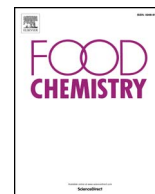




ELSEVIER

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: [www.elsevier.com/locate/foodchem](http://www.elsevier.com/locate/foodchem)

Analytical Methods

## Non-destructive monitoring of apple ripeness using an aldehyde sensitive colorimetric sensor

Yong Hoon Kim<sup>a,\*</sup>, Yun Jae Yang<sup>b</sup>, Jin Se Kim<sup>a</sup>, Dong Soo Choi<sup>a</sup>, Seok Ho Park<sup>a</sup>, So Yeon Jin<sup>c</sup>, Jung Su Park<sup>b</sup><sup>a</sup> Department of Agricultural Engineering, National Institute of Agricultural Sciences, Rural Development Administration, 310 Nonsaengmyeong-ro, Wansan-gu, Jeonju, Republic of Korea<sup>b</sup> Sookmyung Women's University, Department of Chemistry, Cheongpa-ro 47-gil 100, Yongsan-gu, Seoul, Republic of Korea<sup>c</sup> Sookmyung Women's University, Graduate School of Professional Studies Traditional Culture and Arts, Cheongpa-ro 47-gil 100, Yongsan-gu, Seoul, Republic of Korea

### ARTICLE INFO

#### Keywords:

Apple  
Aldehyde  
Ripeness  
Colorimetric sensor

### ABSTRACT

We developed an on-packaging colorimetric sensor label that can detect the aldehyde emission of apples based on Methyl Red. The sensor label was constructed using printable inks on paper medium and relied on the change in basicity caused by the nucleophilic addition reaction between aldehyde and hydroxide via the Cannizzaro reaction. The sensor can be used to detect aldehyde in solution and vapor. Sensitivity and stability toward changes in humidity were achieved by altering the concentration of OH<sup>-</sup>. Under exposure to ripening apples, the label changed color from yellow to orange, and then to red. The degree of ripeness was estimated by a sensory test and texture analysis. The color change of sensor label had showed a similar tendency to the changes in the parameters of the sensory test, soluble solid content, and hardness. Therefore, the sensor label can be used for real time on-package ripeness monitoring of apples during their shelf life.

### 1. Introduction

Apples (*Malus domestica*), a perennial of the Rosaceae family, are representative climatic fruit. The skin surrounding the fleshy parenchyma tissue comprises cuticles, the epidermal layer, and the hypodermal layer. Gas diffusion occurs across its skin at lenticels. During respiration for maturation and ripening, apples emit various organic flavor compounds, including aldehydes, esters, alcohols, ethylene, and ketones (Komthong, Hayakawa, Katoh, Igura, & Shimoda, 2006; Song, Gardner, Holland, & Beaudry, 1997; Zou & Zhao, 2008). These flavors have been used to determine fruit freshness, ripeness, and quality of maturity using non-destructive sensors, such as fluorescence sensors (Betemps et al., 2012), electronic noses (Di Natale et al., 2001; Saevels et al., 2004; Young, Rossiter, Wang, & Miller, 1999), and colorimetric chemosensors (Lang & Hubert, 2012). In particular, the development of naked-eye-detected chemosensors in smart food packaging has received much attention because of their ability to supply on-packaging indicators that provide information on maturity and ripeness to consumers. *RipeSense*<sup>™</sup>, developed by a New Zealand company, is an example of the application of on-packaging colorimetric indicators (Ripesense, 2004).

Colorimetric sensors using ethylene emission as a marker for apple

and kiwi ripeness have been developed for a long time (Cabanillas-Galan et al., 2008; Hu, Li, Park, Kim, & Yang, 2016; Klein, Riley, DeCianne, & Srinavakul, 2006; Lang & Hubert, 2012). However, this method has limited application for apple ripeness sensors, because of its cost and low stability against humidity and UV light.

A pH indicator would be an alternative material for on-packaging colorimetric indicators with respect to cost, sensitivity, and ease of preparation. In addition, aldehyde-sensitive colorimetric sensors using pH indicators have been reported. Vo, Murray, Scott, and Attar (2007) designed a sensor to detect glutaraldehyde in the liquid phase. They suggested that the chemical reaction mechanism was based on the hydrogen bond between glutaraldehyde oligomer formed by an aldol reaction and the sensor. Feng, Musto, and Suslick (2010) developed a formaldehyde detection method using the chemical reaction between formaldehyde and primary amines. In these studies, the color change arises from changes in the basicity of the sensor. Despite extensive researches on aldehyde detection and apple flavor analysis, a colorimetric sensor using aldehyde emission as a marker of apple ripeness has not yet been reported.

