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1 A fast and efficient method for the analysis of α -dicarbonyl 2 compounds in aqueous solutions: development and application

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11 Chromatography

12 Abstract.

13 Among the highly oxygenated species formed *in situ* in the atmosphere, α -dicarbonyl compounds are the most reactive species,
14 thus contributing to the formation of secondary organic aerosols that affect both air quality and climate. They are ubiquitous
15 in the atmosphere and are easily transferred to the atmospheric aqueous phase due to their high solubility. In addition, α -
16 dicarbonyl compounds are toxic compounds found in food in biochemistry studies as they can be produced endogenously
17 through various pathways and exogenously through the Maillard reaction. In this work, we take advantage of the high reactivity
18 of α -dicarbonyl compounds in alkaline solutions (intramolecular Cannizzaro reaction) to develop an analytical method based
19 on high performance ion chromatography. This fast and efficient method is suitable for glyoxal, methylglyoxal and
20 phenylglyoxal which are detected as glycolate, lactate and mandelate anions respectively, with 100% conversion at pH > 12
21 and room temperature for exposure times to hydroxide ranging from 5 minutes to 4 h. Diacetyl is detected as 2,4-dihydroxy-
22 2,4-dimethyl-5-oxohexanoate due to a base catalysed aldol reaction that occurs before the Cannizzaro reaction. The analytical
23 method is successfully applied to monitor glyoxal consumption during aqueous phase HO \cdot oxidation, an atmospherically
24 relevant reaction using concentrations that can be observed in fog and cloud water. The method also reveals potential analytical
25 artifacts that can occur in the use of ion chromatography for α -hydroxy carboxylates measurements in complex matrices due
26 to α -dicarbonyl conversion during the analysis time. An estimation of the artifact is given for each of the studied α -hydroxy
27 carboxylates. Other polyfunctional and pH-sensitive compounds that are potentially present in environmental samples (such
28 as nitrooxycarbonyls) can also be converted into α -hydroxy carboxylates and/or nitrite ions within the HPIC run. This shows
29 the need for complementary analytical measurements when complex matrices are studied.

30 1. Introduction

31 Fast and efficient analysis of small α -dicarbonyl compounds is essential for atmospheric chemistry, biochemistry and food
32 chemistry as these compounds are highly reactive, toxic and ubiquitous in the environment. In the atmosphere, α -dicarbonyl
33 compounds such as glyoxal, methylglyoxal and diacetyl, are primary and secondary highly reactive compounds. They are
34 abundant in the gas, aqueous, and particulate phases. They are produced by the gas-phase oxidation of anthropogenic aromatic
35 hydrocarbons (Volkamer et al., 2001; Calvert et al., 2002; Sato et al., 2012), biogenic terpenes and isoprene (Saunders et al.,
36 2003; Miller et al., 2016; Wennberg et al., 2018) and can potentially originate from marine biogenic fatty acids (Chiu et al.,
37 2017). Alpha-dicarbonyl compounds have a high effective Henry's law constant driven by hydrate (gem-diol) formation
38 (Boreddy and Hoffmann, 1988; Sander, 2015). Therefore, although highly volatile, they partition into the atmospheric aqueous
39 phase (liquid water droplets and/or wet aerosols), where they undergo a specific reactivity that is very different from that in
40 the gas phase, the latter being dominated by direct photolysis. Among the most ubiquitous α -dicarbonyls, glyoxal and
41 methylglyoxal aqueous-phase reactivity leads to the formation of low- or semi-volatile compounds: they can form oligomers
42 *via* hemiacetalisation (Loeffler et al., 2006; Avzianova and Brooks, 2013), acid-catalysed aldol condensation (de Haan et al.,
43 2009a; Nozière et al., 2010) and/or photo-oxidation (Tan et al., 2009; Lee et al., 2011; Zhao et al., 2012). They can be oxidised
44 to oxalic acid, the dominant dicarboxylic acid in the atmosphere, often observed as the most abundant organic species in
45 particle matter (Carlton et al., 2007; Tan et al., 2010; Boreddy and Kawamura, 2018). Although the reactivity of diacetyl in
46 the atmosphere has been much less studied, it has been shown to form light-absorbing products *via* aqueous-phase reactions
47 with ammonia and/or amines, like glyoxal and methylglyoxal (de Haan et al., 2009b; Kampf et al., 2012; Powelson et al.,
48 2014; Laskin et al., 2015; Li et al., 2021; Jimenez et al., 2022; Zhang et al., 2022; Faust et al., 1997; Kampf et al., 2016; Grace
49 et al., 2020). From all these studies, α -dicarbonyl compounds are likely important atmospheric precursors of Secondary
50 Organic Aerosols (SOA) that affect both air quality and climate.

51
52 Alpha-dicarbonyl compounds are also of major interest in food and biochemistry due to their toxicity: they can be generated
53 endogenously and exogenously (Lange et al., 2012). In food, the Maillard reaction occurs between reducing sugars and amino
54 acids and produces various α -dicarbonyl compounds including glyoxal, methylglyoxal and diacetyl (Cha et al., 2019). Previous
55 studies reveal that α -dicarbonyls are also precursors of heterocyclic flavour chemicals in the Maillard reaction (Wang and Ho,
56 2012; Jiang et al., 2013); α -dicarbonyl compounds have been found in fermented food, dairy products and beverages (Degen
57 et al., 2012; Wang et al., 2017; Kim et al., 2021). *In vivo*, glyoxal can be formed through various pathways, including
58 autoxidation of carbohydrates and ascorbate, degradation of glycated proteins and lipid peroxidation (Lange et al., 2012). In
59 addition, α -dicarbonyl compounds can modify proteins and form advanced glycation end products, which are related to the
60 development of many chronic diseases (Lange et al., 2012; Poulsen et al., 2013; Svendsen et al., 2016; Ansari et al., 2018).
61 Finally, α -dicarbonyl compounds are cytotoxic and inhibit the function of human enzymes responsible for DNA repair
62 (Amoroso et al., 2013).

