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ORIGINAL ARTICLE

A SMART methodology for assessment of hexanal in potato crisps using electronic nose technology: sensor screening by scalar machine learning classifier method

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Abstract There is a pertinent need to develop a rapid and accurate methodology for the detection of the onset and the progression of rancidity in the most popular savory product worldwide, *viz*. fried potato crisps for food safety and health concerns. Rancidity in the fried crisps—one set prepared using C18:2-lean deodorized virgin coconut oil under modified deep frying conditions (140 °C, 5 min),—and another set deep fried (170 °C, 3 min) in C18:2-rich oil (simulating commercial frying conditions) was determined by 'rancidity indices' generated (using Mahalanobis distance) from the data obtained by MO-based electronic nose analysis of hexanal (in Likens-Nickerson extract of volatiles from potato crisps), the most prominent rancidity marker, using screened sensors calibrated with standard hexanal, and classified using support vector machine. This also allowed unambiguous discrimination of the two sets of potato fries. The correlation of hexanal contents with the said indices yielded robust regression models which could accurately predict rancidity status of the crisps, forgoing GC-FID analysis of rancidity marker in the same. The 'SMART' models developed would allow rapid-cum-accurate detection of the onset and progression of rancidity in fried potato crisps on an industrial scale, forgoing the need to conduct biochemical analyses.

Keywords Potato crisps · Hexanal · Support vector machines · Electronic nose · Correlation equation

Abbreviations

VOC	Virgin coconut oil
(2,4-De)	Z,z-2,4-decadienal
GC	Gas Chromatography
FID	Flame Ionization Detector
Mo	Metal Oxide
SMART	Specific, measurable, achievable, realistic, and timely
E-NOSE	Electronic Nose
SPC	Standard Plate Count
MDA	Malonalaldehyde
HCA	Hierarchical Cluster Analysis
MUFA	Mono Unsaturated Fatty Acid

Introduction

Potato fries are the most popular savory products worldwide owing to their pleasant sensory appeal, especially crispiness (Loon et al. 2007). However, they have poor storage stability due to lipid oxidation (rancidity) and microbial infestation. The oxidative deterioration products of linoleic acid impart an unpleasant odor and render the fried products not only sensorially unacceptable for human consumption but also pose serious health hazards. Among several compounds, hexanal is considered to be the most prominent molecular marker of rancidity in oil-fried products (Grebenteuch et al. 2021) and its pathway of formation (Fig. S1) from ω-6 linoleic acid (C18:2) is well established (Cao et al. 2014). Besides, homolytic cleavage, followed by peroxidation of C18:2 in frying oil leads to the formation of muta- and neuro-toxin, namely z,z-2,4-decadienal (2,4-De) in fried

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potato crisps (Clarke et al. 2020). Commercially, the most commonly used frying oils are C18:2-rich soybean oil and palm olein oil which favor the formation of 2,4-De.

The drawbacks of deep frying in common frying oils have been successfully circumvented by the usage of an alternate frying oil developed in our laboratory using virgin coconut oil (VCO), deodorized (by removing rancid-acid odor of octanoic acid) by gamma-irradiation at a dose of 4.2 kGy. This deodorized VCO, viz. DVCO possessed a lower amount of C18:2 and a higher amount of medium chain fatty acids, vis-à-vis the common frying oils, and thus potato crisps fried in DVCO [designated as sample set T-22 vide (Bose and Bhattacharjee 2021)] at 140 °C for 5 min (modified deep frying conditions) did not contain 2,4-De; while those fried in soybean oil (designated as experimental control set EC) under deep-frying conditions (170 °C, 3 min) had an appreciable amount of the same (Bose and Bhattacharjee 2021).

Detection of the onset of rancidity is highly important for assuring the safety of fried crisps prior to consumption. Fraudulent practices at commercial production levels such as repeated use of frying oils and merchandise of rancid-fried products to consumers are rampant (Grootveld 2022), thereby increasing the possibilities of the presence of 2,4-De and hexanal in fried potato crisps. Sensorial perception of the onset of rancidity in fried products is obscured not only due to the presence of low concentration of hexanal in the same but is also impeded by the starchy (primarily) potato matrix. Therefore, it is crucial that fried potato crisps are rendered toxin- and hexanal-free to allow delivery of safe-cum-healthy fried products to consumers. Therefore the T-22 and EC sets (post packaging) were subjected to analysis of hexanal during storage envisaging that the concentration of the same would significantly differ between the two sets of potato crisps fried in C18:2-lean and C18:2-rich frying oils, respectively.

