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Quantification of hydroperoxides in liquid fuels: a systematic comparison of titrations and absorption methods and their coupling to HPLC

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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 fuels involve the reduction of ROOH by I^- , yielding iodine (I_2), which can be quantified by titration. The ASTM titration method of ROOH is known to be poorly reproducible and have inadequate lower detection limits and limited dynamic ranges. In this work, several analytical methods for the quantification of hydroperoxides in fuels have been systematically compared for known concentrations of ROOH: titrations of iodine with thiosulfate (ASTM D3703) and triphenylphosphine (TPP) solutions with colorimetric and potentiometric methods and quantification of iodine by UV-visible absorption. *n*-decane was used as a surrogate fuel and tert-butyl hydroperoxide as the ROOH internal standard. Our systematic study shows that the ASTM method based on colorimetric titration using thiosulfate 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 proposed in the literature, using TPP dissolved in *n*-decane as the titrant does not have this miscibility problem. Potentiometric titration is found to be more reproducible and accurate than colorimetric titration. The UV-visible absorption reaches lower detection limits. We show that the combination of the potentiometric titration of iodine with TPP and UV-visible absorption enables ROOH concentrations to be determined with low detection limits and a large dynamic range. The advantages of iodometry and UV-absorption detection methods have been used to develop a new analytical method based on their coupling in HPLC with a post-column reactor.

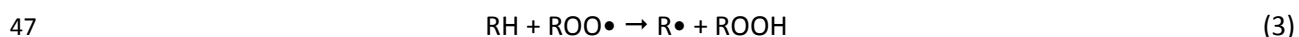
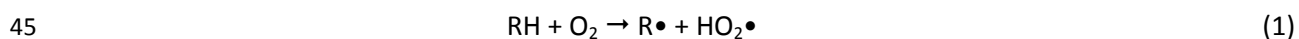
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28 **KEYWORDS:** hydroperoxides, HPLC, autoxidation, surrogate fuel

29 Introduction

30 The oxidation stability of fuels is a key factor for their use in the transport sector [1-3]. Throughout
31 their life cycle, fuels are in contact with air and are subject to significant variations in temperature
32 and pressure. For example, jet fuels can be subject to temperatures up to 150°C because of their use
33 as aircraft coolant [4]. High temperature or pressure conditions favor the liquid phase oxidation of
34 the fuel, also named autoxidation, and this phenomenon is known to change the chemical and
35 physical properties of the fuels (composition, viscosity, freezing point, ...) and ultimately leads to the
36 formation of gum and deposits [3, 5-7]. The fuel autoxidation therefore negatively affects engine
37 operation in terms of efficiency, pollutants and safety. So, it is crucial for the fuels to be oxidatively
38 stable through time. The determination of the oxidation stability of a given fuel can be quantified by
39 numerous physical and chemical criteria: induction period of the fuel, the quantity of gum deposit, or
40 the conductivity of gums [8, 9]. The main measurable chemical quantity that can be linked to the
41 oxidation stability of fuels is the total amount of hydroperoxides [10, 11].

42 Hydroperoxides (ROOH) are highly reactive species that accelerate the autoxidation of hydrocarbon
43 fuels [12, 13]. They are the main autoxidation products of hydrocarbons, up to relatively high extent
44 and are produced by the radical chain mechanism that governs the conversion of the fuel:

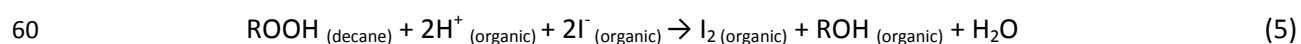


48 ROOH decomposition is the branching reaction of fuel autoxidation:

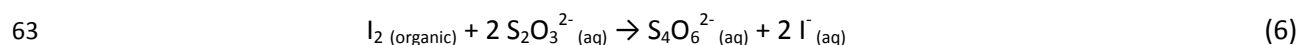


50 and is the most sensitive reaction playing a role on the hydrocarbon fuel conversion [10, 14, 15].

51 Hydroperoxides therefore favor the oxidation of the liquid fuels and are at the origin of gums and
52 deposit formation. They are also known to impair the quality of O-rings and hoses used in the fuel
53 systems [16] and adversely affects Research and Motor Octane Numbers and Cetane Number [17].
54 The quantification of these oxygenated products is therefore of primary importance. An ASTM
55 standard is used to determine the ROOH content in gasoline, diesel and aviation fuels (ASTM D3703).
56 In this standard test, the total hydroperoxide content is determined by iodometry and colorimetric
57 titration. The first step in this method is the reduction of ROOH with iodide ions from potassium
58 iodide in absolute ethanol, in the presence of acetic acid. This reaction produces a yellowish solution
59 of I₂ according to the following equation:



61 Then, the ASTM D3703 method uses thiosulfates in an aqueous medium as the titrant, that reacts
62 with I₂, according to:



64 The titration endpoint is determined by the color change of the solution. However, this titration in
65 aqueous phase is known to be poorly reproducible and have inadequate lower detection limits and
66 limited dynamic ranges [18]. Many works have been performed to determine new methods to better
67 quantify hydroperoxides, and these approaches are mainly based on reduction of ROOH with iodide
68 ions or triphenylphosphine.

