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COMMUNICATION

# A Colour Ripeness Indicator for Apples

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**Abstract** Ripeness and senescence of climacteric fruits are strongly related to the emission of ethylene gas. The ethylene emission of apples can be detected by a new developed ripeness indicator. This indicator is based on the reduction effect of ethylene causing colour changes in selected metal ions. The used molybdenum (Mo) chromophores change under the impact of ethylene in a colour spectrum from white/light yellow to blue because of a partial reduction of Mo(VI) to Mo(V). The sensitivity of molybdenum colour change reactions can be varied by composition and pH values (pH 1.4–pH 1.5) of used ammonium molybdate solution and thus adopted to different fruits and storage conditions. The indicator can be combined with a colour recognition sensor for quantitative measurements of colour change in the frame of the $L^*a^*b^*$ model. The $b^*$-coordinate, reflecting changes from yellow to blue, and the luminance $L^*$ continuously vary with increasing ethylene emission. Results obtained with the indicator system were compared with direct determination of ethylene concentrations by gas chromatography (GC-FID). Furthermore, a descriptive sensory test was used to estimate the degree of ripeness. The indicator can be applied for ripeness gauge on single fruit or in paperboard crates.

**Keywords** Ripeness · Apples · Ethylene · Molybdenum blue · Indicator

## Introduction

A monitoring of fresh perishable produce along the distribution postharvest chain from producer to consumer using non-destructive sensors can avoid quality losses as a result of damages or unfavourable handling conditions. However, the continuous measurement of temperature and ambient humidity, which is used in many cases, provides only indirect information about the quality of fruit. On the other hand, the ripening after harvest of climacteric fruit results in formation of volatile compounds, including ethylene (Li et al. 2011). As illustrated in Fig. 1, the ethylene emission can be used as a marker for ripeness of apple fruit.

Various analytical methods of different performance are known for measuring ethylene in air. Flame ionisation detector (FID)-based gas chromatography is a well-accepted laboratory reference method (Abeles et al. 1992). Several sensitive optical methods (Wahl et al. 2006; Schilt et al. 2009) also have been described for ethylene detection in the range of 0–10 ppm (Saari et al. 2000) and even to the low part per billion to part per million range (nanolitre/litre to microlitre/litre) (Quickert et al. 1975). These methods are still expensive and demand a large experimental setup. Also, the presence of water vapour can introduce measurement errors (Hildenbrand et al. 2008). New sensors on the base of an electrochemical cell (Jordan and Hauser 1997; Blanke 2008) or a semiconductive resistor element using tin or tungsten oxide sensing layers can detect ethylene, too (Giberti et al. 2004; Ivanov et al. 2005; Berger and Fischer 2008; Jadsadapattarakula et al. 2010). These smaller sensors are cost-effective; however, their application is limited due to deficits in sensitivity, selectivity and reliability.

Optical indicators represent another approach to reveal the presence of ethylene by colour changes. For a long time, aqueous solutions of bromine or potassium permanganate were used. The solutions, however, are not stable, and the reaction is not very selective. The reduction of expensive platinum or palladium compounds can also be used for ethylene detection. Promising are

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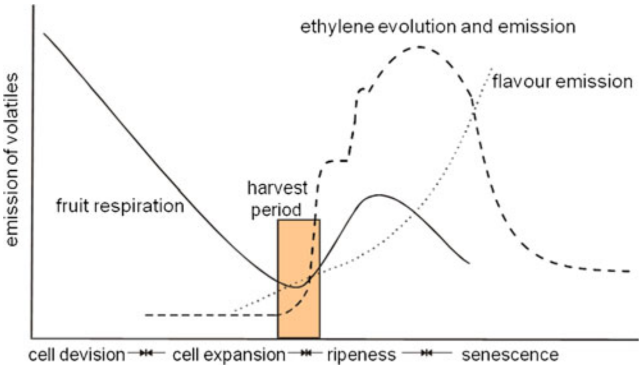

**Fig. 1** The ripening sequence of apple fruit (Dilley 1981; Blankenship and Unrath 1988) and results of ethylene measurements in this paper

molybdenum oxides, because the molybdenum(VI) ions will be fractionally reduced and provoked than the formation of intensively coloured molybdenum blue (Gouzerh and Che 2006). Kim and Shiratori (2006) used a colour reader to objectively determine changes of colour space parameters of an ethylene-responsive film. With this arrangement, ethylene emissions up to 150 ppm could be detected. However, the monitoring of ethylene evolution of fruits seems to be difficult, because most of apples already emit in a larger amount of about 100 μL/kg per hour. Colour indicators on the basis of molybdate species are sensitive to other reducing substances and UV light. Temperature and humidity are influencing parameters, too. This can result in low stability and unwanted colouration without the presence of ethylene. Therefore, the aim of the present study was to develop a stable indicator for in situ detection of ethylene emissions from apples. This can be used for continuous quality control in distribution chain of apples or as a ripening indication label for traders and consumers.