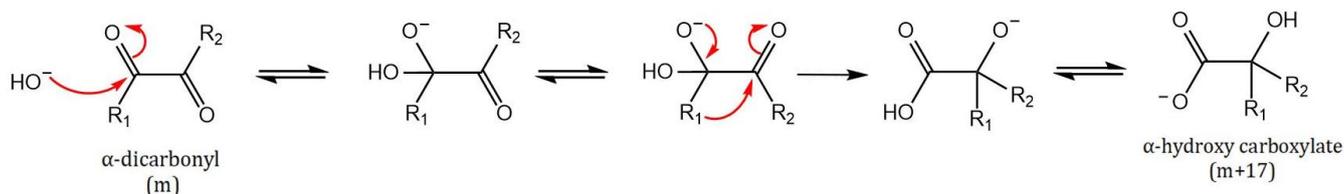
64 Due to their high reactivity, quantitative measurements of α -dicarbonyl compounds are challenging in aqueous samples.
65 Indeed, carbonyl compounds promptly hydrate in water, forming gem-diols that are not detectable by spectrophotometry.
66 Except for diacetyl which can be detected by UV-Visible absorption due to its low hydration in the aqueous phase (Faust et
67 al., 1997; Zuman, 2002), there are currently no methods for the direct detection and quantification of these compounds in the
68 liquid phase. The most widely employed methods for the analysis of these compounds use amino trapping reagents to convert
69 α -dicarbonyl compounds into more stable imine derivative chromophores and/or fluorophores that can be quantified by High-
70 Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC) coupled to UV detection, fluorimetry or Mass
71 Spectrometry (MS) (see SI1). The 3 most common amino trapping reagents ((2,3,4,5,6-pentafluorobenzyl)hydroxylamine
72 (PFBHA), 2,4-dinitrophenylhydrazine (DNPH) and o-phenylenediamine) trap α -dicarbonyl compounds to produce oximes,
73 hydrazones and quinoxalines, respectively. However, amino trapping reagents show some disadvantages for the analysis of α -
74 dicarbonyl compounds. Undesirable formation of mono-derivatives has been reported (Nakajima et al., 2007). Moreover,
75 double derivatisation is generally slower than single derivatisation and leads to the formation of three or four isomers
76 (depending on the symmetry of the α -dicarbonyl compound). For these reasons, derivatisation using a di-amino compound
77 such as o-phenylenediamine appears to be more suitable for efficient trapping of α -dicarbonyl compounds. Furthermore,
78 although some of the amino trapping reagents are very expensive, they are used in large excess to favour the derivatisation
79 reaction. The trapping reagents must then be accurately separated from the imine derivatives for quantification. In addition,
80 the pH of the reaction must be carefully controlled because water elimination in the derivatisation reaction is acid-catalysed
81 but is also reversible under acidic conditions (Layer, 1963). A too low pH, the reaction can also lead to competitive aldol
82 condensation of α -dicarbonyl compounds. Finally, imine derivatives can be poorly water-soluble, affecting the derivatisation
83 in the case of aqueous solutions.

84

85 In this work, a specific method based on High-Performance Ion Chromatography (HPIC) was developed for a simple, fast and
86 accessible analysis of α -dicarbonyl compounds in aqueous solutions. The method has the advantages of high selectivity, high
87 sensitivity, and simple equipment requirement (Chen et al., 2005). The analytical conditions and performances set by Chen et
88 al. (2005) for glyoxal were revisited and complemented by MS detection. The method was extended to other α -dicarbonyl
89 compounds. Methylglyoxal and diacetyl were selected as they are ubiquitous in the environment, and phenylglyoxal was
90 chosen as a proxy for aromatic α -dicarbonyl compounds formed in atmospheric SOA. The developed method was successfully
91 applied to glyoxal monitoring during its aqueous phase HO \cdot -oxidation under atmospherically realistic conditions. The paper
92 discusses the advantages of the method as well as potential analytical artifacts that can occur using HPIC for α -hydroxy
93 carboxylate measurements in complex aqueous environmental samples.

94 2 Materials and methods

95 The method is based on converting α -dicarbonyl compounds into α -hydroxy carboxylates in the presence of a strong base *via*
96 a benzilic acid rearrangement, an intramolecular disproportionation that derives from the Canizzaro reaction (Selman, S., &
97 Eastham, 1960; Fratzke and Reilly, 1986; Burke and Marques, 2007). The reaction consists of HO^- addition, C-C rotation,
98 carbanion migration, and proton relay towards the produced anions (Fig. 1). The formed α -hydroxy carboxylates can then be
99 easily detected using HPIC coupled with conductivity detection and/or mass spectrometry. The chemical conversion can be
100 performed either by addition of a strong base in the sample before analysis, or into the HPIC system using the mobile phase
101 with an appropriate NaOH concentration as reagent. In the latter, the measurement of α -dicarbonyl compounds can be
102 performed without any conversion process before the analysis and thus allows for direct measurement, but with significantly
103 lower performances than the former, as shown in the results.



105 **Fig. 1 – General scheme of the chemical conversion of α -dicarbonyl compounds to α -hydroxy carboxylates in an alkaline solution**
106 **(adapted from Yamabe et al., 2006). Each step is reversible, except for the carbanion migration (3rd step), which is the rate**
107 **determining step.**

108 2.1 Instrumental setup and operating conditions

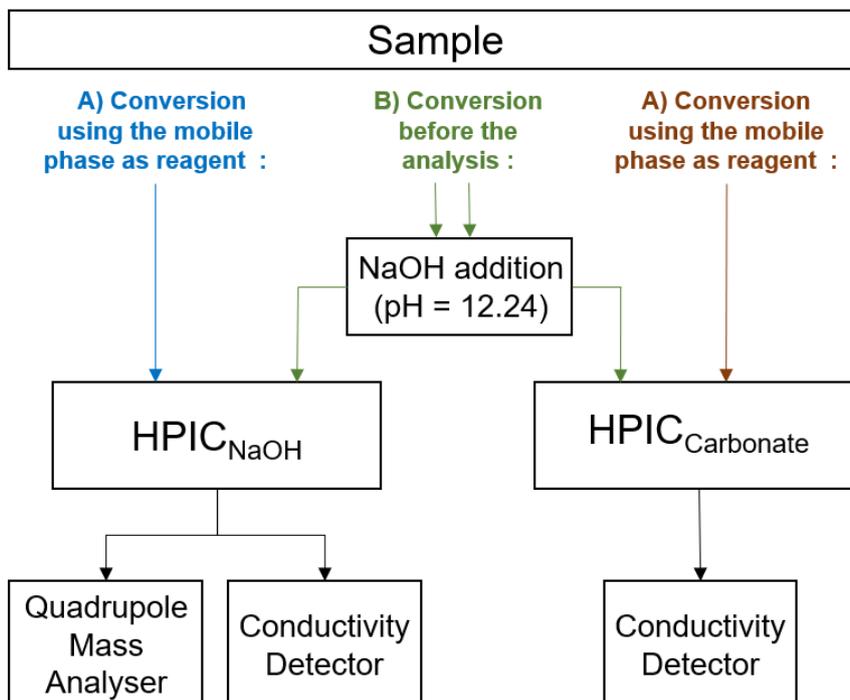
109 Carboxylates were analysed and quantified by two HPIC systems equipped with different mobile phases. The first one was a
110 Dionex ICS-3000 High-Performance Ion Chromatograph driven by Chromeleon® software. The HPIC was coupled with a
111 Dionex CD25 Conductivity Detector (CD) in parallel with a Dionex surveyor MSQ mass spectrometer. In each analysis, the
112 samples were automatically injected using a 100 μL injection loop into a Dionex IonPac AG11-HC precolumn (4 x 50 mm)
113 connected to a Dionex IonPac AS11-HC column (4 x 250 mm) thermostated at 30 $^{\circ}\text{C}$ with a particle size of 9 μm . The HPIC
114 was equipped with a Dionex ACRS 500 chemical suppressor with a constant flow of 50 mM H_2SO_4 at 3.5 mL min^{-1} . The MSQ
115 mass spectrometer was operated in electrospray ionization (ESI) negative mode under a desolvation gas flow of 6 L min^{-1} at
116 600 $^{\circ}\text{C}$ and a capillary voltage of 3.5 kV. The sample cone voltage was set at 35 V and carboxylates were detected and
117 quantified as their deprotonated molecules ($[\text{M}-\text{H}]^-$) with simultaneous full scan and Selected Ion-Monitoring (SIM) for the
118 targeted α -hydroxy carboxylates. In each sample, 1 mg L^{-1} of valeric acid was employed as an internal standard. The injection
119 volume was 100 μL and the flow rate was 1 mL min^{-1} . The mobile phase consisted of an aqueous NaOH solution degassed
120 with purified He and kept under N_2 atmosphere during the analyses. The separation was performed by isocratic elution. Several
121 tests were performed using various NaOH concentrations in the mobile phase, ranging from 17.5 to 45 mM (pH range = 12.24
122 - 12.65), to accelerate the conversion of α -dicarbonyl compounds within the chromatographic column. This system is further
123 designated as $\text{HPIC}_{\text{NaOH}}$.

