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**DETERMINATION OF HYDROPEROXIDES IN LIQUID FUELS: A SYSTEMATIC COMPARISON OF TITRATIONS AND ABSORPTION METHODS AND THEIR COUPLING TO HPLC**

Ryma Benrabah<sup>1</sup>, Zaki El Sayah<sup>1</sup>, Pierre-Alexandre Glaude<sup>1</sup>, Philippe Arnoux<sup>1</sup>, Baptiste Sirjean<sup>1</sup>

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**ABSTRACT**

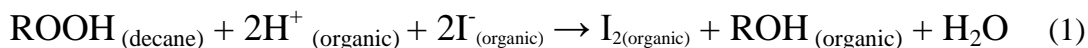
Hydroperoxides are major products in the autoxidation of fuels and play a central role in oxidation kinetics. Their presence affects the oxidation rate, even at low concentrations, and, in turn, the thermal stability of fuels. Standard techniques for the quantification of hydroperoxides (ROOH) in fuel involve the reduction of ROOH by I<sup>-</sup>, yielding iodine (I<sub>2</sub>), which can be quantified by titration. These ASTM methods are known to have poor reproducibility, inadequate lower detection limits and limited dynamic ranges. In this work, several analytical methods for the quantification of hydroperoxides in surrogate fuels have been systematically compared for a known concentration of ROOH: titration of iodine with thiosulfate (ASTM D3703) or triphenylphosphine (TPP) solutions with colorimetric and potentiometric methods and quantification of iodine by UV-visible absorption. *n*-Decane was used as the surrogate fuel and tert-butyl hydroperoxide as the controlled ROOH content. Our systematic study shows that the ASTM method based on colorimetric titration using thiosulfate in aqueous solution is the least accurate because of the non-miscibility of water and *n*-decane, which even makes the UV-visible spectroscopy method ineffective. The other titration method in the literature, using TPP dissolved in *n*-decane as the titrant does not have any miscibility problem. Potentiometric titration is found to be more reproducible and accurate than colorimetric titration. The UV-visible absorption method allows reaching lower detection limits. We show that the combination of the potentiometric titration of iodine with TPP and UV-visible absorption allows for determining ROOH concentrations with low detection limits and a large dynamic range. The advantages of both methods have been used to develop a new analytical method based on their coupling in HPLC.

**KEYWORDS:** hydroperoxides, HPLC, autoxidation

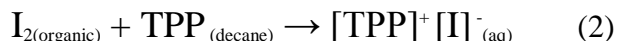
## INTRODUCTION

The thermal oxidation stability of fuels is a key factor in the transportation and the energy fields. This stability can be jeopardized by the slow oxidation of fuels occurring during their storage, manipulation, and use in engines. One of the main chemical markers of fuel oxidation is the formation of hydroperoxides<sup>1,2</sup>. The hydroperoxide content is therefore a key factor to characterize the degree of oxidation of a fuel and its ability to reach the expected specifications for a given engine application. An ATSM standard (D3703) has been used for several years but has been shown to be poorly reproducible.<sup>3,4,5</sup> Indeed, this norm quantifies the total hydroperoxides content of an organic phase (hydrocarbons and organic components) with a method using an aqueous phase, which could lead to miscibility problems. Moreover, many works have been recently performed to determine new methods to better quantify hydroperoxides. These approaches are still based on iodometry.<sup>1,6</sup> **Erreur ! Source du renvoi introuvable.**<sup>7</sup>

Recently, *Roohi and Rajabi*<sup>6</sup> proposed an iodometric titration, based on a visual change of the color to find the endpoint (colorimetric approach). Triphenylphosphine (TPP) is the titrant for the I<sub>2</sub> produced from the reaction of ROOH with iodide ions I<sup>-</sup> in an acidic organic phase. In the first step, ROOH is reduced with iodide ions from potassium iodide in absolute ethanol in presence of acetic acid to produce a yellow solution of I<sub>2</sub> as presented in the equation below:



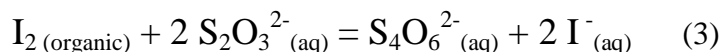
Then, triphenylphosphine is added to react with I<sub>2</sub> producing an uncolored complex [TPPI]<sup>+</sup>[I]<sup>-</sup> as shown below:



The iodine concentration can be determined from the quantity of TPP added and the endpoint is found when the mixture turns transparent.

*Roohi and Rajabi*<sup>6</sup> proposed a colorimetric titration, but the equivalence point can also be found using potentiometry.<sup>7</sup> In this work, we used this method (TPP titrant/potentiometry) for the first time in the literature.

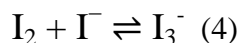
The ASTM D3703 standard uses thiosulfate in aqueous phase as the titrant that reacts with I<sub>2</sub>, according to:



The equivalence point can be determined by colorimetry and potentiometry titrations. The titration methods offer many advantages, including simplicity, not being time and labor-

consuming, accuracy at relatively low concentrations, and, in most cases, easy endpoint determination<sup>3,8</sup>.

Alternatively, the absorbance of the solution formed in equation (1) can be measured by spectroscopy. Indeed, triiodide ion  $I_3^-$  is formed in the presence of  $I_2$  and  $I^-$  (equation 4). In absolute ethanol, triiodide has one of a maximal absorbance at a wavelength of 362 nm.