## Materials and Methods

### Fruit Material and Storage Conditions

Apples of the cultivars ‘Idared’ and ‘Golden Delicious’ were purchased from a local trader and used for the analysis of their ripening in two series. In the first, about 5 Idared apples (1 kg) were stored in a sealed 5-L glass container at 20 °C and relative humidity of 80 to 90%. The accumulated ethylene emission was recorded during a time period of 8 days. Furthermore, the evolution of ethylene of individual Golden Delicious apples was monitored during storage in a paperboard crate at room temperature (20 °C) and a relative humidity of 50 to 60% for 5 weeks.

### Preparation of Ripeness Indicator

Ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), palladium (II) sulphate ($PdSO_4$) and hydrogen peroxide ($H_2O_2$) (purchased from Sigma-Aldrich, St. Louis, USA and Merck, Darmstadt, Germany) were used for the preparation of an aqueous indicator solution. The pH value was stepwise adjusted with $H_2SO_4$ between 1.4 and 1.5 using a pH meter (Hanna Instruments, Kehl am Rhein, Germany). A specific cellulose-free fibre filter (Whatman Ltd., Dassel, Germany) was used as substrate material. Pieces of substrates were punched-out, impregnated with the indicator solution and dried in air. Filter discs, prepared that way, could be directly fixed on individual apples as indicator labels. For investigation in a storage container, the indicator labels were shrink-wrapped with a selective permeable polymer membrane to protect against intrinsic high humidity.

### Colour Recognition Sensor

A colorControl LT1 (eltrotec GmbH, Uhingen, Germany) was used to determine the colour of the indicator and its colour changes due to the reaction with ethylene. According to the $L^*a^*b^*$ colour model (CIELAB; DIN 6174: 2007–10, 2007), quantitative colour components were measured and transferred to a PC for displaying. In two series, two to four indicator labels of each composition were placed in the headspace of 1 kg of Idared apples in the glass container. The colour change of indicator labels and the ethylene emission were measured in intervals of 20 h (series 1). Additionally, a total colour difference (TCD) value ($\Delta E$), which considers the change of all coordinates, was calculated according the following equation (Francis 1983; Azarte-Vázquez et al. 2011):

$$\Delta E = \left[(\Delta L)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2}.$$

### Sensory Test

In order to describe fruit ripeness by sensory impressions, an additional sensory test was performed (DIN 10964: 1996–02, 1996). For sensory analysis, Golden Delicious apples were investigated. At the beginning, each apple was labelled with the ripeness indicator (CF2). After preparation, Golden Delicious apples were stored in a paperboard crate (series 2). During a period of 5 weeks, always six Golden Delicious apples were taken from the board and tasted and scored by a panel consisting of ten people (four male and six female with age from 18 to 60 years). The grading system was based on scores from 1 to 5 (scale) in categories sweetness, softness, juiciness and aroma. In addition, the prevailing subjective status of ripeness was assessed from unripe to overripe. The samples were tasted by the individual taster independently, and the mean value of scores was calculated. Furthermore, colour changes of indicator labels and the evolution of ethylene in the apple core were investigated at intervals of 2 days during a period of 5 weeks.

### Gas Chromatography

For reference analysis of ethylene, a gas chromatograph (HP 6890, Hewlett-Packard, Palo Alto, USA), equipped with flame ionization detector ($t_{\mathrm{FID}}$=250 °C) and 30 m× 0.53 mm×40 μm fused silica capillary column (HP/Plot-Q), was used. Flow rate of the carrier gas (helium) was set to 4.5 mL/min, and the oven was maintained at 40 °C. Ethylene peaks were obtained at a retention time of 3.7 min. From calibration with samples of known ethylene contents, a detection limit of 0.022 μL/L was estimated.