124

125 The second HPIC system used comprised a less alkaline mobile phase to study the effect of the mobile phase pH on the
126 analytical performances. For this purpose, a 761 Compact HPIC System from Metrohm AG was employed including a
127 Metrosep A Supp 4 (4 x 250 mm) column with a particle size of 5 μm . The system comprised a conductivity detector and a
128 suppressor module running at a constant flow of 0.5 mL min^{-1} of 20 mM H_2SO_4 . Samples were manually injected using a 20
129 μL injection loop. The entire HPIC system was thermostated at 20 $^\circ\text{C}$. At a flow rate of 1 mL min^{-1} , an isocratic method with
130 a single eluent consisting of an aqueous solution of 2 mM NaHCO_3 and 1.3 mM Na_2CO_3 (pH = 10.14) was used. This system
131 is further designated as $\text{HPIC}_{\text{carbonate}}$.

132 2.2 Chemicals and sample preparations

133 All chemicals were commercially available and used as supplied as listed in SI2, except for α -nitrooxyacetone that was
134 synthesised following a protocol described in SI3. Conversions of α -dicarbonyl compounds in alkaline solutions were
135 performed either into the HPIC system using the mobile phase as reagent (further designated as method A), or before analysis
136 in amber vials by addition of 17.5 mM NaOH followed by manual shaking for 10 seconds (further designated as method B),
137 as summarised in Fig. 2. The analyses were systematically complemented with blanks including the UHQ water used for
138 dilutions, the NaOH solutions used for the conversion reactions and valeric acid as internal standard. Conversion kinetics
139 experiments were performed using $\text{HPIC}_{\text{NaOH}}$ by repeatedly sampling the same vials after an initial NaOH addition (at pH =
140 12.24) and manual shaking for 10 seconds.



141

142 **Fig. 2 – Summary diagram of the various analytical conditions investigated. Samples were converted either using the mobile phase as reagent**
143 **(method A) or before the analysis (method B) and analysed either by HPIC_{NaOH} or by HPIC_{Carbonate}.**

144 **2.3 Aqueous photooxidation**

145 The study of glyoxal HO \cdot -oxidation in the aqueous phase was performed applying the analytical method developed. The
146 reaction was performed in a 450 mL batch reactor equipped with Pyrex double wall thermostated at 25°C with ethylene glycol
147 and covered by a quartz lid. The reactor was irradiated by a Xenon arc lamp 1000 W (LOT Quantum Design) to mimic the
148 solar irradiance (see SI4). Radiations below 290 nm were filtered by an AM1.5 standard filter (ASTM 892). Homogeneity of
149 the solution was ensured by magnetic stirring.

150

151 HO \cdot radicals were generated by H₂O₂ photolysis. In this experiment, H₂O₂ was monitored by UHPLC-UV analysis (see SI5),
152 pH and dissolved O₂ were continuously monitored in the solution using specific probes (C3020, Consort, and FDO925, WTW,
153 respectively). Aliquots were sampled at regular times in amber vials, which quenched the photolysis reaction. Glyoxal and
154 carboxylate products were analysed from the samples using HPIC_{NaOH}. For glyoxal analysis, the samples were five times
155 diluted and converted before analysis using method B, as described in section 2.2. The photooxidation experiments were
156 performed at a glyoxal initial concentration of 100 μ M, about twice higher than the maximum amounts of glyoxal or
157 methylglyoxal observed in clouds and fogs (Li et al., 2020; Ervens et al., 2013). The initial H₂O₂ concentration (1 mM) was
158 chosen to favor by more than 80 % the HO \cdot reaction towards glyoxal over its reaction with H₂O₂. A series of control
159 experiments were performed using HPIC_{NaOH}: i) dark reaction of H₂O₂ with glyoxal (previously reported by Zhao et al., 2012),
160 ii) direct photolysis of glyoxal (without H₂O₂), and iii) direct photolysis of H₂O₂ (without glyoxal).

161 **3 Results and discussions**

162 **3.1 Method development**

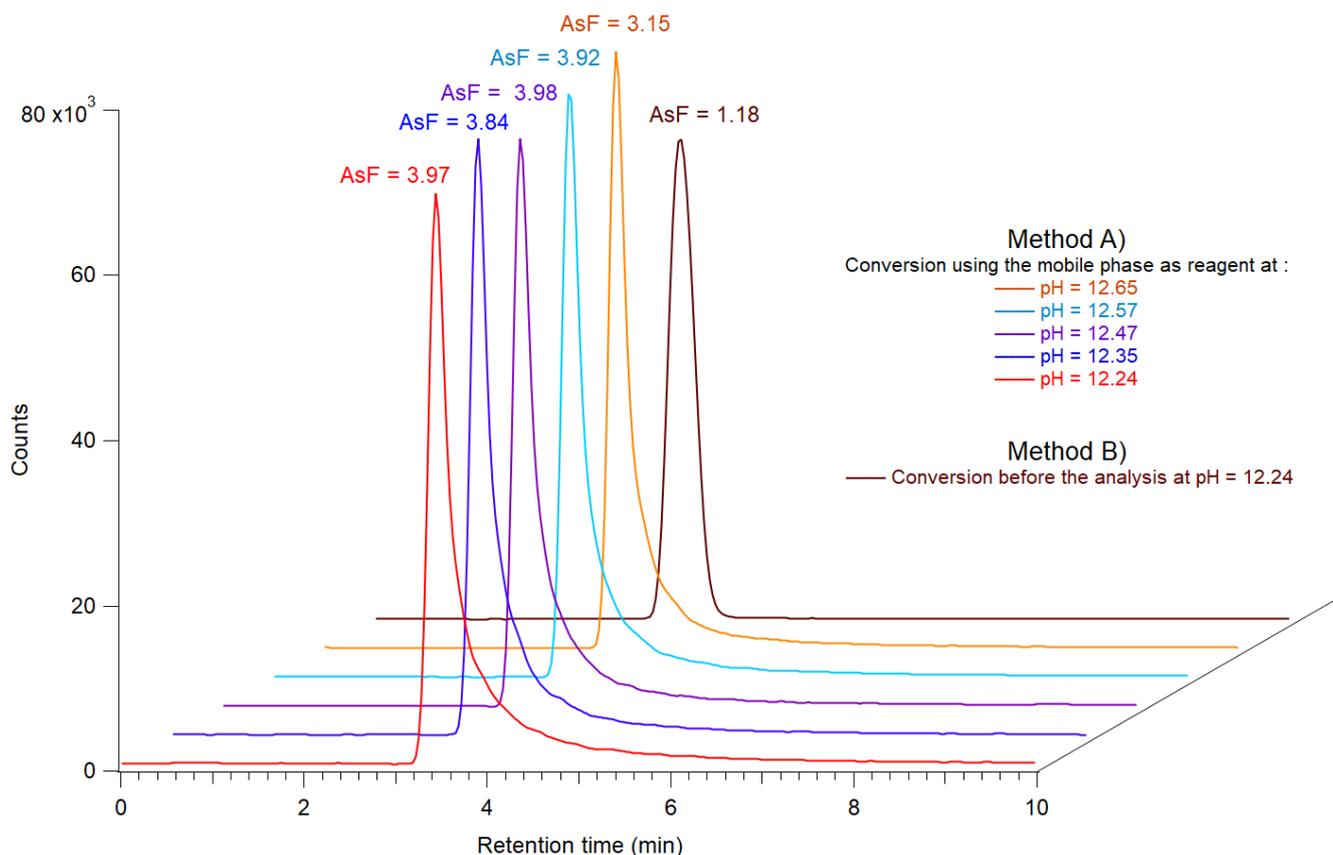
163 Conversion of α -dicarbonyl compounds into α -hydroxy carboxylates through benzilic acid rearrangement is an irreversible
164 reaction occurring in alkaline medium (Fig. 1) that is highly sensitive to pH (Selman, S., & Eastham, 1960; Gill, 1991; Yamabe
165 et al., 2006; Wang, 2010). The influence of pH on the analytical method (using HPIC_{carbonate} and HPIC_{NaOH}) was first studied
166 in details for glyoxal (in sub-section 3.1.1), then it was applied to methylglyoxal, phenylglyoxal and diacetyl (sub-section 3.1.2).
167 For each compound, the conversion kinetics were investigated, as well as their conversion proportions (sub-section 3.1.3). The
168 analytical performances of the method are finally presented in sub-section 3.1.4.