The absorbance depends on the dilution factor of the solution.<sup>8</sup> Since reaction (1) is total,  $[I_2]=[ROOH]$ . The Beer-Lambert law is used to link the absorbance of  $I_3^-$  and its concentration:

$$A = \epsilon l C \quad (5)$$

A: absorbance of the solution at 362 nm

$\epsilon$ : molar extinction coefficient of  $I_3^-$  ( $\text{cm}^{-1} \text{L mol}^{-1}$ )

l: optical length of quartz spectroscopy cell (cm)

C: concentration of  $I_3^-$  ( $\text{mol L}^{-1}$ )

All the above-mentioned methods are usually performed in laboratory flasks (for titration) and cuvettes (UV-Vis absorption). In this study, we will show that reaction (1) and UV-Vis absorption can be combined in a post-column reactor within a High-Performance Liquid Chromatography (HPLC) device. A photodiode array (PDA) detector can also be used to follow the absorbance and the transmission of a colored solution at different wavelengths.<sup>9,10</sup> The high added value of HPLC in this method is its ability to separate the ROOH from other compounds in the oxidized fuel.<sup>10</sup>

This study aims to determine the detection limits of each method and compare their reproducibility and performance for the determination of the total hydroperoxide content of a surrogate fuel containing a known quantity of hydroperoxides.

## EXPERIMENTAL SECTION

### *Reagents*

Potassium iodide (KI), anhydrous sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ; 0.1 N in aqueous solution), and absolute ethanol were purchased from VWR Chemicals. Butylated hydroxytoluene (BHT) ( $\geq 99\%$ ), triphenylphosphine (TPP;  $\geq 99\%$ ), acetic acid ( $\geq 99.8\%$ ), tert-butyl hydroperoxide in *n*-decane (TBHP /  $\text{C}_{10}$ ; 5.5-6.5 M) 2,2,4-trimethylpentane (isooctane;  $\geq 99.5\%$ ) were purchased from Sigma Aldrich. *n*-Decane was provided by ACROS Chemicals. The surrogate fuel is *n*-decane ( $\text{C}_{10}$ ), which is a usual surrogate of diesel and jet fuels<sup>11,12</sup>, and the total ROOH content is represented by the addition of TBHP. To evaluate the performance of the different analytical

methods, TBHP/*n*-decane solutions were prepared with decreasing concentrations of TBHP obtained by dilutions.

### ***Preparation of the solution***

The first reaction used for all types of titrations and the UV-vis spectroscopy is based on the protocol from *Roohi and Rajabi*<sup>6</sup>: 0.5 g of KI and 0.5 mL of acetic acid in 25 mL of absolute ethanol were heated for 5 min in slow agitation (400 rpm) to 68°C. Then, a 1 mL sample of TBHP/*n*-decane blend was added and the mixture was heated at 68°C, at the same agitation, for 15 min to ensure that reaction (1) was complete. The solution was kept warm during the subsequent manipulations.

### ***Colorimetric titration***

A usual setup for titration was used. When TPP is the titrant, a 25 mL burette filed with a 0.08M solution of 2.1g of TPP and 0.01g of BHT in *n*-decane is used to titrate iodine and the endpoint of titration was determined when the solution became transparent. When Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.025M) in water is the titrant, the equivalence point is also reached when the solution becomes transparent. Each experiment was done twice.

### ***Potentiometric titration***

An automated potentiometric titrator (Mettler Toledo G10S Compact Potentiometric Titrator) was used, equipped with a Pt indicator electrode vs. an AgCl / Ag reference electrode. For analysis, 1 ml of the TBHP / C<sub>10</sub> solution was put in the cell stirred at 20%. Two titrants were used: TPP (0.08M-8mM-0.8mM) in *n*-decane and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.025M) in water. Each experiment was repeated 3 times.

### ***UV-spectrophotometric titration***

A sensitive UV-visible double beam spectrophotometer UV-3600 Shimadzu was used to determine the precise amount of peroxides in the TBHP/C<sub>10</sub> solutions. The absorbance of triiodide formed by I<sub>2</sub> with excess iodide ions was measured at 362 nm.<sup>10</sup> Measurements were done in a 4 mL quartz cell of dimensions 10×10×40 mm.

### ***HPLC titration***

An HPLC device combining a separation column in the normal phase (silica) and a post-column reactor was adapted from the work of *Cullis et al.*<sup>10</sup> A HPLC Shimadzu Nexera XR was used at a flow of 1 mL per minute of solvent (isooctane: absolute ethanol 95:5). 1 μL of the sample TBHP/C<sub>10</sub> was injected using an autosampler through the separative column. At the exit of this column, the fractions were mixed with a 10% acetic acid in absolute ethanol (0.2 mL/min) and a

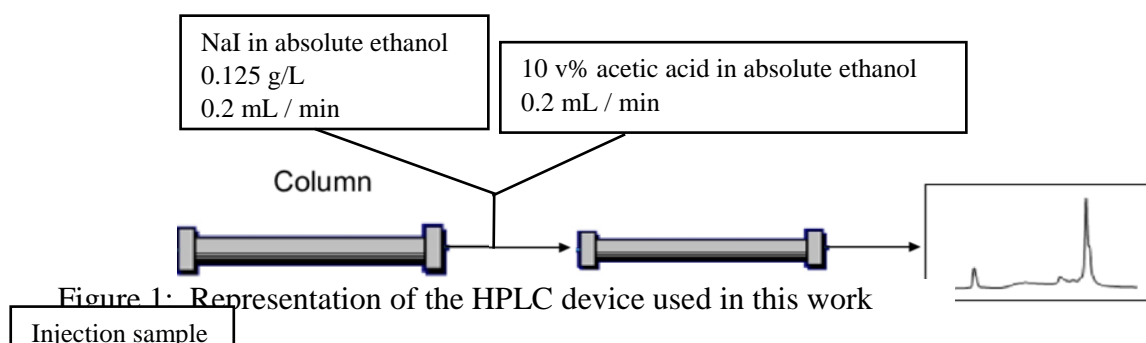


Figure 1. Representation of the HPLC device used in this work

Injection sample

0.125 g/L solution of NaI in absolute ethanol (0.2 mL/min). This mixture passed through a reactive column packed with 30  $\mu\text{m}$  glass beads, heated at 68°C with a residence time of 80 seconds.<sup>10</sup> A chromatogram was obtained at every wavelength between 190 nm and 800 nm, which allows hydroperoxide quantification in the sample after calibration. Figure 1 presents a schematic representation of the HPLC device.