With a gas-tight syringe (SGE Analytical Science, Victoria, Australia), gas samples were taken either directly from the fruit cores or from headspace of sealed glass container filled with apples. For head space analysis, gas samples were taken every 20 h. Then the glass container was opened for gas exchange and sealed again. An aliquot (1 ml) of the gas sample was injected and analyzed by gas chromatography. Sampling was always done in triplicate. The respective ethylene evolution and emission rates are calculated from the peak areas of the chromatograms on the basis of the calibration. The averaged uncertainty of ethylene amount for headspace analysis was estimated by the standard deviation of ±14 μL/L kg and ±170 μL/L kg for apple core measurements.

## Results and Discussion

### Colour Measurement

Ripeness indicators of three colour formulations (CF), prepared at distinct pH, differentially change colour (expressed as $a^*$, $b^*$ and $L^*$) when exposed to ethylene. Ethylene produced by Idared apples in the sealed glass container let all colour parameters continuously alter with increasing ethylene emission (Table 1). The $b^*$ values, representing the colour change from yellow to blue, showed the largest changes. Also lightness $L^*$ decreased due to the blue colouration of the indicator. The composition of the indicator solution largely influenced the ethylene sensibility of indicator tags (Fig. 2). The relation between the measured colour parameters $b^*$ and the ethylene amount exposed to the indicator tags can be fitted by a nonlinear regression with second order polynomial (Table 2). In addition, a correlation between parameters of the colour model ($b^*$ values) and storage time could be established empirically. In fact this implies the ethylene amount, but it can be of interest for application of these indicator tags for fruit monitoring. In Fig. 3, total colour difference $\Delta E$ is displayed in dependence on storage time. Again the data can be fitted by polynomial function of second order. The additional inclusion of the pH values in the regression is possible both for $b^*$ and $\Delta E$ but results in a reduced match. Nevertheless, an increase of acidity resulted in more pronounced colour changes, especially the $b^*$-coordinate decreased toward intensive blue colour. The formed molybdenum blue allows conclusions on the emission of ethylene during the ripening process or the storage time. Therefore, the

**Table 1** Ethylene generated colour change of three different ripeness indicators

| Ethylene amount (in μmol) | CF1 (pH=1.50) | | | | CF2 (pH=1.45) | | | | CF3 (pH=1.40) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $a^*$ | $b^*$ | $L^*$ | $\Delta E$ | $a^*$ | $b^*$ | $L^*$ | $\Delta E$ | $a^*$ | $b^*$ | $L^*$ | $\Delta E$ |
| 0 | −10.0 | −3.8 | 87.9 | 0 | −9.2 | −5.1 | 86.2 | 0 | −10.4 | 6.9 | 82.1 | 0 |
| 4 | | | | | −10.5 | −6.3 | 83.9 | 2.6 | −6.1 | −7.6 | 78.4 | 15.5 |
| 6 | −12.0 | −6.4 | 86.8 | 3.5 | | | | | | | | |
| 9 | | | | | −8.3 | −13.0 | 76.7 | 12.5 | −8.5 | −15.1 | 73.5 | 23.7 |
| 12 | −10.7 | −3.0 | 86.0 | 2.2 | −8.8 | −14.0 | 76.1 | 13.6 | −8.8 | −17.2 | 70.6 | 26.7 |
| 17 | −7.0 | −7.3 | 81.1 | 8.2 | | | | | | | | |
| 20 | | | | | −6.3 | −19.6 | 64.9 | 26.0 | −6.3 | −23.3 | 61.4 | 36.8 |
| 22 | | | | | −5.2 | −23.7 | 60.6 | 32.0 | −5.4 | −25.3 | 57.4 | 40.9 |
| 26 | | | | | −1.9 | −25.4 | 57.7 | 35.9 | −3.1 | −27.4 | 53.6 | 45.2 |
| 28 | −6.9 | −12.8 | 74.6 | 16.4 | | | | | | | | |
| 29 | | | | | −1.8 | −26.9 | 52.8 | 40.7 | −2.0 | −26.8 | 51.2 | 46.5 |
| 31 | −7.5 | −13.9 | 73.6 | 17.7 | | | | | | | | |
| 36 | −7.0 | −16.4 | 70.2 | 21.9 | | | | | | | | |
| 40 | −4.7 | −18.7 | 66.5 | 26.6 | | | | | | | | |