Fried potato-based products are considered to be rancid when hexanal in the same is present at a concentration greater than 0.03 ppm (Agarwal et al. 2018). Commonly, biochemical assays (peroxide values, acid values, and malonaldehyde content) and analytical gas chromatography (GC)-based methods are commonly used for the assessment of rancidity and for analysis of molecular markers of rancidity (chiefly the aldehydes), respectively. However, detection of the onset of rancidity in fat-rich products is not possible by biochemical assays and also by GC-FID (flame ionization detector) analysis since the concentration of hexanal produced at the onset of rancidity is below the LOD (0.89 ppm) and LOQ (2.97 ppm) values of hexanal by either analytical procedure (Aparicio-Ruiz et al. 2018). This problem has been circumvented by several researchers who have developed alternate methodologies for rapid and reliable detection-cum-quantification of remarkably low hexanal concentrations for assessment of the onset of rancidity in fat-rich food products using electronic-nose (e-nose) technology, such as—polymer (conducting) sensor-based e-nose for virgin olive oil (Aparicio et al. 2000); metal-oxide (MO) based e-nose for pork (Tikk et al. 2018), fish (Li et al. 2013), and virgin olive oil (Savarese et al. 2013); HERACLES II electronic nose (Alpha MOS) for study of photooxidation of olive oil (Kishimot 2021); e-nose (FOX-4000, Alpha MOS, Nantes, France) in combination with HS-SPME-GC and GC-TOF/MS for identification of key flavor compounds (including hexanal) in microwaved sesame oil (Jia et al. 2019); MOS-based e-nose for evaluation of virgin olive oil quality in terms of volatile compounds (chiefly hexanal) during storage in dark glass bottles (Martín-Tornero et al. 2023); and GC/MO-based and MS/MO-based e-noses for assessment of rancidity of potato crisps fried in linoleic-acid-rich oil (Vinaixa et al. 2005).

Considering industrial usage of e-nose technology for assessment of the onset and progression of rancidity (rancidity status) in large sample sets of fried potato crisps, the current study endeavored to develop a SMART (specific, measurable, achievable, realistic, and timely) methodology based on a simpler MO-based e-nose model. The specific objectives of the study were: (1) the sensors of e-nose which respond well to hexanal would be first screened using linear support vector machine (SVM) learning tool, followed by calibration of the selected sensors using standard hexanal; (2) the onset and progression of rancidity in fried potato crisps (post packaging) during storage (23 ± 2 °C, 80% RH) would be assessed by determination of their 'spoilage indices' and would be correlated with the concentration of hexanal by regression modeling; (3) consumers' acceptability of the fried crisps would be adjudged in an unbiased way by use of fuzzy logic analysis of sensory evaluation data.

The e-nose analysis in-tandem-with fuzzy logic analysis would allow holistic judgment of the safety (hexanal-free) and overall acceptability of potato crisps by consumers. The best fit regression model if successfully developed would allow researchers/industry personnel to forgo GC-FID analysis or invasive chemical analyses for detection of onset and progression of rancidity in fried food products.

Material and methods

Materials

Mature potato tubers ("Kufri Jyoti") without buds and blemishes were procured from registered farmers/cultivators of Agriculture and Rural Development (ARD) [earlier known as, Faculty Centre of 'Integrated Rural Development and Management' (IRDM)] located at Ramakrishna Mission Ashrama, Narendrapur, South 24 Parganas, West Bengal, India and authenticated by West Bengal Food Processing and Horticulture Development Corporation Limited, Kolkata, India. The potatoes were cultivated without using synthetic fertilizers in loamy soil of pH 6.58 having electron conductivity (EC) of 1.17 mS/m and organic C content of 0.83%. The produce was harvested in the months of January-April 2020. Deodorized virgin coconut oil (linoleic-acid lean and thus less susceptible to rancidity) and soybean oil (linoleic-acid rich and thus highly susceptible to rancidity) was used as frying media for the sample set (T-22) and for experimental control (EC), respectively. All chemicals utilized in this work and different aids utilized for processing the potato crisps have been discussed in the supplementary file (S1).

Preparation of fried potato crisps

Sample/test set designated as T-22

Three parameters namely % L-proline (g/100 g of blanched potato slices), frying time (min), and temperature (°C) were considered as independent variables, and % acrylamide mitigation in fried potato crisps as the response variable to optimize the frying process with the aim to minimize formation of acrylamide in the fried crisps without compromising their sensory attributes (Bose and Bhattacharjee 2021). The test set of fries (comprising of 15 pieces of average dimensions $70 \times 5 \times 10$ mm) were produced by the following sequence of pre-optimized parameters/conditions- (a) aqueous pre-treatment of the potato slices including blanching at 70 °C for 20 min; (b) treatment of the slices by 2% (w/w) L-proline; (3) drying of the treated slices at 60 °C for 130 min; (4) and finally frying in 4.2 kGy-irradiated 28-days-stored DVCO under modified deep frying conditions i.e., 140 °C for 5 min (Bose and Bhattacharjee 2021).

Experimental control set designated as EC set

Sliced potatoes of similar dimensions after washing and drying (*vide supra*) were deep-fried in soybean oil at 170 °C for 3 min (standard deep-frying conditions) at a 1.0 cm^{-1} surface-to-volume ratio using an electric fryer (2270–2500 W, 50 Hz, 220–230 V). This set of fried crisps, designated as the EC set also contained 15 pieces of potato crisps. Use of two frying oils, one less prone to rancidity and one highly susceptible to it was used for the study to enable us to correctly assess rancidity (over a wide range) in the fried potato crisps.

