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# 1 Evaluation of an 'After Opening Freshness (AOF)' *label* for Packaged Ham

2  
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## 6 7 **Abstract**

8 A new type of commercial time-temperature indicator, TTI, namely the 'After Opening  
9 Freshness *Label*', i.e. AOF *label*, is evaluated. The *label* comprises a plastic film colorimetric  
10 CO<sub>2</sub> *indicator* layer encapsulated in a polymer sheath, the permeability of which controls the  
11 rate of diffusion of the CO<sub>2</sub> in to and out of the indicator film. The CO<sub>2</sub>sensitive *indicator*  
12 film inside the *label* is relatively fast in responding (recovering its original colour in 26 min at  
13 25°C) when the ambient atmosphere is changed from that of the MAPed package  
14 (containing 25% CO<sub>2</sub>) to air, but when encapsulated in the polymer sheath used in the AOF  
15 *label*, which uses polyethylene terephthalate, PET, as a gas diffusion barrier, under the same  
16 conditions its recovery time is ca. 30 h (at 25°C). Key to its commercial function –as a  
17 consume within indicator - at 5 °C, the *label's* recovery time is ca. 96 h (i.e. 4 days). While  
18 UV/Vis spectrophotometry is used to characterise the optically transparent CO<sub>2</sub> *indicator*,  
19 photography, coupled with digital image colour analysis is used to characterise the AOF  
20 *label*. A study of the kinetics of colour recovery of the AOF *label* as a function of  
21 temperature revealed an activation energy,  $E_a$ , of colour recovery of ca. 43 kJ mol<sup>-1</sup>, which is  
22 similar to a number of different food spoilage processes. The potential of the AOF *label* as a  
23 'consume within' indicator to help minimise the large amount of unnecessary household  
24 food waste associated with many developed countries is discussed briefly.

25 **Keywords:** Indicator, Freshness, Ham, Packaging, MAP

## 26 1. Introduction

27 The Waste and Resources Action Programme, WRAP, estimate (WRAP, 2017) over 10 million  
28 tonnes of food, valued at £17 bn, is wasted per annum and of which 60% could have been  
29 avoided. Given that 70% of the latter is household food waste, it follows that any  
30 technology that informs the consumer what food in the fridge is still fresh, and so safe to  
31 eat, would be a welcome, useful tool to help reduce this waste. One technology that has  
32 been used for this purpose is the time-temperature indicator, i.e. TTI. A TTI is a smart *label*  
33 that shows the accumulated time-temperature history of a product. TTIs are usually  
34 employed to improve food distribution, reduce food waste and improve shelf-labelling by  
35 highlighting any significant deviations from the recommended refrigeration temperature  
36 (Taoukis, 2001). The shelf-life label used by most packagers assumes correct refrigeration.  
37 An excellent recent review on TTIs is that of Wang and co-workers (Wang, Liu, Yang, Zhang,  
38 Xiang and Tang, 2015).

39 A notable commercial example is the FreshCheck® Freshness 'You Can See™' indicator  
40 (FreshCheck® indicator, 2014) sold by the TempTime Corporation, based on the  
41 polymerisation reaction of colourless diacetylenic monomers. These compounds polymerise  
42 thermally to give very dark, conjugated polymers. The kinetics of the polymerisation  
43 depends upon the type of substitution and so provides a route by which TTIs with different  
44 temperature sensitivities can be produced. In a typical indicator the polymerisation takes  
45 place in the centre of a bulls-eye pattern, with the outer part of the bulls-eye acting as  
46 reference colour ring. Fresh Check® indicators have been used in the past by the Monoprix  
47 supermarket chain in France on selected refrigerated products as well as other chain stores  
48 (Fresh-Check Indicator *Labels* Assure eatZi's Customers Freshness, 2018; Mills, 2009; Wang,  
49 Liu, Yang, Zhang, Xiang and Tang, 2015).

50 The Cryolog Company has developed an irreversible, novel, temperature-activated,  
51 printable TTI *label*, that utilises food-grade micro-organisms to simulate the real  
52 deterioration of food products, called the TOPCRYO™ *label* (TOPCRYO™ technology, 2018).  
53 The growth of these micro-organism parallel that of the micro-organisms found naturally in  
54 the packaged food and produces a pH change in the indicator which is revealed using a pH-  
55 sensitive dye. Thus, the initially green active *label* turns pink if the product has been  
56 incorrectly refrigerated and so is no longer fresh, due to above chill temperature storage.