69 West et al. [18] developed a method to quantify hydroperoxides in jet fuels based on the oxidation of
70 triphenylphosphine (TPP) by ROOH:

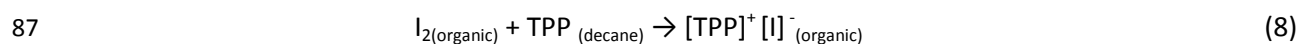


72 TPP will react with ROOH through equation (7) and the TPPO reaction product will be quantified by
73 gas chromatography (GC) with a flame ionization detection (FID). Prior studies that used the
74 measurement of TPPO only measured peroxide concentrations that were rather high (>1 mmol/L),

75 and they excluded measurements in jet fuel matrices [19]. West et al. [18] showed that their method
76 only requires a little amount of fuel (0.5 mL) diluted in toluene, has an extremely low detection limit
77 (0.002 mmol/L), a large dynamic range, and is accurate and repeatable. Their work also identified the
78 alcohol produced in (7), allowing the identification of the original hydroperoxide.

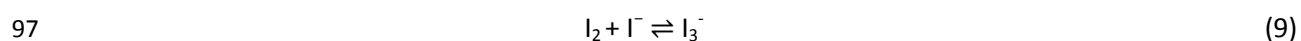
79 Recently, Roohi and Rajabi [20] proposed a water-free iodometric method, based on a visual change
80 of the color to find the titration endpoint. Triphenylphosphine (TPP) in *n*-decane solvent is used as
81 the titrant for the I₂ produced from the reaction of ROOH with iodide ions I⁻ in an acidic organic
82 medium. In the first step, ROOH is reduced with iodide ions (KI in absolute ethanol with acetic acid)
83 to produce a yellow-reddish solution as presented in equation (5).

84 For the reaction (5) to be complete, the solution must be heated at 68°C for 15 minutes. Then, TPP in
85 *n*-decane is used for the titration of I₂, producing an uncolored complex [TPPI]⁺[I]⁻ as shown in
86 equation (8).



88 As seen in equations (5) and (8), the iodine concentration can be determined from the quantity of
89 TPP added and the endpoint of titration is found when the mixture turns transparent. The method
90 proposed by Roohi and Rajabi [20] is based on colorimetry but we showed that the titration endpoint
91 can also be found using potentiometry [10, 21]. The authors reported a ROOH determination error
92 of 4% with their method but did not report detection limits. The lowest concentration mentioned is
93 0.3 wt % of 1-phenyl ethyl hydroperoxide (PEHP) in ethylbenzene ([PEHP] ≈ 6 × 10⁻³ mol/L).

94 Longobardi et al. [22] recently used a spectrophotometric method combined with iodometry to
95 analyze the peroxide value in olive oils. Their method is based on the addition of HCl-ethanol and a KI
96 solution (reaction 5) and the measurement of the absorbance of triiodide ions (reaction 9) at 350 nm.



98 They establish a calibration curve using *tert*-butylhydroperoxide from 1 to 10 m_{eq}O₂/kg
99 (approximately 4.57×10^{-4} to 4.57×10^{-3} mol/L), with a limit of detection of 0.3 m_{eq}O₂/kg
100 (approximately 1.37×10^{-4} mol/L).

101 Cullis et al. [23] determined ROOH concentration using a system based on the work of Deedler et al.
102 [24], using liquid chromatography with a post column reactor, where the iodometric reaction takes
103 place. Normal phase HPLC is used and coupled to the post column reactor fed with the necessary
104 reactants for the reduction of ROOH by I⁻ (reaction 5): sodium iodide in a mixture of iso-propanol,
105 acetic acid and water. The absorbance of I₃⁻ (reaction 9) is measured at 362 nm. The post column
106 reactor placed after the HPLC was shown to be fast and precise for the quantification of
107 hydroperoxides. It was found to detect concentrations of decane hydroperoxides as low as 0.1 µg/L
108 in *n*-decane ($\approx 5.7 \times 10^{-10}$ mol/L). Their study demonstrates that the loss of resolution in
109 chromatograms can be reduced to an acceptable level by a careful design of the post column
110 reaction system.

111 In this work, we propose a new systematic comparison of different methods of the literature for the
112 quantification of the total hydroperoxide content in an alkane fuel. Iodometric titration methods
113 (ASTM D3703 and TPP) with colorimetric and potentiometric detections of the endpoint are
114 performed. The method based on the UV-vis absorbance of triiodide ions from reactions (5) and (9) is
115 also explored for the first time in the literature and compared to iodometric titration approaches.
116 The main purposes of this study are: (1) to provide experimental data on the reproducibility of the
117 different existent methods, (2) to determine the detection range of each technique, and (3) to
118 develop a method in HPLC, with a post-column reactor and determine its detection and
119 quantification ranges. The surrogate jet fuel used in this work is *n*-decane [10] and the hydroperoxide
120 standard is *tert*-butyl hydroperoxide (TBHP).

121 I. Experimental methods

122 1. Reagents

123 Potassium iodide (KI), anhydrous, sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$; 0.1 N in aqueous solution), and
124 absolute ethanol were purchased from VWR Chemicals. Butylated hydroxytoluene (BHT) ($\geq 99\%$),
125 sodium iodide (NaI) ($>99\%$), triphenylphosphine (TPP Reagent plus[®] 99%), acetic acid ($\geq 99.8\%$),
126 *tert*-butyl hydroperoxide in *n*-decane (TBHP / C_{10} ; 5-6 mol/L) 2,2,4-trimethylpentane (isooctane; \geq
127 99.5%) were purchased from Sigma Aldrich. *n*-Decane was purchased from Acros Chemicals. To
128 evaluate the performance of the different analytical methods, TBHP/*n*-decane solutions were
129 prepared with decreasing concentrations of TBHP obtained by dilutions. The most diluted solutions
130 (10^{-6} - 10^{-9} mol/L) were prepared using the AOC-6000 autosampler of Shimadzu and the dilutions for
131 less diluted concentration (10^{-2} - 10^{-5} mol/L) were done with micropipette.

