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Detecting whey adulteration of powdered milk by analysis of volatile emissions using a MOS electronic nose

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ABSTRACT

The ongoing investigation into detecting fraudulent additions to milk powder is a collaborative effort among governmental agencies, industry, and academia. Recent advancements are emphasizing the utilization of fingerprinting methodologies, which involve characterizing the odor of samples using gas sensors and using chemometrics methods to detect "out-of-class" or adulterated samples. We developed an advanced method using an electronic nose (e-nose) equipped with 8 metal oxide semiconductor (MOS) sensors to detect whey adulteration in powdered milk by analyzing volatile emissions. We examined pure powdered milk adulterated with whey at six concentration levels (10%, 20%, 30%, 40%, and 50% v/v) in both dry and rehydrated forms. Statistical analyses, including Principal Component Analysis (PCA) and Artificial Neural Network (ANN), were employed to interpret the sensor output responses from the e-nose. The ANN analysis demonstrated a total variance of 85%, with only eight out of 180 samples (4.4%) being misclassified in detecting whey adulteration in powdered milk. The model achieved an impressive detection accuracy of 95.6%. Notably, sensors MQ9 and TGS822 exhibited the most robust responses to wet samples, while sensors MQ136 and TGS822 showed the highest reactivity to dry test samples. PCA analysis revealed that the first principal component (PC-1) accounted for 90% of the total variance, whereas PC-2 contributed only 4% to the variance. In summary, this article offers insights into the application of an e-nose portable device that enables non-invasive analysis, and it provides a promising tool for rapid quality assessment of commercial powdered milk.

1. Introduction

Milk powder, valued for its high nutritional content, serves as a vital source of nutrition for both infants and the elderly (Huang et al., 2022). Milk in powdered form has become a crucial and important ingredient added to a wide range of prepared food products, including infant formula, chocolates, granola, beverage mixes, seasonings, protein bars, and pastries. Pure dried milk powder offers several storage advantages including longer shelf life before spoilage (when free of additives), reduced storage space (compared to liquid milk), and storage at room temperature with no refrigeration-cooling requirement (Wei, Agarwal, & Subbiah, 2021; Yildirim & Genc, 2017). Powdered milk (PM) has become a large potential target for economically motivated adulteration (EMA) due to its significant global trade volume and increased product demand. Such adulteration poses serious health risks, including malnutrition, gastrointestinal issues, organ dysfunction, anemia, and other related diseases (Huang et al., 2022).The United States Pharmacopeia (USP) defines EMA as the fraudulent addition (dilution), removal, or substitution of inauthentic sub-stances to or from authentic (legitimate) substances by sellers, without the purchaser's knowledge, for economic gain (Jablonski, Moore, & Harnly, 2014). PM products are frequently targeted for EMA, ranking second only to adulterated olive oil in numbers of reported cases according to the USP database on food fraud and economic adulteration (Moore, Spink, & Lipp, 2012). Detecting adulterated milk powder is therefore imperative.

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Conventional methods, currently used for detecting adulteration of powdered milk products (by the addition of cheese whey powder), are divided into two main groups. The first group is based on compositional differences between sweet/acid whey and milk, focusing on determining the casein-to-whey protein ratio. Protein analysis techniques utilize data derived from spectroscopy (Miralles, Bartolomé, Amigo, & Ramos, 2000), electrophoretic separation (Souza, Arruda, BrandÃO, & Siqueira, 2000), and polarography (Mrowetz & Klostermeyer, 1976). The second method group relies on detection of casein-macro peptide (CMP), a specific compound (derived from the cheese-making process) found in whey which serves as a chemical marker for detecting PM adulterated with cheese whey (Ferreira & Oliveira, 2003). During the cheese manufacturing process, milk is hydrolyzed by chymosin and k-casein to form two pep-tides: para-kappa-casein (present in cheese curd), and glycolmacropeptide (GMP) which remain dissolved in cheese whey (Brody, 2000). The presence of these peptides confirms PM adulteration with cheese whey (Neelima, Sharma, Rajput, & Mann, 2013). Various methods have been developed for the quantitative detection of GMP, including Colorimetric Assay (Fukuda, Roig, & Prata, 2004), reverse-phase High-Performance Liquid Chromatography (HPLC) (Elgar et al., 2000), Cation Exchange Chromatography (CEC) (Léonil & Mollé, 1991), Mass Spectrometry (Mollé & Léonil, 2005), Cellulose Acetate Electrophoresis (CAE) (Nakano, Ikawa, & Ozimek, 2007), Starch Gel Electrophoresis (SGE) (Cherkaoui, Doumenc, Tachon, Neeser, & Veuthey, 1997), Sodium Dodecyl Sulfate-Polyacrylamide Gel Electrophoresis (SDS-PAGE), and immunochemical assays such as Enzyme-Linked Immunosorbent Assay (ELISA) (Chávez et al., 2012). Nonetheless, these methods suffer from drawbacks such as complex sample preparation, offline analysis, high costs, requirements of expensive equipment and specialized reagents and significant sample loss (Rasekh, Karami, Wilson, & Gancarz, 2021). Hence, there is a pressing need to develop affordable, reliable, portable, and rapid detection technologies for identifying adulterated milk powder.

The feasibility of using VOC-detection devices, such as e-nose instruments, for evaluating food quality and adulteration assessments of dairy products arises from well documented differences in the VOC emissions of pure powdered milk compared to milk powder adulterated with various contaminating components added because of flaws in the manufacturing process, lack of quality controls, or deliberately for financial gains (EMA fraud). Makhoul et al. (2016), who investigated the QC of semi-finished dairy ingredients by PTR-MS, found statistically significant differences in VOC content between samples of SMP, WMP and WP that effectively differentiate between dairy-product components (ingredients) based on VOCs released. They used a supervised classification model, PLS-DA on WP data, to identify five principal components (PCs) that yielded only a 13.3% classification error rate useful for fraud monitoring. However, such analytical chemistry-based methods, although effective, are quite expensive, time consuming, and require extensive analytical skills for proper quality control (QC) analyses for food safety and authentication assessments.