57 As with FreshCheck™, the TOPCRYO™ TTI is a full history, temperature-only activated  
58 indicators, requiring deep-freeze storage of the label prior to its application. This obviously  
59 limits their use to initially frozen foods and there is, therefore, a clear need for a TTI that is  
60 activated by some other, simple mechanism, other than thawing.

61 Finally, it is worth mentioning the OnVu™ label, which is based on a solid-state  
62 photochromic reaction. Initially colourless, upon activation with UV light the photochromic  
63 pigment turns dark blue, and with time returns back to its colourless form at a rate that is  
64 temperature dependent (Kreyenschmidt, Christiansen, Hubner, Raab & Petersen, 2010).

65 Insignia Technologies Ltd. (Insignia Technologies Ltd., 2017) has recently introduced a new  
66 type of TTI, which they refer to as an 'After Opening Freshness *Label*', or – as we shall refer  
67 to throughout as an 'AOF' *label*, which is initially beige coloured when contained in an  
68 *unopened*, modified atmosphere, CO<sub>2</sub>-containing, package, and only starts to change colour  
69 (to purple) once the food package is *opened* and the CO<sub>2</sub> is released. The key colour-  
70 changing process is therefore due to the desorption of the CO<sub>2</sub> from the label into the  
71 ambient air. Once 'activated' in this way, i.e. once the food package is opened, it takes ca. 4  
72 days to change colour in air provided the package plus label are maintained at 5°C, but is  
73 faster at elevated temperatures, as we shall see. Note, although it is referred to as an 'after  
74 opening freshness' indicator by Insignia Technologies Ltd., the AOF *label* does not measure  
75 food freshness directly. Instead, it is a different type of TTI in that it shows the accumulated  
76 time-temperature history of a product, once the MAPed package is opened. This indicator  
77 was recently made available at selected stores as part of a trial with packages of cooked  
78 British ham slices by Sainsbury's, as illustrated in figure 1(a). Photographs of this AOF *label*  
79 *in situ* after opening as a function of time at 5°C are illustrated in figure 1(b) and show the  
80 gradual transition from an initial beige colour (at time of opening,  $t = 0$ ) to light purple at  $t =$   
81 4 days. The last image of the label shows that the indicator actually continues to darken in  
82 colour after 4 days, until it reaches a deep purple after 7 days, however a colour-matching  
83 scale on the indicator helps identify the 4 day (at 5°C) point.

84 The AOF *label* shows how long the package has been opened when correctly refrigerated  
85 and in so doing indirectly provides advice regarding the freshness of the product, ham in this  
86 case, with the intention that this 'consume within' advice will stop the consumer throwing  
87 out the food unnecessarily while it is safe to eat, by reassuring them of its freshness. As

88 with most packaged foods, the packager sets a time, after opening, for it to be consumed  
89 within, in which the properly refrigerated product will be 'fresh' and 'safe to eat'; how they  
90 arrive at that time (typically 2 days for packaged meat) and what the usual spoilage  
91 mechanisms are outside the scope of this paper, but have been addressed by the work of  
92 others (e.g. Huis in't Veld, 1996; Borch, Kant-Muermans & Blixt, 1996).

93 Reassurance of food freshness and safety are required particularly by the many that forget  
94 when their refrigerated food packages were opened and so are unable to follow the  
95 'consume within' advice that is usually printed on such packages, such as 'consume within 2  
96 days' for the Sainsbury's ham, for example. The discrepancy in 'consume within' times  
97 between the AOF *label* (4 days at 5°C) and the printed advice (2 days) arises because the  
98 latter errs on the side of caution, since research shows that many (over 70% in the UK, for  
99 example, and similar figures for the USA and Europe; James, Evans & James, 2008)  
100 household fridge temperatures exceed 5°C. In contrast, MAP packaged ham refrigerated at  
101 5°C or less, is safe to eat up to 3-5 days after opening (Foodsafety.gov, 2018).

102 In this paper the indicator used in the Insignia Technologies AOF *label* is characterised and  
103 evaluated using UV/Vis spectroscopy and digital image under different conditions of  
104 temperature and CO<sub>2</sub>. The results provide a better understanding of the features and  
105 possible limitations of this new TTI.