132 2. Preparation of the solution

133 The first solution used for all of the titrations and the UV-vis spectroscopy was prepared using the
134 protocol from Roohi and Rajabi [12]: 0.5 g of KI (in excess) and 0.5 mL of acetic acid in 30 mL of
135 absolute ethanol were heated for 5 min in medium agitation (400 rpm) to 68°C. Then, a 1 mL sample
136 of TBHP/*n*-decane blend of known concentration was added and heated at 68°C, at the same
137 agitation rate, for 15 min to ensure that reaction (5) was complete. The solution was kept warm
138 during the subsequent manipulations.

139 3. Colorimetric titration

140 A usual colorimetric dispositive for titration was used. When TPP is the titrant, a 25 mL burette filled
141 with a 0.08 mol/L solution of 2.1g of TPP and 0.01g of BHT in 100mL of *n*-decane is used to titrate
142 iodine and the endpoint of titration was determined when the solution became transparent. When
143 $\text{Na}_2\text{S}_2\text{O}_3$ (0.025 mol/L) aqueous solution was the titrant (ASTM D3703), the titration endpoint is also
144 reached when the solution becomes transparent. Each experiment was repeated twice.

145 4. Potentiometry

146 An automated potentiometric titrator (Mettler Toledo G10S Compact Potentiometric Titrator) ~~was~~
147 ~~used~~, equipped with a Pt indicator electrode vs. an AgCl / Ag reference electrode was used. For the
148 analysis, the TBHP/I⁻/C₁₀ solution was put in the cell stirred at 20% and two titrants were used: TPP
149 (0.08; 8.0 × 10⁻³; 8.0 × 10⁻⁴; 8.0 × 10⁻⁵ mol/L) in *n*-decane and Na₂S₂O₃ (0.025 mol/L) in water. Each
150 experiment was repeated 3 times

151 5. UV-visible spectroscopy

152 An alternative to the titration of iodine is to measure the absorbance of the solution formed in
153 equation (5). Indeed, the color is due to the formation of triiodide I₃⁻ in the presence of I₂ and I⁻ in the
154 same solution (reaction 9). In absolute ethanol, triiodide has one of its maximal absorbances at a
155 wavelength of 362 nm.

156 The absorbance depends on the dilution factor of the solution [25]. The Beer-Lambert law is used to
157 link the absorbance of I₂ and its concentration:

$$158 \qquad \qquad \qquad A = \epsilon l C \qquad \qquad \qquad (10)$$

159 A: absorbance of the solution at 362 nm

160 ϵ : molar extinction coefficient of I₂ (cm⁻¹ L mol⁻¹)

161 l: optical length of quartz spectroscopy cell (cm)

162 C: concentration of I₂ (mol L⁻¹)

163 A sensitive UV-visible double beam spectrophotometer UV-3600 Shimadzu was used to determine
164 the amount of hydroperoxides in the TBHP/C₁₀ solutions. The absorbance of triiodide formed by the
165 reduction of peroxides and the reaction of I₂ with excess iodide ions was measured at 362 nm for the
166 sample essay [26]. Measurements were done in a 1 mL quartz cell and the cell dimensions were
167 10x10x40 mm.

168

169

6. High Performance Liquid Chromatography (HPLC)

170 An HPLC (high-performance liquid chromatography) device combining a separation column in the

171 normal phase (silica) and a post-column reactor (P-cR) was adapted from the work of Cullis et al.[23].

172 A HPLC Shimadzu Nexera XR was used at a flow of 1 mL per minute of solvent (isooctane: absolute

173 ethanol / 95:5). 10 μ L of the sample TBHP/C₁₀ was injected using an autosampler through the

174 separative column. This separative column separates oxygenated products thanks to their polarity. At

175 the exit of this column, the fractions were mixed with a 10% acetic acid in absolute ethanol (0.2

176 mL/min) and a 12.5 g/L solution of NaI in absolute ethanol (0.2 mL/min). The change of iodide salt is

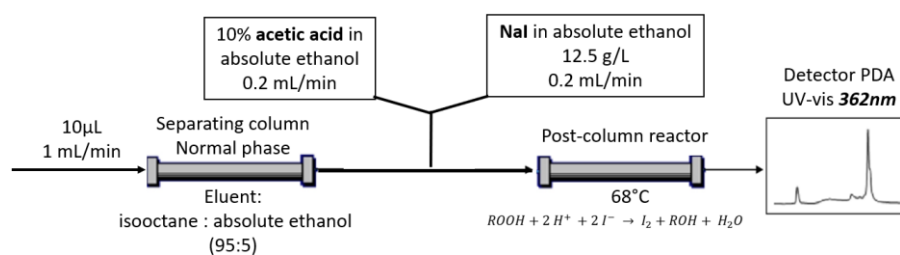
177 due to the ability of KI to obstruct the microfluidic in the HPLC device. This mixture passed through a

178 reactive column packed with 30 μ m glass beads, heated at 68°C, with a corresponding residence time

179 of 90 seconds [23]. This residence time was verified by passing toluene, throughout the system with

180 and without the post column reactor.

