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Quality tracing of peanuts using an array of metal-oxide based gas sensors combined with chemometrics methods

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ABSTRACT

Quality tracing models were set up for both unshelled peanuts and peanut kernels by applying an array of 18 metal-oxide (MOX) based gas sensors. Acid value, peroxide value and content of crude fat of the peanuts at different storage times were measured by traditional methods as a reference. Classification results for both unshelled peanuts and peanut kernels at different storage times based on Linear Discriminant Analysis (LDA) and Support Vector Machine (SVM) were acceptable Storage time, acid value, peroxide value and content of crude fat of peanuts were predicted by Partial Least Squares Regression (PLSR) and SVM on the basis of different normalized datasets. Original datasets, datasets normalized in [0,1] and in [−1,1] were considered. PLSR and SVM provided better prediction results when normalized in [0,1] and [−1,1], respectively. Correlations between adulterated levels (stale peanuts blended in fresh peanuts at levels of 0%, 25%, 50%, 75% and 100%) and sensor signals were researched by PLSR and SVM. It was found that the sensor signals and adulterated levels exhibited good correlation ($R^2 > 0.801$ for training and testing sets by both methods). Meanwhile, The R^2 for training and testing sets were 0.941 and 0.896 by applying SVM, respectively, and both of them were correspondingly higher than the R^2 for training and testing sets by PLSR (training: $R^2 = 0.812$; testing: $R^2 = 0.802$). The research indicates that the 18 MOX based gas sensors combined with appropriate chemometrics methods can be used as a non-destructive method in detecting peanut quality.

1. Introduction

Peanuts (Arachis hypogaea Linn.) are one of the most important oilseed crops cultivated and consumed in most parts of the world. Due to the high nutritive value (about 26% protein, 50% oil, and 3% fiber), peanuts are processed into products such as oil and butter (Wang et al., 2012). During storage, peanut quality decreases due to storage conditions, such as temperature, oxygen and humidity or some improper processing methods. In addition to environmental factors, adulteration directly affects the quality of peanuts.

Physicochemical methods, typically acid and peroxide values, are commonly used in peanut quality evaluation. However, physicochemical methods need intensive labor and organic solvents which are bad for health (Kardash and Tur'yan., 2005). These drawbacks have limited the application of physicochemical methods in detecting peanut quality. Currently, there are also some modern techniques used in peanuts analyzing, such as GC/MS (Liu et al., 2013), high performance liquid chromatography (HPLC) (Hepsag et al., 2014), which are time-consuming, requiring for specific instruments and need complex preprocessing for samples. Machine vision (Chen et al., 2008) and visible spectroscopy/near infrared spectroscopy (VIS–NIRS) (Wang et al., 2009a,b), which bases on the detection of appearance of samples and could avoid sundry preprocessing, have been applied in detecting peanut quality. However, limited change on the peanut shells occur even the inside quality of peanuts changes a lot and limit their usefulness of internal quality monitoring for peanuts.

One of the most important quality problems for peanuts is rancidity of lipid and protein during storage, which could be induced by oxidation and produce undesirable off-flavors (Mate et al., 1996; Agbo et al., 1992). The off-flavor, related to the seed protein (s) that is lipoprotein in nature and is rich in oleic acid (Basha and Young, 1996; Basha et al., 1998), would change with storage time increasing. The porous structure of peanut shell creates possibility for the off-flavor emanating from inside. Hence, it is possible to detect the changes of peanut quality by detecting the volatile organic compounds (VOCs). Although gas chromatography–mass spectroscopy (GC–MS) is commonly used in analyzing VOCs, it is expensive and requires complex preprocessing for samples as mentioned above. Sensory analysis,

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on account of volatiles released from peanuts, is another way for peanut quality detection. The disadvantage of the sensory analysis is the difficulty to avoid the subjective caused by some personal issues existing in even the best trained panelists, which would affect the stability and the reproducibility of the results (Berna et al., 2004).

The readily available sensors, based on metal-oxide semiconductor sensor of electronic nose (e-nose) technology, were used in this research in order to address the drawbacks of previous works. An e-nose system consists of sensor array and computerized multivariate statistical data processing tools. The volatiles of samples flow through the sensor array with broad and partly overlapping selectivity, and the sensor response signals are recorded as "fingerprint" for analysis. Multivariate statistical technique is applied to identify "fingerprint" signals and is crucial for the analysis procedure. E-nose, actually known as simulation of human nose, has offered a fast and non-destructive alternative by sensing aroma for conventional techniques in odor analysis. The e-nose has demonstrated its diverse applications in many fields, especially in food industry. Fruit (Baietto and Wilson, 2015; Zhang et al., 2008, 2012), juice (Wang et al., 2016; Qiu et al., 2015a,b), wine (Bellincontro et al., 2013; Yu et al., 2014), meat (Musatov et al., 2010; Tian et al., 2013; Hong et al., 2012), egg (Wang et al., 2009a,b) and milk (Wang et al., 2010; Verma and Yadava, 2015) have been researched for their ripeness, spoilage, freshness, adulteration and flavors by e-nose.