## RESULTS AND DISCUSSION

The colorimetric and the potentiometric methods using two different titrants are compared, as well as UV-spectrophotometric measurement, to determine the concentration of total peroxide content in the TBHP / C<sub>10</sub> solutions. HPLC using a PDA detector (spectroscopy UV-vis) is also used.

### *Comparison and limits of colorimetric titration using TPP and aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>*

Figure 2 presents a comparison between the experimental and the theoretical (vendor certifications for the stock solution) concentrations of TBHP in *n*-decane. TBHP concentrations were measured by colorimetry with two titrants: a solution of TPP in *n*-decane and a solution of sodium thiosulfate in the aqueous phase. The results of Figure 2 are also given in Tables 1 and 2.

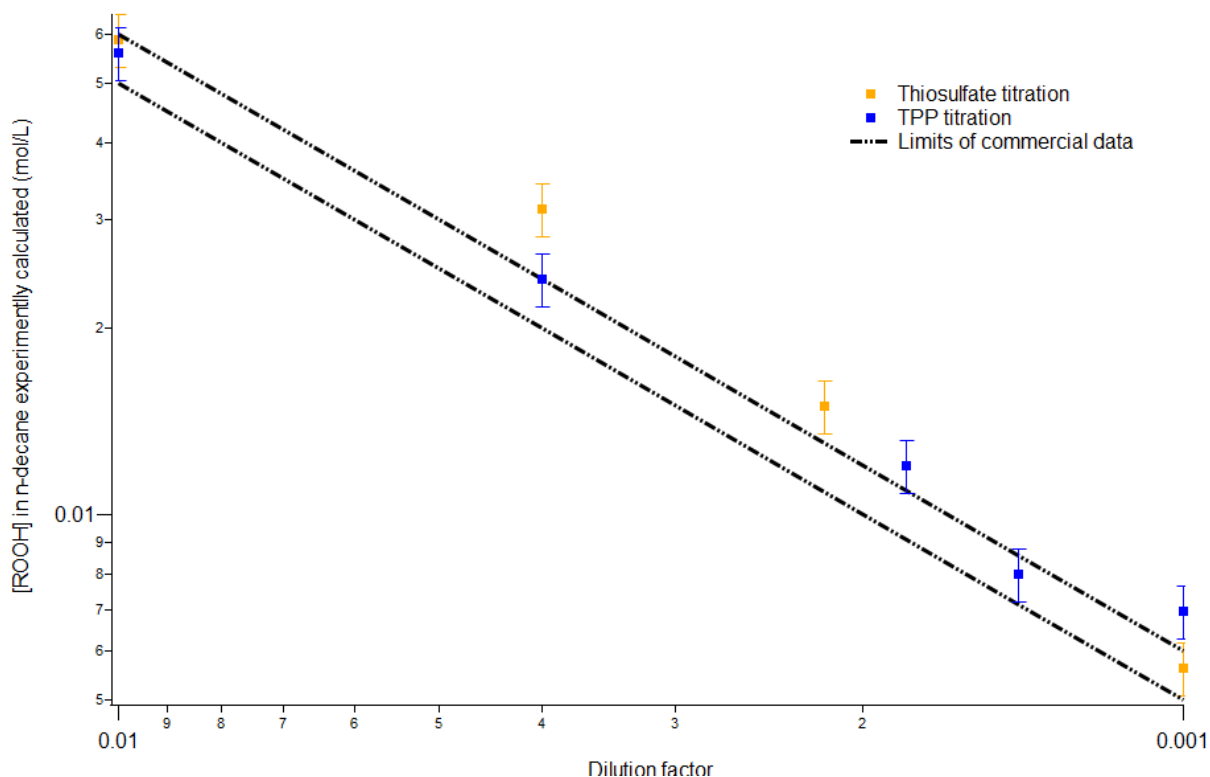


Figure 2: Comparison of experimental and theoretical (commercial certifications) TBHP (ROOH) concentrations as a function of dilution. Experimental method: colorimetric titration with thiosulfate in water and TPP in *n*-decane titrants.

Sigma-Aldrich indicates that the concentration of TBHP in *n*-decane (our stock solution) ranges between 5.5 and 6.5M. It is worth noting that their measure of the TBHP concentration is performed by iodometry using the thiosulfate and colorimetric method. Therefore, we decided to represent these limits on the graph (black dashed straight line) to ensure that the concentration found with each solution remains in these data.

Table 1: Molar concentration and titration volume of ROOH in TBHP / C<sub>10</sub> after iodometric titration with TPP in *n*-decane titrant.