181 Figure 1 presents a schematic representation of the HPLC device.



182

183

Figure 1: Representation of the HPLC-P-cR device used in this work

184 A chromatogram such as the one presented in Figure 1 at 362 nm was obtained, which allows the

185 indirect hydroperoxide quantification (I_2 absorbance at 362 nm) in the sample, after calibration. It

186 can be noted that the PDA (Photo-Diode Array detector) allowed us to record chromatograms for

187 every wavelength between 190 nm and 800 nm.

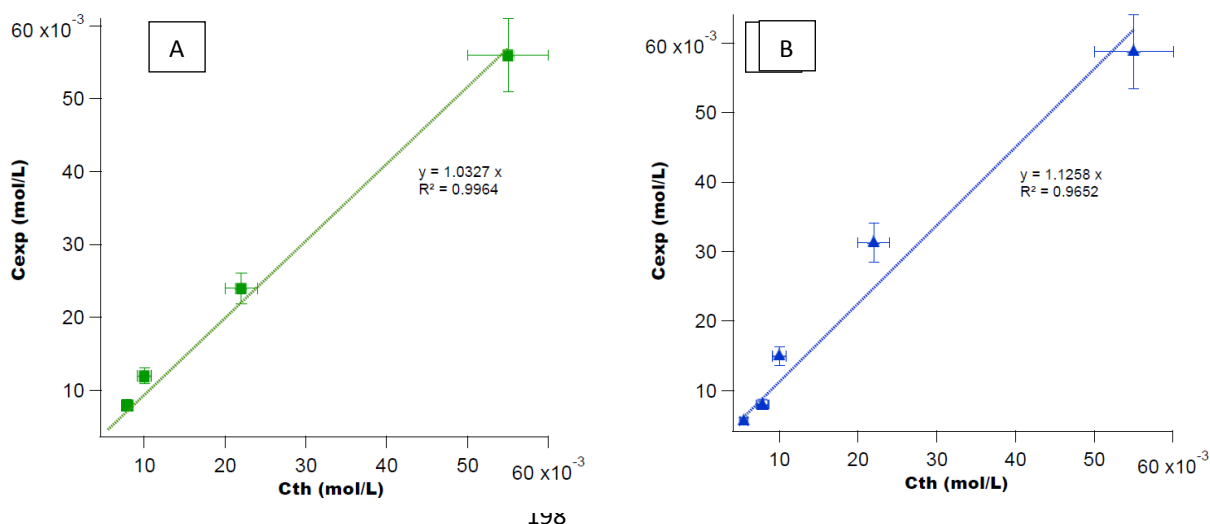
188 II. Results

189 The colorimetric method, using two different titrants, is compared to the potentiometric method, as
190 well as UV-spectrophotometric measurement and HPLC coupled to a P-cR using a PDA detector is
191 also used.

192 1. Colorimetric titration

193 TBHP concentrations were measured by the colorimetric method with two titrants: a solution of TPP
194 in *n*-decane and a solution of sodium thiosulfate in the aqueous phase. Figure 2 presents a
195 comparison between the experimental and the theoretical (vendor certifications for the stock
196 solution) concentrations of TBHP in *n*-decane.

197



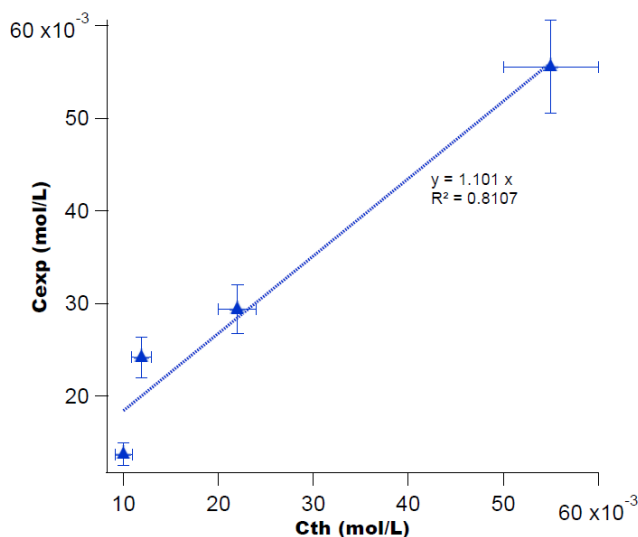
199 *Figure 2: Comparison of experimental and theoretical (commercial certifications) TBHP (ROOH)*
200 *concentrations as a function of dilution. Experimental method: colorimetric titration with different*
201 *titrants: TPP in n-decane (A) and thiosulfate in water (B).*

202 Sigma-Aldrich indicates that the concentration of TBHP in *n*-decane (our stock solution) ranges
203 between 5 and 6 mol/L. It is worth noting that their measure of the TBHP concentration is performed
204 using the thiosulfate and colorimetric method. The theoretical data used here are assumed to be the
205 dilution of a 5.5 mol/L stock solution.

206 Figure 2 shows that with $\text{Na}_2\text{S}_2\text{O}_3$, the data are scattered with a low correlation coefficient and a
207 deviation in the parity plot ($y = 1.13x$), while with the TPP titrant, the correlation coefficient is near 1
208 and the results are close to parity between theoretical and measured values. Using TPP titrant, we
209 observed that the data are well reproducible up to 6.0×10^{-2} mol/L. The detection of the titration
210 endpoint with the colorimetric method quantifies hydroperoxides for concentrations as low as $6.0 \times$
211 10^{-2} mol/L. For more diluted concentrations, the change of color at the endpoint was no longer
212 visually detectable. The upper limit of detection with this approach was found to be equal to the
213 maximum concentration that we could reach, the one of the stock solution: 5.5 mol/L.