Use of an electronic nose (e-nose) device for detecting food adulteration and food quality was a newer, alternative method based on analysis of product volatile emissions (Wilson, 2013). Electronic nose devices consist of a collection of chemical sensors, forming a sensor array that collectively detect volatile emissions from organic sources in the form of volatile organic compounds (VOCs) (Wilson, 2018). Sensory outputs from an e-nose sensor array are often analyzed using pattern recognition and chemometric statistical methods to detect and classify simple and complex aromas derived from organic samples(Rasekh, Karami, Kamruzzaman, Azizi, & Gancarz, 2023). Electronic noses are used extensively to investigate food quality and freshness because of their capability of providing fast, accurate, and reliable results in evaluating the quality of commercial food products (Wilson, 2018). The efficacy of e-nose devices for food quality application assessments are well establish in available literature, recently reviewed by Karami, et al. (2024a).

Recent literature, specifically Yakubu, Kovacs, Toth, and Bazar (2022), has reviewed the applications of E-nose technology in the dairy sector, encompassing milk, yogurt, and cheese. In the context of fresh milk, E-nose has been utilized for various purposes, including monitoring microbial growth(Carrillo-Gómez, Acevedo, & García-Rico, 2021; Phukkaphan, Eamsa-Ard, Chairanit, & Kerdcharoen, 2021), discriminating between milk based on farming systems (Mu, Gu, Zhang, & Zhang, 2020), detecting traces of detergent in (Tohidi, Ghasemi-Varnamkhasti, Ghafarinia, Bonyadian, & Mohtasebi, 2018), and distinguishing milk from cows fed on different Alpine pastures (Falchero et al., 2009).

Since no study has been conducted on the detection of milk powder adulteration using an electronic nose, this study aimed to investigate the detection of whey adulteration at different levels (10−50%) in milk powder (both in dry and wet states). The analysis focused on differences in VOC emissions to evaluate the e-nose's ability to classify milk powder samples based on whey adulteration levels, aiming to find more effective means of ensuring the quality and purity of milk powder products, which are essential for regulatory compliance and consumer protection.

2. Materials and methods

2.1. Preparation of powdered milk samples

Powdered milk (PM) and cheese whey powder (WP) were obtained from a commercial dairy product distribution source (Nestlé NAN OPTIPRO 1, Tehran, Iran) to prepare samples for e-nose analyses. PM samples were defined into two sample types, including pure unadulterated powdered milk (UPM) samples that served as controls, and 2) powdered milk samples having whey adulteration (at five levels) by adding whey powder (WP) to pure powdered milk in separate lots at incremental proportions of 10%, 20%, 30%, 40%, and 50% v/v) to create artificial PM adulteration mixtures.

Sample controls (pure PM) and UPM samples were further prepared for testing in two distinct sample states (consistencies): 1) in the dry state (powdered form) and 2) in a wet state (powder mixed with boiling water). For dry sample tests, pure dry UPM samples were labeled samples A, while other dry samples were labeled B through F (corresponding to 10−50% whey adulteration, respectively) in the dry state. For wet sample tests, pure UPM wet samples were labeled samples G, and adulterated samples were labeled H through L (corresponding to 10−50% adulteration, respectively) in the wet state. Wet samples were prepared by mixing the dry milk powder with boiling water. The water-to-dry powder mixture dilution ratio of (90:14.5) or (16.1% w/v) was based on the instructions provided on the packaging of infant formula milk, indicating the addition of 90 mL (90 g) of water for every 3 scoops of powdered milk (14.5 g). Thus, a total of 1862.06 mL of deionized water was mixed with 300 g of powdered milk powder, equivalent to 62.1 mL of de-ionized water added for every 10 g of powdered milk.

Fifteen sample replications ($n = 15$) were prepared and analyzed for each sample type including pure UPM samples and for WP milk samples (with multiple levels of whey adulteration) for both wet and dry experiments. All samples were prepared in 300 g portions (for each level of adulteration) and divided into 30 samples of 10 g aliquot increments each for conducting e-nose analysis for sample replications. The dry weight of powdered milk samples was measured using a precision digital Sartorius TE-64 balance (Sartorius

AG, Göttingen, Germany) with an accuracy of 0.0001 g. Adulterated samples were divided into 15 containers with each container containing 10 g of sample mixture. To maintain the integrity and functionality of the electronic nose system, no other experiments were conducted in the laboratory workspace. This precaution was taken to prevent any potential interference or disruption to the electronic nose system operations. Individual samples were prepared for e-nose analysis by placing a 10 g sample, comprising a mixture of powdered milk and cheese powder (for adulterated milk samples), placed in-side a small polyethylene plastic container. A total of 180 samples were prepared for dry and wet sample tests with 30 containers of 10 g each (for each level of adulteration) for powdered milk samples in both wet and dry states.

2.2. Electronic nose system

The experimental electronic nose system used in this study was composed of two major components: hardware and software. The hardware components of the electronic nose system included a data acquisition system, eight metal oxide semiconductor (MOS) gas sensors, a sensor chamber, a sample chamber, a power supply, connections and accessories, an electric valve, an air pump, and an air filter.