Therefore, we prepared various colorimetric sensors using available pH indicators to overcome the problems noted in previous studies and applied them to detect aldehyde emission as a marker for apple

\* Corresponding author.

E-mail address: [yhkim0420@korea.kr](mailto:yhkim0420@korea.kr) (Y.H. Kim).

<https://doi.org/10.1016/j.foodchem.2018.02.110>

Received 14 February 2017; Received in revised form 12 October 2017; Accepted 20 February 2018

0308-8146/© 2018 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

maturity. The colorimetric sensors that showed controllable sensitivity, selectivity, and stability in different humidities at an acceptable cost were prepared by commercially applicable printing inks and applied to determine apple ripeness.

## 2. Experiments

### 2.1. Materials

Methyl Red ( $C_{15}H_{15}N_3O_2$ , 2-(4-dimethylaminophenylazo)benzoic acid), Methyl Red Sodium salt ( $C_{15}H_{14}N_3O_2Na$ ), methanol (MeOH), gallic acid ( $C_7H_6O_5$ , 3,4,5-trihydroxybenzoic acid), Quercetin ( $C_{15}H_{10}O_7$ , 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one), sodium hydroxide (NaOH), Bromocresol Purple ( $C_{21}H_{16}Br_2O_5S$ , 4,4'-(1,1-dioxido-3H-2,1-benzoxathiole-3,3-diyl)-bis(2-bromo-6-methylphenol), Bromocresol Green ( $C_{21}H_{14}Br_4O_5S$ , 2,6-dibromo-4-[7-(3,5-dibromo-4-hydroxy-2-methyl-phenyl)-9,9-dioxo-8-oxa-9 $\lambda$ 6-thiabicyclo [4.3.0]nona-1,3,5-trien-7-yl]-3-methyl-phenol), Methyl Orange ( $C_{14}H_{14}N_3NaO_3S$ , sodium 4-([4-(dimethylamino)phenyl]diazenyl)benzene-1-sulfonate), and aldehydes were purchased from Sigma-Aldrich. A vehicle solution for ink jet printing, a wet-acrylic polymer (Newplex RB-4NF) for silk-screen printing, and apples (Fuji) were obtained from a domestic market. The vehicle solution is composed of refined water (55 v/v%), glycerin (40 v/v%), and antifreeze (5 v/v%). A binder for flexographic printing (Etistar P Trans White) was obtained from the Flint Group (Malaysia). Filter paper was obtained from Advantec Ltd (125 g/m<sup>2</sup>) and Whatman (No.2). Water used was high purity Milli-Q water (Millipore, > 18 M $\Omega$  cm). All analytical grade reagents (Sigma-Aldrich) were used without further purification.

### 2.2. Preparation of the colorimetric sensors

**Sensor 0:** Methyl Red and Methyl Red Sodium salt were dissolved in a mixed solvent (MeOH (250 mL): water (210 mL): glycerol (40 mL)). The final concentrations of the two chemical species were 1.2 mM. The solution was stirred for approximately 2 h. NaOH pellets were added to the solution and stirred at 21 °C for approximately 2 h. The final concentration of NaOH was 8 mM. The yellow-tinged solution was poured in a petri dish and a filter paper (Whatman, No.2) was immersed in it for 1 h. The wet filter paper was dried at 21 °C in the dark overnight. The filter-paper sheet was then cut into disks using a manual puncher (diameter, 12.5 mm).

**Sensor 1:** Methyl Red (0.05 g), Methyl Red Sodium salt (0.05 g), and NaOH (0.5 g) were dissolved in 10 mL of vehicle solution. The yellow-tinged ink was printed by a stamp marker on the photocopy paper. The sensor paper was dried at 100 °C for 100 s, and then cut in to pieces to test its colorimetric response toward an aldehyde.

**Sensor 2:** Methyl Red (0.2 g), Methyl Red Sodium salt (0.2 g), and NaOH (9.0 g) were dissolved in 15 mL of a mixed solvent (MeOH: water, 1v:1v). After stirring for approximately 30 min, the solution was mixed with 250 mL of a flexographic printing binder (Etistar P Trans White). The yellow-tinged ink was printed by a stamp marker. The other procedures were the same as those for the preparation of *Sensor 1*.

**Sensor 3:** Methyl Red (0.8 g), Methyl Red Sodium salt (0.7 g), and NaOH (4.75 g) were dissolved in a mixed solvent (MeOH (10 mL): water (10 mL)). After stirring for approximately 30 min, the solution was mixed with 200 g of a wet-acrylic polymer (Newplex RB-4NF). The ink slurry was printed by a silk-screen press. The other procedures were the same as those for the preparation of *Sensor 1*.