Storage studies of T-22 and EC sets for their shelf life assessments

The T-22 and EC sets post-frying were wrapped in food-grade Al foil and packaged in Ziploc LDPE (20 μ) pouches. Nitrogen was flushed into them before self-sealing. Thereafter, the pouches were kept at 23 ± 2 °C, 80% RH for a total period of 6 and 4 days, respectively. The duration of storage of these two sets was based on the results of microbiological analyses of the two sets (*vide infra*). Each day, around 10 samples were withdrawn from each of the above sets; and biochemical, analytical, e-nose, and sensorial analyses were performed until the end of their respective shelf lives. Analysis of hexanal by e-nose and GC was conducted for 7 days (*vide infra*).

Micobiological analyses of T-22 and EC sets

The "standard plate count" (SPC); and the "yeast and mold counts" of T-22 and EC sets were evaluated with time (days) in accordance with standard methods described in IS5402: 2012 and IS5403: 1999, RA 2018. The counts have been expressed in cfu/g of fried potato crisps.

Preparation of "deliberately rancid" or training sets of crisps

Sets of "deliberately-rancid" samples were prepared from freshly prepared T-22 and EC sets. Rapid rancidity development in these crisps was achieved by storing these samples in an accelerated rancidity chamber for a period of four days. The conditions that prevailed in this chamber have been elaborately described in our previous publication (Mondal et al. 2022). The deliberately-made rancid fried potato crisp sets were removed from the "conservation chamber" and designated as TT22 and TEC (labeled in concordance with the T-22 and EC sets) comprised of 180 fried potato crisps each. Biochemical analyses of 60 fried potato crisps were performed from the above set while the remaining 180 crisps were analyzed chromatographically and by e-nose technology. The samples analyzed were labeled on the basis of their day of analysis, viz. T-22:1, TT-22-1 (T-22, TT22 set respectively, on day 1).

Biochemical assays of T-22 and EC sets

Standard biochemical assays such as analyses of peroxide values (PVs), acid values (AVs), and malonalaldehyde (MDA) contents were performed with T-22 and EC sets on days 0, 1, 2, 3, 4, 5, and 6 and their "deliberately-rancid" counterparts on days 1, 2, 3 and 4 for analyzing their rancidity status during storage (Table S1). The details of these analyses have been discussed in supplementary file S1.

Extraction of hexanal from fried potato crisps by Likens-Nickerson's steam-distillation-cum-solvent extraction method

The VOCs of the fried potato crisps (T-22 and EC sets) during storage were extracted and concentrated by the Likens-Nickerson (L-N) concurrent steam-distillation-solvent extraction method followed by concentration of the extract using Vigreux fractional distillation column (Bhattacharjee et al. 2005) to precisely assess the rancidity marker i.e., hexanal forgoing other undesirable starchy and/or oily odor notes of the same. The details of the process have been provided in supplementary file S1.

GC analysis of hexanal of T-22 and EC sets

Hexanal analysis of extracted VOC concentrates of T-22 and EC sets of fried potato crisps (during storage) were performed on GC (Trace GC 700; Thermo Fischer Scientific) following our previously developed method (Bose et al. 2023). The oven temperature was programmed as follows: 70 °C (2 min hold), 70–120 °C raised at 5 °C min^{-1}, then increased to 260 °C at 10 °C min^{-1} and finally held at 260 °C for 7 min. Extracted VOCs (dissolved in HPLC-grade DCM) were injected in split-less mode into the GC column. Identification of hexanal was performed using the pure standard of the same (Fig. S2). Prior to sample analyses, a calibration curve of hexanal (50–75 mg/ml) was developed using a pure standard of hexanal in HPLC-grade DCM. Standard hexanal solution was diluted to the required concentration immediately before injection into the GC column. The hexanal content was expressed as mg/kg (ppm) of crisps.

Analysis of fried potato crisps by e-nose

Operating conditions for qualitative analysis of hexanal In our current investigation, the e-nose system, ENOVISION Ver.1.Q (developed by M/s Centre for Development of Advanced Computing, Kolkata, India) equipped with eight MOS sensors ("TGS 816, TGS 823, TGS 830, TGS 832, TGS 2600, TGS 2610, TGS 2611, and TGS 2626") was used for assessment of rancidity in T-22 and EC sets w.r.t hexanal (prominent rancidity marker). Prior to performing the e-nose analyses of the said samples, several preliminary trials were conducted with operating parameters such as sample size, sampling, and purging time. The maximum response received from each sensor was under the following operating conditions: sample size-100 µL of extracted VOC concentrate; acquisition rate-600 ppb; headspace generation time-30 s; sampling time-50 s; purging time-450 s. The e-nose analysis of their respective training sets ("deliberately-rancid" sets, vide supra) i.e., TT-22 and TEC were performed under similar operating conditions.

