sub>2</sub>.

### Flow Injection System

The Fast Peroxide Analyzer (FPA) is based upon a flow injection technique and uses an Agilent 1260 Infinity II HPLC system configured with a pump, an autosampler, a DVLS reaction module and a UV-VIS detector. Figure One displays the Fast Peroxide Analyzer next to a titration system.

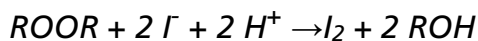
### Boosting laboratory efficiency



Figure One: The Fast Peroxide Analyzer versus the Iodometric Titration

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 yellow-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.

# Determination of Peroxide Traces in Styrene



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.

Figure Two shows a calibration curve of Dibenzoyl Peroxide (DBP) in 1-Propanol (NPA) ranging from 213 to 0.4 mg/kg H<sub>2</sub>O<sub>2</sub> analyzed by the FPA. The lower detection limit of the FPA is 0.1 mg/kg H<sub>2</sub>O<sub>2</sub>.

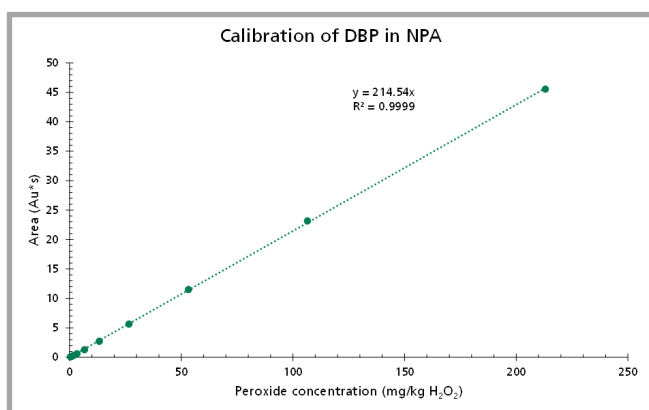


Figure Two: the calibration curve of DBP in 1-Propanol

## Experimental

Two production batches of polymerization grade Styrene were analyzed during transshipment using both ASTM D2340 and the DVLS FPA. Duplicate samples from both batches were taken during loading of the barges and from the shoretank after discharge. Each sample was analyzed in tenfold on the FPA.

Table One shows the analysis results of the FPA and the ASTM D2340 method. All concentrations are reported in mg/kg H<sub>2</sub>O<sub>2</sub>.

Batch, movement, sample	FPA H <sub>2</sub> O <sub>2</sub> (mg/kg)	D2340 H <sub>2</sub> O <sub>2</sub> (mg/kg)
Batch 1, during loading, sample 1 (1L1)	2.7	2
Batch 1, during loading, sample 2 (1L2)	2.5	2
Batch 1, after discharge, sample 1 (1D1)	2.7	2
Batch 1, after discharge, sample 2 (1D2)	2.6	2
Batch 2, during loading, sample 1 (2L1)	2.7	5
Batch 2, during loading, sample 2 (2L2)	2.3	5
Batch 2, after discharge, sample 1 (2D1)	2.7	2
Batch 2, after discharge, sample 2 (2D1)	2.7	2

Table One: H<sub>2</sub>O<sub>2</sub> in Styrene results of the FPA and the D2340 method

Table Two lists the determined concentrations of the replicates, all concentrations are reported in mg/kg H<sub>2</sub>O<sub>2</sub>. The repeatability stated in ASTM D2340 is 6 mg/kg Hydrogen Peroxide. The highest repeatability of the FPA (listed in Table Two) is 0.17 mg/kg.

Figure Three displays an overlay of the first sample of batch 2 after discharge.