The response of the eight MOS sensors in the sensor array was monitored by a data acquisition system connected to a computer via USB connection. The data acquisition process consisted of three sequential operational stages: 1) baseline correction, 2) sample injection, and 3) sensor cleaning between each sample analysis (Khorramifar et al., 2023). In the data acquisition stage, a suitable amount of the sample (10 g) was placed in the sample chamber. During this stage, the baseline was established by passing clean reference (room) air, maintained within a narrow relative humidity range (maximum 5–6% variation) over the sensor array to purge VOC contaminants and clean the sensors. In dry experiments, this process lasts for 150 s, while wet sample analyses took 100 s. The additional purpose of the clean air sensor-purge stage was to bring the sensor responses to a stable state. In the sample injection stage, VOCs emitted from the sample were moved to the glass sensor chamber (containing the 8 MOS sensor array) using an air pump. This stage involves exposing the sensors to volatile components emitted from the samples within the sensor chamber. In dry sample experiments, the sensor exposure duration was 300 s, while in wet experiments, it was 200 s. As VOCs within the sample gases enter the sensor chamber and contact the sensor surfaces, VOC adsorption induces changes in the output voltage of each sensor. This variation is proportional to the type of sensor used and its sensitivity. Upon receiving the VOCs from the sample, the sensors produce and output response, transferred and recorded by the data acquisition system. The data acquisition system contains a transducer that converts the analog sensor response into digital data, transmitted to a computer via a USB cable (Khorramifar et al., 2022). Data were evaluated by signal preprocessing using pattern recognition methods and analyzed statistically using principal component analysis (PCA), artificial neural networks (ANN), and first-order linear discriminant analysis (LDA). The final stage involves comparing the results with standard reference samples (Karami, Rasekh, & Mirzaee-Ghaleh, 2020a). In the sensor and chamber cleaning stage between samples, clean air was passed over the sensors to stabilize the sensor array's response baseline. The pump was used to remove any residual VOCs inside the sample chamber. This step takes 150 s for dry experiments and 100 s for wet experiments, preparing the system for the next sample accordingly. The voltage response of the sensors was recorded for 600 s in dry experiments and 400 s in wet experiments (Karami, Rasekh, & Mirzaee-Ghaleh, 2020b).

The experimental e-nose was comprised of eight MOS sensors. Each sensor responds to all volatile compounds emitted from the samples. These durable MOS sensors possess advantages such as high chemical stability, long lifespan, low sensitivity to humidity, cost-effectiveness, and high sensitivity. They can be utilized for a wide range of food and chemical substances (Karami et al., 2024b). Table 1 provides the sensitivity and detection range specifications of individual MOS sensor types present within the sensor array of this e-nose sys-tem.

2.3. Data processing and statistical analyses

During the data collection process, the relative humidity and temperature of the VOC sampling chamber environment were maintained in a narrow range of variability (temperature 20 ± 2.0 °C and relative humidity of 30–40%). The room air temperature also was controlled at 20 ± 0.5 °C during the sample preparation and detection to help minimize changes in the carrier input air relative humidity prior to input in the VOC sampling chamber (Tatli, Mirzaee-Ghaleh, Rabbani, Karami, & Wilson, 2022). The signals received from the sensor array were initially recorded and stored as raw data. The next stage involves preprocessing the sensor signals, which significantly impacts the performance of pattern recognition methods. The specific preprocessing steps may vary depending on the type of detectors used. Data preprocessing consisted of three stages: 1) baseline correction, 2) data compression, and 3) sensor output normalization. The objective of baseline correction was to compensate for sensor drift and enhance the quality of sensor responses (Zorpeykar, Mirzaee-Ghaleh, Karami, Ramedani, & Wilson, 2022).

A fractional method based on (Equation (1)) was used for data normalization in addition to baseline correction. The fractional method was commonly employed in normalizing data from semiconductor metal oxide sensors (Rasekh et al., 2022).

$$y_s(t) = \frac{x_s(t) - x_s(0)}{x_s(0)} \quad (1)$$

Table 1
Sensor types and sensitivities within the 8-MOS electronic nose sensor array (Karami, Rasekh, & Mirzaee-Ghaleh, 2021).

Sensor no.	Sensor name	Primary gases detected (response sensitivity)	Detection ranges (ppm)[a]
1	MQ3	Alcohol	10–300
2	TGS822	Organic solvents	50–500
3	MQ136	Sulfur dioxide (SO_2)	1–200
4	MQ9	Carbon monoxide (CO), combustible gases	10–1000 (CO), 100–1000 combustible gases
5	TGS813	Methane, propane, butane	500–10,000
6	MQ135	Ammonia, benzene, sulfide	10–10,000
7	TGS2602	Hydrogen sulfide, ammonia, toluene	1–30
8	TGS2620	Alcohol, organic solvents	50–500

[a] Sensor detection ranges given in parts per million (ppm) concentration ranges.

The baseline response (xs (0)) was the smallest sensor response obtained when clean air was introduced into the sensor chamber during the low-pulse aroma stage prior to sample acquisition. The resulting value was divided by the baseline response, generating a dimensionless normalized component called the processed response (ys (t)). This processed response can compensate for both high and low response rates of each sensor (Karami et al., 2024b).

The evaluation metrics used for analyzing the system performance included accuracy, precision, recall, specificity, area under the curve, and F-score. The evaluation metrics are derived from the confusion matrix, which utilizes parameters such as false positive (FP), true positive (TP), false negative (FN), and true negative (TN) (Aghili, Rasekh, Karami, Azizi, & Gancarz, 2022; Tatli et al., 2022).

$$\text{Specificity} = \frac{TN}{TN + FP} \tag{2}$$

$$\text{Precision} = \frac{TP}{TP + FP} \tag{3}$$

$$\text{Recall} = \frac{TP}{TP + FN} \tag{4}$$

$$\text{Accuracy} = \frac{TP + TN}{TP + TN + FN + FP} \tag{5}$$

$$\text{AUC} = \frac{\text{Sensitivity} + \text{Precision}}{2} \tag{6}$$

$$\text{F} = \frac{2 \times PR}{P + R} \tag{7}$$

From the total dataset, 60% were randomly selected for training, 20% for testing, and 20% for validation. Data analysis and classification were conducted, following data preprocessing, using the artificial neural network (ANN) statistical model method by the MATLAB R2013b software (The MathWorks Inc., Natick, MA, USA). Principal component analysis (PCA), linear discriminant analysis (LDA), and support vector machine (SVM) methods were implemented using the Unscrambler X, version 10.4, software (Aspentech, CAMO Analytics, Bedford, MA, USA). Data normalization and visualization of multiple graphs were performed using Microsoft Excel 2019 software (Microsoft Corp., Redmond, Washington, USA).