## 106 **2. Materials and methods**

### 107 *2.1 Materials*

108 Packets of Sainsbury's 7 cooked British ham slices, with their Insignia Technology AOF *labels*,  
109 were purchased from a local Sainsbury's store between June 2017 and January 2018. In all  
110 cases the AOF *labels* were stuck inside to the clear plastic film lidding (50 µm thick) of the  
111 ham package. In this paper, all tests of the AOF *label* were conducted with the label still  
112 stuck onto the lidding. The structure of the AOF *label* was probed using FT-IR and Scanning  
113 Electron Microscopy (SEM) and the latter results are illustrated in figure 2(a). SEM,  
114 combined with optical and FT-IR microscopy, showed that the AOF *label* comprised: a  
115 relatively thick (70 µm), purple-coloured low density polyethylene (LDPE) plastic film CO<sub>2</sub>-  
116 sensitive *indicator* layer sandwiched between a thin (30 µm) white PET layer – on its 'food'  
117 side and a thick polypropylene layer (50 µm) on its 'lidding' side. Adhesive binds all the

118 layers together, as well as the *label* to the lidding (50  $\mu\text{m}$ ) which appears (from FTIR) to be  
119 made of polyethylene terephthalate, PET, with a coating of EVA; the thicknesses of the EVA  
120 and adhesive layers could not be readily determined by SEM. A schematic illustration of the  
121 *label* attached to the lidding is given in figure 2(b).

122 In part of this study the AOF *label* was peeled apart so as to enable the purple-coloured  
123 plastic film CO<sub>2</sub>-sensitive *indicator* to be characterised in its uncovered, i.e. **naked**, form. In  
124 all such work, the **naked** AOF plastic film *indicator* is referred to as the AOF *indicator*, in  
125 order to distinguish it from the combined system, illustrated in figure 2(b), the AOF *label*.  
126 All gases, e.g. CO<sub>2</sub>, 25% CO<sub>2</sub> in air and air were purchased from BOC.

## 127 2.2 Methods

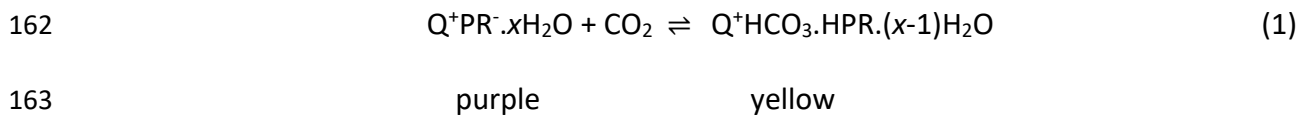
128 Calibration of the AOF *indicator* and *label* was achieved using different mixes of CO<sub>2</sub> with Ar.  
129 In this work, the appropriate gases were blended together using a Cole-Parmer – rotameter  
130 based – gas blender. An Anéolia Legend O<sub>2</sub>/CO<sub>2</sub> gas analyser was used to verify the level of  
131 CO<sub>2</sub>, i.e. the %CO<sub>2</sub>, in final gas mixture. All UV/ Vis absorbance measurements were made  
132 using an Agilent Technologies CARY 60 UV-vis spectrophotometer. All FT-IR spectra were  
133 recorded using a Perkin Elmer model Spectrum 1 FT-IR spectrometer. SEM measurements  
134 were carried out using a FEI Quanta™ 250 SEM with a spot size of 4 mm, working distance  
135 of 10 mm and an accelerating voltage of 20 kV. Prior to SEM analysis, samples were sputter  
136 coated with a 10 nm layer of gold using a Quora Q150R S rotary pumped sputter coater. All  
137 digital photographs were taken using a Cannon 600D digital camera.