TBHP / C <sub>10</sub> Dilution factor	[TBHP / C <sub>10</sub> ] buffer (mol. L <sup>-1</sup> )	[TPP/C <sub>10</sub> ] (mol. L <sup>-1</sup> )	V <sub>titration</sub> (mL)	[ROOH] (mol. L <sup>-1</sup> )
100	5.50E-02	0.08	0.80	6.40E-02
250	2.20E-02	0.08	0.30	2.40E-02
550	1.00E-02	0.08	0.15	1.20E-02
700	7.86E-03	0.08	0.10	8.00E-03
1000	5.50E-03	0.08	8.7E-02	6,97E-03

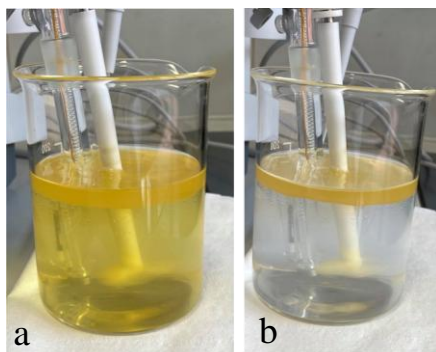
Table 2: Molar concentration and equivalence point volume of ROOH in TBHP / C<sub>10</sub> after iodometric titration with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> / water solution.

<b>TBHP / C<sub>10</sub> Dilution factor</b>	<b>[TBHP / C<sub>10</sub>] buffer (mol. L<sup>-1</sup>)</b>	<b>[Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> / water] (mol. L<sup>-1</sup>)</b>	<b>V<sub>titration</sub> (mL)</b>	<b>[ROOH] (mol. L<sup>-1</sup>)</b>
100	5.50E-02	0.025	4.70	5.88E-02
250	2.20E-02	0.025	2.50	3.13E-02
460	1.00E-02	0.025	1.20	1.50E-02
700	7.86E-03	0.025	0.64	8.00E-03
1000	5.50E-03	0.025	0.45	5.63E-03

The comparison between the results obtained by colorimetric titration with TPP in *n*-decane (mean relative deviation (MRD) with the theoretical value of 14.8%) and sodium thiosulfate in water (MRD of 20.7%) shows better results between the experimental and commercial concentrations in the case of the titration using TPP. All the colorimetric titration results seem to show that the TBHP concentration is within the upper limit of the vendor certifications. It is important to note that the main difference in the titration with an aqueous titrant and an organic titrant lies in the formation of two phases which brings accuracy issues in the colorimetric (and potentiometric) methods. Figure 3 illustrates the non-miscibility problems observed when thiosulfate is used as the titrant.



**Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**



**TPP**



Figure 3: Pictures representing the different states of colorimetric titration (before the equivalence volume (a, c) and after (b,d) of iodine using an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and using TPP.

Figures 3b and 3c clearly show that two phases are involved when water is involved in the titration. The colorimetric determination of the endpoint can even be challenging as illustrated in Figure 3c.

#### *Comparison and limits of potentiometry using TPP and aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>*

Potentiometry has also been used for the determination of the equivalence point in thiosulfate and TPP titrations. The results using two different titrants are shown in Figure 4 and detailed in Table 3. TPP in *n*-decane titrant (0.08 M-8mM and 0.08mM) was used since the volume of a droplet in the potentiometer is small compared to the one in the burette.

Table 3: Molar concentration and equivalence point volume of ROOH in TBHP / C<sub>10</sub> after potentiometric titration with organic TPP / C<sub>10</sub> solution.

<b>TBHP / C<sub>10</sub> Dilution factor</b>	<b>[TBHP / C<sub>10</sub>] buffer (mol. L<sup>-1</sup>)</b>	<b>[TPP/C<sub>10</sub>] (mol. L<sup>-1</sup>)</b>	<b>V<sub>titration</sub> (mL)</b>	<b>[ROOH] (mol. L<sup>-1</sup>)</b>
10	5.50E-01	0.08	7.79	6.23E-01
100	5.50E-02	0.08	8.0E-01	6.40E-02
250	2.20E-02	0.08	2.9E-01	2.32E-02
550	1.00E-02	0.08	1.6E-01	1.28E-02
700	7.86E-03	0.08	1.00E-02	8.18E-03
1000	5.50E-03	0.08	8.72E-02	6.97E-03

2500	2.40E-03	8.00 E-03	6.16E-01	4.93 E-03
5000	1.20E-03	8.00 E-03	3.60E-01	2.88 E-03
10000	6.00E-04	8.00 E-03	1.07E-01	7.17 E-04
500000	1.20E-04	8.00 E-04	2.54	2 E-04
700000	8.57E-05	8 E-04	2.00	7.14 E-05
1000000	6E-05	8 E-04	1.00	5.0 E-05

The experimental results of the quantification of peroxides in the different samples of TBHP in *n*-decane and the commercial concentrations agree well (MRD of 32.7%), as shown in Table 3. The limit of detection of this method is considerably lower than the colorimetric approach with the same reagents and titrants. Figure 2 presents the variation of the different concentrations obtained by potentiometric titration with TPP titrant, within the range of concentration given by the vendor.