169 **3.1.1 Optimisation of glyoxal analysis**

170 Using method A, no conversion of glyoxal to glycolate was observed using HPIC_{carbonate} in contrast to the results obtained
171 using HPIC_{NaOH}. As shown in Fig. 3 a strong glycolate signal was observed using a highly alkaline mobile phase. These results

172 are in very good agreement with the kinetic model of Fratzke and Reilly (1986) which predicts complete conversion of glyoxal
173 in the analysis timescale (10 min) at pH = 12.24 (conversion half-life of glyoxal < 10 s, see SI6). Glyoxal measurements can
174 therefore be performed using HPIC_{NaOH} without any conversion process before the chromatographic analysis, thus allowing
175 its direct measurement. However, under these conditions, glycolate quantification was complicated by low-quality
176 chromatograms due to large peak tailing (Fig. 3). This phenomenon can be explained by the reaction medium successive
177 conditions encountered by the sample in the HPIC. The reaction started as soon as the sample was in contact with the mobile
178 phase in the injection loop. When the sample entered the HPIC column, the early formed glycolate molecules were retained,
179 while the unconverted non-ionic glyoxal molecules were not retained, but were continually converted during the elution
180 process. The reaction was promoted by the exchangeable counterions of the stationary phase. The reaction then also took place
181 at the outlet of the column and up to the chemical suppressor where the pH was lowered thus stopping the reaction. Ranging
182 from 17.5 to 45 mM NaOH concentration as HPIC_{NaOH} mobile phase (pH range = 12.24 – 12.65) the asymmetry factor slightly
183 decreased (Fig. 3) as the reaction rate and elution were accelerated. Nevertheless, the glycolate peak asymmetry factor was
184 much lower and closer to 1 using method B and HPIC_{NaOH} (Fig. 3).

185 Using method B and HPIC_{carbonate}, a glycolate signal was also observed showing the irreversibility of the reaction. However,
186 the strong OH⁻ signal due to the high NaOH concentration in the sample and the unsuitable suppressor conditions overlapped
187 the glycolate signal and resulted in a low-quality chromatogram (not shown).

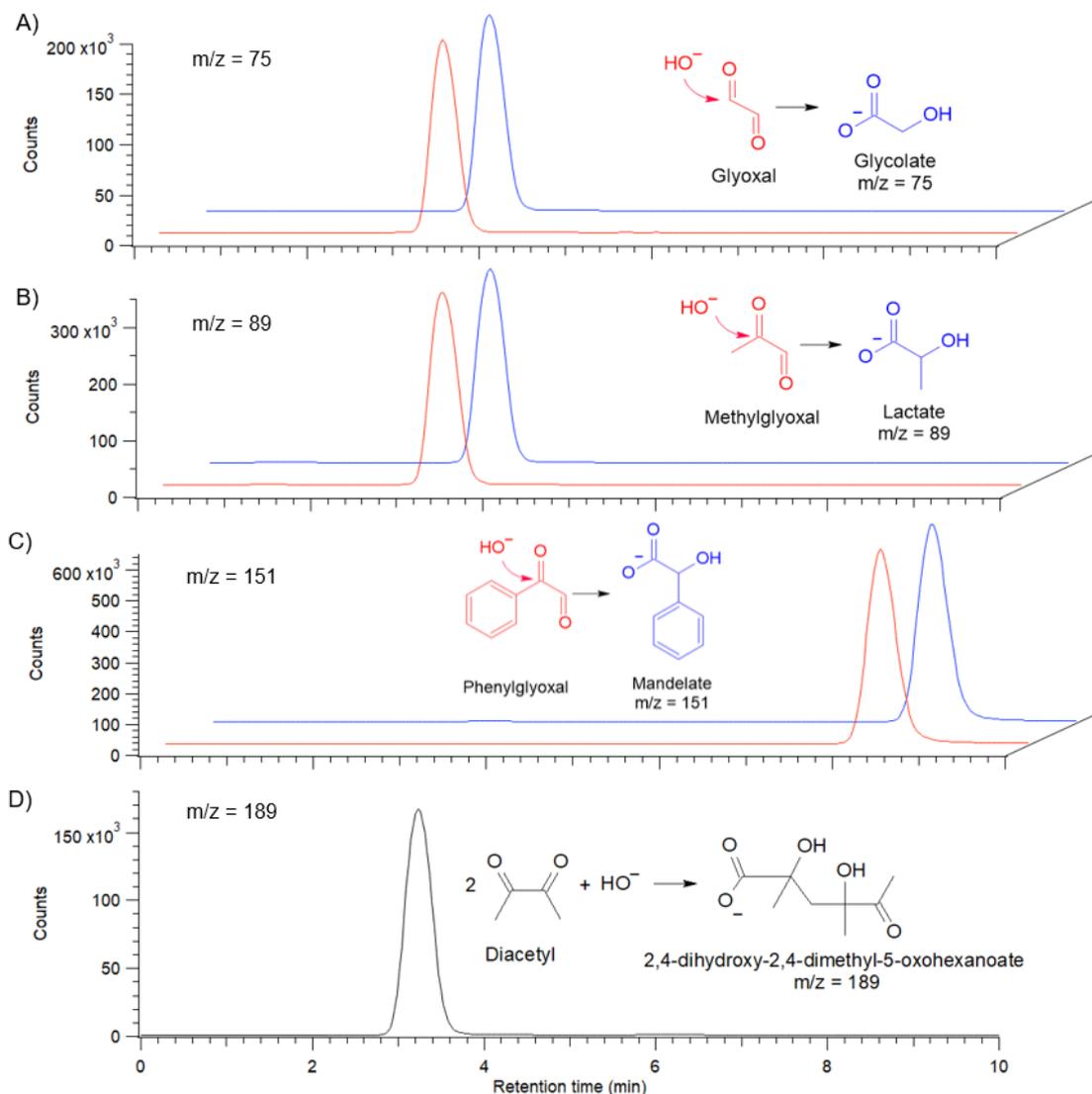


189

190 **Fig. 3 – HPIC_{NaOH} SIM chromatograms at $m/z = 75$ of a $5 \mu\text{M}$ glyoxal solution using either method B (conversion before the analysis**
 191 **at pH 12.24), or method A (conversion using the mobile phase as reagent), at various NaOH concentrations, corresponding to the**
 192 **indicated pH. The peak asymmetry factors (AsF) are indicated at the top of each peak with the corresponding colors. The asymmetry**
 193 **factor was calculated at 10% of the peak height.**

