Thermochimica Acta 649 (2017) 63–68

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Effects of ascorbic acid and light on reactions in fresh-cut apples by microcalorimetry

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ARTICLE INFO

Article history:
Received 5 August 2016
Received in revised form 13 January 2017
Accepted 18 January 2017
Available online 22 January 2017

Keywords:
Microcalorimetry
Fresh-cut fruit
Ascorbic acid
UV-C light
Pulsed light

ABSTRACT

During the manufacturing of fresh-cut apples, a number of biochemical events, overall exothermic, contribute to increasing the reaction rate of the fruit and the browning of its wounded surface. This work applied isothermal microcalorimetry to compare the overall effect of such complex events before and after treatments with ascorbic acid solutions, pulsed lights or UV-C lights. Briefly, apple samples were cut into cylinders and dipped in solutions containing ascorbic acid (0–2.5%) or exposed to high energy doses of light (from 6 to 175 kJ/m^2). In general, the heat-flow signal recorded by microcalorimetry was inversely proportional to the intensity of the applied treatment. In case of treatments with ascorbic acid, the heat-flow signal was empirically deconvoluted in three distinctive signals, respectively, (I) an exponential decay, (II) a gaussian central curve and (III) a final logistical function. The first and the third functions were constant regardless of the concentration of ascorbic acid used. Only the second Gaussian function was correlated with the concentration of ascorbic acid and the area was used to evaluate the efficacy of the process. Overall, this work contributes to the understanding of the heat produced by fruit after wounding and, from a practical standpoint, can help compare the effects of different treatments on fresh cut fruits.

1. Introduction

Fresh-cut products are defined as fruits or vegetables that are processed (i.e. washed, trimmed, peeled, cut, etc.) into high quality and ready-to-eat products [1]. Their quality is typically assessed by external attributes, such as size, shape, color, glossiness, surface cleanliness and absence of defects [2]. Following cutting operations, a number of biochemical events, overall exothermic, contribute to increasing the reaction rate of the fruit and the browning of its wounded surface [3]. The rate of these physiological events affects the product shelf-life [4]. Especially the browning of fruits is a major problem in the fresh-cut fruit industry and is believed to be one of the main causes of quality loss.

To control the occurrence of these reactions, fresh-cut fruits can be submitted to different chemical or physical treatments [5]. The former includes traditional dipping of apple slices into a solution containing antioxidants (e.g. ascorbic acid) and/or chelants (e.g. citric acid) and/or salts (i.e. $CaCl_2$). More recently, to control fruit reactions, some innovative technologies have been also proposed, such as the application of electromagnetic waves in either continuous or pulsed mode. For instance, the exposure of fruits to UV-C and pulsed light has been demonstrated to inactivate polyphenol oxidase, minimizing enzymatic browning reactions in cut apples [6,7].

To evaluate the effects of such treatments on fruit reaction, the rate of change of some quality attributes (i.e. color, acidity, pH, soluble solids, texture, water loss, phenolic profile, vitamin C, carotenoids or the sensorial profile) is generally monitored. This approach makes use of destructive measurements that may require time consuming and expensive analytical techniques (i.e. chromatographic analysis of phenols, vitamins and carotenoids) on pre-treated samples [8].

Among the techniques used for measuring reaction rate in foods, animal and vegetable tissues, microcalorimetry has played a crucial role. One of the main advantages of this technique is that it measures the rate of heat production (or heat-flow) of samples contained in an ampoule, regardless of their physical state (i.e. liquid, solid or gas), non-destructively and without any previous pre-treatment. A number of studies have applied this technique to the measurement of metabolic rates in fruits under different con-

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http://dx.doi.org/10.1016/j.tca.2017.01.008
0040-6031/

ditions [9]. Other applications include the evaluation of the shelf life [10] and fresh-cut fruits metabolism [11].

Despite the importance of microcalorimetry, there has been very little research directly investigating the possibility to use heat flow data to discriminate the contribution of the reactions occurring on fruit samples after cutting. Accordingly, this work aimed to apply isothermal microcalorimetry to evaluate the effect of ascorbic acid on the resulting heat of reaction of fresh-cut apples (*Malus domestica* cv. *Golden Delicious*). Also, microcalorimetry was applied to evaluate the effect of UV-C and pulsed-light treatments. The experimental work presented here contributes to extending the possible uses of microcalorimetry and provides an opportunity to advance our knowledge on the effect of traditional and innovative technologies on foods.

2. Methods

2.1. Fresh cut apple samples

Golden delicious apples (*Malus domestica* cv. *Golden Delicious*) were purchased from the local market. Apples of uniform size and color were used in the experiments. Fruits were washed with tap water, rinsed and air-dried. All cutting utensils were sanitized with ethanol (99.8%) prior to use. The washed-apples were cut into 55 ± 2 mm long cylinders of 5 mm diameter, using a sharp stainless steel corer. The length of the cored apple cylinder was cut to 35 mm. The cylindrical apple samples from different apples were treated with dipping treatments or light treatments. Each experiment was replicated 3 times.