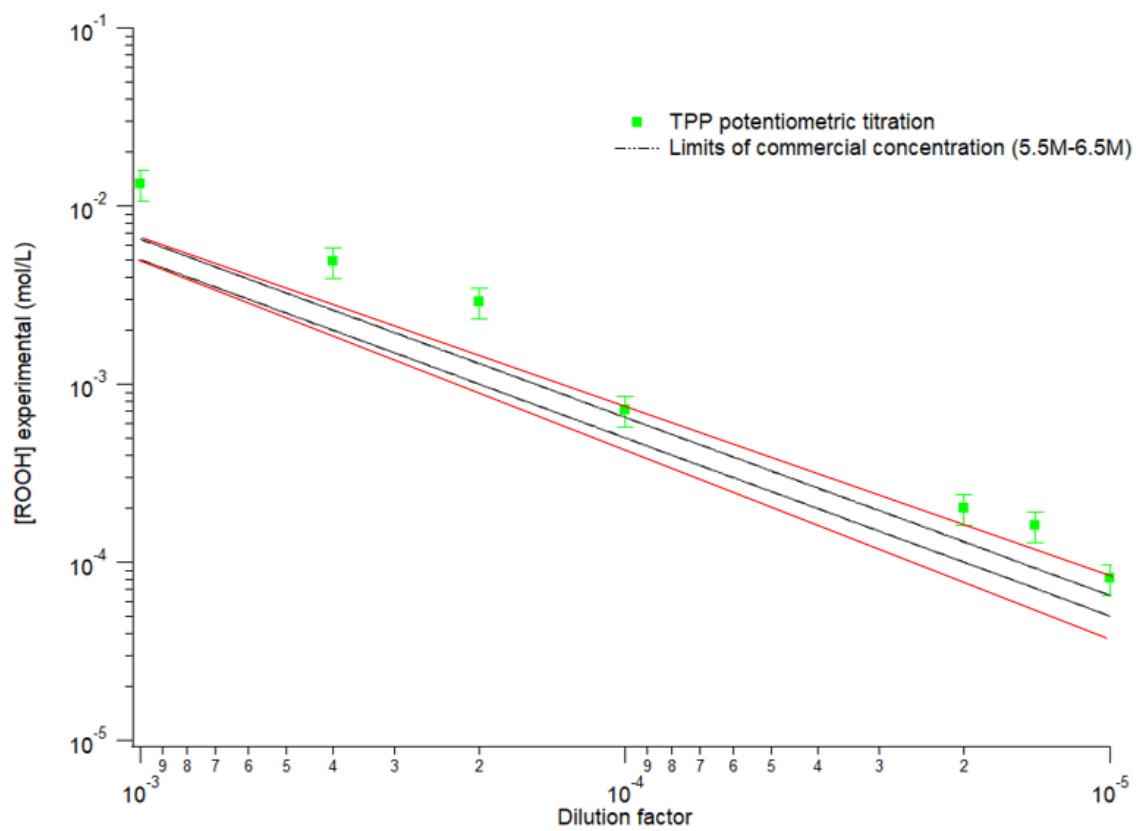
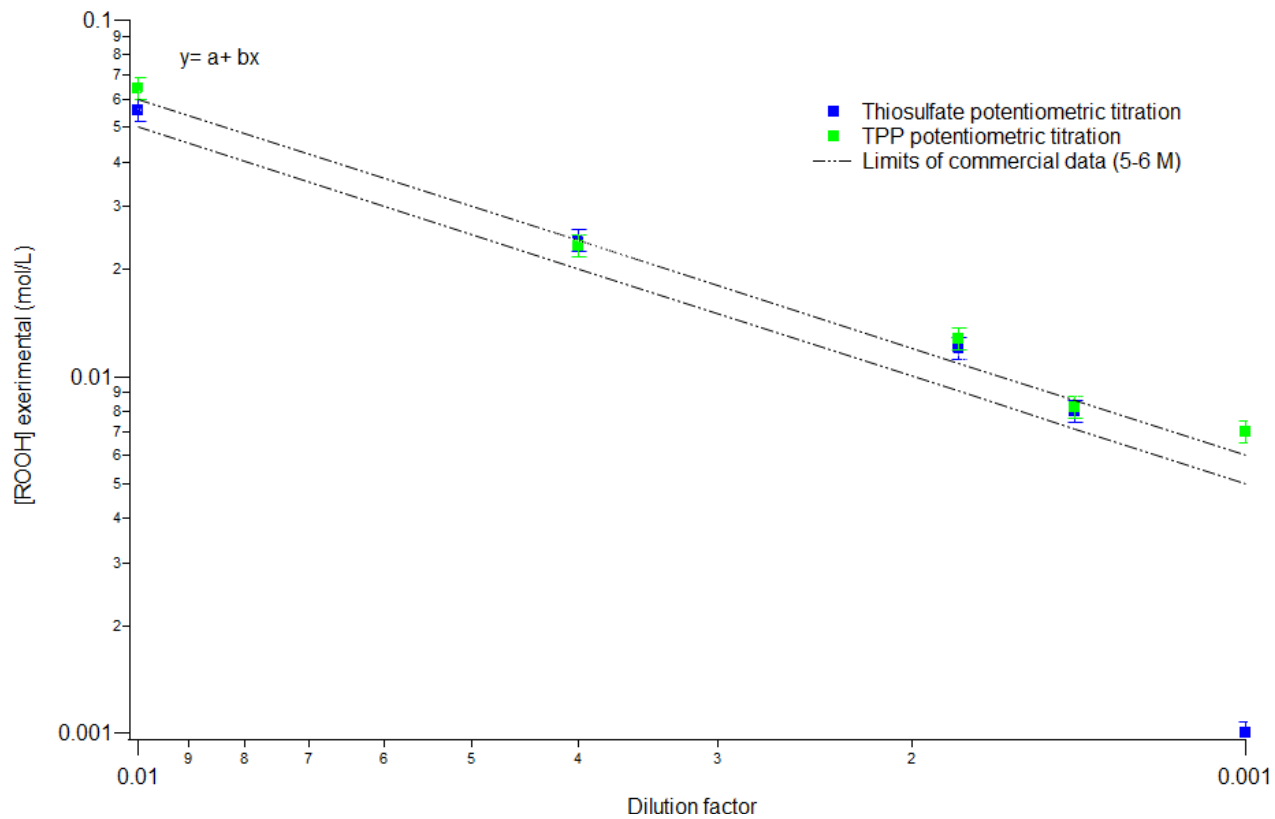


Figure 4: Comparison between experimental and theoretical (vendor certification) TBHP concentrations. Potentiometric titration with TPP and thiosulfate titrants. Theoretical concentrations (black lines 5,5-6,5M) and the corrected concentration due to repeated dilutions (red lines) are represented.