214 2. Potentiometric titration

215 Potentiometry has been used for the determination of the titration endpoint with thiosulfate and
216 TPP titrants. The experimental results are shown in Figure 3. TPP in *n*-decane was used at different
217 concentrations (0.08 mol/L, 8×10^{-3} mol/L, 8×10^{-5} mol/L) since the volume of a droplet in the
218 potentiometer need to stay small compared to the one in the burette.



219

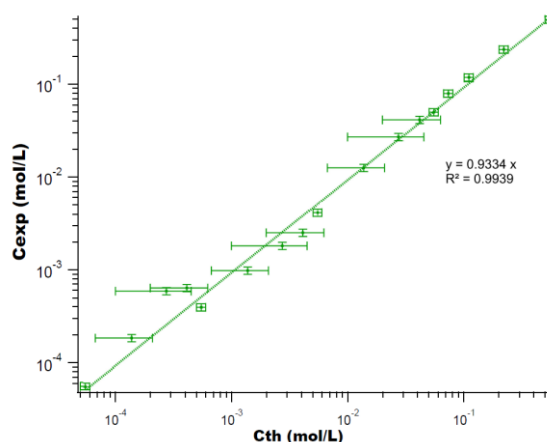
220 *Figure 3: Comparison between experimental and theoretical (vendor certification) TBHP*
221 *concentrations in n-decane. Potentiometric titration with thiosulfate.*

222 The potentiometric method using $\text{Na}_2\text{S}_2\text{O}_3$ (0.025 mol/L) in water as titrant shows a scattering of the
223 experimental points (Figure 3). The miscibility issues induced by the use of an aqueous titrant led to
224 problems. For this reason, only a limited number of dilution points were explored. These miscibility

225 issues are discussed in more details later in the text. Only a high concentration of peroxides can be
226 measured as the measure fails at ROOH concentration below 1.0×10^{-2} mol/L. Indeed, the highest
227 concentration leads to a higher immiscibility, which determine the limitation of this method.

228 Figure 4 presents the parity plot between theoretical and experimental ROOH concentrations,
229 obtained by potentiometric titration with TPP in *n*-decane.

230



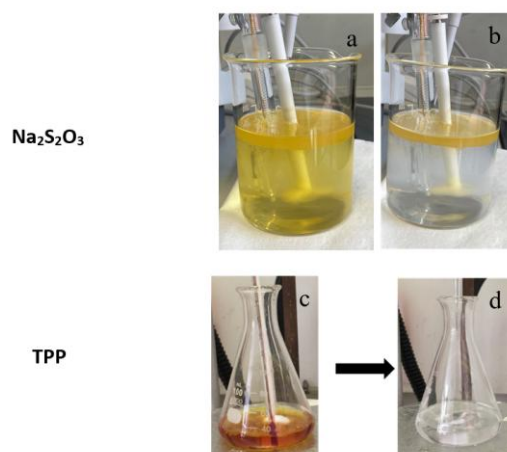
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232 *Figure 4: Comparison between experimental and theoretical (vendor certifications in x error bars)*
233 *TBHP concentrations and potentiometric titration with TPP in n-decane.*

234 Figure 4 shows a very good agreement between the theoretical and experimental concentrations for
235 the different concentrations of TBHP in *n*-decane, highlighting the efficiency of the potentiometric
236 titration method with TPP in *n*-decane in organic solutions. ROOH concentrations as low as 5.5×10^{-5}
237 mol/L can be reached and the highest concentration is 5.5×10^{-1} mol/L, which is restricted by the
238 detection limit of the potentiometer. The experimental results of the quantification of peroxides in
239 the different samples of TBHP in *n*-decane agree well (Mean relative deviation (MRD) of 32.7%) with
240 the commercial concentrations. The limit of detection of this method is considerably lower than the
241 colorimetric approach with the same reagents and titrants

242

243 The MRD obtained by colorimetric titration with TPP in *n*-decane as titrant is 14.8%, while the that
244 with sodium thiosulfate in water titrant is 20.7%. As already mentioned, the TPP in *n*-decane titrant is
245 better suited for the titration of hydroperoxydes in organic solvent because of miscibility issues when
246 aqueous thiosulfate is used in these solvents. Indeed, the main difference in the titration with an
247 aqueous phase titrant and an organic phase titrant lies in the formation of a biphasic medium which
248 brings accuracy issues in the colorimetric (and potentiometric) methods. Figure 5 illustrates the non-
249 miscibility problems observed when thiosulfate is used as the titrant. Figures 5a and 5b clearly show
250 that two phases are involved when water is involved in the titration. The colorimetric determination
251 of the endpoint of titration can even be challenging as illustrated in Figure 5c.