194 3.1.2 Application to other α -dicarbonyl compounds

195 Using method A, as observed for glyoxal, no chemical conversion of methylglyoxal and phenylglyoxal was obtained using
 196 HPIC_{carbonate}, but a strong signal of conversion was observed using HPIC_{NaOH}. Under these conditions, lactate and mandelate
 197 were detected respectively for methylglyoxal and phenylglyoxal, as expected from the mechanism (Fig. 1). However, in the
 198 same manner as for glyoxal, the chromatograms showed large peak tailing and the deformations were solved using method B
 199 (Fig. 4). These conversion observations are in very good agreement with the kinetic model predictions of Fratzke and Reilly
 200 (1986) and Hine et al. (1971), (conversion half-life of methylglyoxal and phenylglyoxal are 7 and 8 min respectively) as
 201 detailed in SI6.



202

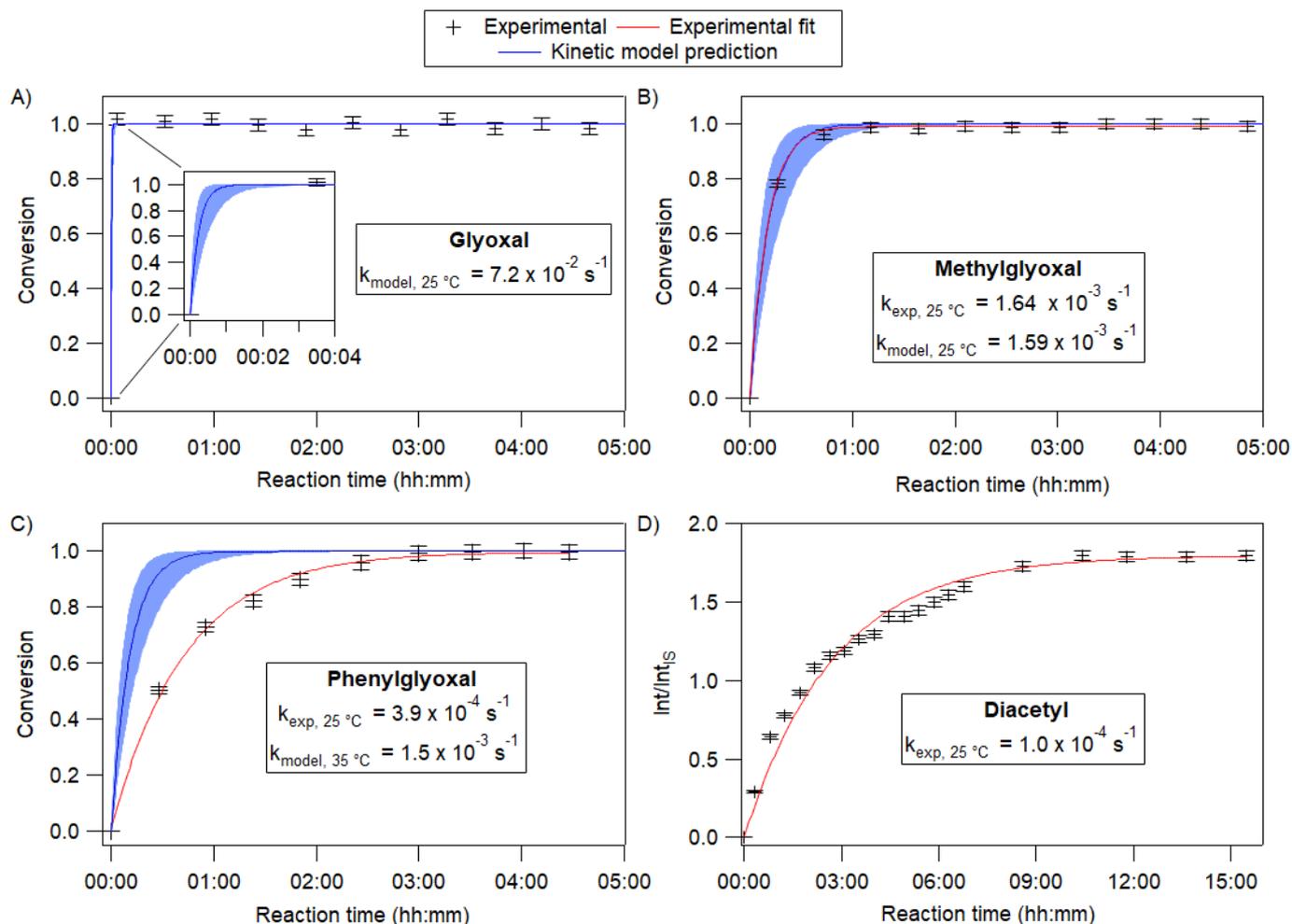
203 **Fig. 4 – HPLC_{NaOH} selected-ion monitoring (SIM) chromatograms A) at $m/z = 75$ of glyoxal (red) and glycolate (blue) solutions B) at**
 204 **$m/z = 89$ of methylglyoxal (red) and lactate (blue) solutions C) at $m/z = 151$ of phenylglyoxal (red) and mandelate (blue) solutions.**
 205 **D) SIM chromatogram at $m/z = 189$ of a diacetyl solution. The concentration of each compound was $10 \mu\text{M}$, the conversion time was**
 206 **5, 120, 240 and 720 min for glyoxal, methylglyoxal, phenylglyoxal and diacetyl, respectively.**

207 Concerning diacetyl, no signal was detected at $m/z = 103$ which corresponds to 2-methylactate, expected from the mechanism
 208 shown in Fig. 1. Instead, a strong signal was observed at $m/z = 189$ (Fig. 4D) which shows that a more complex chemical
 209 process occurs under alkaline conditions. This was explained by an additional mechanism shown in Fig. SI7: diacetyl bears
 210 enolisable hydrogens which allow aldol condensation to compete with the benzilic rearrangement. Diacetyl thus undergoes
 211 base catalysed aldol condensation and forms an α -dicarbonyl dimer that is converted to 2,4-dihydroxy-2,4-dimethyl-5-
 212 oxohexanoate (shown in Fig. 4D) *via* the benzilic acid rearrangement (Machell, 1960). The latter compound is not

213 commercially available, therefore no quantitative comparison with a standard product could be done. Although methylglyoxal
214 bears enolisable hydrogens on its methyl group as well, no product from a similar mechanism was detected, probably due to
215 its fast conversion kinetics (see next section) and the smaller number of hydrogens in the molecule.
216 In summary, the chemical conversion measurement method is also applicable to methylglyoxal, phenylglyoxal and diacetyl
217 detected as lactate, mandelate and 2,4-dihydroxy-2,4-dimethyl-5-oxohexanoate, respectively, and is more efficient for
218 quantification using method B than method A.

