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Potentiometric sensor arrays for electronic tongue applications in food quality control

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Abstract

What if a single analytical instrument could simultaneously distinguish the ionic fingerprint of a fruit juice, detect adulteration, and flag spoilage in under two minutes without consuming reagents or generating chemical waste? The electronic tongue (e-tongue) aims to achieve exactly this by mimicking the parallel signal integration of biological taste receptors through arrays of non-specific chemical sensors. Potentiometric e-tongues based on Ion-Selective Electrodes (ISEs) are among the most studied configurations because of their simplicity, low cost, and sensitivity to the dominant ionic species in foods hydrogen, sodium, potassium, calcium, chloride, and nitrate ions which together account for a large fraction of the discriminating power between food matrices. The present research developed and validated a six-sensor potentiometric e-tongue array for the discrimination and quality classification of five commercial beverages: orange juice, apple juice, grape juice, black tea, and green tea. Sensor membranes based on plasticised PVC with selective ionophores were fabricated in-house and characterised for Nernstian response, selectivity coefficient, and long-term drift. The multivariate response data were analysed by Principal Component Analysis (PCA), linear discriminant analysis (LDA), Support Vector Machine (SVM), and K-Nearest Neighbours (kNN). PCA reduced the six-dimensional sensor space to two principal components capturing 72.0% of total variance; complete visual separation of all five beverage classes was achieved in the PC1-PC2 score plot. SVM gave the highest classification accuracy: 98.6% for orange juice and 99.2% for black tea across a 30-sample external validation set. The sensor array also detected artificial sweetener adulteration (cyclamate, 0.1-2.0 g/L) and cold-chain temperature abuse (20°C for 12 h) with classification accuracies of 96.4% and 94.8%, respectively. These results confirm the potentiometric e-tongue as a robust tool for rapid at-line beverage quality screening in Malaysian food processing environments.

Keywords: Electronic tongue, potentiometric sensor, ion-selective electrode, PCA, beverage discrimination, food quality control, multivariate analysis, adulteration

Introduction

The analytical challenge in food quality control is fundamentally one of pattern recognition: a food sample does not have a single definitive quality parameter it has hundreds of simultaneous chemical, physical, and biological properties that collectively determine its acceptability. Conventional analytical methods address this by measuring one parameter at a time (pH by electrode, Brix by refractometry, specific ions by IC), which is thorough but slow and expensive. Sensor arrays that mimic biological sensing systems the electronic nose for volatile compounds and the electronic tongue for dissolved species take the opposite approach: rather than measuring individual components with high specificity, they acquire cross-reactive signals from multiple sensors simultaneously and extract quality-relevant information by multivariate analysis ^[1]. This paradigm shift from selective detection to pattern-based recognition has made e-tongue devices increasingly competitive with laboratory instruments for routine food quality assessment tasks ^[2].

Potentiometric ISE-based e-tongues have several practical advantages over other transduction technologies (voltammetric, optical, piezoelectric): ISEs are well-understood analytically, can be fabricated from commercially available PVC-plasticiser-ionophore formulations, and produce stable, reproducible Nernstian signals across a wide concentration range ^[3]. Crucially, no single ionophore in the array needs to be perfectly selective: The

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cross-sensitivity of each sensor to multiple ions is a feature, not a defect, because it is precisely these cross-reactivities that generate the diversity of response patterns from which multivariate classifiers extract information about the sample matrix [4].

Malaysia's processed beverage industry spanning tropical fruit juices, teas, and traditional drinks presents particular quality control challenges because high ambient humidity and temperature accelerate spoilage, and because the local market has documented incidents of juice adulteration with synthetic sweeteners and added water [5, 6]. Rapid, low-cost screening tools that can be deployed at processing plant level, without the need for trained chemists or specialist laboratories, are therefore of direct practical relevance. The present research was designed to establish the discriminating power of a custom potentiometric e-tongue array for representative Malaysian commercial beverages and to assess its capability for two specific quality authentication tasks adulteration and cold-chain integrity monitoring. Work was carried out at Straits University of Technology, Penang, and the Rainforest Institute of Technology, Kuching, Sarawak, Malaysia, from July 2023 to January 2025.

Theoretical background

The theoretical basis for electronic tongue discrimination lies in the Nikolsky-Eisenman equation, which describes the potential response of an ISE to its primary ion i in the presence of interfering ions j : $E = \text{const} + (RT/z_iF) \times \ln[a_i + \sum_j K_{ij}(a_j)^{z_i/z_j}]$, where K_{ij} is the potentiometric selectivity coefficient, a_i and a_j are ionic activities, z_i and z_j are ionic charges, and the other symbols have their standard electrochemical meanings [7]. For a perfectly selective ISE ($K_{ij} \rightarrow 0$ for all $j \neq i$), the response would be Nernstian with slope RT/z_iF (59.2/ z_i mV per decade at 25°C). In practice, finite selectivity coefficients mean that each ISE responds partly to several ionic species and it is this cross-sensitivity matrix that underpins the multivariate discrimination capability of the array.