**Sensor 4:** Bromocresol Purple, Methyl Orange, and NaOH were dissolved in a mixed solvent (MeOH (250 mL): water (250 mL)). The final concentrations of the chemical species were 5 mM, 5 mM, and 40 mM respectively. The other procedures were the same as those for the preparation of *Sensor 0*.

**Sensor 5:** Bromocresol Purple (0.05 g), Methyl Orange (0.03 g), and NaOH (0.2 g) were dissolved in 10 mL of vehicle solution. The other

procedures were the same as those for the preparation of *Sensor 1*.

**Sensor 6:** Bromocresol Purple (0.2 g), Methyl Orange (0.2 g), and NaOH (9 g) were dissolved in 15 mL of a mixed solvent (MeOH: water, 1 v:1 v). The other procedures were the same as those for the preparation of *Sensor 2*.

**Sensor 7:** Bromocresol Purple, Bromocresol Green, Methyl Orange, and NaOH were dissolved in a mixed solvent (MeOH (250 mL):water (250 mL)). The final concentrations of chemical species were 5 mM, 5 mM, and 40 mM respectively. The other procedures were the same as those for the preparation of *Sensor 0*.

**Sensor 8:** Bromocresol Purple (0.05 g), Bromocresol Green (0.02 g), Methyl Orange (0.03 g), and NaOH (0.2 g) were dissolved in 10 mL of vehicle solution. The other procedures were the same as those for the preparation of *Sensor 1*.

**Sensor 9:** Bromocresol Purple (0.2 g), Bromocresol Green (0.2 g), Methyl Orange (0.2 g), and NaOH (9 g) were dissolved in 15 mL of a mixed solvent (volume ratio, MeOH:water, 1:1). The other procedures were the same as those for the preparation of *Sensor 2*.

### 2.3. Ultraviolet-visible (UV-VIS) and pH measurement

The UV-VIS spectra were obtained using a DR 5000 instrument (HACH, Germany) at 0.5 nm spectral resolution in quartz cuvettes (Hellma) with an optical pass length of 2 mm. Methyl Red and Methyl Red Sodium salt solutions (0.2 mM) were used for the absorption measurement. At the given concentration, 100 equivalents (equiv.) of propionaldehyde ( $CH_3CH_2CHO$ ) were added sequentially to basic Methyl Red solution titrated by 4 equiv. of NaOH. The mixture was ultrasonicated for 5 min before measurement. The pH measurements were performed using an ORION 3 star (Thermo Scientific, USA) equipped with a ROSS pH electrode.

### 2.4. Measurements of colorimetric response to aldehydes

In the constant illumination chamber shown in Fig. S1B, 1.5  $\mu$ L of aldehydes were dropped directly onto *Sensor 0* and the color change was recorded using a digital camera (Canon Mark III equipped with a zoom lens (aperture f/4, 24–70 mm focal length)). To investigate the response to vapors, 20  $\mu$ L of aldehyde were dropped onto the bottom of a glass vial (Fig. S1A). *Sensor 0* was hung at the top of the glass vial (55 mL) to detect aldehyde vapors, and its response was recorded until the color was saturated.

### 2.5. Measurements of colorimetric response in apple flavor

Apples (3.0 kg) and the colorimetric sensors were loaded into a desiccator. The release valves were opened to maintain atmospheric pressure. Colorimetric sensors were attached onto the surface of the apples. The desiccator was put into a thermostatic chamber fixed at 18 °C. Discoloration was recorded using a digital camera (Canon Mark III) over 24 h. RGB color values of the images were calculated using the “Eyedropper Tool” of adobe photoshop in a randomly selected area.

### 2.6. Measurements of apple hardness and soluble solid content (SSC)

Apple hardness was measured using a texture analyzer (TA-XT2, Stable Micro System Ltd., Haslemere, UK). The measurement conditions were: Pre-test speed 5.0 mm/s, test speed 1.0 mm/s, Post-test speed 5.0 mm/s, test distance 10.0 mm, and a trigger force 5 g. All experiments were performed five times.

The soluble solid content (SSC) denoted by Brix% was obtained using a saccharometer (Pocket pal-1, ATAGO, Tokyo, Japan). All experiments were performed five times.

Download English Version:

<https://daneshyari.com/en/article/7584408>

Download Persian Version:

<https://daneshyari.com/article/7584408>

[Daneshyari.com](https://daneshyari.com)