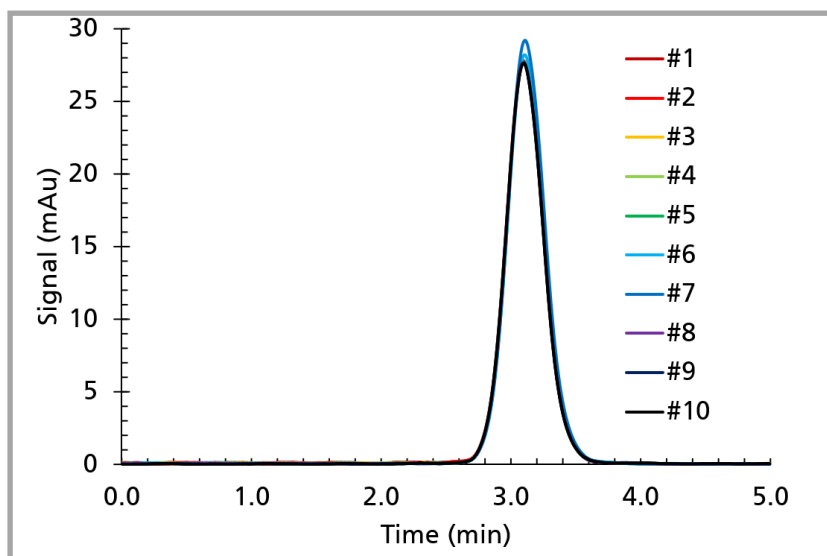


Figure Three: Overlay of the Batch 2 Styrene sample #1 after discharge

# Determination of Peroxide Traces in Styrene by the Fast Peroxide Analyzer (FPA) as an alternative to Iodometric Titration

Replicate	1L1 H <sub>2</sub> O <sub>2</sub> mg/kg	1L2 H <sub>2</sub> O <sub>2</sub> mg/kg	1D1 H <sub>2</sub> O <sub>2</sub> mg/kg	1D2 H <sub>2</sub> O <sub>2</sub> mg/kg	2L1 H <sub>2</sub> O <sub>2</sub> mg/kg	2L2 H <sub>2</sub> O <sub>2</sub> mg/kg	2D1 H <sub>2</sub> O <sub>2</sub> mg/kg	2D2 H <sub>2</sub> O <sub>2</sub> mg/kg
#1	2.64	2.54	2.65	2.53	2.70	2.20	2.72	2.67
#2	2.61	2.44	2.64	2.65	2.70	2.20	2.70	2.67
#3	2.63	2.46	2.67	2.53	2.70	2.32	2.69	2.72
#4	2.64	2.51	2.78	2.53	2.71	2.33	2.70	2.81
#5	2.75	2.54	2.79	2.52	2.70	2.23	2.69	2.72
#6	2.75	2.54	2.64	2.55	2.84	2.22	2.75	2.66
#7	2.62	2.54	2.66	2.52	2.84	2.22	2.85	2.67
#8	2.62	2.43	2.65	2.56	2.70	2.23	2.70	2.68
#9	2.61	2.41	2.65	2.63	2.70	2.33	2.70	2.66
#10	2.65	2.41	2.64	2.63	2.69	2.32	2.68	2.68
Average	2.65	2.48	2.68	2.57	2.73	2.26	2.72	2.69
Repeatability	0.15	0.16	0.16	0.14	0.17	0.16	0.14	0.13

Table Two: the repeatability of the FPA

## Conclusion

Traces of Peroxides in Styrene monomer can be analyzed fast and accurately with the DVLS Fast Peroxide Analyzer (FPA); a flow injection system. The comparison with the iodometric titration method ASTM D2340 demonstrates that the FPA greatly improves the repeatability, reproducibility and LOD as shown in Table Three.

Specifications	DVLS FPA	Iodometric Titration ASTM D2340
Reproducibility	0.17 mg/kg H <sub>2</sub> O <sub>2</sub>	6 mg/kg H <sub>2</sub> O <sub>2</sub>
Lower limit of detection	0.1 mg/kg H <sub>2</sub> O <sub>2</sub>	1 mg/kg H <sub>2</sub> O <sub>2</sub>
Method range	50 mg/kg H <sub>2</sub> O <sub>2</sub>	60 mg/kg H <sub>2</sub> O <sub>2</sub>
Calibration method	External calibration with DBP	Standardization to potassium dichromate

Table Three: Comparison of the DVLS FPA with the Iodometric Titration method D2340

The FPA analysis also allows a better monitoring of the Peroxide content during custody transfer of Styrene, which is indicated by the analysis results. The titration results of samples 2L1 and 2L2 are suspect as shown in Table One, they may have been reported too high due to O<sub>2</sub> (air) interference.

## More information

- Application Note: Determination of Peroxides in Various Chemical Products by the Fast Peroxide Analyzer: Publication number: DVE.36.01
- Application Note: Determination of Peroxide Traces in 1,3-Butadiene by the Fast Peroxide Analyzer (FPA) as an alternative to ASTM D5799 ; Publication number: DVE.34.01

Publication number: DVE.33.01

DA VINCI LABORATORY SOLUTIONS B.V.  
P.O. Box 12103, 3004 GC Rotterdam - The Netherlands  
T: +31 (0)10 258 1870 - E-mail: solutions@davinci-ls.com

www.davinci-ls.com