Figure 4 shows the agreement between the concentrations obtained experimentally and theoretically of the different TBHP in *n*-decane, highlighting the efficiency of the potentiometric titration method with TPP in *n*-decane for the quantification of hydroperoxides in an organic phase. ROOH concentrations as low as  $5 \cdot 10^{-5} \text{ mol L}^{-1}$  can be reached.

The same potentiometric method can be used with  $\text{Na}_2\text{S}_2\text{O}_3$  ( $0.025 \text{ mol. L}^{-1}$ ) in water. It was done in this work to see the effect of an aqueous phase on the potentiometry. The results are shown in Table 4.

Table 4: Molar concentration and titration volume of ROOH in TBHP /  $\text{C}_{10}$  after potentiometric titration with  $\text{Na}_2\text{S}_2\text{O}_3$  in water.

<b>TBHP / <math>\text{C}_{10}</math> Dilution factor</b>	<b>[TBHP / <math>\text{C}_{10}</math>] buffer (mol. <math>\text{L}^{-1}</math>)</b>	<b>[<math>\text{Na}_2\text{S}_2\text{O}_3</math> / water] (mol. <math>\text{L}^{-1}</math>)</b>	<b><math>V_{\text{titration}}</math> (mL)</b>	<b>[ROOH] (mol. <math>\text{L}^{-1}</math>)</b>
100	5.50E-02	0.025	4.44918	5.56E-02
250	2.20E-02	0.025	2.34941	2.94E-02
460	1.19E-02	0.025	1.9332	2.42E-02
550	1.00E-02	0.025	1.097	1.37E-02
1000	5.50E-03	0.025	0	0

The results of the potentiometric titrations of 4 samples of TBHP represented in Table 4 show convergent experimental and theoretical concentrations. However, only a high concentration of peroxides can be measured as the measure fails at ROOH concentration below  $1 \cdot 10^{-2} \text{ mol L}^{-1}$ . This is due to the non-miscibility observed in Figure 3.

#### *Comparison and limits of potentiometry and UV-vis spectroscopy*

Absorbance is known to poorly follow linearly Beer-Lambert law when  $\text{OD}=1$ . The results presented in Figure 5 show that the absorbance of the mixture containing  $\text{I}_3^-$  is linear with its dilution so its concentration for the sample diluted more than  $10^3$ . The linearity is shown with a correlation coefficient of 0.99751. Despite this absorbance, the concentration calculated thanks to

the potentiometric titration is less linear. It can be explained by the different uncertainty of repeated dilutions of TBHP stock solution (5.5-6.5M).

