

QUALITY ASSESSMENT OF DICED ONION (*ALLIUM CEPA* L.) USING AN ELECTRONIC NOSE

L. ABBEY AND D. C. JOYCE

L.A.: Institute of BioScience and Technology, Cranfield University, Silsoe, Bedfordshire, MK45 4DT, UK; D.C.J.: Institute for Horticultural Development, Agriculture Victoria, Private Bag 15, Ferntree Gully Mail Centre, Victoria 3156, Australia

Abstract

Evaluation of diced onion (*Allium cepa* L.) quality using a potentially more efficient 32 conducting polymer sensor electronic nose (E-nose) was investigated. Diced (ca. 6 mm³) brown onion was sealed in 50 µm thick polyethylene bags and stored for 3, 6 and 9 days at 4 °C. E-nose sensor response (%dR/R) to samples headspace gas did not change significantly ($P > 0.05$) over the initial 6 days of storage but significantly ($P < 0.05$) reduced from 1.91 per cent on day 0 to 1.70 per cent on day 9. Mahalanobis distance (D^2) values for separation of headspace volatiles data set clusters increased with increasing storage period. Pyruvic acid concentration reduced significantly ($P < 0.01$) by 12, 13 and 27 per cent on 3, 6 and 9 days, respectively. Greatest reduction in dry-matter content, from 18 to 16 per cent, was recorded between days 0 and 3. Time to maximum lachrymatory potency (hotness) increased from 34 s response time on day 0 to 42 s on day 3, after which it could not be sensed. A positive linear correlation ($r = 0.803$) was found between %dR/R (Y) and pyruvic acid concentration (X). Overall, the results suggest that the conducting polymer sensor E-nose could be used to monitor quality of minimally processed onion.

Résumé

ABBEY, L. & JOYCE, D. C.: *Evaluation qualitative d'oignon (Allium cepa L.) coupé en cube utilisant un nez électronique.* Evaluation de la qualité d'oignon (*Allium cepa* L.) coupé en cube utilisant le nez électronique (nez - E) détecteur polymère à conducteur 32 qui est potentiellement plus efficace était enquêtée. L'oignon brun coupé en cube (ca. 6 mm³) était emballé dans les sachets en polyéthylène de 50 µm épais et mis en stock pour 3, 6, et 9 jours à 4 °C. La réaction (%d R/R) du détecteur nez - E aux gaz à la tête de l'espace d'échantillons n'a pas changé considérablement ($P > 0.05$) pendant les 6 jours initiaux de stockage mais réduisait considérablement ($P < 0.05$) de 1.91 pour cent au jour 0 à 1.70 pour cent au jour 9. Les valeurs de la distance mahalanobis (D^2) pour la séparation d'un set de données groupées des gaz volatils à la tête de l'espace, augmentaient avec l'augmentation de la période de stockage. La concentration de l'acide pyruvique réduisait considérablement ($P < 0.01$) par 12, 13 et 27 pour cent respectivement aux jours 3, 6 et 9. La plus grande réduction en teneur de matière sèche, de 18 à 16 pour cent était enregistrée entre les jours 0 et 3. Le temps à la puissance lacrymatoire maximum augmentait de 34 s du temps de réaction au jour 0 à 42 s au jour 3, après quoi on ne le détectait plus. Une corrélation linéaire positive ($r = 0.803$) était découverte entre %d R/R (Y) et la concentration de l'acide pyruvique (X). D'ensemble les résultats suggèrent que le nez-E détecteur polymère à conducteur pourrait être utilisé pour contrôler la qualité d'oignon à peine traité.

Introduction

Onions (*Allium cepa* L.) are eaten for their distinctive aromas and tastes (Block, 1992). There is a trend of increasing consumer demand for minimally processed foods (Resurreccion & Prussia, 1986), including fresh cut onion.