3. Results

3.1. Principal component analysis

PCA was used to reduce dimensionality of eight variables to two principal components (PCs) while preserving the essential information content of the data. This method detected differences between PM sample types (through score plots) and helped identify the factors contributing most to response differences by using loading plots. Score plots are used to identify patterns, classify data, and express similarities and differences. They provide a visual representation of the data that reveals relationships and variations. Loading plots provide insights into the relative contributions of variable groups to specific evaluation components. They clarified the role and contribution of each sensor in providing discrimination in the classification process. If the loading value of a sensor was closer to the primary components (near the outer circle), it implies that the sensor plays a more significant role in identifying and detecting differences in sensor output patterns.

The PCA analysis utilized normalized sensor responses to the odors of different samples of powdered milk. The results revealed that PC-1 accounted for 90% of the total variance, while PC-2 accounted for 4% of the variance. The cumulative variance of the samples reached 94% in the resulting score plot (Fig. 1). The model constructed using the first two principal components discriminated the samples based on their olfactory characteristics and accurately detected the presence of adulterated cheese powder in moist powdered milk with good accuracy. The left side of the figure represents PCA plotting results for dry powdered milk samples (labeled with green letters A to F) in which A represents dry pure powdered milk and B through F representing various levels of whey adulteration. The right side of the figure represents PCA plotting

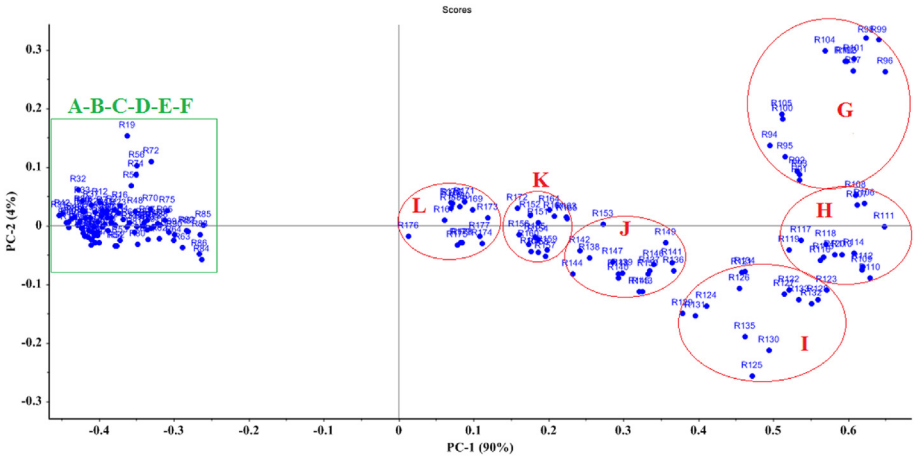

Fig. 1. PCA analysis results for detecting fraudulent whey-adulterated powdered milk samples in separate dry and wet sample tests. Sample labels are divided into two groups for (a) dry sample tests (represented by samples A–F within the green box at left), and (b) wet sample tests (represented by samples G–L within red circles at right). Sample type letter symbols: A = pure dry unadulterated PM; B–F = whey-adulterated dry PM samples with 10–50% adulteration levels, respectively, at 10% increasing increments); G = pure wet unadulterated PM; H–L = whey-adulterated wet PM samples with 10–50% adulteration levels, respectively, at 10% increasing increments).

results for wet powdered milk samples (labeled with red letters G through L) in which G represents wet pure unadulterated powdered milk and samples H through L representing various levels of whey adulteration. Whey-adulterated milk samples (at different levels) exhibited significant overlap (for dry samples) that were not distinguishable statistically from pure unadulterated powdered milk. However, the various adulteration levels of PM in a moist state were well distinguished into separated data clusters and statistically different from pure unadulterated powdered milk. Thus, whey adulteration of PM was detected effectively only in wet samples.

PCA data of pure powdered milk samples (green A–F samples) were in a tight cluster and well separated from all whey-adulterated powdered milk samples (red G–L samples) with no overlap and at least 0.3 mapping distance units apart.

3.2. E-nose sensor contribution analysis

The Unscrambler-X software data output of the loading plot provided information about the effectiveness of the e-nose sensor array in discriminating between PM sample types based on differences in VOC emissions. The contribution of each individual sensor to each principal component (and sample discriminations) was indicated in the loading plot (Fig. 2). The plot consists of two circles in which the inner circle represents 50% and the outer circle represents 100% of the total variance of e-nose sensory data. The role of a sensor in detection and classification was determined by its loading coefficient, with sensors closer to the outer circle playing a more substantial role. Therefore, sensors located on the outer larger circle have a greater impact on data classification and discrimination. The loading plot showed the role of sensors in separating PM samples, specifically in detecting whey adulteration in wet milk tests. Based on the loading plot, the sensors with the highest contributions to sample discriminations were, in descending order, MQ9, TGS813, and TGS2620. The MOS e-nose sensor array was not effective in detecting WP adulteration in dry PM samples. Consequently, the role of individuals in sample discrimination and classification were not possible for dry PM samples.

A higher loading value for a sensor in the loading plot indicates a greater influence on the detection and differentiation of PM samples. By eliminating sensors with lower contributions to sample differentiation, not only can the cost of sensor production be reduced, but the complexity of data evaluation stages may also be minimized (Tohidi et al., 2018). In this case, all sensors had significant roles in identifying levels of WP fraud and discriminating between PM sample classes.