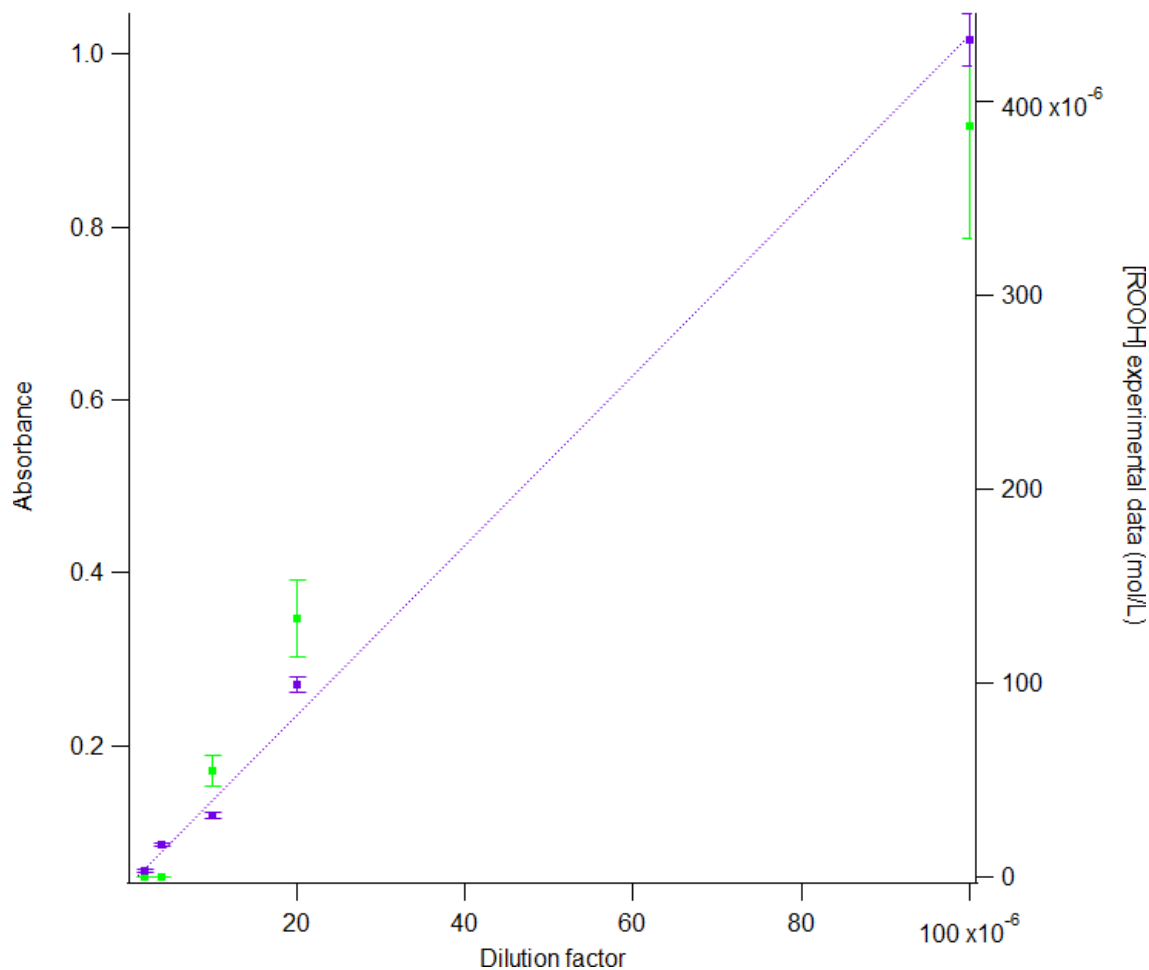


Figure 5: Comparison of absorbance of the reactive solution and the concentration obtained using potentiometric titration with TPP (green) and the Beer-Lambert law (purple).

Table 5: Experimental concentration of ROOH in TBHP / C<sub>10</sub> after potentiometric titration with TPP solution and the absorbance of the solution before the titration

<b>TBHP / C<sub>10</sub> Dilution factor</b>	<b>[ROOH] experimental TPP/C<sub>10</sub> potentiometry (mol/L)</b>	<b>Absorbance</b>
<b>1.00E-03</b>	1.97E-03	2.95E+00
<b>4.00E-04</b>	1.64E-03	2.93E+00
<b>2.00E-04</b>	9.61E-04	2.26E+00
<b>1.43E-04</b>	2.85E-04	9.80E-01

<b>1.00E-04</b>	3.87E-04	1.02E+00
<b>2.00E-05</b>	1.33E-04	2.71E-01
<b>1.00E-05</b>	5.45E-05	1.19E-01
<b>4.00E-06</b>		8.60E-02
<b>2.00E-06</b>		5.50E-02
<b>1.43E-06</b>		4.10E-02
<b>1.00E-06</b>		4.40E-02

The absorbance technique seems to be more reproducible than potentiometric since the standard deviation of each point is less than 5%. The error in the successive dilution of the stock solution of TBHP seems to be linear enough to not affect the linearity of absorbance due to Beer-Lambert law.

Results of Table 5 show that lower concentration (up to  $1.0 \cdot 10^{-6} \text{ mol L}^{-1}$ ) of TBHP can be measured experimentally compared to the potentiometric titration with TPP. We also see that a higher concentration of ROOH cannot be measured by this absorption method because the absorbance exceeds 1 for concentrations above about  $3.0 \cdot 10^{-4} \text{ mol L}^{-1}$ .

#### *Quantification of hydroperoxides using HPLC device*

Experiments consisted of the injection of 10  $\mu\text{L}$  or 40  $\mu\text{L}$  of a solution of TBHP in eluent (isooctane: absolute ethanol 95:5) inside the separative column. PDA detector records a chromatogram shown in Figure 6. Absolute ethanol was used because of its resistance to autoxidation. Isopropanol, which is commonly used in this type of experiment, has the property of easily autoxidizing which produces hydroperoxides<sup>6</sup>. A new solution of absolute ethanol was used every day and the baseline check was done each time. For these results, the baseline check showed an error  $\pm 0.497 \text{ mAU}$ . We can determine a peak if its height is at least 10 times higher than this error.

Table 6: Experimental absorption of ROOH in TBHP / iso-C<sub>8</sub> after injection in HPLC after the reactive column.

<b>TBHP / iso-C<sub>8</sub> Dilution factor</b>	<b>Volume of injection (<math>\mu\text{L}</math>)</b>	<b>Area (mAU)</b>	<b>Intensity (mAU)</b>
<b>1.00E-04</b>	10	8639.526	643.323
<b>1.00E-06</b>	40	8855.279	201.097
<b>1.00E-07</b>	40	3767.283	114.99
<b>1.00E-08</b>	40	165.309	8.2725

