

*Supplementary Information*

## **Voltammetric Electronic Tongue for Discrimination of Milk Adulterated with Urea, Formaldehyde, and Melamine** *Chemosensors* 2014, 2, 251-266

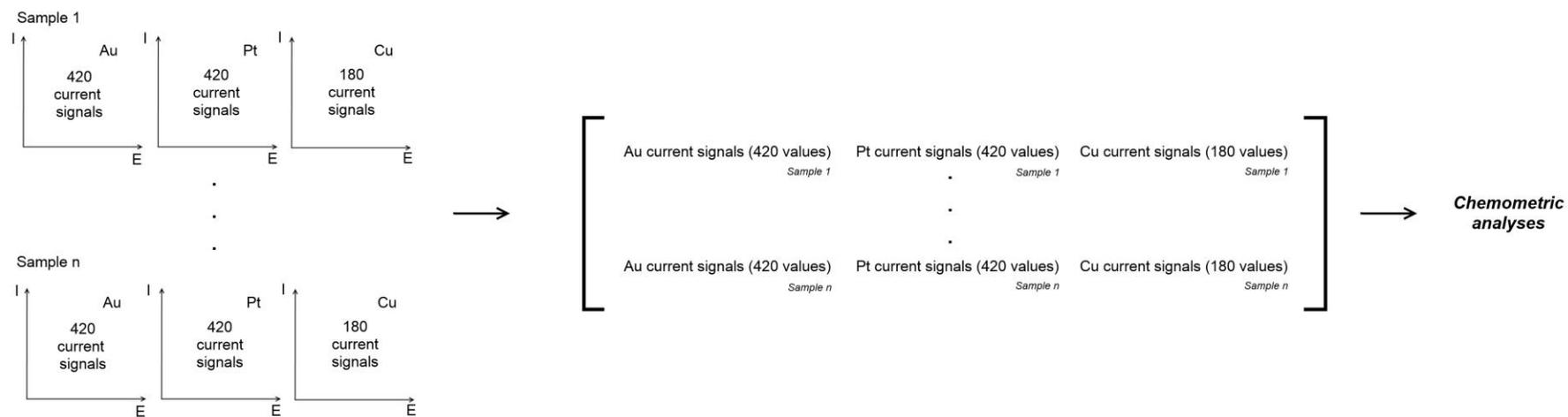
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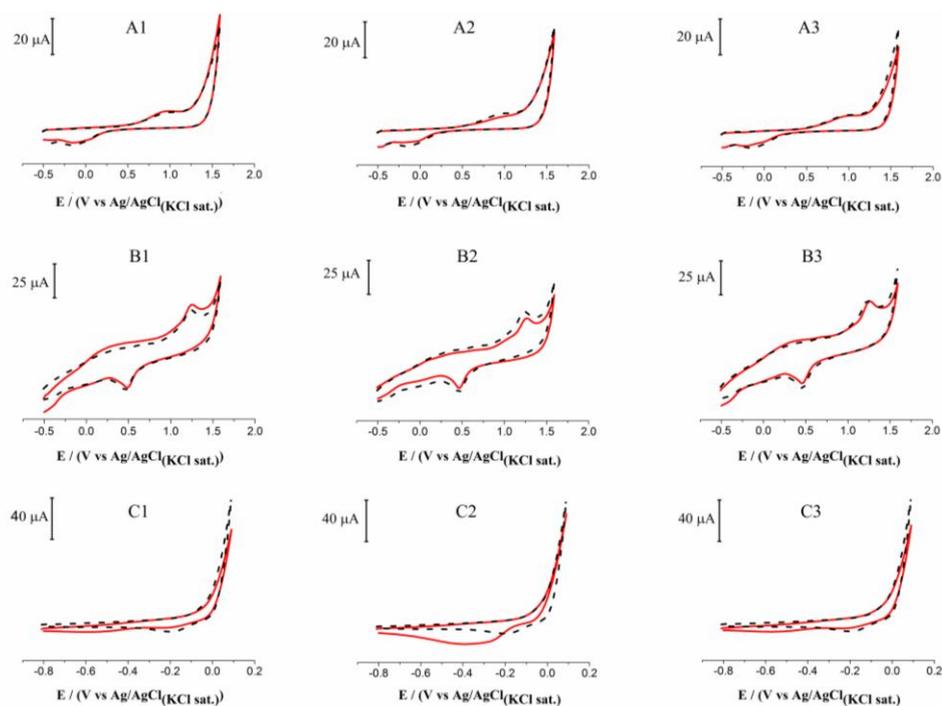
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Tel.: +55-11-3091-9150.