## 138 3. Theory of CO<sub>2</sub>-based indicators; how the AOF *label* works

139 The AOF *label* contains a purple-coloured plastic *indicator* film that changes colour  
140 (ultimately bright yellow in 100% CO<sub>2</sub>) when exposed to carbon dioxide. The packaged ham,  
141 illustrated in figure 1, has a modified atmosphere comprising ca. 25% CO<sub>2</sub>: 75% N<sub>2</sub>, so as to  
142 extend the shelf-life of the food. As a result, when in the sealed package of ham, the AOF  
143 *label* is beige coloured, but not bright yellow, which requires a much higher level of CO<sub>2</sub>.  
144 When the package is opened, the CO<sub>2</sub>-rich atmosphere is replaced rapidly by air, which only  
145 has 0.04% CO<sub>2</sub>, and so the AOF *label* slowly recovers its original (purple) colour over a time  
146 period that depends upon temperature. This slow recovery is due to the diffusion of the  
147 CO<sub>2</sub> in the *indicator* film, slowly diffusing out through the white PET overlayer, i.e. (iv) in

148 figure 2(b), into the ambient air. As a consequence, the AOF *label*, illustrated in figure 1,  
 149 changes from beige to light purple over a period of 4 days after opening when refrigerated  
 150 at 5°C, as illustrated in figure 1.

151 The purple-coloured plastic film CO<sub>2</sub>-sensitive *indicator* film that forms part of the AOF *label*,  
 152 see figure 2(b), is an example of one of a number of smart plastic films developed originally  
 153 by this group (Mills, Skinner & Grosshans, 2010; Mills & Yusufu, 2016a,b). It comprises a  
 154 CO<sub>2</sub>-sensitive pigment dispersed uniformly throughout an extruded polymer which, in this  
 155 case, is low density polyethylene, LDPE. The pigment comprises fine particles (BET surface  
 156 area = 130 ± 25 m<sup>2</sup>/g), of hydrophilic silica coated with a pH sensitive dye, in this case  
 157 phenol red, PR; the identity of the latter was determined using UV/Vis absorption  
 158 spectroscopy. In the dye coating the silica particles the PR is in its highly coloured (purple)  
 159 deprotonated form, PR<sup>-</sup>, and ion-paired with a quaternary ammonium, Q<sup>+</sup>, cation. The  
 160 resulting complex, Q<sup>+</sup>PR<sup>-</sup>.xH<sub>2</sub>O, reacts with CO<sub>2</sub> *via* the following colour-changing  
 161 equilibrium reaction:



164 From eqn(1) it follows that:

$$165 \quad R = [\text{HPR}]/[\text{PR}^-] = \alpha \times \% \text{CO}_2 \quad (2)$$

166 where [HPR] and [PR<sup>-</sup>] are the concentrations of Q<sup>+</sup>HCO<sub>3</sub>.HPR.(x-1)H<sub>2</sub>O and Q<sup>+</sup>PR<sup>-</sup>.xH<sub>2</sub>O,  
 167 respectively, α is a proportionality constant (units: %<sup>-1</sup>), which provides a measure of the  
 168 sensitivity of the CO<sub>2</sub>-sensitive optical sensor under test, and R is a measure of the  
 169 transformation of the dye from the deprotonated to protonated form due to the presence  
 170 of CO<sub>2</sub>. Experimentally, the value of R can be calculated from the measured absorbance of  
 171 the indicator film at a known value of %CO<sub>2</sub>, Abs, at the wavelength of maximum  
 172 absorbance for, say PR<sup>-</sup>, i.e. λ<sub>max</sub>(PR<sup>-</sup>) = 592 nm, since, from reaction (1) and eqn (2) it follows:

$$173 \quad R = (\text{Abs}_0 - \text{Abs})/(\text{Abs} - \text{Abs}_\infty) = [\text{HPR}]/[\text{PR}^-] \quad (3)$$

174 Where, Abs<sub>0</sub> is the value of absorbance due to the PR dye at λ<sub>max</sub>(PR<sup>-</sup>) when %CO<sub>2</sub> = 0 (i.e.  
 175 when all the dye is in its deprotonated form) and Abs<sub>∞</sub> is the absorbance of the film when all  
 176 the dye is in its protonated form, HPR, i.e. when %CO<sub>2</sub> = ∞; the latter absorbance is assumed

177 here to be that measured when the %CO<sub>2</sub> = 100 %. The characterisation of other CO<sub>2</sub>-  
178 sensitive plastic films, based on this principle, using, for example, the pH sensitive dyes:  
179 meta-cresol purple, thymol blue and hydroxypyrene trisulfonic acid (HPTS), has been reported  
180 previously by this group (Mills, Skinner & Grosshans, 2010; Mills & Yusufu, 2016a,b). Other  
181 work shows that for such sensors a variation in relative humidity, RH, from 40-100% at  
182 room temperature, has little effect on the response features of such indicators although a  
183 shift from 0 to 40% usually lowers the sensitivity of the indicator by a factor of ca. 3 (Mills &  
184 Yusufu, 2016a) and the PR indicator film reported here is assumed to behave in a similar  
185 fashion.