252

253 *Figure 5: Pictures representing the different states of colorimetric titration of iodine (before the*
254 *equivalence volume (a, c) and after (b, d) using an aqueous solution of Na₂S₂O₃ and using TPP.*

255

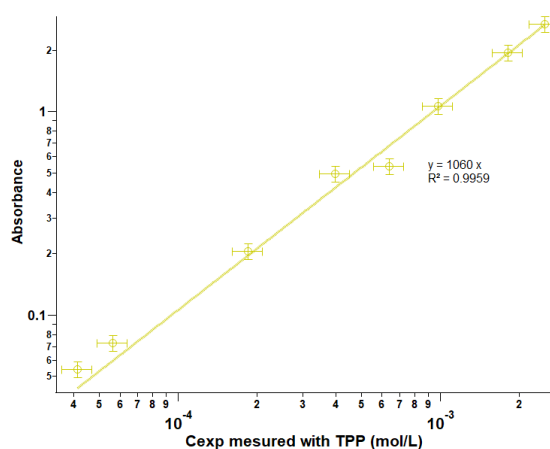
256 Potentiometry cannot be effective on two-phase solutions since the potential of the solution is not
257 homogeneous. In the potentiometric titration, the potential of the indicator electrode in relative to
258 the reference electrode is measured as a function of the titrant volume. In this titration, after adding
259 drops of titrant, the cell potential (in millivolts) is tested and recorded. The volume of titrant added is
260 reduced as the system gets closer to the endpoint of titration. The MRD of TPP with potentiometric
261 titration is 13.0%, which is lower than the detection of endpoint with color change. Note that dilution
262 uncertainties are preponderant in the reported MRD because successive dilutions increase the

263 uncertainty in the reference TBHP concentrations. We demonstrate that potentiometry with TPP in
264 *n*-decane is accurate, easy to program with an automated titrator and allows a wide range of ROOH
265 quantification.

266 It can be noted that all the colorimetric titration results show that the TBHP concentration is within
267 the upper limit of the supplier certifications (between 5 and 6 mol/L).

268 3. UV-visible spectroscopy

269 The titrations methods are based on the quantification of I₂ formed in the iodometric reaction (5) by
270 its reaction with TPP or thiosulfate. I₂ can also be directly detected by UV-vis absorption and we
271 explored this approach in this section. The absorbances at 362 nm of the diluted solutions of TBHP in
272 *n*-decane, from higher concentrations to 1 × 10⁻⁷ mol/L, and subjected to the protocol of Roohi and
273 Rajabi [20] (reaction (5)) were systematically measured and the results are presented in **Erreur !**
274 **Source du renvoi introuvable..**



275
276 *Figure 6: Absorbance at 362 nm of TBHP in n-decane solutions and the concentrations obtained using*
277 *potentiometric titration.*

278
279 Figure 6 shows that the absorbance of the mixtures is linear with concentration over 3 orders of
280 magnitude. The linearity is established with a good correlation coefficient of 0.996 with the
281 experimental concentration determined by the potentiometric titration using TPP. This reference

282 concentration was used rather than the vendor one because we demonstrated that potentiometric
283 titration with TPP is more accurate (see discussion section below) than the colorimetric thiosulfate
284 titration used by the vendor. The main uncertainties observed can be explained by the repeated
285 dilutions of TBHP stock solution (5.5-6.5M). Indeed, the errors seem to be correlated with the syringe
286 precision used for the dilution and increase with the different double or triple dilutions.

287 Using UV-vis absorbance, lower concentrations as low as 1.0×10^{-6} mol/L of ROOH can be detected
288 compared to potentiometric titration with TPP, and concentrations as low as to 1.0×10^{-5} mol/L can
289 be quantified rigorously. We also see that a higher concentration of ROOH cannot be measured by
290 this absorption method because the absorbance is above 2 for concentrations above about 5.0×10^{-3}
291 mol/L. Above 2, absorbance is known to poorly follow linearly Beer-Lambert law with a
292 spectrophotometer.

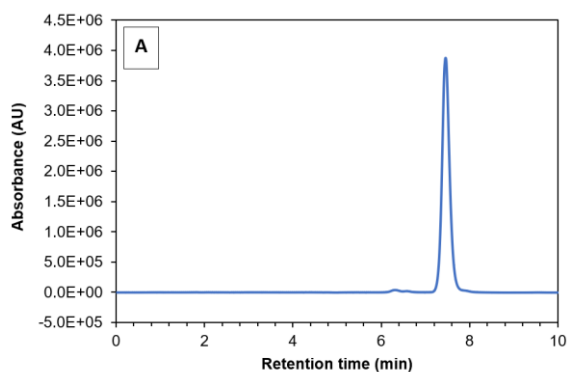
293

294 The absorbance technique seems to be more reproducible than potentiometry since the standard
295 deviation of each point is less than 9% for the lower concentrations and the mean standard deviation
296 of each point for the potentiometric titration is 13% as specified in Table S1. The error of the dilution
297 of the stock solution of TBHP seems to be linear enough to not affect the linearity of absorbance in
298 the Beer-Lambert law.

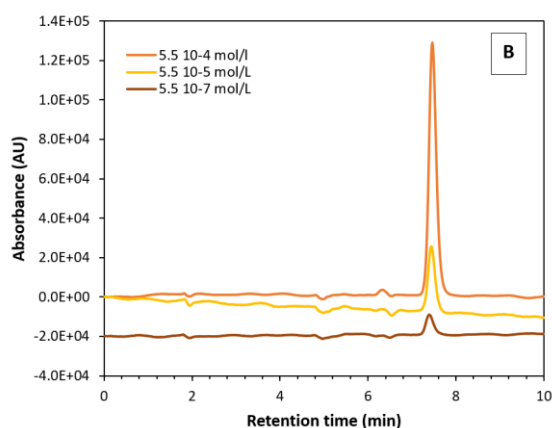
299 Spectroscopy UV-vis is a useful and easy tool widely applied in the scientific fields for its easy use and
300 the detection and the quantification limits are mostly limited by the absorbance of the solution and
301 the path length of the cell. However, with the spectroscopy method, a calibration curve is needed
302 based on a standard solution. This is different from the titration methods, which give an absolute
303 content of ROOH. The accuracy of the UV-vis method will therefore depend on the accuracy of the
304 external calibration done with a peroxide or iodine solution. The MRD increase with the
305 concentration so this method is not adapted for high concentration above 5.5×10^{-3} mol/L.