Screening of e-nose sensors Prior to "rancid-acid" odor analyses of T-22 and EC sets, the sensors were screened by training with deliberately-made rancid fried potato crisps viz. by TT-22 and TEC sets in accordance with our previously published reports (Chatterje et al. 2014; Dutta et al. 2017). The sensors were successively calibrated against standard hexanal so as to enable unambiguous distinction of the rancid (just onset) samples from the non-rancid ones. Hexanal in the concentration range of 0.005–0.04 mg was used to calibrate the sensors. Although Vinaixa et al. (2005) worked on GC/MO-based and MS/MO-based e-noses for assessment of rancidity of potato crisps fried in linoleic-acid-rich oil, sensor screening and their calibration with hexanal for rapid-cum-reliable assessment of rancidity in fried potatoes have not been reported by them. Sensor screening was performed using "SMLC (Matlab® R2020a; Mathworks, Inc. Natick, MA, USA)". The data generated from the sensor array was obtained using Eq. (1) for T-22 and EC sets of fried potato crisps.

$$(|\Delta R|/R)_{hexanal} = /\left(R_{TS} - R_{hexanal}\right)//R_{hexanal} \tag{1}$$

where R_{TS} is the resistance of sensor(s) towards the VOCs of training sets (vide supra); R_S is the resistance of sensor(s) towards the VOCs of experimental samples on days 0, 1, 2, 3, 4, 5 and 6; and $R_{hexanal}$ is the resistance of sensor(s) towards standard hexanal. The volume of hexanal to be used for sensor calibration was optimized to be 0.024 mg (an amount greater than this oversaturated the sensors and baseline correction was rendered impossible even after purging the sensors with air several times).

These data were fed into different models of SMLC. The running conditions were: (a) fivefold cross-validation and (b) distribution of data set as 80:20::training data set: test data set. Selection of the model was performed on the basis of % accuracy and prediction speed of each model (code provided in S1). Responsible sensors were recognized using the best-fit model (*vide infra*).

E-nose analysis of T-22 and EC sets during storage

In this investigation, ENOVISION with selected sensors was employed to evaluate the rancidity profiles of T-22 and EC sets during storage under operating conditions similar to those used for hexanal calibration (*vide supra*) by computing sensor responses using Eq. (2).

$$(|\Delta R|/R)_{hexanal} = /\left(R_S - R_{hexanal}\right)//R_{hexanal} \tag{2}$$

where, R_S is the resistance of the sensor towards the VOCs of experimental samples on days 0, 1, 2, 3, 4, 5, and 6; and $R_{hexanal}$ is the resistance of the sensor(s) towards standard hexanal (0.024 mg).

Hierarchical cluster analysis (HCA) of rancidity status of T-22 and EC sets In the current investigation, HCA was employed to find the association based on similarities of selected sensor responses towards VOCs of "rancid-acid" odor of T-22 and EC sets during storage (represented as a dendogram). The rancid status of the samples in terms of their freshness, onset of rancidity, and progression of rancidity have been clearly exhibited in corresponding figures (described later).

Determination of 'spoilage indices' for fried potato crisps

Screened sensor responses generated numerical values (scalar in nature) for T-22 and EC sets using the Mahalanobis distance method (Chatterjee et al. 2014). This was nomenclatured as 'spoilage indices' for fried potato crisps. In this study, the Mahalanobis distance (d^2) for T-22 and EC sets was determined using matrix operation as has been described by Chatterjee et al. (2014). The data set of screened sensors i.e., N (811×2) was considered as the "baseline vector". On each day of storage, the matrix i.e., M_i (811×2) was created from the data generated by the screened sensors. "Mahalanobis distance (Eq. 3) was calculated between the matrix (M_i) and matrix (N) which generated 'd^2'.

$$d^2 = (x - m)^T \cdot V^{-1} \cdot (x - m) \tag{3}$$

where $x^T = \{x_1, x_2, \ldots, x_n\}$ vector for a single multivariate observation; $m_t = \{\mu_1, \mu_2 \ldots, \mu_n\}$ vector representing the population mean and V is co-variance matrix" (Chatterjee et al. 2014). Greater distance of mean of ($|\Delta R|/R$) values of fresh sets of T-22 and EC from the baseline matrix implied higher rancidity. The spoilage indices were plotted against the hexanal concentrations of T-22 and EC sets during storage. The regression equations thus developed would allow unambiguous determination of concentration (> 0.03 ppm) of hexanal generated in fried potato crisps consequent to rancidity.

Sensory evaluation of T-22 and EC sets

Objective sensory evaluation of T-22 and EC sets using the standard 9-point sensory scale during storage was performed inside a department classroom at 24 ± 1 °C in bright light as per the procedure described by Stone and Sidel (2004). Details of the sensory evaluation performed by the 30-member-panel can be accessed in our previous publication (Bose et al. 2023). Panelists evaluated the potato crisps in terms of color, odor, texture, flavor, after-taste, and overall acceptability. During testing, the panelists were monitored by the authors. Unsalted crackers and water were also given to the panelists for refreshing their palates before tasting subsequent samples (Korley et al. 2020).