3.3. Radar plots of E-nose sensor outputs

Radar plots of sensor response patterns (radial smellprint signatures) provided indications of visual differences in sensor responses to VOC emissions derived from pure UPM and WP adulterated samples in both dry and wet sample tests. The average sensor output responses of the electronic nose sensors, after normalization, are plotted in two separate radial plots for dry and wet PM sample tests (Fig. 3a,b).

Dry sample tests showed sensor response intensities to UPM dry milk samples (letter A, black line) were significantly lower for most sensors in the sensor array than WP adulterated samples (indicated by letters B, C, D, E, and F with 10–50% adulteration), except for sensor MQ 136, for which only 40% and 50% WP adulterated samples had higher sensor intensities (Fig. 3a).

Wet UPM samples represented by the letter G (purple line), caused sensor responses that were significantly higher than for WP adulterated samples only for sensor MQ9 (Fig. 3b). By contrast, sensor response intensities to WP adulterated samples were mostly greater than UPM samples (represented by letters H, I, J, K, and L) at increasing levels of whey adulteration with 50% adulteration (indicated by the letter L, black line) having the lowest sensor intensity responses by all sensors. Sensor responses became more attenuated at higher levels of WP adulteration in wet samples. By contrast, sensor response intensities tended to increase with increasing WP adulteration in dry samples.

Dry sample test results indicated that sensors MQ136 and TGS822 exhibited the strongest responses to VOC emissions, while the remaining sensors showed lower responses to PW samples. Wet sample test results were different, indicating that the standard deviation of sensor responses to VOC emissions from WP adulterated samples yielded the highest sensor responses in sensors MQ9 and MQ136 to wet PM samples (combined with steam).

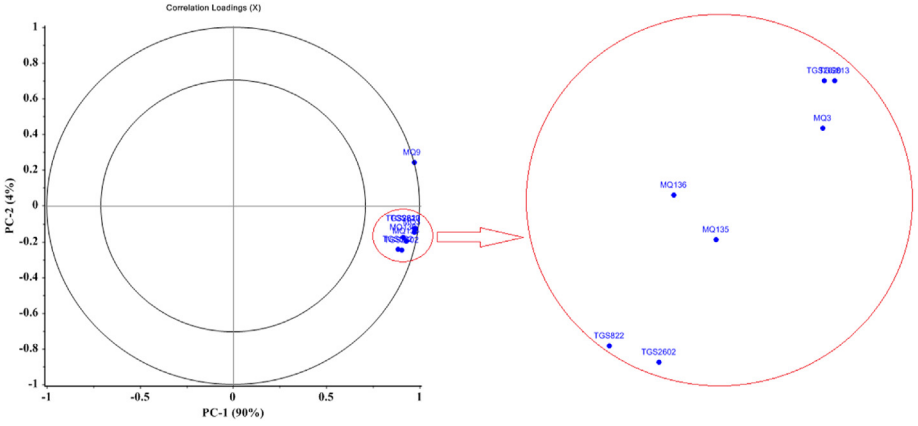

Fig. 2. Loading PC plot to identify the effectiveness of individual sensors in detecting whey adulteration of powdered milk samples tested in the wet state. Levels of sensor contribution to sample discriminations are indicated by the distance of each plotted sensor name from the center of the plot. Indications of individual positions of each sensor are shown more clearly in the enlarged view at right (red circled area).

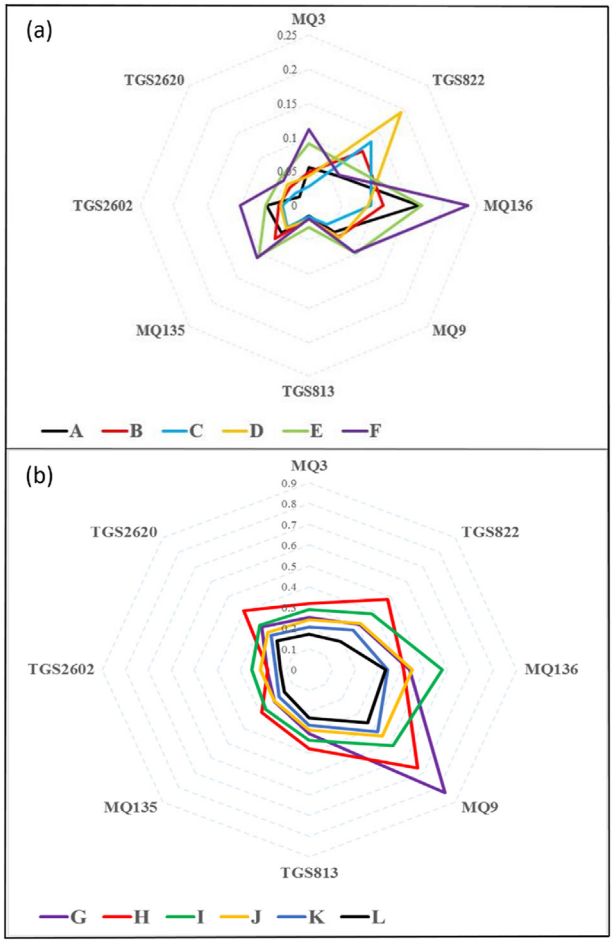

Fig. 3. Radar plot of 8-MOS e-nose sensor array responses to milk volatile emissions from milk samples in the (a) wet state, and (b) dry state in separate tests. Sample type letter symbols: A = pure dry unadulterated PM; B–F = whey-adulterated dry PM samples with 10–50% adulteration levels, respectively, at 10% increasing increments); G = pure wet unadulterated PM; H–L = whey-adulterated wet PM samples with 10–50% adulteration levels, respectively, at 10% increments).