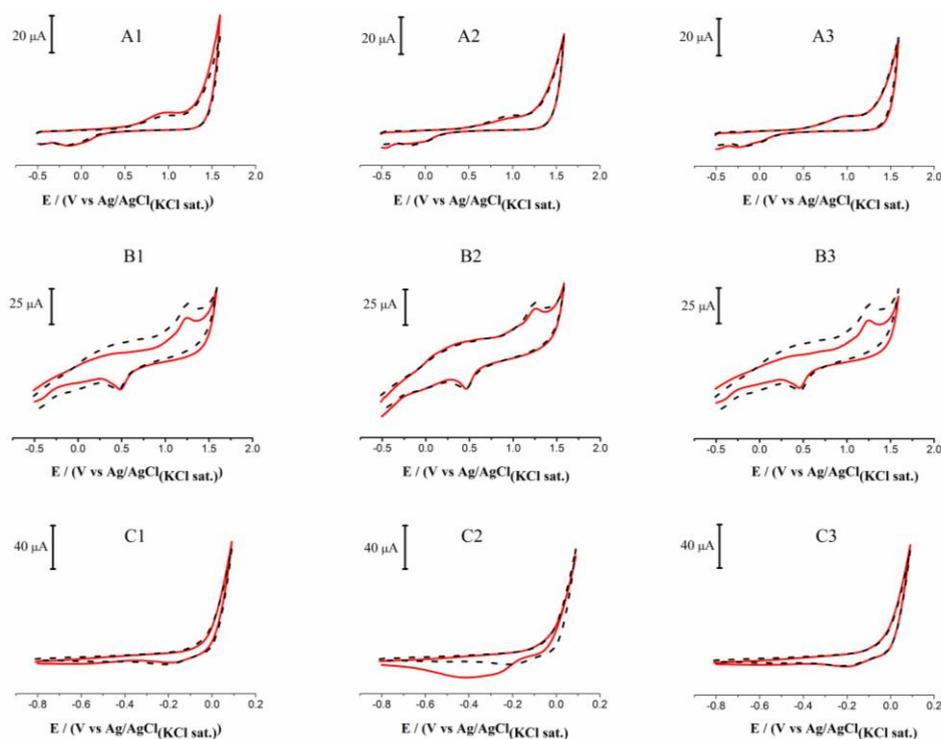
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**Scheme S1.** Schematic illustration of how the current signals were organized in order to use the Statistica software.

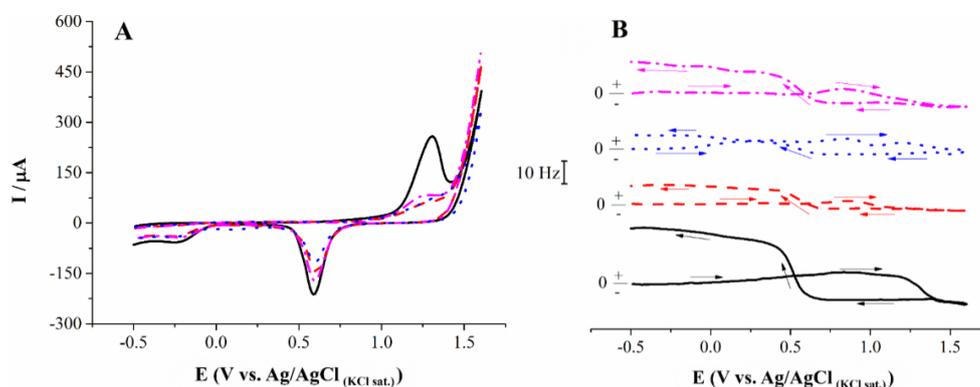
**Figure S1.** Cyclic voltammograms recorded directly in skimmed milk using platinum (A), gold (B), and copper (C) working electrodes, in the absence (dashed lines) and presence (full lines) of 10.0 mmol L<sup>-1</sup> of formaldehyde (1), 0.95 mmol L<sup>-1</sup> of melamine (2), and 4.16 mmol L<sup>-1</sup> of urea (3). Scan rate = 100 mV s<sup>-1</sup>.