Preference for minimally processed food can be attributed to produce freshness, safety, availability and convenience. However, minimally processed fresh foods have short shelf life compared with their intact counterparts (Ohlsson, 1994). Thus, it is important to monitor their quality, which is

currently done mostly by sensory methods (Pal, Sachdev & Singh, 1995; Giese, 2000).

The harvested onion bulb is a living organ prone to stress leading to alteration of normal metabolic activities and to senescence (Kader, 1992; Zagory, 1999). Cutting of onion bulbs initiates biochemical, physiological and microbiological processes that reduce shelf life. Minimal processing techniques such as dicing, wedging, slicing and ringing of onion bulbs cause tissue injury and reduce shelf life (Howard *et al.*, 1994; Blanchard *et al.*, 1996). For example, reductions in sugar concentration and other food reserves are faster in diced onion bulbs compared to intact bulbs (Blanchard *et al.*, 1996). Such differences can be attributed to increased rates of respiration due to an increase in oxygen influx into diced onion tissues. Rapid superficial microbial development fuelled by the release of cellular fluid during cutting processes also increases overall respiration rate, and enhances discolouration of fresh cut onion (Howard *et al.*, 1994; Khatoon & Hakim, 1999).

Headspace flavour volatiles for diced onion in modified atmosphere package (MAP) bags reduce in concentration with increasing duration of storage (Howard *et al.*, 1994). Similarly, total flavour, as indicated by pyruvic acid content, reduces with increasing storage period (Blanchard *et al.*, 1996). Moreover, reduction in flavour quality of minimally processed onion in MAP bags is associated with increases in off-flavour compounds such as methanethiol and propanethiol (Toivonen, 1997). Anaerobic conditions created as tissue senesces, and as a result of microbial activity, may also contribute off-flavour compounds; including ethanol, ethyl acetate and acetaldehyde (Larsen & Watkins, 1995; Keshri & Magan, 2000).

Quality assessment of foods in general, including minimally processed onion, is conventionally by sensory and analytical tests (Pal, Sachdev & Singh, 1995; Giese, 2000). However, these conventional tests can be costly,

time-consuming and technically complex. In addition, results from sensory appraisals of onion samples may be neither reliable nor repeatable due to panellist fatigue and inconsistencies even though it is a single most important and widely used quality evaluation method (D. O'Connor; personal communication). Recently, relatively novel electronic nose (E-nose) technology has been used to evaluate storage qualities of tomato (Sinesio *et al.*, 2000), meat, fish, edible oils and fats (Adechy, Shiers & Squibb, 2000) and milk (Korel & Balaban, 2002). The genotypic differences amongst garlic, leek, chive, bulb onion and spring onions were discriminated using E-nose (Abbey, Joyce & Aked, 2001). Cluster analysis and principal component analysis (Mark & Tunnell, 1985; Wold, Esbensen & Geladi, 1987), along with changes in E-nose sensor conductivity, were used to discriminate odour quality of these alliums.

The conducting polymer-based E-nose sensor comprised an array of tiny elements that interact with headspace volatile molecules. Conductance of the various individual polymer units alters upon absorption and desorption of volatiles. Resultant resistance signals are processed using mathematical algorithms to yield output data that fingerprint the odour characteristics of the sample presented (Gopel *et al.*, 1998; Giese, 2000). E-nose devices are safe, easy to use and cost-effective. Relatively large numbers of samples can be analysed per unit time, and automation of odour evaluation is possible (Payne, 1998; Giese, 2000).

The study investigates the use of a 32-conducting polymer sensor E-nose for monitoring quality changes in diced onion, processed and packaged, by a UK wholesale food supply company.

Experimental

Sample preparation

Brown onion bulbs were peeled and left for 24 h to equilibrate to room temperature in a commercial

food processing factory (Parrapak Foods Ltd, UK). The peeled onion bulbs were disinfected by dipping in $5 \mu\text{g l}^{-1}$ chlorine water before dicing to about 6 mm^3 . The diced onion (250 g) was sealed in 1.3-l capacity $50 \mu\text{m}$ thick transparent polyethylene film bags with an oxygen permeability of $49,500 \text{ cm}^3 \text{ O}_2 \text{ linear}^{-1} \text{ m}^{-1} \text{ day}^{-1} \text{ atm}^{-1}$ (P-Plus, Danisco Flexible Ltd, UK).