3.4. Artificial neural network (ANN) analysis models

The ANN's input layer receives normalized data from 8 metal oxide sensors, while the output layer comprises 12 distinct groups of dry milk, serving as the target for model development. The configuration of the hidden layer was determined through trial and error. The dataset was divided into three subsets: 60% for training, 20% for validation, and the remaining 20% for testing purposes.

The ANN models, obtained based on different topologies, were evaluated using metrics including as Correct Classification Rate (CCR), R-squared or coefficient of determination (R^2), and Root Mean Square Error (RMSE). The evaluation of the ANN model for all topologies are presented in Table 2. The best ANN performance was obtained for the 8-13-12 topology among all topologies tested. Specially, R^2 values obtained for the training and test sets for were 0.973 and 0.945, respectively. The corresponding RMSE values were 0.534 for the training set and 0.610 for the test data set.

We examined different topology configurations for assessing the best models and methods for sample discriminations. Among the tested topologies, the 12-13-8 configuration delivered the best results with an R^2 value of 0.973 (for the training data set) and 0.945 for the test data set. The corresponding RMSE values were 0.534 for the training data set and 0.610 for the test data set, reflecting a model accuracy of 95.6%. The confusion matrix indicates that out of a total of 180 data points, only 8 were misclassified, indicating the model's high detection accuracy of 95.6%. The model's performance was quantified by the following metrics: Accuracy, Precision, Recall, Specificity, AUC (Area Under the Curve), and F-score for powdered milk. These results included an AUC of 99.3%, Specificity of 0.956, Recall of 0.956, Precision of 0.996, Accuracy (Area Under the Curve) of 0.976, and an F-score of 0.955.

The confusion matrix results are presented in Fig. 4. Horizontal rows (A–L) on the vertical y-axis represent the predicted output classes from the network, whereas horizontal columns (A–L) represent the actual target classes. The diagonal cells represent the number and percentage of correct classifications by the ANN. The cells outside the diagonal represent the misclassified samples. Based on the confusion matrix, out of a total of 180 data points, 8 data points have been incorrectly classified for detecting cheese whey powder adulteration. The ANN model achieved a detection accuracy of 95.6%.

Performance metrics obtained from ANN models in the experiments are presented in Table 3. Average values for AUC for ANN analyses, for detecting whey powder adulteration, include Specificity, Recall, Precision, Accuracy, and F-Score were 0.976, 0.996, 0.956, 0.956, 0.993, and 0.955, respectively. Letters A and G represent pure powdered milk in dry and wet state, whereas letters B to F represent adulteration 10 to 50 percent for milk samples in the dry powder state. Letters H to L represent adulteration 10 to 50 percent for milk samples in the wet state.

Table 2
ANN model-evaluation based on root mean square error (RMSE), coefficient of determination (R^2), and correct classification rate (CCR) performance metrics.

Topology[a]	Training		Test		CCR (%)[b]
	RMSE	R^2	RMSE	R^2	
8-9-12	0.499	0.926	0.991	0.856	90.0
8-10-12	0.473	0.917	0.941	0.899	88.9
8-11-12	0.522	0.954	0.697	0.899	93.3
8-12-12	0.455	0.946	0.916	0.917	91.7
8-13-12	**0.534**	**0.973**	**0.610**	**0.945**	**95.6**
8-14-12	0.511	0.963	0.992	0.917	93.3
8-15-12	0.417	0.926	0.841	0.899	91.7

The bold numbers in the table represent the best topology with highest CCR.

[a] Topology: The notation (8–13–12) in network topology denotes the network's arrangement of nodes and connections. The first number represents input layers from eight sensors. The second number signifies hidden layers, determined through trial and error. The third number indicates output layers reflecting the 12 powdered milk groups.

[b] The correct classification rate (CCR) in artificial neural networks (ANN) represents the accuracy of the model in correctly classifying instances within a dataset. It is calculated as the ratio of correctly classified instances to the total number of instances in the dataset, expressed as a percentage.

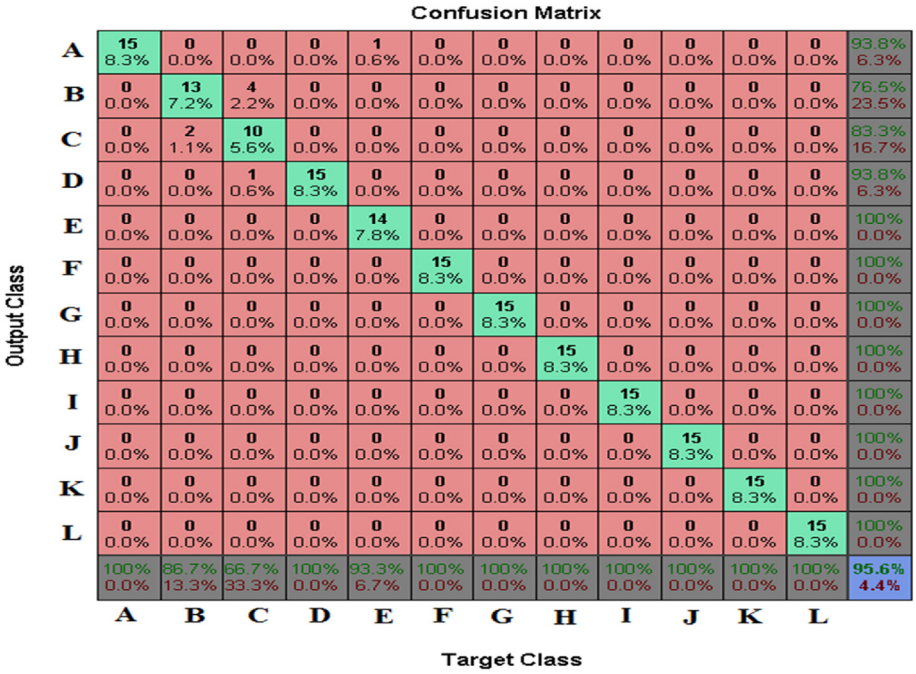

Fig. 4. Confusion matrix of ANN statistical model derived from sensor response outputs of the MOS e-nose sensor to VOC emissions from powdered milk sample tests. Output and target class results from powdered milk sample tests run in separate tests: 1) dry state tests for samples labeled A (dry pure PM) and labeled B through F (for dry samples with 10–50% whey adulteration, respectively), and 2) wet state tests for samples labeled G (wet pure PM) and samples H through L (for wet samples with 10–50% whey adulteration, respectively).