219 3.1.3 Conversion kinetics

220 In addition to being strongly dependent on pH, the conversion kinetics at 25°C were observed to be highly different from one
221 α -dicarbonyl compound to the other as shown in Fig. 5 where they are compared to the kinetic model predictions proposed by
222 Fratzke and Reilly (1986) for glyoxal and methylglyoxal and by Hine et al. (1971) for phenylglyoxal. For glyoxal, the
223 conversion was extremely fast (conversion half-life of glyoxal < 10 s) and reached its maximum within less than 4 minutes.
224 For methylglyoxal, phenylglyoxal and diacetyl, the conversion kinetics were slower (conversion half-life of methylglyoxal,
225 phenylglyoxal and diacetyl was 7 min, 29 min and 2 h, respectively) likely because of the more complex mechanisms of the
226 reaction conversion. In this mechanism (Fig. 1), the migration step of the R₁ group is rate-determining (Yamabe et al., 2006),
227 therefore, the reaction kinetics depend on the nature of the R₁ and/or R₂ groups. Compared to glyoxal, methylglyoxal and
228 phenylglyoxal bear a methyl and a phenyl group, respectively, that probably slows down the conversion reaction by steric
229 hindrance. Furthermore, diacetyl possesses two enolisable methyl groups which allow for more competitive aldol condensation
230 kinetics. In this case, the conversion reaction occurs after the dimerisation step 1 (Fig. SI7), which likely explains the globally
231 slower kinetics. Therefore, in addition to low-quality chromatograms, method A results in incomplete conversion of α -
232 dicarbonyl compounds with slow conversion kinetics (for methylglyoxal, phenylglyoxal and diacetyl) and thus much lower
233 performances.



234

235 **Fig. 5 – Temporal evolution of the conversion of A) glyoxal to glycolate (the inner graph shows a zoom in the first 4 minutes), B)**
 236 **methylglyoxal to lactate, C) phenylglyoxal to mandelate and D) diacetyl to 2,4-dihydroxy-2,4-dimethyl-5-oxohexanoate using SIM**
 237 **at $m/z = 75, 89, 103$ and 151 , respectively. Chromatographic peak integrated areas (Int) were normalised to integrated areas of**
 238 **valerate, the internal standard (Int_S) and compared to the signal of the corresponding α -hydroxy carboxylate, when possible, to**
 239 **compute the chemical conversion. Experimental error bars represent the standard deviation between triplicates. Red lines are the**
 240 **experimental fit using pseudo first-order kinetics: $1 - \exp(-kt)$. Blue lines (and shaded blue areas) show the kinetic model prediction**
 241 **at $\text{pH} = 12.2 (\pm 0.2)$ set by Fratzke et al. (1986) for glyoxal and methylglyoxal and by Hine et al. (1971) for phenylglyoxal.**

242 Fig. 5 shows that all the experimental kinetics are first-order, in very good agreement with the kinetic results by Hine et al.
 243 (1971) and Fratzke and Reilly (1986). Using exponential fits, pseudo first-order conversion rate constants of methylglyoxal,
 244 phenylglyoxal, and diacetyl were respectively $k_{\text{exp, methylglyoxal}} = 1.6 \times 10^{-3} \text{ s}^{-1}$, $k_{\text{exp, phenylglyoxal}} = 3.9 \times 10^{-4} \text{ s}^{-1}$, $k_{\text{exp, diacetyl}} = 1.0 \times 10^{-4}$
 245 s^{-1} . These values are compared in Fig. 5 to the kinetic model predictions developed by Fratzke and Reilly (1986) and Hine et
 246 al. (1971) that predict k as a function of pH (see SI6). Although no rate constant of glyoxal conversion could be determined in
 247 this work due to its very fast kinetics under our experimental conditions, Fig. 5 shows excellent agreements between our kinetic
 248 results and those predicted by Fratzke and Reilly (1986) for glyoxal and methylglyoxal at 25°C . A significantly slower kinetics

249 is observed for phenylglyoxal when compared to the kinetic model prediction by Hine et al. (1971) that was established at 35
250 °C only. The temperature effect probably explains the kinetic differences observed. Assuming an Arrhenius dependence of the
251 pseudo first order rate constant of glyoxal conversion and from the work of Fratzke and Reilly (1986), the activation energy
252 of the glyoxal conversion is 61.2 kJ mol⁻¹ at pH = 12.24 (see SI8). A rough estimation of the activation energy of the conversion
253 of phenylglyoxal at pH = 12.24 using the value obtained by Hine et al. (1971) at 35 °C and our rate constant determined at 25
254 °C results in an activation energy of approximately 100 kJ mol⁻¹. Although this value is a rough estimation and should be
255 confirmed by more experimental data at various temperatures, it is significantly higher than that of glyoxal and may be
256 explained by steric hindrance due to the phenyl group of the phenylglyoxal.

257 **3.1.4 Analytical method performances**

258 The performances were evaluated from the optimal pH and kinetics conditions for each compound using method B, i.e.
259 conversion before analysis into amber vials at pH > 12 for 5 minutes to 12 h and MS analysis using HPIC_{NaOH}. The resulting
260 SIM chromatograms are shown in Fig. 4. The reaction yield was determined, when possible, at the end of the reaction by
261 comparison of the α -hydroxy carboxylate signal in the converted α -dicarbonyl samples and the signal of authentic α -hydroxy
262 carboxylate standard samples, using the two HPIC systems. The performances obtained for the four α -dicarbonyl compounds
263 are shown in Table 1. For glyoxal, methylglyoxal and phenylglyoxal the yields were higher than 97 %, whereas no conversion
264 yield could be derived for diacetyl due to the lack of standard of 2,4-dihydroxy-2,4-dimethyl-5-oxohexanoate. The peak area
265 of each α -hydroxy carboxylate showed a good linearity ($R^2 > 0.99$) using concentrations of the corresponding α -dicarbonyl
266 compounds ranging from 0.1 to 20 μ M (see SI9) with good reproducibility (variation coefficient < 2.5 %). No interaction was
267 observed in mixture samples of the four α -dicarbonyls and the same values as in single samples were recovered. The detection
268 limits for the four α -dicarbonyls ranged from 9 nM to 66 nM (determined using Signal/Noise = 3) and are of the same order
269 as other recently published results using traditional derivatisation measurement methods (Rodigast et al., 2015). Glyoxal and
270 methylglyoxal show average concentrations in cloud and fog water ranging respectively from 0.6 to 96 μ M and from 0.3 to 93
271 μ M (Ervens et al., 2013; Li et al., 2020). The method developed in this work thus presents the performances needed by
272 environmental samples and has the advantage of being simple and fast.