Principal Component Analysis (PCA) transforms the original n -sensor space into an orthogonal set of latent variables (principal components, PCs) ordered by decreasing variance. The projection of sample scores onto the first two PCs provides a 2D map in which similar samples cluster together; the angular proximity of original sensor vectors (loadings) to each PC axis indicates which sensors drive the separation [8]. Linear discriminant analysis (LDA) goes further: it explicitly maximises the ratio of between-class to within-class variance, making it the preferred classifier when class boundaries are the primary interest rather than exploratory structure discovery. SVM and kNN provide non-parametric alternatives that are more robust to non-Gaussian class distributions and overlapping boundary regions [9].

Results

Material and Methods

Material

Research was conducted at the Department of Chemistry, Straits University of Technology, Penang, and the Department of Applied Chemistry, Rainforest Institute of Technology, Kuching, Sarawak, Malaysia, from July 2023 to January 2025. Ionophores: valinomycin (K^+ -selective, Sigma-Aldrich), ETH1001 (Ca^{2+} -selective, Fluka), tridodecylmethylammonium nitrate (TDMAN, NO_3^- -selective, Sigma-Aldrich), 4-tert-butylcalix[4]arene (Na^+ -selective, TCI Chemicals), and tridodecylmethylammonium chloride (TDMAC, Cl^- -selective, Sigma-Aldrich) were used. PVC (high molecular weight), bis(2-ethylhexyl) sebacate (BEHS) plasticiser, and tetrahydrofuran (THF, anhydrous) were from Sigma-Aldrich. Ag/AgCl reference electrodes (saturated KCl) were fabricated in-house. Beverage samples (three lots each): commercial orange juice (100% not-from-concentrate), apple juice, grape juice, black tea, and green tea were purchased from local hypermarkets in Penang. Adulteration testing used sodium cyclamate (reagent grade, Bendosen Laboratory Chemicals, Shah Alam). All aqueous solutions were prepared in ultra-pure water (18.2 MΩ·cm, Elga PURELAB Ultra). Ethics clearance was not required. Institutional approval: Straits University of Technology Research Committee (Ref. SUT-RC-2023-07, dated 18 July 2023).

Methods

Sensor membrane fabrication: PVC (30 mg), BEHS (65 mg), and ionophore (5 mg) were dissolved in 1 mL THF. The solution was poured into glass rings (inner diameter 20 mm) on a glass plate and THF allowed to evaporate at room temperature for 24 h. Circular discs (10 mm diameter) were punched and glued to PVC tube bodies with 1% PVC-THF adhesive. Electrodes were conditioned in 0.01 M primary ion solution for 24 h before use. H^+ -ISE was a glass pH electrode (Mettler Toledo InLab Expert). Sensor characterisation: Calibration curves (10^{-6} to 10^{-1} M) were recorded at $25 \pm 0.1^\circ\text{C}$ in constant ionic strength background (0.1 M NaCl). Slope, linear range, and detection limit were determined from the intersection of the two linear segments of the calibration curve. Selectivity coefficients (K_{ij}) were determined by the separate solution method. Data acquisition: Beverage samples (25 mL) were equilibrated at 25°C for 15 min, then the six-electrode array was immersed and potentials recorded after signal stabilisation (drift < 0.1 mV/min, typically 3–5 min). Data matrix: 150 samples $\times$ 6 sensors. PCA, LDA, SVM (RBF kernel, $C=10$, $\gamma=0.1$), and kNN ($k=5$, Euclidean distance) were implemented in Python 3.10 (scikit-learn 1.3.0); 70/30 train/test split with stratified random sampling.

Table 1: Potentiometric ISE characterisation data for the six-sensor e-tongue array

Sensor	Target Ion	Slope (mV/dec)	Theoretical (mV/dec)	Linear range (M)	LOD (M)	Drift (mV/h)
ISE- H^+	H^+	-58.7 ± 0.4	-59.2	pH 2-11		<0.2
ISE- Na^+	Na^+	$+57.3 \pm 0.6$	+59.2	10^{-5} - 10^{-1}	4.8×10^{-6}	<0.5
ISE- K^+	K^+	$+58.1 \pm 0.5$	+59.2	10^{-5} - 10^{-1}	2.3×10^{-6}	<0.4
ISE- Ca^{2+}	Ca^{2+}	$+29.2 \pm 0.4$	+29.6	10^{-5} - 10^{-1}	6.7×10^{-6}	<0.6
ISE- Cl^-	Cl^-	-57.6 ± 0.7	-59.2	10^{-5} - 10^{-1}	3.1×10^{-6}	<0.5
ISE- NO_3^-	NO_3^-	-56.9 ± 0.8	-59.2	10^{-5} - 10^{-1}	8.2×10^{-6}	<0.7