Since the panel members were semi-trained, variation in their sensorial perceptions of the onset of rancidity would certainly influence their decisions while performing the sensory evaluation. Therefore, fuzzy logic analysis of the sensory scores was performed to mitigate these variabilities and arrive at an unbiased evaluation of the organoleptic quality of the fried potato crisps.

Fuzzy logic analysis of T-22 and EC sets

To remove ambiguity in the sensory scores provided by the panel, the panelists re-evaluated the fried crisps (EC and T-22) using sensory scale factors and the linguistic data provided by them was subjected to fuzzy logic analysis. Using the "triangular fuzzy membership distribution function", defuzzified scores were calculated which were classified as 'Excellent', 'Good' etc. in accordance with the categories defined by Das et al. (2005). The details of the fuzzy logic analysis can be accessed in the publications of Das et al. (2005) and Bose and Bhattacharjee (2018). The main steps of fuzzy modeling of sensory evaluation have been discussed in S1.

Statistical analysis

All experiments were conducted in triplicate i.e., three independent runs were conducted under each experimental condition and the results have been reported as mean ± SD of three sets of independent experimental data. The dendogram was obtained using SPSS-20.0 software (IBM). A $p \leq 0.05$ was used to verify the significance of the tests.

Results and discussion

Microbiological data of T-22 and EC sets during storage

The acceptable limits of SPC and TFC were $\leq 2.0 \times 10^5$ cfu/g and $\leq 1.0 \times 10^5$ cfu/g, respectively following WHO

Table 1 Microbiological analyses of EC and T-22 sets during storage

Microbiological parameters	Set of fried potato crisps	0	1	2	3	4	5	6
SPC (30 ℃, 72 h.) ($\times 10^3$ cfu/g)	EC	NG	12.2^{a}	70.5^{b}	87.8^{c}	167.7$^{\mathbf{d}}$	–	–
	T-22	NG	3.7^{a}	19.3^{b}	40.2^{c}	68.3^{d}	81.5^{e}	161.9$^{\mathbf{f}}$
Yeast and mould count or TFC (25 ℃, 5 days) ($\times 10^3$ cfu/g)	EC	NG	22.6^{a}	44.1^{b}	75.3^{ab}	106.6$^{\mathbf{d}}$	–	–
	T-22	NG	9.8^{a}	28.7^{b}	47.9^{ab}	68.7^{c}	89.7^{d}	105.3$^{\mathbf{e}}$

Values in the same column with different superscript ($^{a-e}$) are significantly different ($p<0.05$); Mean in a row with similar superscripts are not significant different at $p \leq 0.05$

Yeast and mould count showing < 10 on day 0 imply that the count is below LOQ

NG No growth

Table 2 Hexanal content of T-22 and EC sets of fried potato crisps during storage

Day	Hexanal content (ppm)	
	T-22	EC set
1	N.D	N.D
2	N.D	N.D
3	N.D	3.82 ± 0.04
4	N.D	4.79 ± 0.03
5	2.98 ± 0.02^{a}	6.33 ± 0.04^{b}
6	3.42 ± 0.04^{a}	8.96 ± 0.05^{b}
7*	4.66 ± 0.03^{a}	15.98 ± 0.05^{b}

Mean ± S.D of three samples of one experimental set

^{a,b}Different letters in a row indicates significant difference ($p<0.05$); 7*: The study period was 5 days. However, to make correlation study with spoilage index, hexanal analysis was continued for 7 days in case of T-22 sets and EC sets

N.D Not detected as hexanal content was below LOD and LOQ

guidelines (1994). For T-22 and EC sets, visible fungal growth was found on day 6 and day 4, respectively, corresponding to their SPC and TFC values (Table 1), and had exceeded the aforementioned limits. Therefore, T-22 and EC sets can be stored up to day 5 and day 3, respectively. The antimicrobial activities of the monounsaturated fatty acids (MUFA) present in DVCO (Ghosh et al. 2016; Huang et al. 2011) possibly accounted for their preservation until the said days.

Biochemical assay values of T-22 and EC sets during storage

The biochemical assay results (Table S1) have been elaborately discussed in S1. From the comparison of these findings with those of the respective training sets, it is evident that the onset of rancidity in T-22 and EC sets occurred on day 5 and 3, respectively.