273

| α -dicarbonyl | | | Detected α -hydroxy carboxylate | | | Analytical performances | | | | |
|----------------------|-----|---|---|-----|---|--|---------------------|------------------------------------|----------------------|---|
| Name | m/z | Structure | Name | m/z | Structure | Yield of the conversion reaction (reaction time) | Linearity (R^2) | Sensitivity (μM^{-1}) | Detection limit (nM) | Variation coefficient between triplicates |
| Glyoxal | 58 |  | Glycolate | 75 |  | $100 \pm 4 \%$ (5 min) | 0.9969 | 0.13 | 33 | 2.3% |
| Methylglyoxal | 72 |  | Lactate | 89 |  | $97 \pm 5 \%$ (2 hrs) | 0.9985 | 0.31 | 43 | 1.7% |
| Phenylglyoxal | 134 |  | Mandelate | 151 |  | $101 \pm 5 \%$ (4 hrs) | 0.999 | 1.16 | 9 | 2.5% |
| Diacetyl | 86 |  | 2,4-dihydroxy-2,4-dimethyl-5-oxohexanoate | 189 |  | not determined | 0.9984 | 0.2 | 66 | 1.9% |

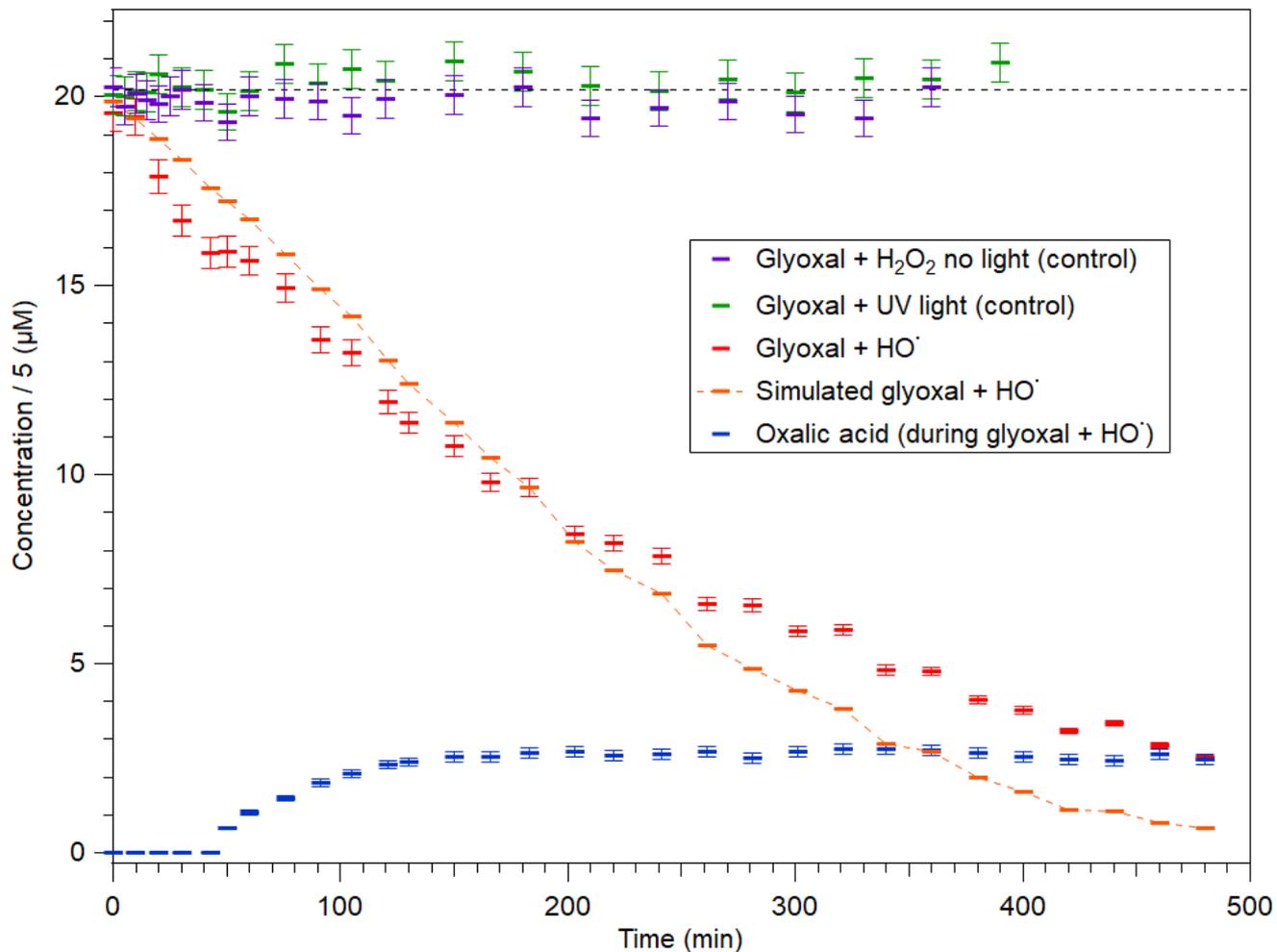
274

275 **Table 1 – Analytical performances of HPIC_{NaOH} analysis of α -dicarbonyl compounds after chemical conversion to α -hydroxy**
 276 **carboxylate anions in NaOH solutions at pH>12 (method B).**

277 3.2 Application to aqueous phase photooxidation of glyoxal

278 The chemical conversion method for α -dicarbonyl analysis shows good performances, is simple, fast and requires simple
 279 instrumentation and cheap solvents. This makes it very suitable for laboratory studies on specific α -dicarbonyl compounds
 280 such as aqueous glyoxal $\cdot\text{OH}$ -oxidation. The results (Fig. 6) show that control experiments revealed no significant direct
 281 photolysis of glyoxal in the aqueous phase, as expected from glyoxal hydration that suppresses the carbonyl groups and leads
 282 to the reversible formation of gem-diol, with a high hydration equilibrium constant reached within less than a second (hydration
 283 half-life of glyoxal is < 0.1 seconds as compiled by Ervens and Volkamer, 2010). This reaction thus prevents the radiation
 284 absorption by the molecule in water (Montoya and Mellado, 1994). The reaction between glyoxal and H_2O_2 reported previously
 285 (Zhao et al., 2012) was not observed under our experimental conditions, probably due to our low initial concentrations that
 286 slowed down the formation of hydroxyhydroperoxides. In the presence of HO^\bullet radicals (produced from $\text{H}_2\text{O}_2 + \text{h}\nu$), glyoxal
 287 concentrations decreased exponentially by one order of magnitude within 7h of reaction, while H_2O_2 concentrations decreased
 288 by a factor of 11% (SI10). These kinetics allowed us to derive some values of the rate constants of the limiting reactions, i.e.
 289 H_2O_2 direct photolysis $J_{\text{H}_2\text{O}_2}$, and glyoxal HO^\bullet oxidation k_{OH} . Assuming steady state concentrations for HO^\bullet and HO_2^\bullet radicals,
 290 the glyoxal and H_2O_2 concentration time profiles were simulated using the Microsoft® Excel® Solver routine. Both $J_{\text{H}_2\text{O}_2}$, and
 291 k_{OH} were optimized to minimize the sum of the square differences between calculated and experimental data (see SI10). The
 292 results show a good agreement between the simulated and the experimental concentrations (Fig. 6 and SI10), and a value of
 293 $k_{\text{OH}} = 1.07 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was derived. Although this value is a rough estimation due to the steady state approximations, it is in
 294 good agreement with the values of 1.1×10^9 and $0.92 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ determined by Buxton et al. (1997) and Schaefer et al. (2015)
 295 respectively. The main photooxidation reaction product detected was secondary oxalic acid, in agreement with previous studies
 296 (Tan et al., 2009; Lee et al., 2011; Lim et al., 2013; Schaefer et al., 2015). The measurement method developed in this work

297 has thus proven to be simple and efficient to monitor glyoxal during a reaction of atmospheric interest, under concentrations
298 similar to those observed in clouds and fogs.