186 The patent associated with this technology is currently licensed to Insignia Technologies Ltd  
187 (Mills, Grosshans and Skinner, G. 2014).

## 188 **4. Results and discussion**

### 189 *4.1 Characterisation of the AOF indicator*

190 The 'naked' AOF *indicator* was fixed in a gas cell (see Supplementary information, figure S1  
191 for a schematic illustration of the gas cell and set up), and then exposed to different levels  
192 of CO<sub>2</sub> at room temperature (25 °C) for 15 mins and its UV/Visible spectrum measured and  
193 digital photograph take at each level. The results of this work are illustrated in figure 3(a),  
194 including an insert plot of  $R$ , calculated using eqn (3), vs %CO<sub>2</sub>, which revealed a good  
195 straight line of gradient (which is a measure of the sensitivity of the indicator)  $\alpha = 0.62 \pm$   
196  $0.02 \text{ \%}^{-1}$ . This same procedure was carried out at number of different temperatures so as to  
197 determine the temperature sensitivity of  $\alpha$ . An Arrhenius plot of the data, i.e.  $\ln(\alpha)$  vs  $1/T$ ,  
198 illustrated in figure 3(b) yielded a good straight line, from the gradient of which an  
199 activation energy,  $E_a$ , of  $45 \pm 1 \text{ kJ mol}^{-1}$  was calculated for reaction (1). This value is near to  
200 that reported elsewhere for a similar type of plastic film CO<sub>2</sub> indicator, using the sodium salt  
201 of the fluorescent dye, 8-hydroxypyrene-1,3,6-trisulfonic acid, i.e.  $E_a = 38 \pm 2 \text{ kJ mol}^{-1}$   
202 (Mills & Yusufu, 2016b). The results of this work reveal that the CO<sub>2</sub> indicator films become  
203 increasingly sensitive towards CO<sub>2</sub> the lower the ambient temperature, i.e.  $\alpha$  increases with  
204 decreasing  $T$ , which is not surprising given the negative entropy associated with reaction (1)  
205 and reactions of this type.



206 As suggested by eqn (3), all CO<sub>2</sub> indicators based on reaction (1) show a hyperbolic, rather  
207 than linear, response towards CO<sub>2</sub>, and as a result exhibit response and recovery profiles  
208 that are asymmetric (Mills & Chang, 1992), as illustrated in figure 4, for the AOF *indicator*,  
209 when exposed to alternating cycles of argon (0% CO<sub>2</sub>) and 25% CO<sub>2</sub>.

210 From these profiles it is possible to calculate the average 90% response,  $t_{90\downarrow}$ , and recovery  
211 times,  $t_{90\uparrow}$ , of 1 and 26 min, respectively, which are also similar to those observed for the  
212 HPTS and thymol blue containing CO<sub>2</sub>-sensitive plastic films, which were typically 2-3 min  
213 and 32-38 min, respectively (Mills & Yusufu, 2016ab). In such CO<sub>2</sub> indicators, the response  
214 and recovery times depend directly upon the rate of permeation of the CO<sub>2</sub> into and out of  
215 the indicator film, respectively, with a proportionality constant that is inversely proportional  
216 to the square of film thickness (Mills & Chang, 1992). The very long recovery of the AOF  
217 *label* (> 4 days at 5 °C, see figure 1), compared to the *indicator* (26 min at 25 °C), is due to  
218 the additional barrier to CO<sub>2</sub> permeation, namely the 30 µm layer of white PET.  
219 Permeability data for CO<sub>2</sub> in different polymers is given in the supplementary Information  
220 section, Table S1. Other experiments conducted using the *label* with additional barrier films  
221 on the lidding, or on the white PET side of the *label*, show, not surprisingly, that the  
222 combination of a gas diffusion barrier of 50 µm PET/EVA and 50 µm of PP, on the 'lidding'  
223 side, provides an even greater barrier to CO<sub>2</sub> permeation than the thin (30 µm) white PET  
224 layer on the food side, thus the rate of recovery of the original colour of the AOF *label* is  
225 primarily due to diffusion of the CO<sub>2</sub> from the indicator film through the white PET layer, as  
226 noted earlier. PET is known to have a relatively low permeability towards CO<sub>2</sub> (Ashley, 1985  
227 and Table S1) and, indeed, that is why it is often used to package carbonated drinks. The  
228 AOF plastic film *indicator*, with its 90% response and recovery times of 1 and 26 min at 25°C,  
229 respectively, utilises LDPE as the polymeric encapsulation medium, which has a permeability  
230 that is > 200 x's that of PET (Ashley, 1985 and Table S1), so that it is little wonder that the  
231 recovery time of the AOF *label* is much greater, i.e. > 4 days at 5°C, than that of the (naked)  
232 CO<sub>2</sub> *indicator*.

