Supplementary Information

Voltammetric Electronic Tongue for Discrimination of Milk Adulterated with Urea, Formaldehyde, and Melamine

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Scheme S1. Schematic illustration of how the current signals were organized in order to use the Statistica software.
**Figure S1.** Cyclic voltammograms recorded directly in skimmed milk using platinum (A), gold (B), and copper (C) working electrodes, in the absence (dashed lines) and presence (full lines) of 10.0 mmol L\(^{-1}\) of formaldehyde (1), 0.95 mmol L\(^{-1}\) of melamine (2), and 4.16 mmol L\(^{-1}\) of urea (3). Scan rate = 100 mV s\(^{-1}\).

**Figure S2.** Cyclic voltammograms recorded directly in semi-skimmed milk using platinum (A), gold (B), and copper (C) working electrodes, in the absence (dashed lines) and presence (full lines) of 10.0 mmol L\(^{-1}\) of formaldehyde (1), 0.95 mmol L\(^{-1}\) of melamine (2), and 4.16 mmol L\(^{-1}\) of urea (3). Scan rate = 100 mV s\(^{-1}\).
**Figure S3.** (A) Voltammogram recorded in 0.10 mol L$^{-1}$ acetate buffer (pH 4.5) (full line) after the addition of formaldehyde (dashed line), melamine (dotted line), and urea (dashed dotted line) at a final concentration of 9.5 mmol L$^{-1}$. Scan rate = 50 mV s$^{-1}$. (B) Frequency shifts versus potential plots for gold quartz crystal registered at the same time as the voltammograms.

**Figure S4.** The HCA algorithm and Euclidian distances using whole milk data extracted using gold (A), copper (B), and platinum (C) electrodes with a Ag/AgCl$_{\text{KCl sat}}$ reference electrode. Samples were analysed in triplicate.
Figure S5. The HCA algorithm and Euclidian distances using data extracted from commercial (Elege®) (RF S.A.–Entreposto Usina, Teutônia, RS, Brazil) whole milk samples using three working electrodes (gold, platinum, and copper) with a Ag/AgCl(KCl sat) reference electrode. Samples were analysed in triplicate.

![HCA diagram](image1)

Figure S6. The PCA loading plot [tri-dimensional view (A) and top view (B)] using the input data reported in Figure. 4. Symbols: Au (red circles), Pt (green circles) and Cu (blue circles).

![PCA loading plot](image2)
**Figure S7.** PCA 3D plots of commercial (Parmalat®) (Laticínios Bom Gosto S.A. Usina de Beneficiamento, Tapejara, RS, Brazil) milk samples: unadulterated samples (black squares), and samples adulterated with 10.0 mmol L⁻¹ of formaldehyde (red circles), 0.95 mmol L⁻¹ of melamine (blue up triangles), and 4.16 mmol L⁻¹ of urea (green down triangles). Whole milk (A), skimmed milk (B), and semi-skimmed milk (C). Samples were analysed in triplicate.

**Figure S8.** PCA 3D plots of commercial (Qualita®) (Usina de Beneficiamento de Leite da Cooperativa dos Suinocultores de Encantado Ltda, Arroio do Meio, RS, Brazil) milk samples: unadulterated samples (black squares), and samples adulterated with 10.0 mmol L⁻¹ of formaldehyde (red circles), 0.95 mmol L⁻¹ of melamine (blue up triangles), and 4.16 mmol L⁻¹ of urea (green down triangles). Whole milk (A), skimmed milk (B), and semi-skimmed milk (C). Samples were analysed in triplicate.
Figure S9. PCA 3D plots of commercial (Elegê®) (BRF S.A. – Entreposto Usina, Teutônia, RS, Brazil) whole milk samples: unadulterated samples (black squares), and samples adulterated with 100 mmol L\(^{-1}\) of formaldehyde (red circles), 9.5 mmol L\(^{-1}\) of melamine (blue up triangles), and 41.6 mmol L\(^{-1}\) of urea (green down triangles). Samples were analysed in triplicate.

Figure S10. PCA 3D plots of commercial (Elegê®) (BRF S.A.–Entreposto Usina, Teutônia, RS, Brazil) whole milk sample: unadulterated samples (black squares), and samples adulterated with 10 mmol L\(^{-1}\) (red circles) and 100 mmol L\(^{-1}\) (open red circles) of formaldehyde; 0.95 mmol L\(^{-1}\) (blue up triangles) and 9.5 mmol L\(^{-1}\) (open blue up triangles) of melamine; and 4.16 mmol L\(^{-1}\) (green down triangles) and 41.6 mmol L\(^{-1}\) (open green down triangles) of urea. Samples were analysed in triplicate.
Figure S11. PCA 3D plots of commercial (Elegê®) (BRF S.A.–Entreponto Usina, Teutônia, RS, Brazil) whole milk samples: unadulterated samples (black squares), and samples adulterated with 10 mmol L\(^{-1}\) (red circles) and 100 mmol L\(^{-1}\) (open red circles) of formaldehyde; 0.95 mmol L\(^{-1}\) (blue up triangles) and 9.5 mmol L\(^{-1}\) (open blue up triangles) of melamine; and 4.16 mmol L\(^{-1}\) (green down triangles) and 41.6 mmol L\(^{-1}\) (open green down triangles) of urea. Samples were analysed in triplicate. All the input data was pre-treated using a local technique transformation reported in the manuscript.