306 4. High Performance Liquid Chromatography

307 Experiments consisted in 10 μL or 40 μL injections of diluted TBHP solutions in eluent (isooctane:
308 absolute ethanol 95:5) in the HPLC chain described in Figure 1. Chromatograms that measured the
309 signal of I_3^- at 362 nm are presented in **Erreur ! Source du renvoi introuvable.**



310



311

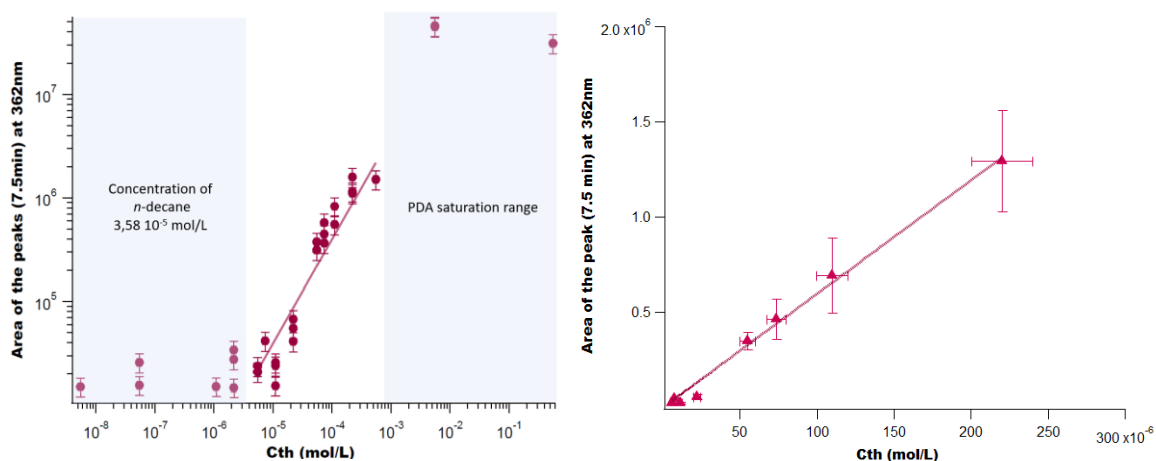
312 *Figure 7: Chromatograms of different diluted solutions injected in the HPLC-P-cR device measured at*
313 *362 nm (10 μL injected at 1 mL/min for 10 min). Chromatogram A: solid blue line: $[\text{ROOH}] = 5.5 \times 10^{-3}$*
314 *mol/L; Chromatogram B: orange line: $[\text{ROOH}] = 5.5 \times 10^{-4}$ mol/L, yellow line: $[\text{ROOH}] = 10^{-5}$ mol/L and*
315 *brown line: $[\text{ROOH}] = 5.5 \times 10^{-7}$ mol/L.*

316

317 It can be noted that in our HPLC-P-cR method, absolute ethanol was used instead of isopropanol,
318 which is commonly used in this type of experiment, because we observed that it has the property of
319 readily producing hydroperoxides, probably due to its facile autoxidation. A new solution of absolute
320 ethanol was used every day of experiments and the baseline was checked each time. For these
321 results, the baseline check showed an error ± 0.497 mAU. We can determine a peak if its height is at
322 least 10 times higher than this error. Every peak included in this work outlined this error bar.

323 The results presented in Figure 7 show that the HPLC set-up used can detect I_3^- , produced in the post-
324 column reactor (reactions (5) and (10)) for concentrations as low as 10^{-7} mol/L. The presence of
325 peaks at the retention time of 7.5 ± 0.15 min and the difference of retention times is due to the
326 quantity of TBHP injected in the HPLC. This method is reproducible: each experiment was repeated at
327 least 2 times and the deviation is generally 1.45 mAU which is adequate and the detailed mean
328 standard deviation is shown in table S4.

329 Using the THBP / *n*-decane solutions of known concentrations, we calibrated the response of the
330 HPLC-P-cR. Figure 8 presents the results obtained for ROOH concentrations ranging between 0.55
331 and 5.5×10^{-9} mol/L.