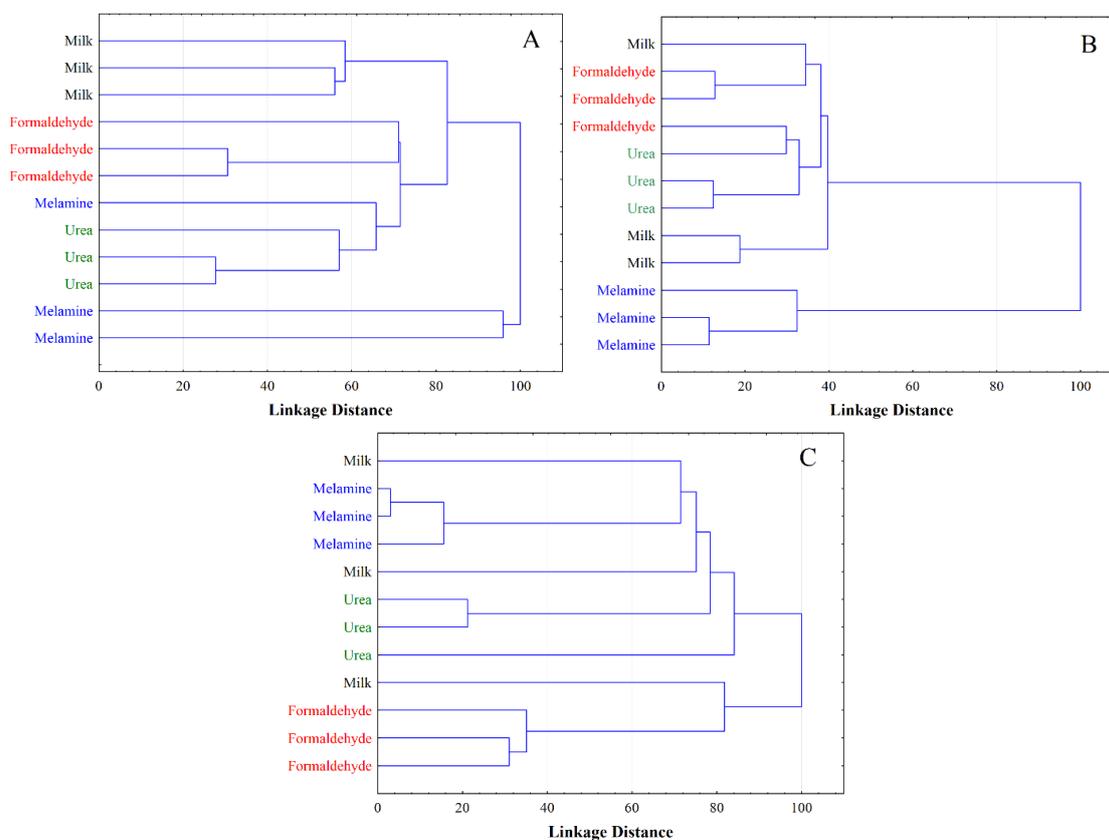
**Figure S2.** Cyclic voltammograms recorded directly in semi-skimmed milk using platinum (A), gold (B), and copper (C) working electrodes, in the absence (dashed lines) and presence (full lines) of 10.0 mmol L<sup>-1</sup> of formaldehyde (1), 0.95 mmol L<sup>-1</sup> of melamine (2), and 4.16 mmol L<sup>-1</sup> of urea (3). Scan rate = 100 mV s<sup>-1</sup>.