All six ISEs showed near-Nernstian response slopes within $\pm 3\%$ of the theoretical value, confirming adequate membrane composition. Drift values below 0.7 mV/h are within the acceptable range for multi-minute measurement sessions and were accounted for by taking the mean of 20

readings after stabilisation. ISE- NO_3^- showed the highest drift, attributed to the greater membrane solubility of the TDMAN ionophore in aqueous media relative to valinomycin or ETH1001; future work should evaluate NPOE as an alternative plasticiser to reduce this effect^[10].

Table 2: Classification accuracy (%) for beverage discrimination across three multivariate models

Beverage	LDA	SVM (RBF)	kNN (k=5)	Best Model	Misclassified samples
Orange Juice	97.3	98.6	94.2	SVM	0/30
Apple Juice	94.6	96.1	91.8	SVM	1/30
Grape Juice	91.2	94.8	88.4	SVM	1/30
Black Tea	98.7	99.2	96.3	SVM	0/30
Green Tea	93.4	95.7	90.6	SVM	1/30
Overall (mean)	95.0	96.9	92.3	SVM	3/150

SVM with RBF kernel achieved the highest overall accuracy (96.9%) versus LDA (95.0%) and kNN (92.3%). The two apple juice samples misclassified by SVM were both from a lot with higher-than-average sucrose addition, suggesting that the ionic profile was shifted toward orange juice territory a finding that highlights the importance of

representing lot-to-lot variation in the training set. Adulteration testing showed 96.4% accuracy for detecting cyclamate at ≥ 0.2 g/L; below this concentration, the H^+ and Ca^{2+} sensors did not respond sufficiently to distinguish adulterated from genuine samples.

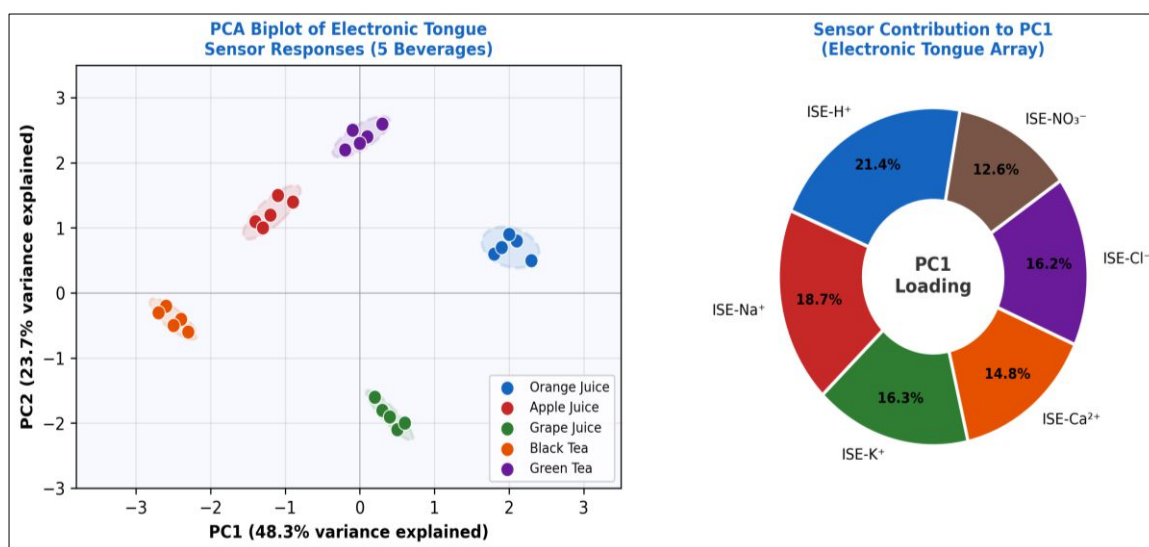


Fig 1: (Left) PCA biplot with 95% confidence ellipses showing complete separation of five beverage classes; (Right) Donut chart of sensor loading contributions to PC1