332
333 *Figure 8: Area of the peaks at 362nm as a function of the theoretical concentration of TBHP (10 μ L*
334 *injected at 1 mL/min for 10min). Left panel: all data over the full range of concentrations explored.*
335 *Right panel: zoom on the linearity zone ($R^2 = 0.9925$); triangles are the mean values of the repeated*
336 *measurements.*

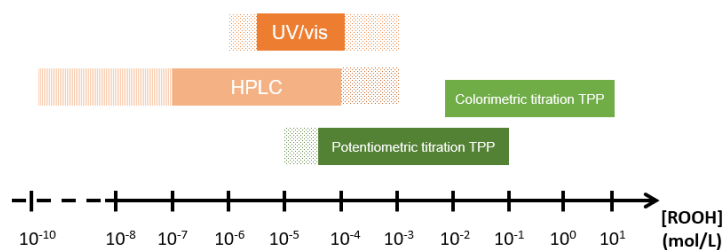
337
338 In Figure 8, we can observe that the area of the peaks decreases with the dilution factor. However,
339 this decrease is not linear and three concentration zones appear, that establish the detection and the
340 quantification limits of this technique. We observe that the response is linear from 1.0×10^{-3} to
341 5.0×10^{-5} mol/L. Above 1.0×10^{-3} mol/L, the absorbance is too high and the Beer-Lambert
342 law no longer applies. Below 5.0×10^{-5} mol/L, the hydroperoxide content in fresh *n*-decane

343 which is the diluent has to be considered. Indeed, the fresh bottle of *n*-decane was found to
344 contain 3.59×10^{-5} mol/L of hydroperoxides, from the natural aging of the liquid, and explains the
345 plateau observed for the lower concentrations. This artifact due to the presence of hydroperoxides in
346 the diluent highlights the importance of the checking for the presence of hydroperoxides in the
347 solvents used in HPLC-P-cR. Commercially available hydroperoxides are scarce and the only
348 molecules available in organic solvents were TBHP in *n*-decane and cumylhydroperoxide in cumene.
349 It is expected that dilutions with cumene to study cumylhydroperoxide would suffer from the same
350 problems because cumene is prone to autoxidation. In order to determine the potential lowest limit
351 of detection of our method, a I_2 solution in absolute ethanol mixed with NaI and acetic acid was
352 injected in the device after removing the 2 columns (analytic and P-cR). The lowest detection limit of
353 I_3^- at 362nm in the PDA cell was determined to be 2.5×10^{-11} mol/L.

354 Figure 8 also shows that concentrations up to 0.55 mol/L can be detected until the saturation of the
355 detector occurs. It can be noted that in Figure 8, the absorbances are plotted as a function of the
356 theoretical concentration, and not the one from potentiometric titration, because it was not possible
357 to quantify [ROOH] with potentiometric titration for the lowest concentration range (below 5.5×10^{-5}
358 mol/L).

359 The HPLC-P-cR setup quantifies ROOH in solution by determining the concentration of I_3^- using an
360 easy and reproducible method, for a large range of concentrations. In addition, this method has the
361 potential to separate and quantify different ROOH structures in a mixture of oxidized components.
362 Adsorption chromatography is well suited for oxidized fuels, since it leads to the formation of
363 oxygenated low molecular mass products. Since the analytical column is normal phase, an efficient
364 separation of polar and non-polar fractions can be achieved. Hydroperoxides are very polar
365 molecules so these molecules will be well retained and elute at the end of each analysis.

366 An overview of the different methods explored in this work for the quantification of hydroperoxides
367 is given in Figure 9, along with their detection and quantification limits.



368

369 *Figure 9: Detection limits and quantification range of each techniques | Dotted part are detection*
 370 *limits and plain part are quantification range*

371 From Figure 9, it appears that the titration methods with TPP in *n*-decane allow ROOH to be detected
 372 and quantified for the higher concentration ranges. The use of potentiometry enable the measure of
 373 considerably lower concentrations compared to colorimetry. ROOH quantifications based on the
 374 absorbance of I_3^- ions at 362 nm in a standard UV-vis spectrometer and in the HPLC-P-cR chain, are
 375 efficient for the lowest ROOH concentration ranges. The use of a post-column in HPLC is found to
 376 have the larger detection range among all the methods. The quantification of traces of ROOH,
 377 meaning an extension of the lower limit of quantification, require the use of solvent free of
 378 hydroperoxides and it should be pointed out that for HPLC, as for UV-vis used in the latter method,
 379 an external calibration is required to obtain the iodine response, which was not necessary with the
 380 potentiometric titrations. It may be noted that the detection limits presented here are the
 381 intrinsic values of the methods and that the upper detection limit could be extended by
 382 sample dilution. However, as noted several times in the manuscript, successive dilutions
 383 inevitably lead to an increase in measurement uncertainty.

384 Conclusion

385 This work compared the reproducibility and detection limits of different techniques of
 386 hydroperoxides quantification in fuels. The change of color and potential in iodometric titrations and
 387 the UV-Vis absorbance of the solutions were monitored during different methods. A commercial
 388 solution of TBHP in *n*-decane was used as standard and diluted. Potentiometric and colorimetric

389 titrations showed to be reproducible at high concentrations, especially when using TPP as titrant in
390 an organic phase. The use of thiosulfate in an aqueous phase as a titrant is poorly reproducible and
391 explains the limitations of this ASTM standard method. The potentiometric method gives
392 reproducible results until a concentration of 10^{-4} mol/L. Below that value, experimental uncertainties
393 take a larger place and biased the results. Spectroscopy using UV-vis absorption at 362 nm is able to
394 quantify hydroperoxides in a reproducible way until 10^{-6} mol/L. The results obtained with the new
395 HPLC coupled with a post-reactor column for the iodometric reduction of hydroperoxides are very
396 promising because concentration as low as 10^{-11} mol/L can be detected and ROOH were quantified
397 for concentrations as low as 10^{-7} mol/L. HPLC is also interesting thanks to the possibility of this device
398 to separate hydroperoxides in an aged fuel and quantify their concentrations in a more complex
399 mixture.

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