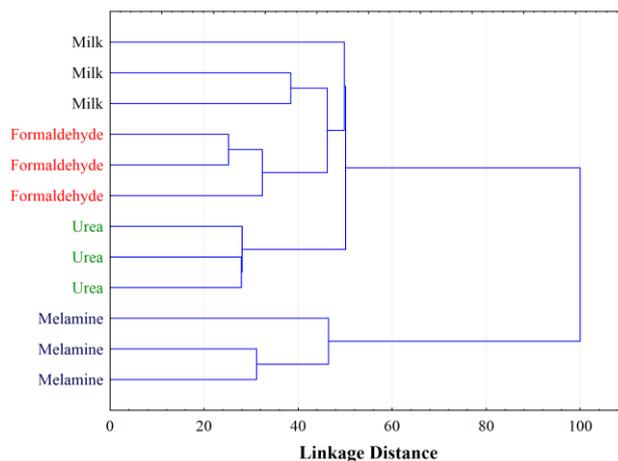
**Figure S3.** (A) Voltammogram recorded in 0.10 mol L<sup>-1</sup> acetate buffer (pH 4.5) (full line) after the addition of formaldehyde (dashed line), melamine (dotted line), and urea (dashed dotted line) at a final concentration of 9.5 mmol L<sup>-1</sup>. Scan rate = 50 mV s<sup>-1</sup>. (B) Frequency shifts versus potential plots for gold quartz crystal registered at the same time as the voltammograms.



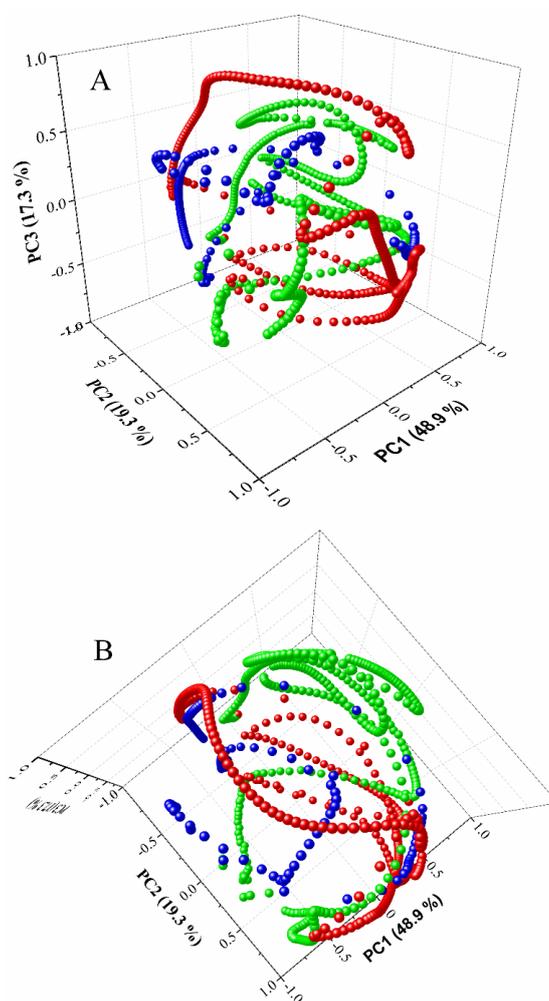
**Figure S4.** The HCA algorithm and Euclidian distances using whole milk data extracted using gold (A), copper (B), and platinum (C) electrodes with a Ag/AgCl(KCl sat) reference electrode. Samples were analysed in triplicate.