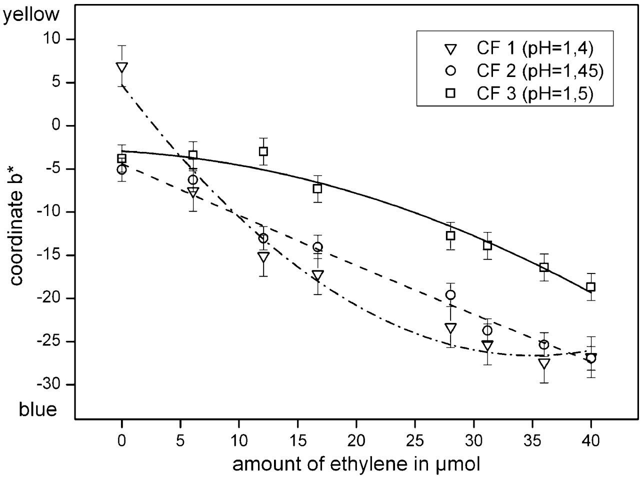

**Fig. 2** Changes of *b**-coordinate of three different colour formulations (CF) due to integrated accumulated amount of ethylene in the headspace of glass container filled with Idared apples where the sensor is placed

ripening of apples can be characterised in relation to the expected ethylene emission rate.

## Mechanism of Colour Change

The chemical reactions of ethylene with molybdenum oxides, which are responsible for the colour change, are not completely known and studied in detail yet (De-Liang et al. 2010).

The molybdate anion $[Mo_7O_{24}]^{6-}$ partly decomposes in acidic solutions of pH<2, and various isopolymolybdate species like $[MoO_4]^{2-}$, $[Mo_8O_{26}]^{4-}$ or $[Mo_{36}O_{112}\,(H_2O)_{16}]^{8-}$ are formed. Their amounts will change in dependence on Mo/$H_2O$ ratio and pH value (Pope 1983). In preliminary investigations, it was observed that colour indicators on the basis of isopolymolybdate species are sensitive to other reducing substances and UV light. Temperature and humidity do have an influence on the colour change. This can result in low stability and unwanted colouration already without presence of ethylene. In contrast, it was found that more stable and robust indicators in comparison to polymolybdate can be prepared by the use of peroxymolybdate (Klein et al. 2006). The formation of peroxymolybdate can be described for instance by the following equation:

$$[Mo_8O_{26}]^{4-} + 4H_2O_2 \rightarrow \left[Mo_8O_{24}(O_2)_2(H_2O)_2\right]^{4-} + 2H_2O. \quad (1)$$

This species was chosen as an example because an $(NH_4)_4[Mo_8O_{24}(O_2)_2(H_2O)_2]{\cdot}4H_2O$ can be precipitated from an acidic ammonium molybdate solution of pH 1.5 to 2.8 (Trysberg and Stomberg 1981). The impact of ethylene will cause a decomposition of the peroxomolybdate:

$$2C_2H_4 + \left[Mo_8O_{24}(O_2)_2(H_2O)_2\right]^{4-} \rightarrow 2C_2H_4O + \left[Mo_8O_{26}(H_2O)_2\right]^{4-}. \quad (2)$$

In addition, a partial reduction of molybdenum(VI) takes place and gives species with mixed valence and blue colour:

$$C_2H_4 + \left[Mo_8O_{26}(H_2O)_2\right]^{4-} \rightarrow C_2H_4O + \left[Mo_8O_{25}(H_2O)_2\right]^{4-}. \quad (3)$$

Of course, further, other more complex species with a relative molar mass of more than 800 atoms and mixed valence of molybdenum ions are known for "molybdenum blue" (Csanyi 1989; Müller et al. 1995). Nevertheless, the reduction of the molybdenum(VI) ion by ethylene is retarded in the peroxymolybdate anion compared to the polymolybdate. This may be caused by a higher, protective oxygen coordination of the molybdenum ion (Zhou et al. 2004). Also the previous reaction of ethylene with the peroxy group takes place. In addition, ethylene also reacts first with the peroxo group of the molybdate according to Eq. 2. Palladium ions in the indicator solution support the reaction, probably the electron transfer. Palladium ions can be reduced to dark metallic palladium particles, which also contribute to a decrease of *L**.