2.2. Dipping treatments

Dipping treatments were carried out at room temperature in aqueous solutions containing increasing concentrations of ascorbic acid from 1 to 3% (w/v) (Sigma Aldrich, Steinheim, Germany). Additional control samples were dipped in distilled water. After 60 s dipping, samples were removed from the solution. Excess surface moisture was removed by drying with a cold air blower. Samples were then introduced in the calorimetric ampoules and hermetically sealed.

2.3. Pulsed light treatments

Pulsed light (PL) treatments were carried out by using a pulsed light mobile decontamination unit (Claranor, Rouaine, France) equipped with 4 xenon lamps (JA series, Verre et Quartz, Bussy Saint Georges, France) with maximum emission in the range 200–1000 nm (200–400 nm: 41%; 400–700 nm: 51%; 700–1000 nm: 8%). Apple samples were placed on a 5 mm thick quartz plate at a distance of 10 mm from the lamps positioned above, below and at the two sides of the sample, and exposed at increasing light fluence up to 175.0 kJ/m^2, by modifying capacitor voltage (1000–3000 V). Each light pulse had a duration of 50 μs and a frequency of 0.5 Hz. After treatments, samples were incubated for 8 h in the icebox, then, introduced into the calorimetric ampoules and hermetically sealed.

2.4. UV-C treatments

UV-C light treatments were carried out using 15 W lamps (OF, OSRAM, GmbH, Germany) with a maximum emission of 253.7 nm. UV-C lamps were positioned into a thermostated cell (Climacell 222, MMM Medcenter, Einrichtungen GmbH, Graefelfing, Germany) operating at 8 °C and equipped with a system of air moisture control settled at 95% ERH to avoid sample dehydration during the treatment. Apple samples were exposed between two parallel UV-C lights for increasing time up to 120 min. Relevant fluence on the samples was equal to 6, 12 and 24 kJ/m^2. After treatments, samples were incubated for 8 h in the icebox, then, introduced into the calorimetric ampoules and hermetically sealed.

2.5. Isothermal microcalorimetry

A TAM III isothermal heat conduction calorimeter (TA instruments, New castle, Delaware, USA) was used. The instrument is a multichannel microcalorimeter able to analyze 24 ampoules simultaneously. The 4 mL glass ampoules were used. Apple samples were placed inside the ampoules, crimp sealed, and positioned inside the microcalorimeter. After an equilibration time of 45 min, the heat flow signal emitted from the ampoule containing the sample was measured at 30 °C until the signal dropped to approximately zero. The heat flow data for each treatment were normalized on the basis of the sample weight.

The enthalpy change (ΔH) of the overall metabolic response can be estimated from integration of the heat flow (φ) during the experiment time t [9].

$$\Delta H = \frac{\int_{t=0}^{t} \phi_t \cdot dt}{mol} \quad (1)$$

Finally, with the knowledge of the enthalpy of the process, the heat flow curve provides a direct estimate of the rate of the process (r) [12]:

$$r = \frac{\phi}{\Delta H} \quad (2)$$

2.6. Oxygen measurement

A Fibox 4-trace fiber-optic oxygen meter (PreSens GmbH, Regensburg, Germany) equipped with inner pressure sensors (10–1200 mbar), 5 mm Pst3 luminescence oxygen sensors, resistance temperature detectors PT 100 (0–50 °C) and 2 mm PMMA fibers was used to measure the oxygen consumption in the same ampoules as used in the calorimeter. The Pst3 oxygen sensors were used for oxygen concentration ranges from 0 to 100% with LOD 0.03% and response time <6 s. The sensors were glued to the inner surface of the ampoule with silicone (RS components, Mörfelden-Walldorf, Germany) at ½ height between the bottom and neck before the experiment. Two-point calibration in oxygen-free environment and air-saturated environment was used. Oxygen free water (100 mL) was obtained by mixing 1 g sodium sulfite (Na_2SO_3) and 50 μL cobalt nitrate ($Co(NO_3)_2$) standard solution (1000 mg/L in nitric acid 0.5 mol/L). Air saturated water was obtained by bubbling air, while stirring the solution. To prove the accuracy of the sensors, oxygen measurements were performed in ampoules filled with nitrogen and ambient air prior to measurement.

Cylindrical apple samples were placed into the ampoule and sealed with an aluminum cap to monitor the oxygen kinetics. The calorimetric ampoules were kept in a water bath at controlled temperature (30.0 °C ± 0.3). The polymer optical fibers of Fibox 4-trace were fixed perpendicularly on the sensors spot from the outside of the ampoule. The Fibox 4-trace is completely stand-alone device, controlled by PC and data manager software (version 2.0.0.57, ©GmbH, Germany). Oxygen concentration inside the ampoule was recorded every 30 min.

3. Results and discussions

3.1. Calorimetric signal

Fig. 1 shows the heat flow curves from apple cylinders, after treatment with a solution of ascorbic acid.