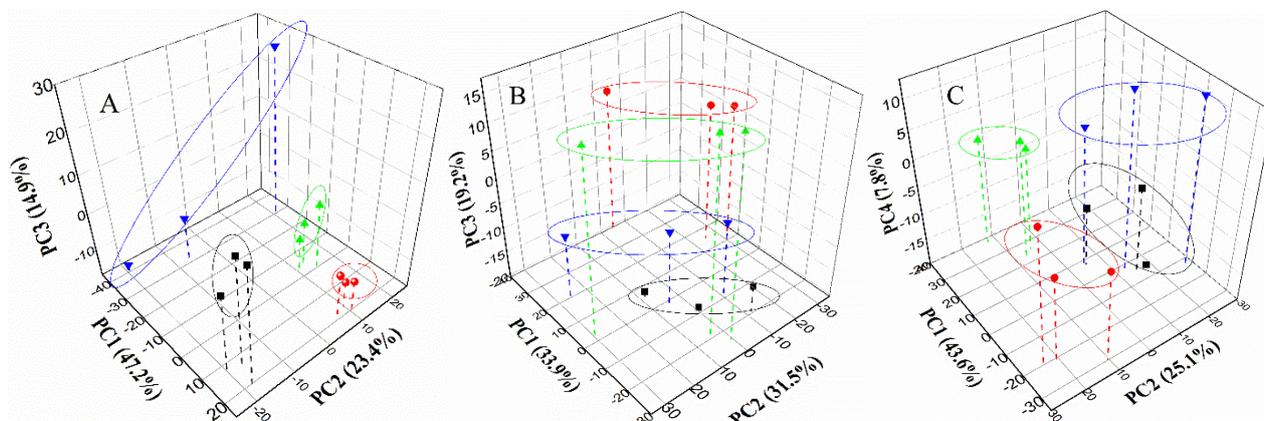
**Figure S5.** The HCA algorithm and Euclidian distances using data extracted from commercial (Elegê®) (RF S.A.–Entrepôsto Usina, Teutônia, RS, Brazil) whole milk samples using three working electrodes (gold, platinum, and copper) with a Ag/AgCl<sub>(KCl sat)</sub> reference electrode. Samples were analysed in triplicate.



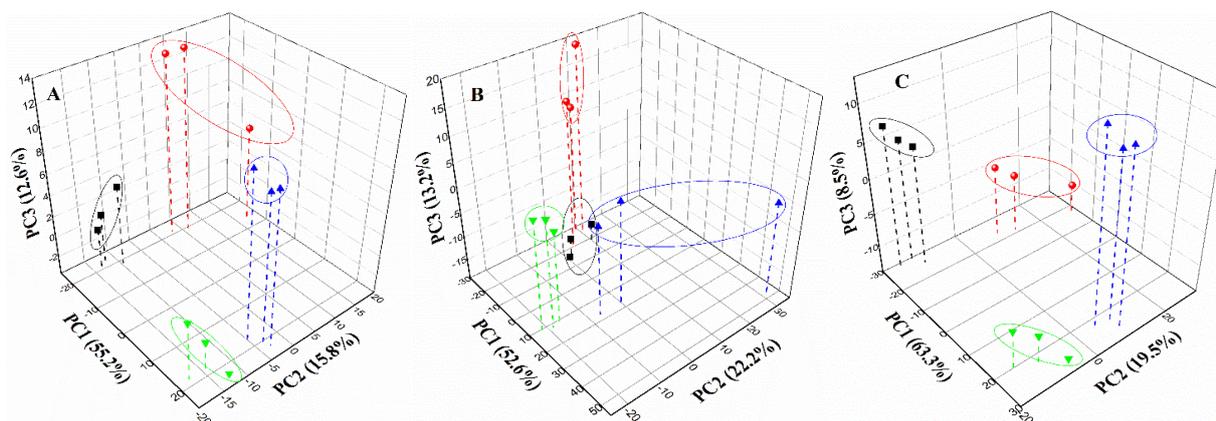
**Figure S6.** The PCA loading plot [tri-dimensional view (A) and top view (B)] using the input data reported in Figure. 4. Symbols: Au (red circles), Pt (green circles) and Cu (blue circles).