**Table 2** Fitting parameters

| No. | Regressand | pH | Parameter | | | | | $R^2$ | RMSE | RPD |
|---|---|---|---|---|---|---|---|---|---|---|
| | *b** | | *a* | *b* | *c* | *d* | *e* | | | |
| 1 | *b** | 1.4 | 4.744±1.764 | −1.789±0.215 | 0.0255±0.0051 | – | – | 0.97 | 2.37 | 5.7 |
| 2 | *b** | 1.45 | 4.391±1.135 | −0.6078±0.1383 | 8.604E-4±0.003 | – | – | 0.98 | 0.97 | 6.4 |
| 3 | *b** | 1.5 | −2.943±1.070 | −0.0799±0.1303 | −0.0082±0.0031 | – | – | 0.96 | 0.8 | 5.0 |
| 4 | *b** | 1.4–1.5 | 0 | 1.282±0.291 | 88.98±26.34 | 0.01854±0.0080 | 61.05±18.00 | 0.76 | 4.72 | 2.0 |
| 5 | Δ*E* | 1.4 | 0 | 0.5262±0.0599 | −0.00157±0.00037 | – | – | 0.98 | 4.0 | 8.3 |
| 6 | Δ*E* | 1.45 | 0 | 0.2259±0.0265 | −7.722E-5±1.632E-4 | – | – | 0.99 | 1.77 | 14.1 |
| 7 | Δ*E* | 1.5 | 0 | 0.0928±0.0219 | 2.305E-4±1.348E-4 | – | – | 0.99 | 1.46 | 10.4 |
| 8 | Δ*E* | 1.4–1.5 | 0 | 1.809±0.3231 | 217.15±29.23 | 0.02152±0.00889 | −150.12±19.97 | 0.89 | 5.25 | 3.0 |

The following functions were fitted: Lines 1–3: $b^* = a + b \cdot x_1 + c \cdot x_1^2$; Line 4: $b^* = a + b \cdot x_1 + c \cdot x_2 + d \cdot x_1^2 + e \cdot x_2^2$; *b** colour coordinate, $x_1$ ethylene amount, $x_2$ pH value. Lines 5–7:$\Delta E = a + b \cdot x_1 + c \cdot x_2 + d \cdot x_1^2$; Line 8: $\Delta E = a + b \cdot x_1 + c \cdot x_2 + d \cdot x_1^2 + e \cdot x_2^2$; Δ*E* averaged colour change, $x_1$ storage time, $x_2$ pH value

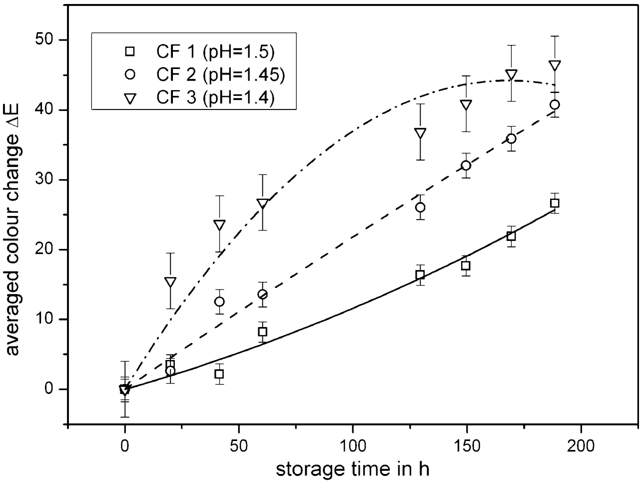

**Fig. 3** Changes of total colour differences of indicator labels due to ethylene formation in headspace during storage of Idared apples in glass container

## Sensory Analysis

After general assessment, the apples' ripeness, flavour, taste, sweetness, aroma and juiciness were appraised. Even the results of aroma sensory test scatter due to the subjective perception; however, the following tendencies can be deduced. During ripening, the colour of the pericarp of Golden Delicious apples changed from light green to yellow-orange, while the pulp remains white to light yellow. The change of consistency reflects the water loss, cell wall disintegration and starch degradation of apples during ripening and senescence. Senescence is also noticeable by the perceived odour. The smell of both pericarp and pulp changes from "aromatic and fresh" to "musty, old and sticky". The results of the classification of ripeness criteria in the sensory analysis are given as a polar plot in Fig. 4 (Mota et al. 2011). As expected, the estimated general ripeness state as well as softness of skin and pulp increased during the storage, whereas juiciness and aroma content decreases. The sweetness remains nearly constant, which is typical for these apples.