Hexanal content of fried potato crisps during storage

GC-FID chromatograms for hexanal present in T-22 and EC sets are presented in Fig. S3-S4. In this study, LOD and LOQ of hexanal by GC-FID were found to be 0.89 ppm (mg/kg of sample) and 2.97 ppm (mg/kg of sample), respectively. The hexanal content in the T-22 set was first identified and quantified on day 5 (Fig. S3c) and was found to be 2.98 ppm while the same for the EC set, first identified and quantified on day 3 (Fig. S4c) was found to be 3.82 ppm (Table 2). Although the concentration of hexanal increased linearly with time for both the sets, it's amount differed significantly ($p<0.05$) between T-22 and EC sets, which can be attributed to the difference in C18:2 contents of the frying oils of the two sets, viz. PUFA-lean DVCO (1.8%) and PUFA-rich soybean oil (50.9%). The hexanal contents of T-22 and EC sets on days 5 and day 3, respectively, were significantly greater ($p< <0.05$) than 0.03 ppm, attesting to the fact that the onset of rancidity occurred earlier than day 5 and day 3 in T-22 and EC sets, respectively.

Screened sensors of e-nose for determination of hexanal

The responses of each sensor towards VOCs of "deliberately rancid" or training sets (samples withdrawn from the rancidity chamber on days 1, 2, 3, 4) served as inputs to each of the 26 SMLC models (Table S2). The best-fit model thus obtained was that of linear SVM having 93.90% accuracy and a prediction speed of 4600 s. $|\Delta R|/R_{hexanal}$ values of all eight MOS generated a scatter plot wherein appreciable segregation between the sensors exhibiting high and low responses was represented by a linear hyper-plane with maximal margin (discussed in S1). From Fig. 1 it is evident that within the 8-sensor array, TGS 2626 and TGS 832

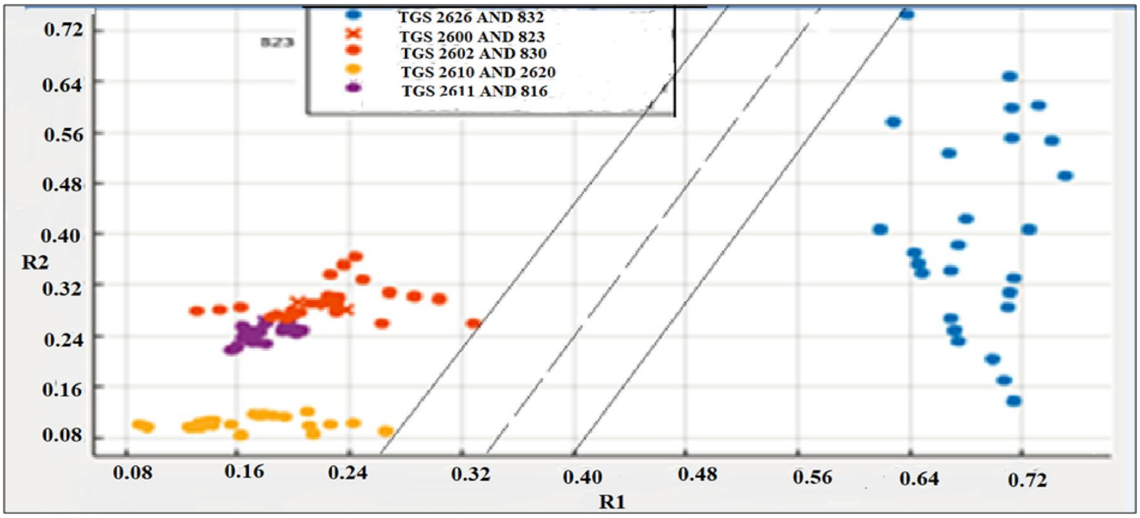

Fig. 1 Storage analyses of samples performed with screened sensors TGS 2626 and 832

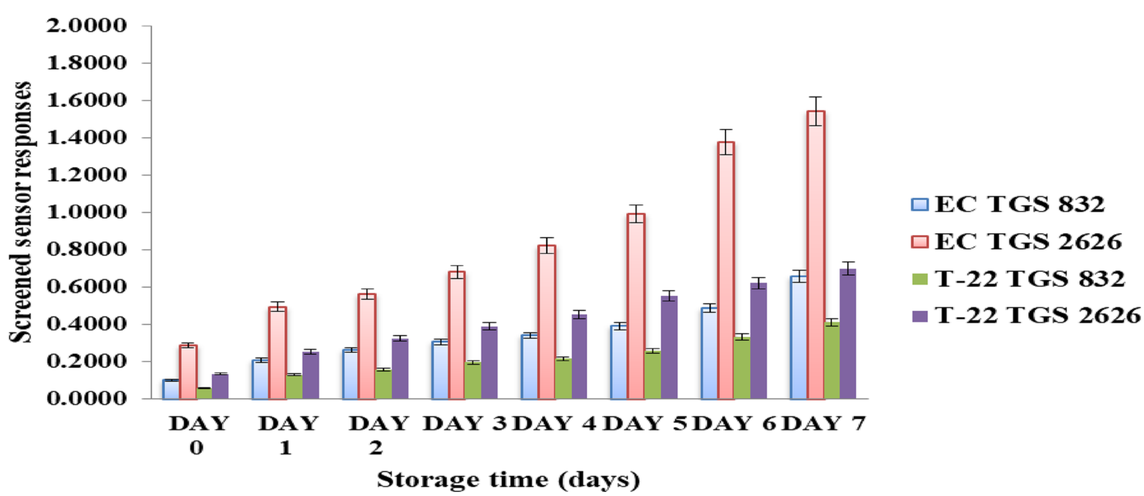

Fig. 2 E-nose analyses of fried potato crisps with the screened sensors during storage