Storage and experiment design

The diced onion, sealed in polyethylene film bags, was stored at 4°C . A randomised complete block design was adopted with three replications. Each block (a tray) was comprised of two sample bags of sealed diced onions for each storage period of 3, 6 and 9 days. Thus, there were six bags arranged in a single layer on each tray. Diced onion for initial assessment (day 0) was stored under the same conditions for 20 h before analysis. This delay was adopted because minimally processed onion from the factory reaches sales destinations within 24 h of processing, packaging and handling at low temperature.

Data collection and statistical analyses

E-nose discrimination. Diced onion for each time treatment from each of the three blocks was homogenised in a Moulinex (Tipo 753; Patendo, Spain) mixer at room temperature. After 20 min, this bulk homogenate was mixed (1:1 w/v) with 5 per cent trichloroacetic acid (TCA) for 20 s to terminate alliinase activity. One ml of the resultant solution was placed in a 100-ml Schott bottle and moved into the sample station of an AromaScan LabStation System (Model A32/8S; Osmetech, UK) to equilibrate for 10 min at 25°C and 30 per cent R.H. Headspace gas was then sampled for a period of 70 s at a gas flow rate of 50 ml/min. The response of the E-nose 32-conducting polymer sensor to the headspace volatiles was processed and analysed using A32S Microsoft Windows Version 3.24B software (AromaScan Plc., UK).

Pyruvic acid concentration. One ml aliquots

of homogenate/TCA (1:1 v/v) solution were dispensed into conical flasks. Then, 1 ml aliquots each of 0.0125 per cent (w/v) 2,4-dinitrophenylhydrazine (2,4-DNPH) and deionised water were added. This cocktail was mixed for 20 s and then warmed in a water bath at 37°C for 10 min. Five ml of 0.6 N NaOH was then added and the cocktail mixed for another 20 s. An UV/VIS spectrophotometer (Model PU8730; Unicam, UK) was used to measure absorbance at 420 nm. Absorbance was converted to $\mu\text{mole pyruvic acid g}^{-1}$ fresh weight using a sodium pyruvate standard calibration curve (Schwimmer & Weston, 1961; Randle & Bussard, 1993).

Sensory appraisal of lachrymatory potency. A simple assessment of lachrymatory potency (LP) of the diced onions was carried out. Diced onion samples (20 g) from each block were placed on glass plates and labelled with two digit numbers. Samples were selected at random and the time to maximum lachrymatory potency (time-intensity of hotness), as sensed by the tongue during chewing, was recorded with a stopwatch (Larmond, 1982). Each test was repeated three times.

Total soluble solids content. Diced onion samples were homogenised. A hand-held refractometer (Model PR1; Atago Co. Ltd, Japan) was used to determine the total soluble solids (TSS) content of the homogenate.

Dry matter content. Diced onion samples were weighed before and after oven drying at 65°C for 48 h. Percentage dry-matter (%DM) content was then calculated on fresh weight basis.

Data analysis and presentation

E-nose data set clusters of headspace volatiles for the different storage periods were compared in a two-dimension (2D) principal component analysis (PCA) plot. The PCA was used to reduce the size of the data from the 32 E-nose sensor polymers, and for outlier detection and estimation of correlation structure between the variables (Wold, Esbensen & Geladi, 1987). Eigenvalues