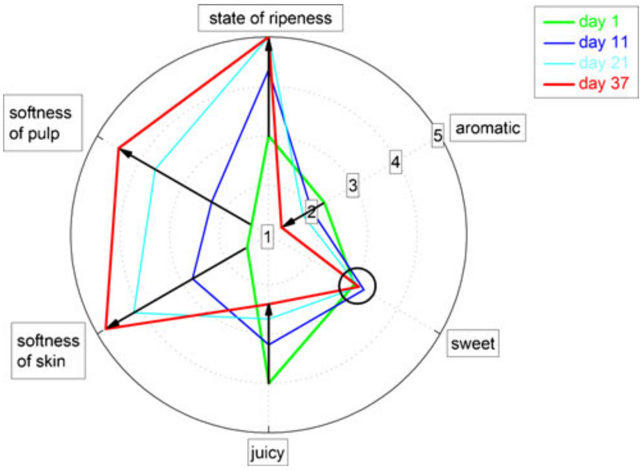

**Fig. 4** Polar plot for Golden Delicious apple ripening according to sensory properties (quality level from 1 to 5)

## Correlation of Colour Indication and Sensory Test

In order to demonstrate a correlation between different methods for description of ripeness, Golden Delicious apples were investigated from unripe to overripe states in a period of 37 days. The comparison of results from sensory ripeness testing and ethylene gas detection from the fruit core (IEC) by GC-FID with colour change will allow a verification of the developed indicator. Figure 5 outlines the findings for individual fruit stored in a paperboard crate. As expected, the amount of produced ethylene gas increased continuously. The observed saturation at longer storage time corroborates the chronological ripeness sequence of apples illustrated in Fig. 1. Although there is a scatter in the ripening process of individual apples, a correlation between the increasing sensory ripeness and the indication of the colour paper tags is emerging. The subjectively appraised degree of sensory ripeness of the apples rises in the scale of 3 to 5. Colour changes from white to blue of the ripeness indicator labels on the apples were clearly visible over the studied time.

The first molybdenum blue appeared on the indicator labels CF2 only after 17 days. The ripening indicator shows a partial step by step and finally integrated blue colouring over the whole substrate area. An intense dark blue colour of the indicator labels was obviously reached in final ripening stage. Colour changes of indicator labels can be quantified by the optical sensor (compare Figs. 2 and 3).

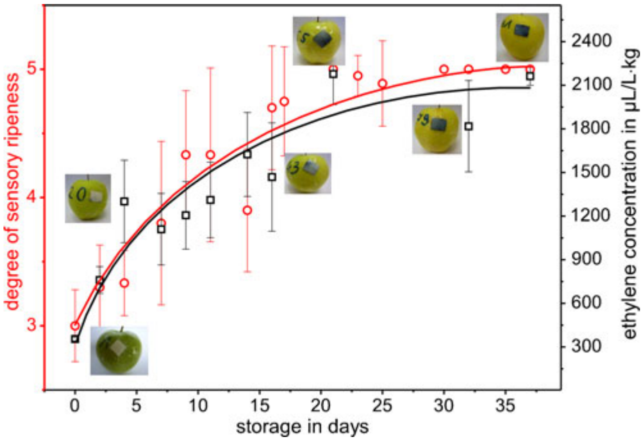

**Fig. 5** Ripening process of Golden Delicious apples during storage in paperboard crate at 18 to 20 °C, indicated by ethylene concentration, measured in the fruit core, degree of sensory ripeness and colour indicator (CF2)

Thus, indicator labels enable a rapid non-destructive detection and continuous monitoring of the ripening behaviour of the Golden Delicious apples during a storage period of up to 5 weeks. The indicator sensitivity can be adopted by variation of pH value and composition to different fruits and storage conditions. The obtained information can contribute to avoid quality losses in the postharvest processing of apples.

## Conclusions

A colour indicator on the basis of molybdenum blue can contribute to specify the ripeness of apples. The colour change from white/yellow to blue is caused by the partial reduction of the peroxymolybdate by ethylene. The colour change correlates with the amount of ethylene emitted from a single fruit (IEC) or with exposition time in an ethylene containing atmosphere of storage gas. The ripeness indicator is suggested for quality monitoring in fruit logistic chain or as display of the degree of ripeness for traders and consumers.

The application of colour indicator on the basis of molybdenum blue will be investigated on the ripeness process of further climacteric fruits as a next step.

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