sensors showed relatively better responses towards progression of rancidity with time, i.e., their $|\Delta R|/R_{hexanal}$ values were discrete. The responses of the remaining sensors did not linearly increase with the increase in the rancidity of the samples. Therefore, their response values appeared as clusters and were distinctly separated from those of the former sensor set (comprising of TGS 2626 and TGS 832 sensors). Thus, the SVM analysis established TGS 2626 and TGS 832 as the best sensor duo for assessment of the rancidity status of fried potato crisps during storage.

E-nose data of fried potato crisps during storage and its classification by HCA

The e-nose analysis of T-22 and EC sets was performed up to day 7 with screened sensors (TGS 2626 and TGS 832) and the responses were plotted (Fig. 2). To build the dendrogram and to discriminate the samples with respect to their freshness status, the screened sensor responses of either sample set were considered up to day 5. From these data, an HCA (Fig. 3) plot was generated which was used to obtain homogeneous clusters of sample sets of similar rancidity status.

In Fig. 3, it is clearly seen that T-22:0, T-22:1, T-22:2, T-22:3, and EC:0, EC:1 formed group A. T-22:4 and EC:2 exhibited association with each other and are therefore together in group B. TT22-1, TT22-2 TT22-3, TT22-4, TEC-1, TEC-2, TEC-3, TEC-4, T-22:5, EC:3; and EC:4

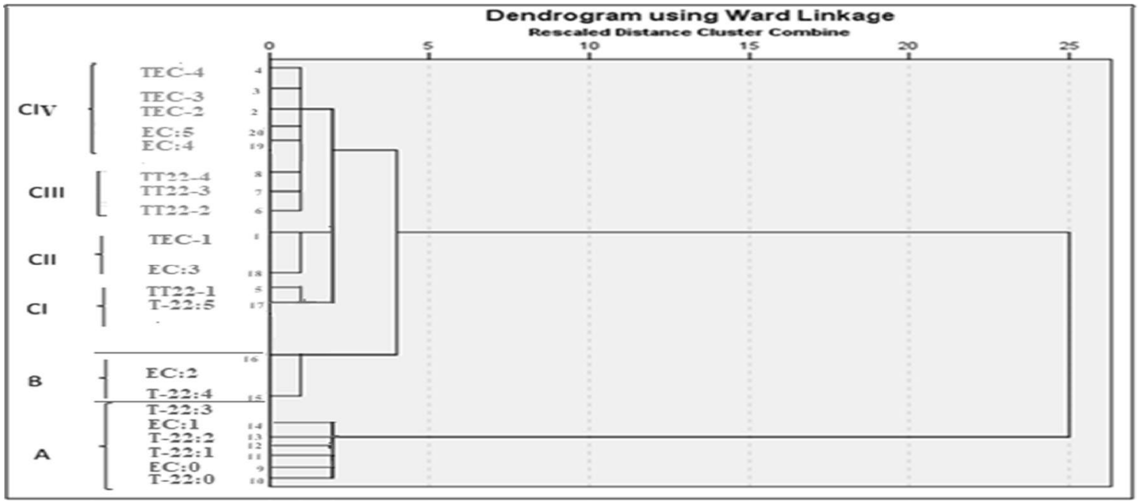

Fig. 3 Hierarchical cluster analysis of T-22 and EC sets, and their corresponding training sets based on screened sensor responses towards VOCs (Dendogram) up to day 5

and EC:5 formed group C. Among these clusters, T-22:5, TT22-1; and EC:3, TEC-1 formed subgroups of CI and CII within group C. TT22-2, TT22-3, TT22-4; and EC:4, EC:5, TEC-2, TEC-3, and TEC-4 formed subgroups of CIII and CIV, respectively, within group C. A good classification among different groups and subgroups based on the variations in progression of rancidity was obtained, and their rancidity status was found to be in the following order: from fresh to rancid: group A (fresh) > group B > group CI (rancid) > group CII > group CIII > group CIV (extreme rancid).

It is evident from the above results that the quality status of group 'B' is neither fresh nor rancid which imply that the onset of rancidity in T-22 and EC sets occurred on day 4 and day 2, respectively. Therefore, e-nose with screened MOS sensors could accurately predict both the onset and the progression of rancidity w.r.t hexanal in T-22 and EC sets, vis-à-vis the conventional analytical methods. Thus, the safe period for consumption of T-22 and EC sets was day 3 and day 1, respectively.