E-nose has also been used in detecting the quality of nuts, like Chinese pecans and peanuts (Jiang and Wang, 2016). As for peanuts, it has been applied in studying the influence of cured temperature on off-flavor releasing (Osborn et al., 2001a) or in investigating the capability of electronic nose in separating peanuts with different levels of destruction (Osborn et al., 2001b). But few researchers focused on the application of electronic nose as a non-destructive method in detecting peanut quality. There is another case concentrating on unshelled peanuts and researching the ability of e-nose to detect and monitor quality changes in both unshelled peanuts and peanut kernels (Wei et al., 2015). But the sensors in their study were different from the sensors based on a Fox 4000 (ALPHA MOS, Toulouse FR) with three Metal-Oxide Sensors chambers equipped with 18 sensors (S1: LY2/AA, S2: LY2/G, S3 LY2/gCT, S4: LY2/gCTl, S5: LY2/Gh, S6: LY2/LG, S7: P10/1, S8:P10/2, S9: P30/1, S10: P30/2, S11: P40/1, S12: P40/2, S13: PA2, S14: T30/1, S15: T40/2, S16: T70/2, S17:T40/1, S18: TA2) and there was no deep investigation for the quality of adulterated peanuts by e-nose. Beyond that, the quality detection of unshelled peanuts by e-nose was hardly reported in any other researches. The current work mainly aims to use an array of 18 metal-oxide based gas sensors combined with physicochemical methods to achieve the following objectives: (1) To ensure whether the e-nose based on an array of 18 metal-oxide gas sensors could be applied as a non-destructive method in detecting the quality changes in peanuts during storage by combining PCA, LDA, SVM. (2) To set up the peanut quality tracing models based on e-nose signals to predict the physicochemical indices (acid value, peroxide value and content of crude fat) and storage time by utilizing PLSR and SVM, and try to select the best regression model by comparing the differences of using different normalized interval of datasets in PLSR and SVM. (3) To explore the ability of e-nose in tracing the adulterated levels of peanuts by using PLSR and SVM.

2. Experimental

2.1. Materials and grouping

The peanuts for this research were mini-baisha that were harvested in Shanzhuang town, Rizhao city, Shandong province in September 2014. Good quality peanuts with uniform size were used as experimental samples and were randomly divided into 6 groups (there were nine samples for each group, around 0.026 kg for each sample). The peanut samples were stored at 27 °C and 85–90% humidity to accelerate deterioration of peanut quality. One group of samples were removed for the e-nose measurements every two days. After e-nose measurement, acid value, peroxide value and contents of crude fat of the peanut kernels were tested according to national standard methods. Stale peanuts harvested in September 2013 had been stored with room temperature at 20 °C ± 2 °C for one year. The adulterated samples were made by mixing the fresh peanuts (harvested in September 2014) with stale ones at levels of 0%, 25%, 50%, 75% and 100%. Peanuts mass and detection replicates were the same as above.

2.2. Electronic nose detection

The odor analysis experiments were performed by a Fox 4000 (ALPHA MOS, Toulouse FR) e-nose, which consists of 18 metal-oxide semiconductor type chemical sensors. Table 1 shows the response characteristics of the 18 metal-oxide sensors. The response signal output from sensors is R (resistance value) and the maximum value would be extracted from sensor signals for the latter data processing.

Table 1
The response characteristics of 18 metal-oxide sensors.

Sensor chamber	NO.	Sensors	Sensitive characteristics	Reference volatiles
Sensor chamber 1	1	LY/LG	oxidizing gas	chlorine, fluorine
	2	LY/G	toxic gas	ammonia, amine compounds
	3	LY/AA	organic compounds	Ethanol
	4	LY/Gh	toxic gas	ammonia, amine compounds
	5	LY/gCTL	toxic gas	hydrogen sulfide
	6	LY/gCT	inflammable gas	propane, butane
Sensor chamber 2	7	T30/1	organic compounds	organic compounds
	8	P10/1	inflammable gas	Hydrocarbon
	9	P10/2	inflammable gas	Methane
	10	P40/1	oxidizing gas	Fluorine
	11	T70/2	aromatic compounds	methylbenzene, xylene
	12	PA/2	organic compounds, toxic gas	ethanol, ammonia, amine compounds
Sensor chamber 3	13	P30/1	inflammable gas, organic compounds	hydrocarbon, combustion products
	14	P40/2	oxidizing gas	Chlorine
	15	P30/2	organic compounds	ethanol, combustion products
	16	T40/2	oxidizing gas	Chlorine
	17	T40/1	oxidizing gas	Fluorine
	18	TA/2	organic compounds	Ethanol