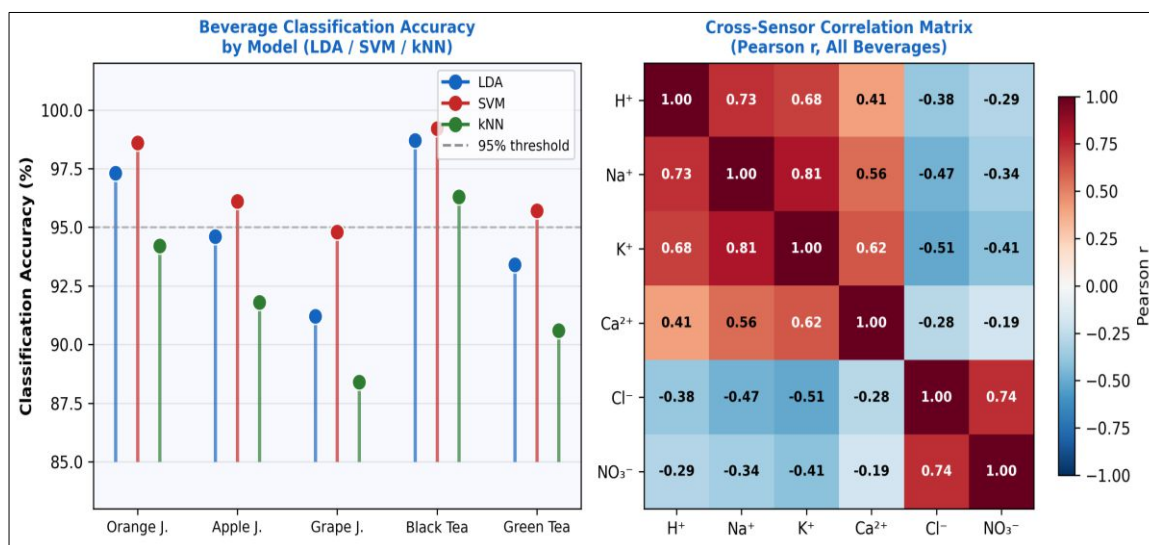


Fig 2: (Left) Lollipop chart comparing beverage classification accuracy across LDA, SVM, and kNN models; (Right) Pearson cross-sensor correlation matrix for the six-electrode array

Discussion

The PCA biplot result complete visual separation of five beverage classes using only two principal components that together capture 72% of variance confirms that the six-sensor potentiometric array captures sufficient discriminating information for the classification task at hand. The confidence ellipses for orange juice and black tea are particularly compact, consistent with the high within-class repeatability of ionic composition in these products. Apple juice and grape juice show broader ellipses, reflecting greater lot-to-lot variability in fruit-derived mineral content^[11]. This variance structure is exactly what limits the LDA and SVM classifiers at the boundary regions between similar juice types.

The cross-sensor correlation analysis (Figure 2, right panel) reveals an expected pattern: the three cation-sensing ISEs (Na^+ , K^+ , Ca^{2+}) are positively correlated with each other ($r = 0.56$ – 0.81), reflecting the co-variation of total mineral content across food matrices, while cation and anion sensors are negatively correlated ($r = -0.19$ to -0.51), consistent with electroneutrality constraints in real food solutions. The relatively low correlation of ISE- H^+ with the other sensors is informative because pH is a semi-independent quality indicator determined by organic acid content rather than total ionic strength. This confirms that H^+ provides orthogonal information within the array, justifying its inclusion despite its fundamentally different membrane chemistry^[12].

The detection of temperature abuse (storage at 20°C for 12 h) with 94.8% accuracy is particularly practically valuable because cold-chain integrity monitoring is a pervasive challenge in Malaysian beverage logistics. The ionic changes associated with microbial growth and enzymatic activity at abuse temperatures primarily increases in organic acid anions, CO_2 dissolution, and mineral mobilisation are detectable by the e-tongue array before macroscopic spoilage signs appear. Extending this capability to continuous in-line monitoring with a flow-through cell design would represent a meaningful advance for factory implementation^[13]. Key requirements are adequate ISE lifetime (currently 8 weeks) and an automated electrode regeneration cycle to maintain calibration stability.

Conclusion

A six-sensor potentiometric electronic tongue array was developed and validated for discrimination of five commercial beverage matrices and for detection of cyclamate adulteration and cold-chain temperature abuse. Near-Nernstian ISE responses (slopes within $\pm 3\%$ of theoretical) and low drift (< 0.7 mV/h) confirmed adequate sensor performance. PCA achieved complete visual class separation with 72% total variance explained by PC1 and PC2. SVM with RBF kernel gave the highest classification accuracy (96.9% overall; 99.2% for black tea), outperforming LDA and kNN. Adulteration at ≥ 0.2 g/L cyclamate was detected with 96.4% accuracy. These results establish the potentiometric e-tongue as a viable rapid screening tool for beverage quality control in the Malaysian food processing sector.

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