Table 3
Functional parameters obtained from ANN model based on 8-13-12 topology.

Topology	Class	Accuracy	Precision	Recall	Specificity	AUC	F-score
8-13-12	A	0.994	0.938	1.000	0.994	0.966	0.968
	B	0.967	0.765	0.867	0.976	0.870	0.813
	C	0.961	0.833	0.667	0.988	0.911	0.741
	D	0.994	0.938	1.000	0.994	0.966	0.968
	E	0.994	1.000	0.933	1.000	1.000	0.966
	F	1.000	1.000	1.000	1.000	1.000	1.000
	G	1.000	1.000	1.000	1.000	1.000	1.000
	H	1.000	1.000	1.000	1.000	1.000	1.000
	I	1.000	1.000	1.000	1.000	1.000	1.000
	J	1.000	1.000	1.000	1.000	1.000	1.000
	K	1.000	1.000	1.000	1.000	1.000	1.000
	L	1.000	1.000	1.000	1.000	1.000	1.000
Average per class		0.993	0.956	0.956	0.996	0.976	0.955

4. Discussion

International law strictly prohibits the addition of whey to milk due to its association with fraudulent milk adulteration. This deceptive practice implicates every entity in the production chain, from producers to consumers, through distributors, carrying both nutritional and legal ramifications. Consequently, there is an urgent need for precise, efficient, rapid, trustworthy, accessible, and quantitative techniques. Implementing such methods is essential for both governmental regulatory bodies and the dairy industry to safeguard the quality of milk for consumers (Vera-Bravo et al., 2022). That is why this study focused on detection of whey adulteration of powdered milk, and further classification of various levels of whey adulteration based on differences in VOC emissions from powdered milk samples. Sample were analyzed with an 8-sensor MOS experimental e-nose from which sensory data were compared by advanced statistical analysis models, including PCA and ANN methods. In the current study, PCA was used to help reduce dimensionality while preserving essential e-nose sensory data information, effectively capturing cumulative variance to facilitate sample discrimination. Previous studies have shown that score plots help to visually identify similarities and differences in e-nose sensory response patterns, while loading plots reveal the specific in the e-nose sensor array that contribute most to discriminations between sample types (Ayari, Mirzaee-Ghaleh, Rabbani, & Heidarbeigi, 2018). We used this approach to precisely discriminate between VOC emissions from PM samples based on e-nose sensor response patterns.

The consistency (dry vs. wet) of PM sample types analyzed here had a significant impact on the effectiveness of whey-adulteration detection and discrimination between sample types. Wet samples exhibited greater differentiation between powdered milk sample types presumably resulting from potential VOC alterations that occurred during reconstitution with boiling water. During the reconstitution of powdered milk with boiling water, chemical changes may occur, potentially altering or releasing new VOCs compounds from milk powder. Certain volatile compounds may undergo heat-induced chemical changes (degradation, oxidation, and conversion) that could impact the aroma characteristics of powdered milk emissions. Wet adulterated PM samples also produce significantly more VOC emissions than dry samples (Makhoul et al., 2016). These explanations may account for our divergent results (based on PM sample consistency) which indicated that superior differentiation between UPM and WP adulterated powdered milk samples, based on sample VOC-emission differences, were obtained from analyzing wet samples.

Sensor response intensities from Radial plot (smellprint) signatures revealed that e-nose sensors MQ9 and TGS822 within the sensor array exhibit the highest sensor intensity responses to VOCs emissions from wet milk samples (in the presence of steam), whereas sensors MQ136 and TGS822 had the highest sensor responses to VOCs from dry milk samples. These results underscoring

the importance of assessing sensor array response analyses (i.e., the testing of individual sensor within the array that are most responsiveness to expected targeted sample VOCs) which vary depending on sample type and consistency. Evaluating individual sensor effectiveness was essential for detecting specific VOC-emission differences in milk samples adulterated with cheese whey powder. The varying sensor responses emphasize the importance of selecting the appropriate sensors (within the sensor array) for specific testing conditions, contributing to improved accuracy and reliability of sample discrimination and adulteration detection in dairy products.

A comparison of our PM test results, using PCA and ANN statistical methods for product adulteration detection, to results of similar previous e-nose studies of product quality and adulteration for various other plant and dairy products using comparable statistical methods, indicated encouraging results for using a combination of e-nose and ANN analyses for assessing product quality. Mohammadian, Ziaiifar, Mirzaee-Ghaleh, Kashaninejad, and Karami (2023), investigated the capabilities of an e-nose to detect adulteration and additives in lemon juice based on e-nose sensory pattern recognition and ANN techniques. They found the ANN method demonstrated superior performance in sample discrimination using e-nose analysis data. Similarly, Kasbe et al. (2018) used ANN and PCA to discriminate between healthy and unhealthy post-harvest tomato fruits, achieving a classification accuracy of 95%. The ANN method effectively distinguished between different tomato samples based on quality, demonstrating successful performance in classification and highlighted the capability of the e-nose instrument in detecting plant fruit quality status. Cevoli et al. (2011) utilized an e-nose with an ANN approach to classify Pecorino cheeses based on ripening time and manufacturing techniques aimed at improving production applications with different pre-treatments. They obtained better classification performance using PCA (100% correct sample classification) compared to other pre-processing systems. Aghdamifar, Sharabiani, Taghinezhad, Szymanek, and Dziwulska-Hunek (2023) utilized several statistical data analysis techniques (PCA, PLSR, LDA, and ANN) to detect various amounts of caffeine present in coffee.