299
300

301 **Fig. 6 – Experimental and simulated glyoxal time profiles during its aqueous phase reaction using SIM at $m/z = 75$ (glycolate). At**
302 **$m/z = 89$ oxalate was also monitored as the main secondary reaction product. Error bars represent the standard deviation between**
303 **analytical triplicates. The samples were diluted by a factor of 5 before analysis.**

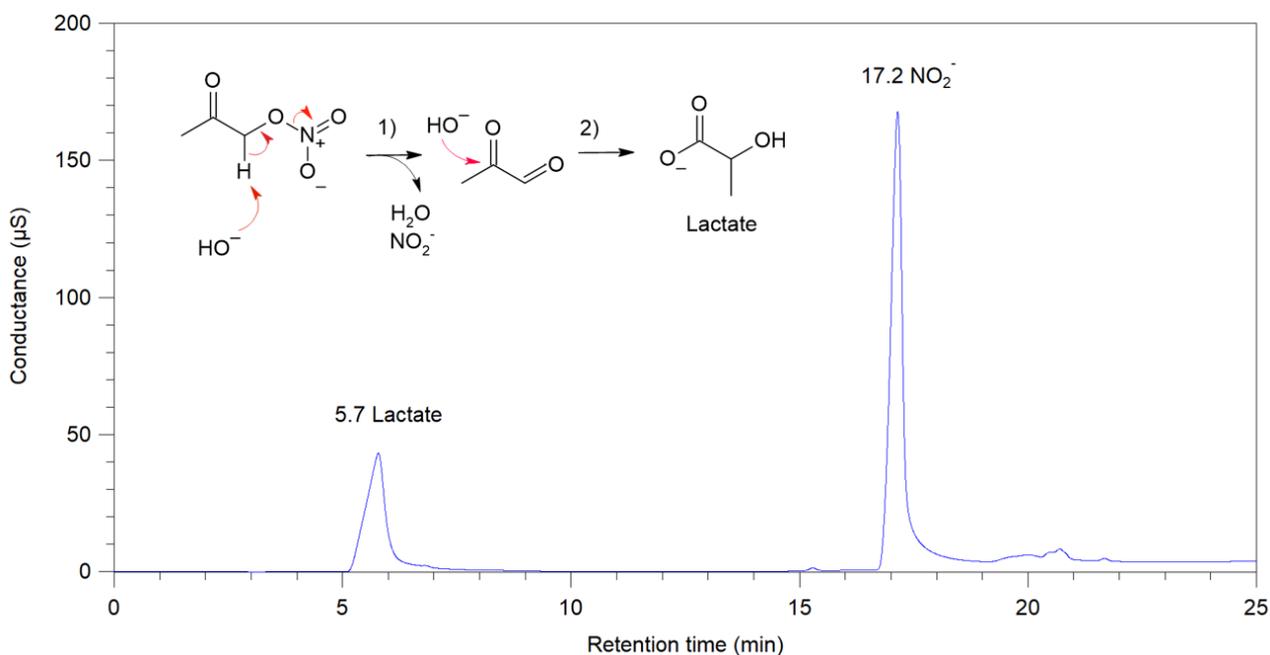
304 3.3 Discussions on environmental analysis

305 The method also shows some disadvantages and should therefore be used with caution, especially for complex environmental
306 samples. Concentrations of α -dicarbonyls may be overestimated if the samples contain the corresponding α -hydroxy
307 carboxylate. In this case, it is necessary to perform a preliminary α -hydroxy carboxylate quantification at lower pH, to prevent
308 the conversion of any α -dicarbonyl compound (see SI11 for more details). For this reason, the method is more suitable for
309 targeted laboratory studies but remains applicable to environmental samples.

310 Our results also show that the presence of α -dicarbonyl compounds can induce overestimation biases especially when looking
311 for organic acids and carboxylates in environmental samples. To evaluate the importance of the conversions that may occur, a
312 simple calculation was performed for the two most abundant α -dicarbonyl compounds, glyoxal and methylglyoxal.
313 Considering the kinetics model proposed by Fratzke and Reilly (1986) and our results, using a typical HPIC method (Wang,
314 2009) whose pH gradient is often used for environmental analysis, up to 24 and 3% of glyoxal and methylglyoxal can be
315 converted to their corresponding hydroxy carboxylates respectively. However, the induced biases on the quantification of α -
316 hydroxy carboxylates depend on the relative abundance of α -dicarbonyl to α -hydroxy carboxylate concentrations in the sample.
317 Note that other α -dicarbonyl compounds can also interfere with gluconate, malate, 2-hydroxyvalerate, mucate, tartarate, citrate
318 and isocitrate measurements. Specific analyses should thus be performed using our methodology (i.e. HPIC_{NaOH} and
319 HPIC_{carbonate}) to determine the importance of these biases in environmental samples.

320 Other pH-sensitive compounds can be converted into α -dicarbonyls and hydroxy-carboxylates during HPIC analysis using
321 highly alkaline mobile phases, especially compounds prone to base-catalysed hydrolysis. For example, seeking for any
322 contaminants during the synthesis of α -nitrooxyacetone, large quantities of lactate and nitrite were detected using HPIC_{NaOH}
323 (see Fig. 7 and SI12 for chromatographic conditions). This phenomenon was explained by the prompt base-catalysed
324 hydrolysis of α -nitrooxyacetone that produced nitrite ions and methylglyoxal which was then converted into lactate during the
325 HPIC_{NaOH} analysis (see the mechanism in Fig. 7). Particular care should therefore be taken when performing routine HPIC
326 analysis of environmental samples which likely contain polyfunctional and pH-sensitive compounds, especially for the
327 measurement of glycolate, lactate and nitrite ions.

328



329

330 **Fig. 7** HPIC_{NaOH} chromatogram of an aqueous solution of α -nitrooxyacetone. In the figure: Reaction mechanism of α -
331 nitrooxyacetone in alkaline medium. 1) Basic hydrolysis 2) Benzilic acid rearrangement.

332 **4. Conclusions**

333 In this work, we took advantage of the high reactivity of α -dicarbonyl compounds in alkaline solutions (intramolecular
334 Cannizzaro reaction) to develop an analytical method based on HPIC. The chemical conversion can be performed in the sample
335 before analysis or in the HPIC system during elution using the mobile phase as reagent. The required mobile phase pH depends
336 on the targeted α -dicarbonyl compound, the analysis time and the temperature of the HPIC system. However, when the
337 chemical conversion was performed using the mobile phase as reagent, chromatographic distortions were observed under our
338 analytical conditions that were solved by performing the chemical conversion before analysis. When the chemical conversion
339 was performed before analysis, the analytical method performances were comparable to other recently published traditional
340 derivatisation methods and allowed for laboratory experiments, such as aqueous phase HO-oxidation of glyoxal, to be
341 conducted in concentration ranges similar to those observed in the atmosphere. Compared to the previous derivatisation
342 methods, this alkaline chemical conversion method is much simpler, faster and cheaper but is more suitable for targeted
343 laboratory experiments. Indeed, potential interferences of α -hydroxy carboxylates in complex environmental samples can
344 occur, they need to be treated with caution, for example, using two different elution methods, i.e. mildly alkaline eluents such
345 as carboxylates and highly alkaline eluents such as sodium or potassium hydroxide solutions.

346

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