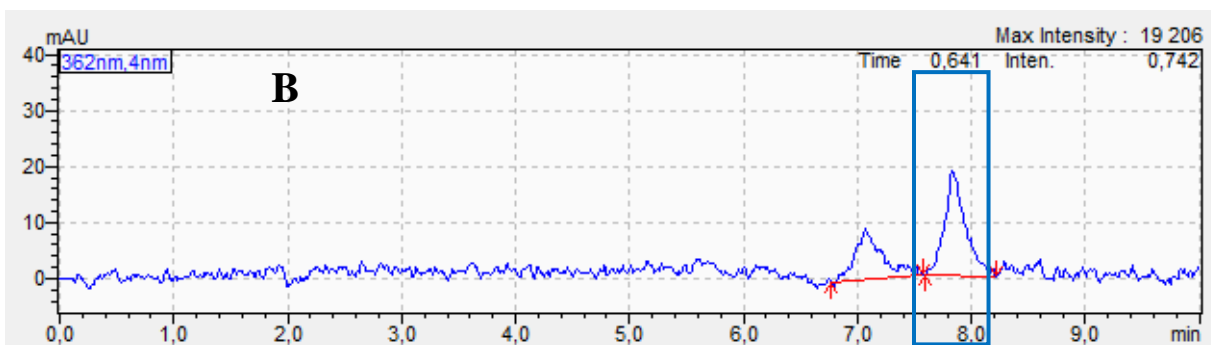
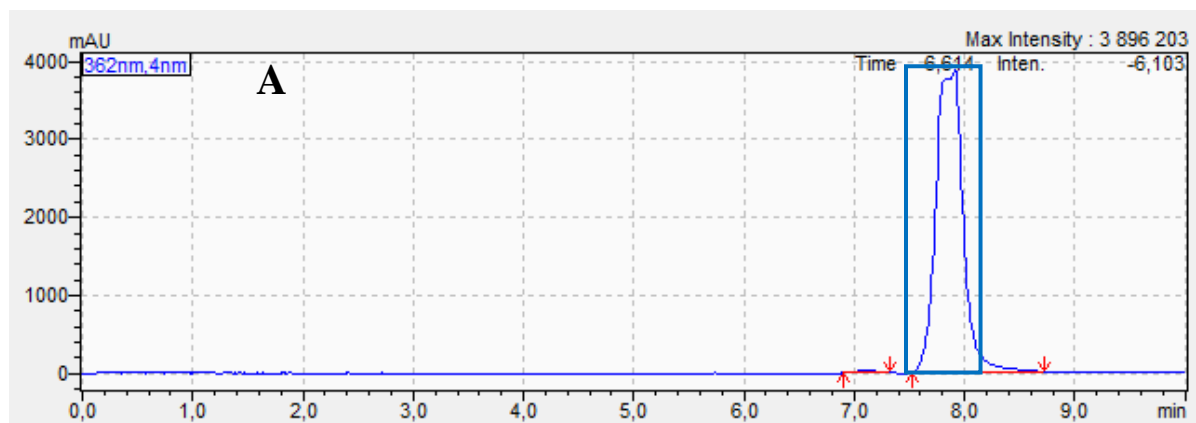
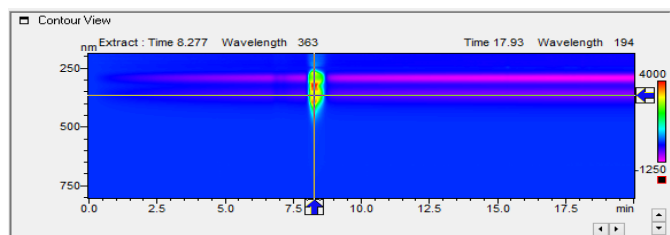


Figure 6: Chromatogram of TBHP (framed in blue) at 362nm A: diluted  $10^4$  times (10  $\mu$ L injected at 1 mL/min for 9.2 min) B: diluted  $10^8$  times (40  $\mu$ L injected at 1 mL/min for 15min)

The results presented in Figure 6 show that the HPLC set-up used can detect  $I_3^-$  which result from a reaction between TBHP and iodide. We can detect a TBHP solution diluted  $10^8$  fold (Table 6).

The presence of peaks at different retention times results from the difference of the quantity of TBHP injected in the HPLC. Moreover, this detection is reproducible, each experiment was repeated at least 2 times and the deviation is generally 1.45 mAU which is adequate. In Table 6, we can observe that the area and the height of the peaks decrease with the dilution factor. However, this decrease is not linear, which can be explained by the uncertainty of multiple dilutions of TBHP the same as the uncertainties using potentiometric quantification of hydroperoxide.

This HPLC setup quantifies ROOH in solution by determining the concentration of  $I_3^-$  using an easy and reproducible method. This method will be improved to have a stable retention time for ROOH to be able at term to isolate and quantify ROOH in a mixture of oxidized components.

## CONCLUSIONS

This work aimed to determine the detection limits of different techniques quantification of hydroperoxides in fuels. The standard ASTM method is known to be little reproducible. Colorimetry, potentiometry and UV adsorption spectroscopy were compared to quantify iodine formed during the iodometric titration of peroxides. To better determine the limits of each technique, a standard solution of TBHP in *n*-decane was diluted. Potentiometric and colorimetric titrations were performed at 70°C. These techniques are well reproducible at high concentrations. The potentiometric method gives reproducible results until a concentration of  $10^{-4}$  mol/L. Below that value, experimental uncertainties take a larger place and biased the results. On the other hand, UV-vis absorption spectroscopy at 362 nm allows to quantify iodine and indirectly hydroperoxides in a reproducible way until  $10^{-6}$  mol/L. The results obtained with the HPLC, coupled with a post-column iodometric reactor, are very promising because we can detect concentration until  $10^{-8}$  mol/L. HPLC is also interesting because of the possibility of this device to separate hydroperoxides in an aged fuel and quantify their concentration in a more complex mixture.

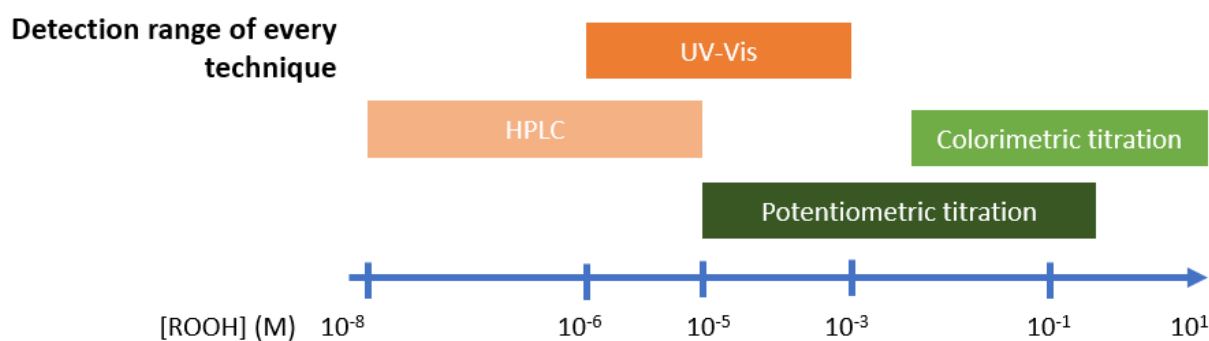


Figure 7: Detection range of each method in organic media mentioned in this study

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