#### 233 4.2 UV/Visible spectroscopy and digital colour image analysis

234 When it comes to comparing the performance of the AOF *indicator* to the AOF *label*, there  
235 appears to be a potential problem in that the latter does not allow the transmission of light  
236 and so cannot be probed using UV/Vis absorption spectroscopy. However, an increasingly

237 popular, simple way to monitor quantitatively the colour change exhibited by opaque  
238 samples is through photography and digital image colour analysis (Knutson et al., 2015;  
239 Williams et al., 2007). In its simplest form, as used here, photographs are taken of the  
240 indicator under test and its image analysed for the red, green and blue components, i.e.  
241  $RGB(\text{red})$ ,  $RGB(\text{green})$  and  $RGB(\text{blue})$ , respectively, which will have values between 0 and  
242 255, and which, when taken together, defined the observed colour of the indicator in the  
243 photograph. In the Insignia AOF *indicator* and *label*, the colour change is from purple to  
244 yellow and the colour component that changes most strikingly is red. Thus, when analysing  
245 photographic images of the AOF *indicator*, or *label*, here we use an apparent absorbance,  
246  $Abs(\text{red})$ , (Knutson et al., 2015; Williams et al., 2007) based on the average red component  
247 of the digital image,  $RGB(R)$ , of the AOF label, as a substitute for absorbance in eqn (3), in  
248 order to calculate a value for  $R$ , where

$$249 \quad Abs(\text{red}) = \log(255/RGB(\text{red})) \quad (4)$$

250 In order to validate this method of analysis its ability to generate a value for  $\alpha$  for the AOF  
251 *indicator* was tested and compared to that value, determined using UV/Vis  
252 spectrophotometry for the same *indicator*, reported earlier in this work. Thus, figure 3(a)  
253 illustrates the digital photographs taken on the AOF *indicator* taken at the same time as the  
254 absorbance measurements illustrated in figure 3(a) for different levels of %CO<sub>2</sub>. Digital  
255 image colour analysis of these images of the indicator yielded a range of  $Abs(\text{red})$  values,  
256 calculated using eqn (4), as a function of %CO<sub>2</sub>, which were then used to generate a straight  
257 line plot of  $R$  vs %CO<sub>2</sub>, via eqn (3), which had almost the same gradient, i.e. same value of  $\alpha$   
258 (0.59 %<sup>-1</sup>) as that determined by UV/Vis spectrophotometry for the same *indicator* (see  
259 insert plot in figure 3(a)), i.e.  $\alpha = 0.62 \text{ \%}^{-1}$ . As found for other indicator systems, this work  
260 shows that simple colour-based indicators, such as the PR *indicator* film studied here, can be  
261 analysed quantitatively using the much simpler, less expensive method of digital  
262 photography coupled with colour analysis, rather than the more expensive and less  
263 amenable (for opaque samples at least) method of UV/Vis spectrophotometry. As a result,  
264 in the subsequent study of the AOF *label*, described in section 4.3, all colour measurements  
265 used the digital colour image analysis method outlined above, rather than UV/Vis  
266 spectrophotometry – which could not be applied due to the opaque nature of the label.