(variances) were calculated by multiplying the proportion of explained variance by the number of variables for each axis; these being principal component 1 (PCA 1) on the X-axis and principal component 2 (PCA 2) on the Y-axis. Each PCA explains the percentage variance in the data. Mahalanobis distance (D^2) statistic was used to determine the degree of significance of separation between PCA 1 and PCA 2 data sets of headspace volatile clusters in the 2D PCA plot (Mark & Tunnell, 1985). D^2 is determined from principal component scores, and assumes a multivariate normal distribution for a given population. Mathematically, D^2 is defined as $D_i^2 = [(x_i - \mu)\Sigma^{-1}(x_i - \mu)']$; where x_i = distance from i th sample, μ = class centroid for the population, Σ = population variance which explains data dispersion around the centroid (Shah & Gemperline, 1989). $AD^2 > 3.0$ (i.e. three standard deviations) between two data set clusters is considered significant separation (Mark & Tunnell, 1985).

A dendrogram was plotted by hierarchical

cluster analysis of observations using Minitab for Windows Version 12.23 software (Minitab Inc., USA) to show relationships among E-nose data set clusters. E-nose sensor response data sets, determined by relative changes in sensor resistance ratio (%dR/R), were transformed by the square-root transformation rule in preparation for ANOVA (Gomez & Gomez, 1984) using Minitab. However, for convenience of interpretation, the original data for %dR/R are tabulated. ANOVAs for balanced designs were also performed on pyruvic acid concentration, lachrymatory potency, total soluble solids content and percentage dry-matter. The least significant difference (LSD) method was used to separate treatment means at $P = 0.05$.

Results and discussion

E-nose data set clusters for headspace volatiles of the sealed diced onion separated in space with increasing storage period (Fig. 1 and 2). PCA 1 and PCA 2 explained nearly 76 per cent of the

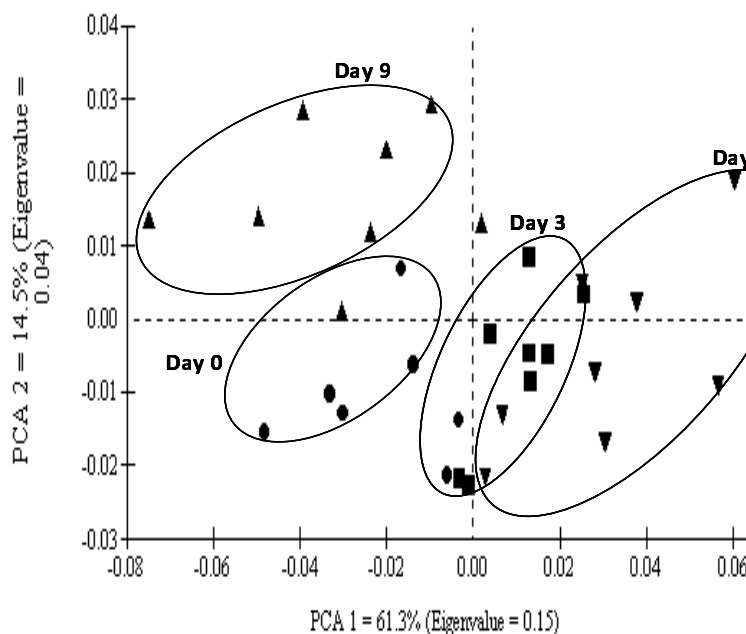


Fig. 1. Two-dimensional (2D) principal component analysis (PCA) plot of E-nose data set clusters for headspace volatiles of diced onion in sealed polyethylene film at three different storage periods