Yu, Wang, and Xu (2007) previously investigated methods for monitoring powdered milk adulteration based on aroma data from an electronic nose to evaluate food quality. The study utilized a PEN 2 e-nose, containing 10 MOS sensors in the sensor array. The experiment involved liquid whole milk, reconstituted milk powder, and adulterated liquid milk with varying proportions of water or milk powder, conducted over a 7-day storage period. The results were analyzed using principal component analysis (PCA) and linear regression analysis (LDA). Three sample types, including skimmed milk, skimmed milk adulterated with reconstituted milk, and adulterated skimmed milk with water were well-differentiated in both LDA and PCA plots. The PEN 2 e-nose demonstrated the capability of detecting milk purity in adulterated skimmed milk. The e-nose also was capable of distinguishing between milk samples aged for varying duration with clear separation up to day 4. Moreover, In another investigation, the blending of detergent powder as adulterant in raw milk up to the concentration level of 0.3% was examined by Tohidi et al. (2018). The score plot of PCA explained 91% of the variations in the e-nose data. To achieve enriched grouping accuracy, linear discriminant factor and SVM approaches were employed. SVM method improved accuracy to 90%. However, the results of LDA (66.6%) grouping method did not improve on the PCA method. The separation was indistinguishable for class 0.3% adulteration in LDA.

Significant differences in MOS e-nose sensor array responses to VOC emissions from pure unadulterated milk powder UMP compared to whey-adulterated samples, indicated in both radar plot (smellprint) signatures and in ANN classifications, could be explained by the distinct chemical composition of VOCs present in each sample as well as differences in the quantities of certain VOCs in common with both sample types. Previous research has demonstrated that there are at least three VOCs found in whey powder (WP), including (2-propanone, 5-methyl-2(3H) furanone, and a third unidentified compound) that are unique to WP and not found in UMP (Makhoul et al., 2016). In addition, they found at least twenty-five VOCs in UMP such as 2-propanal, acetaldehyde, methane thiol, butanal, 2-pentenal, 2-heptenal, ethyl furan, and 18 other VOCs) are unique to UMP and absent among the volatiles of WP. Of the 390 total VOCs identified in emissions from UMP and WP, about 107 of these VOCs were present in emissions from both sample types but occurred at significantly different quantities and molar ratios within the gas analytes from each sample type (Makhoul et al., 2016). Thus, distinctly different VOC emissions from UMP and WP are the clear basis for the capability of the MOS e-nose to detect differences in volatile emissions between pure and whey-adulterated powdered milk.

The increase in additional volatiles released from whey-contaminated powdered milk in storage, associated with spoilage compounds and off-flavor, contribute to additional sources of chemical differences in VOC emissions between UMP and WP-contaminated powdered milk. The US dairy industry standard for WMP shelf life is 6–9 months (Lloyd, Hess, & Drake, 2009) primarily linked to whey lipid oxidation. Straight-chain aldehydes, particularly hexanal associated with linoleic acid oxidation, are the main volatiles released from the oxidation of various whey lipids (Jadhav, Singh, & Salunkhe, 1972). Javidipour and Qian (2008) reported that dimethyl disulfide emission levels, derived from microbial degradation of whey proteins, also increased in whey-amended products stored for 15 weeks after production, indicating further means for detecting whey-adulterated powdered milk in storage. Commercial whey powder typically contains 2–5% lactose and 3–7% lipids that make milk powder susceptible to off-flavor production during storage (Laye, Karleskind, & Morr, 1995).

Whey also affects the flavor and physicochemical properties of powdered milk, decreasing product quality by the addition of chymosin (a milk clotting enzyme) that changes the properties of milk by affecting its protein content (diminishing stability), microbiological activities, and ultimately causing changes in VOC emissions (Gallardo-Escamilla, Kelly, & Delahunty, 2005; Vera-Bravo et al., 2022). Dimethyl disulfide, a breakdown product of the sulfur-containing amino acids cysteine and methionine, may contribute to VOCs associated with off-flavor, resulting from the oxidation of fatty acids that forms aldehydes, methyl ketones, alcohols, and furans (Tunick et al., 2016). Some volatiles are breakdown products of microbial activities.

Electronic tongue devices and certain biosensors also may potentially offer other cost-effective alternative means of detecting milk adulteration by certain other substances such as urea. Poonia et al. (2017) provided a comprehensive review comparing suitable methods for detecting and determining sources of milk adulteration.

5. Conclusions

This study contributes significantly to addressing concerns surrounding food adulteration, particularly within the dairy food industry. Traditional methods for detecting adulteration, often costly and time-intensive, require specialized technical skills. In contrast, our novel approach focuses on non-invasive volatile analysis of milk powder emissions, presenting a marked advancement over conventional chemical analysis methods. By employing electronic nose (e-nose) analyses in conjunction with PCA and ANN

techniques, we demonstrate the efficacy of accurately detecting whey adulteration levels in powdered milk. Importantly, these methods hold potential for assessing the quality of various commercial dairy products. Our findings offer a promising solution to enhance food quality and safety assessments, presenting a faster and more economical alternative to traditional chemical analysis methods.

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CRediT authorship contribution statement

Pouya Darvishi: Writing – original draft, Data curation. **Esmaeil Mirzaee-Ghaleh:** Visualization, Validation, Supervision, Software, Resources, Project administration, Conceptualization. **Zeynab Ramedani:** Writing – review & editing, Visualization, Supervision, Project administration. **Hamed Karami:** Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Formal analysis, Conceptualization. **Alphus Dan Wilson:** Writing – review & editing, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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