#### 267 4.3 Characterisation of the AOF label

268 The sensitivity of the AOF *label towards* CO<sub>2</sub> should be similar, if not identical, to that of the  
269 AOF *indicator*, since the *label* is simply a polymer film encapsulated *indicator*. In order to  
270 confirm this prediction, a number of identical AOF *labels* were placed in sealed jars, each  
271 previously flushed with different CO<sub>2</sub>/argon gas mixtures, left to equilibrate for at least 48 h,  
272 and then photographed at room temperature (25 °C) and then at 5 °C. Digital image colour  
273 analysis of the photographs allowed the calculation of values of *Abs(red)*, which were used,  
274 as a substitute for 'spectrophotometric' Abs, in eqn (3), in order to generate the plots of *R* vs  
275 %CO<sub>2</sub> for the AOF *label* at 25 and 5 °C, which are illustrated in figure 5. The straight lines  
276 plots in Figure 5, reveal  $\alpha = 0.58 \%^{-1}$  and  $2.1 \%^{-1}$  values for the AOF *label* at 25 and 5 °C.  
277 Note, as expected, the former (for the AOF *label*) value of  $\alpha$  is almost identical to that of the  
278 AOF *indicator*,  $\alpha = 0.59 \%^{-1}$ . These results confirm that the CO<sub>2</sub> *sensitivity* of the AOF  
279 *indicator* is not markedly affected by the addition of the two polymer films, i.e. layers (ii)  
280 and (iv) in figure 1, both of which act as barriers to the permeation of CO<sub>2</sub> to and from the  
281 indicator film, (iii) in figure 2 (b), into the ambient air.

282 As noted earlier, key to the function of the AOF *label* is, after the food package is opened,  
283 the diffusion of CO<sub>2</sub> from the *label* to the ambient air. In order to probe this feature more  
284 thoroughly, this recovery - of the original colour - process for a typical AOF *label* was studied  
285 as a function temperature, over the range 1 to 25 °C. In all cases the *labels* were initially  
286 beige coloured, as they were stored in an atmosphere containing 25% CO<sub>2</sub> (75% N<sub>2</sub>) for at  
287 least 48 h before use. After 'opening' - and rapid substitution of the CO<sub>2</sub> atmosphere for air  
288 - these *labels* were monitored photographically until their original (CO<sub>2</sub> free) purple colour  
289 was well developed, and well beyond the pale purple colour used by Insignia technologies to  
290 signify the food product (ham in this case) is 'past best', see figure 1. The plots of some of  
291 the different data sets generated as a result of this work, in the form of *Abs(red)* vs  
292 (recovery) time, are illustrated in figure 6. The broken horizontal red line signifies the point  
293 time,  $t_{pb}$ , in the recovery when the indicator has reached the pale purple colour associated  
294 with the food product being 'past best', as illustrated in figure 1. Thus, it can be seen that  
295  $t_{pb}$  for the AOF *label* is ca. 4 days at 5 °C, as reported by Insignia Technologies Ltd. (Insignia  
296 Technologies Ltd., 2017) and that  $t_{pb}$  decreases with increasing temperature.

297 The variation of the 'past best' times,  $t_{pb}$ , can then be used to determine an approximate  
298 activation energy for recovery of the initial purple colour of the *label*,  $E_A(\text{recovery})$ , via a plot

299 of  $\ln(1/t_{pb})$  vs  $1/T$ , from which a value of the activation energy for recovery,  $E_a'$ , of  $43 \pm 5$  kJ  
300  $\text{mol}^{-1}$  was determined. This value is not too surprising since  $E_a$  for small molecule gases  
301 (such as  $\text{CO}_2$ ;  $\text{O}_2$  and  $\text{N}_2$ ) diffusion in polymers in general is typically  $50 \text{ kJ mol}^{-1}$  (Yam, 2009)  
302 and, although  $E_a$  can vary from 28-65  $\text{kJ mol}^{-1}$  for  $\text{CO}_2$  diffusion when considering a wide  
303 range of polymers, for polyethylene it is  $38.5 \text{ kJ mol}^{-1}$  (Pauly, 1999), which compares well  
304 with the value of  $43 \pm 5 \text{ kJ mol}^{-1}$  reported above.