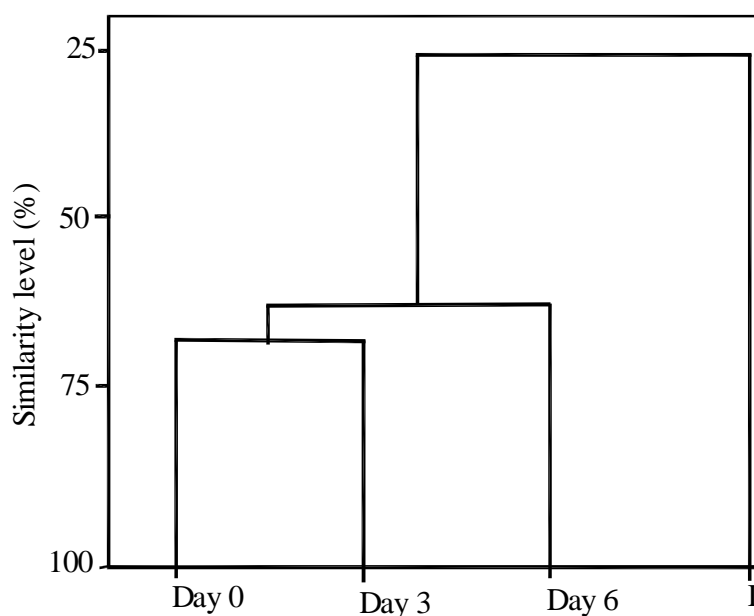


Fig. 2. Dendrogram of E-nose sensor responses for headspace volatiles of diced onion in sealed polyethylene film at three different storage periods

total variance in headspace volatiles. PCA 1 accounted for over 61 per cent (Eigenvalue = 0.15) of the total variance as compared with 15 per cent (Eigenvalue = 0.04) accounted for by PCA 2. The relative location of each data set cluster of headspace volatiles in the PCA map was dependent on the storage period for the diced onion. Data set clusters for headspace volatiles shifted from left to right across the PCA map as storage period was extended from day 0 (initial assessment before storage) to day 6. The increase in storage duration resulted in significant ($D^2 > 3.0$) increases in the distances between E-nose data set clusters for each of days 3 ($D^2 = 3.6$), 6 ($D^2 = 5.8$) and 9 ($D^2 = 7.0$) with reference to day 0 (Table 1). Thus, even after just 3 days, there was a change in headspace volatiles for the diced onions.

Interestingly, the position of data set cluster for day 9 deviated from the trend observed from day 0 up to day 6. This cluster was located up

TABLE 1

Mahalanobis distance (D^2) values for E-nose data set cluster separation on a 2D PCA plot for diced onion headspace volatiles at three different storage periods

	Day 0	Day 3	Day 6
Day 3	3.6	-	-
Day 6	5.8	4.3	-
Day 9	7.0	10.1	11.6

above day 0 on the left hand-side of the PCA map. The position of the data set cluster for day 9 explains the greater D^2 values for days 3 or 6 *versus* day 9, these being 10.1 and 11.6, respectively, compared to 7.0 for day 0 *versus* day 9. The deviation from the established trend may reflect significant changes in tissue metabolism and microbial load, which, perhaps, were due to the onset of anaerobic respiration and favourable conditions for microbial growth (Howard *et al.*,

1994; Khatoon & Hakim, 1999). Further work is required to test this proposition.

Three different sets of E-nose data clusters for diced onion headspace volatiles were identified in the cluster analysis dendrogram (Fig. 2). Cluster one consisted of an overlap of data sets for days 0 and 3, while days 6 and 9 comprised separate clusters two and three, respectively. Thus, the dendrogram suggests differences for diced onion flavour volatiles over the first 3 days of storage compared to samples stored for longer. The similarities in headspace volatiles showed in the dendrogram (Fig. 2) support those evident in the 2D PCA plot (Fig. 1).

Increases in off-flavours in modified atmosphere packaged (MAP) diced onion headspace (Howard *et al.*, 1994; Toivonen, 1997) presumably contributed to the observed trends for separation of E-nose data set clusters in the PCA plot and the dendrogram (Fig. 1 and 2). Volatiles production by spoilage organisms (Keshri & Magan, 2000), loss through the semi-polyethylene film of low molecular weight aromatic

sulphur volatiles that comprise onion flavour, degradation of flavour compounds by enzymes and/or reduced alliinase activity due to prolonged storage at low temperature (Lewis *et al.*, 1977), and metabolic switches from aerobic to anaerobic respiration (Larsen & Watkins, 1995) can all increase production of off-flavours. Such processes apparently differentially influenced responses of the E-nose sensor elements over time.