Table 3 "Spoilage index" of T-22 and EC sets of fried potato crisps obtained during storage using Mahalanobis distance methodology

Day	Spoilage index	
	T-22 set	EC set
1	0.58[a]	0.96[b]
2	0.73[a]	1.54[b]
3	1.27[a]	2.06[b]
4	1.56[a]	3.42[b]
5	1.76[a]	4.53[b]
6	2.11[a]	6.59[b]
7*	2.86[a]	8.32[b]
Day	Spoilage index	
	TT-22 set	TEC set
1	1.79[a]	2.08[b]
2	2.05[a]	3.58[b]
3	2.29[a]	5.62[b]
4	2.59[a]	7.55[b]

[a–b]Different letters in a row indicates significant difference ($p < 0.05$); 7*: The study period was 5 days. However, to make correlation study with spoilage index, e-nose analysis was continued for 7 days in case of T-22 sets and EC sets

Spoilage indices for fried potato crisps

From the HCA plot, screened sensors of e-nose could effectively discriminate fresh and rancid T-22 and EC sets on the basis of their "rancid-acid" odor. Spoilage indices (obtained from screened sensor responses for the 7-day period) generated by the Mahalanobis distance method (Table 3) represented the extent of spoilage of the samples. From the ANOVA study, it was found that there was significant ($p < 0.05$) enhancement in spoilage indices for either set with storage. The spoilage index of T-22 set having a storage period of 4 days (1.56) was slightly lower ($p = 0.0481$) than that of TT22-1 (1.79); whereas the same for T-22:5 (1.76) was similar ($p > 0.05$) to that of TT22-1. The spoilage index of EC:2 (1.54) was slightly lower ($p = 0.0484$) than that of TEC-1 (2.08); however, the same for EC:3 (2.06) was similar ($p > 0.05$) to that of TEC-1. These findings are in consonance with those visualized in the HCA plot.

Correlation of spoilage indices of T-22 and EC sets with biochemical parameters

From the experimental data obtained from e-nose and GC-FID analyses of T-22 and EC sets, regression (linear) correlations were established between their spoilage indices (Table 3) and hexanal contents (from day 0 to day 7) to predict the rancidity status of the above sets. These regression model Eqs. (4) and (5) were used for the determination of hexanal contents of T-22 and EC sets of fried crisps as a function of their respective spoilage indices, forgoing GC analysis.

$$Hexanal = 1.5472\,(Spoilage\ index) + 0.2157 \tag{4}$$

$$Hexanal = 2.2951\, e^{0.2232(Spoilage\ index)} \tag{5}$$

The p- and F-values justified the fitness of these regression models. The p-values of 0.0000 and the reasonably high F-values of 686.00 and 687.05 corresponding to Eqs. (4) and (5), respectively, indicated that the regression models (between hexanal contents and screened sensors responses) were good fits having good regression coefficients [R^2 values of Eqs. (4) and (5) were 0.99 and 0.98, respectively]. Thus Eqs. (4) and (5) allowed direct and accurate assessment of the prominent molecular marker of rancidity in potato crisps (viz. hexanal), fried in DVCO (linoleic acid-lean) and soybean (linoleic acid-rich) frying oils, respectively. The correlations of hexanal concentrations in fried potato crisps with e-nose sensor responses are reported here for the first time.

Fuzzy logic analysis of sensory scores of T-22 and EC sets during storage

From the defuzzified scores (Tables S3 and S4), it is evident that the panelists had shown an increasingly low preference for T-22 and EC sets with time. Thus, T-22 shifted from category "good" to "moderate" on day 4, and to "not significant" on day 5; whereas, the EC set underwent a shift from category "good" to "moderate" on day 2, and to "not significant" on day 3. Therefore, T-22 and EC sets could be consumed up to a 'maximum' of 4 days and 2 days, respectively. However, the 'highest acceptability' of T-22 and EC sets remained up to day 3 and day 1, respectively.

Conclusion

The inevitable phenomenon of rancidity in fried potato crisps could be reduced significantly by adopting a modified frying process and by replacing the commonly used commercial frying medium with linoleic acid-lean deodorized coconut oil. Although reduced, accurate assessment of rancidity in the crisps poses an additional challenge especially when industrial production is concerned, which could be successfully resolved by employing MO-based-e-nose technology. The sensors of the e-nose system were first screened with respect to their responses towards hexanal, calibrated using standard hexanal, and classified using SVM. Rancidity in the crisps was quantitated by the use of 'rancidity indices' generated (using Mahalanobis distance) from the data obtained from the screened e-nose sensors. The correlations of the indices with concentrations of hexanal (GC-FID analysis) obtained by regression modeling yielded good model fit equations which allowed direct and accurate assessment of the prominent rancidity molecular marker in the crisps for small as well as large sample sets; forgoing the need to conduct complex, time-consuming-cum-expensive analytical assays.

For industrial-scale production of fried crisps, the SMART approach developed in this study will certainly render rancidity assessment of samples fast, reliable, and inexpensive. The methodology developed in this study could also be safely extrapolated to allied fried food products.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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