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310 Table 1 lists the activation energy of some popular commercial TTIs from which it can be  
311 seen that the value of  $E_a'$  for the AOF *label* ( $43 \pm 5 \text{ kJ mol}^{-1}$ ) is very similar to that reported  
312 for the MonitorMark<sup>TM</sup> TTI, which is based on the diffusion of a coloured liquid along a wick  
313 ( $30\text{-}50 \text{ kJ mol}^{-1}$ ; Pocas, 2008). Other reported TTI activation energies include:  $84\text{-}100 \text{ kJ mol}^{-1}$   
314 for Fresh-Check<sup>TM</sup> (Pocas, 2008) and  $97\text{-}106 \text{ kJ mol}^{-1}$  for OnVu<sup>TM</sup> (Kreyenschmidt,  
315 Christiansen, Hubner, Raab & Petersen, 2010).

316 Ideally, any TTI *label* should have an activation energy similar to the major spoilage  
317 mechanism associated with the food. However, the latter are many (Maroulis & Saravacos,  
318 2003; Maroulis & Saravacos, 2011) and varied so that their associated  $E_a$  values span a wide  
319 range which cannot be covered by just one TTI. Thus, for example,  $E_a$  for enzymic spoilage is  
320 usually low, ( $4 - 60$ )  $\text{kJ mol}^{-1}$  whereas protein denaturation is very high ( $300 - 500$ )  $\text{kJ mol}^{-1}$ .  
321 Interestingly, common microbial spoilage lies in between these extremes ( $60\text{-}120$ )  $\text{kJ mol}^{-1}$   
322 (Labuza, Fu & Taoukis, 1992).

323 It follows that the AOF *label* would be best suited when used with foods for which the major  
324 spoilage process has an  $E_a$  value that is  $< 50 \text{ kJ mol}^{-1}$ , which includes enzymic spoilage,  
325 chlorophyll and ascorbic acid degradation, non-enzymic browning and lipid oxidation  
326 (Maroulis & Saravacos, 2003; Maroulis & Saravacos, 2011). Unfortunately, in the case of  
327 packaged ham, in which microbial spoilage is often a major process after opening, the AOF

328 label is not ideally suited to respond (to temperature changes) in a manner that reflect that  
329 of the likely spoilage mechanism associated with ham and many food stuffs. However, that  
330 isn't its primary function, which is to signal when the recommended 2 day period is up,  
331 when the food is stored under the recommended refrigeration conditions.

### 332 **Conclusions**

333 The 'After Opening Freshness *Label*', i.e. AOF *label*, currently being trialled by Sainsbury's  
334 comprises a plastic film colorimetric CO<sub>2</sub> *indicator* layer encapsulated in a polymer sheath  
335 that limits the rate of diffusion of the CO<sub>2</sub> into and out of the indicator film. The system is  
336 designed to change from a beige colour, when in the presence of ca. 25% CO<sub>2</sub>, in a MAPed  
337 package of ham, to purple, 4 days after opening the package, when held at 5 °C. When used  
338 in this way it provides an indirect indication if the food is still 'fresh' and so safe to eat by  
339 measuring the CO<sub>2</sub> loss from the sensor which is correlated to 'freshness' and 'safety'. The  
340 basic principle of this novel commercial consume within indicator has be outlined earlier by  
341 this group using an O<sub>2</sub> indicator (Mills et al., 2012). The indicator itself utilises the pH  
342 sensitive dye phenol red and is fast responding (recovering its original colour in 26 min at  
343 25°C), but this response time is greatly increased when encapsulated in the polymer sheath  
344 used in the AOF *label*, where its recovery time is ca. 30 h (at 25°C) – which is tripled to 96 h  
345 (i.e. 4 days) at 5°C. The activation energy for colour recovery is ca. 43 kJ mol<sup>-1</sup>, which is  
346 similar to a number of different food spoilage processes, although not the very temperature  
347 sensitive ones, such as protein denaturation and bacterial spore destruction for which E<sub>a</sub> is  
348 typically > 200 kJ mol<sup>-1</sup>. Overall, the AOF *label* is a promising new technology which, if  
349 embraced by the general public, could help minimise the large amount of unnecessary  
350 household food waste associated with many developed nations. In order to use it as an AOF  
351 *label* for many other very different foods, further possible work includes: a study of how the  
352 film response time varies with the %CO<sub>2</sub> in the headspace and humidity and attempts to  
353 reformulate the indicators so that it exhibits and activation energy which is nearer to that  
354 for microbial spoilage, (60-120) kJ mol<sup>-1</sup> (Labuza, Fu & Taoukis, 1992).

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