Nonetheless, relative changes in the E-nose sensor resistance ratio (%dR/R) of the 32-conducting polymer sensor were not significantly ($P > 0.05$) different for days 0, 3 and 6 (Table 2). However, a small but significant ($P < 0.05$) difference in %dR/R was recorded for day 9. Thus, the PCA-based approach to analysing the data was the more sensitive method.

Total pyruvic acid concentration in the MAP diced onion reduced with increasing storage duration between day 0 and day 9 (Table 2). Percentage reductions in pyruvic acid concentration on days 3, 6 and 9, as compared to

TABLE 2

E-nose conducting polymer sensor resistance ratio (%dR/R), pyruvic acid content, lachrymatory potency (LP), total soluble solids and dry matter contents of diced onion in sealed polyethylene film bag at different storage periods (mean \pm standard error)

Day	%dR/R	Pyruvic acid content $\mu\text{mole g}^{-1}$ fresh weight	Time intensity of LP (s)	Total soluble solids (%)	Dry matter (%)
0	1.91 \pm 0.03a	8.99 \pm 0.05a	34.0 \pm 0.8b	10.7 \pm 0.1a	18.0 \pm 0.2a
3	1.87 \pm 0.03a	7.97 \pm 0.06b	42.4 \pm 1.0a	10.6 \pm 0.1a	16.0 \pm 0.1b
6	1.94 \pm 0.06a	7.79 \pm 0.10b	ND	10.7 \pm 0.5a	15.1 \pm 0.3bc
9	1.70 \pm 0.08b	6.60 \pm 0.07c	ND	10.6 \pm 0.1a	14.9 \pm 0.1c
Mean	1.85 \pm 0.04	7.83 \pm 0.22	38.2 \pm 1.9	10.7 \pm 0.7	16.0 \pm 0.7
LSD _{0.05}	0.14*	0.24*	3.4*	NS	1.0**

ND - not detected.

*,** Significant difference at $P < 0.05$ and $P < 0.01$, respectively.

NS, no significant difference at $P < 0.05$.

Data within a single column with the same letter indicates no significant ($P < 0.05$) difference in quality parameter with reference to storage duration.

day 0, were 11.6, 13.3 and 26.6, respectively. The difference between days 3 and 6 was not significant ($P > 0.05$). There was a positive linear association between total pyruvic acid (flavour) concentration (X) versus %dR/R (Y); where $Y = 1.166 + 0.879X$; $r = 0.803$; $P > 0.05$; and $n = 4$.

Lachrymatory potency, as determined by time-intensity sensory data for hotness, reduced significantly ($P < 0.05$) from 34 s response time on day 0 to 40 s on day 3 (Table 2). After day 3, lachrymatory potency was completely lost. The lachrymatory factor, thiopropanal sulphoxide, is known to be unstable. It either vaporised and escaped the tissue at low temperature or was chemically converted to trans-3,4-diethyl-1,2-dithietane 1,1-dioxide (Block, 1992).

The total soluble solids content of the diced onion did not change over 9 days of storage (Table 2). Blanchard *et al.* (1996) observed that an increase in CO₂ concentration reduced physiological activity in diced onion stored for 14 days in air and in a controlled atmosphere system at 10 per cent CO₂ with or without 2 per cent O₂. Percentage dry-matter content significantly ($P < 0.05$) reduced with increasing storage period (Table 2). The greatest reduction in dry matter content from 18 to 16 per cent was recorded after 3 days of storage. At this early time, dry matter might have been consumed in increased physiological and biochemical activities following the severe tissue wounding.

Conclusion

A correlation was shown to exist between the E-nose data and more conventional means of determining the flavour quality of diced onion. This correlation suggests that the E-nose could be used in commerce for the assessment of minimally processed onion quality. The E-nose could save time, reduce financial cost, provide reliable results and offer relative ease of use.

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