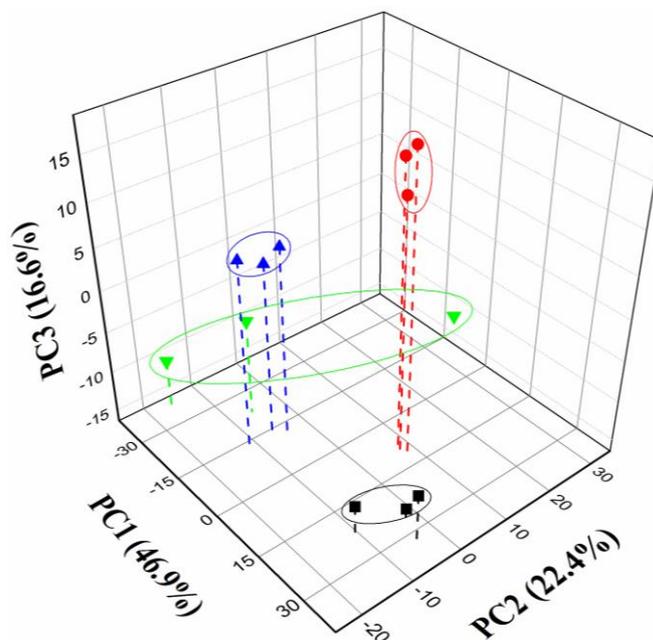
**Figure S7.** PCA 3D plots of commercial (Parmalat®) (Laticínios Bom Gosto S.A. Usina de Beneficiamento, Tapejara, RS, Brazil) milk samples: unadulterated samples (black squares), and samples adulterated with 10.0 mmol L<sup>-1</sup> of formaldehyde (red circles), 0.95 mmol L<sup>-1</sup> of melamine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



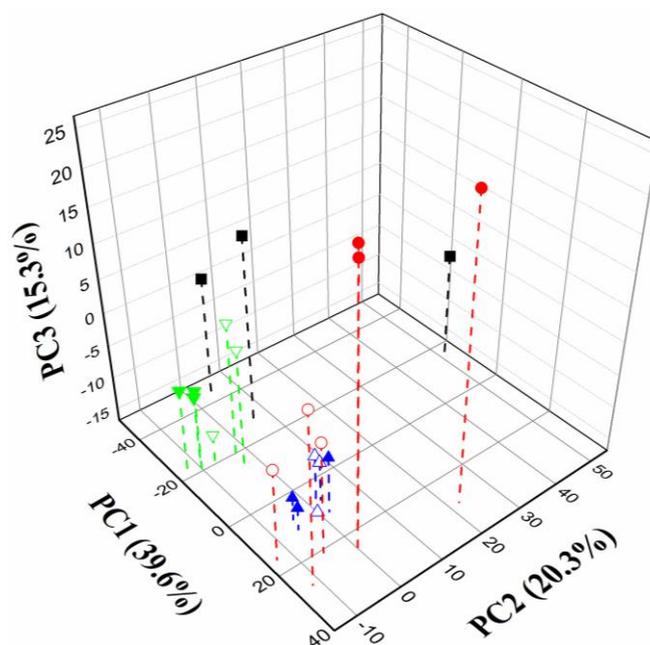
**Figure S8.** PCA 3D plots of commercial (Qualitã®) (Usina de Beneficiamento de Leite da Cooperativa dos Suinocultores de Encantado Ltda, Arroio do Meio, RS, Brazil) milk samples: unadulterated samples (black squares), and samples adulterated with 10.0 mmol L<sup>-1</sup> of formaldehyde (red circles), 0.95 mmol L<sup>-1</sup> of melamine (blue up triangles), and 4.16 mmol L<sup>-1</sup> of urea (green down triangles). Whole milk (A), skimmed milk (B), and semi-skimmed milk (C). Samples were analysed in triplicate.



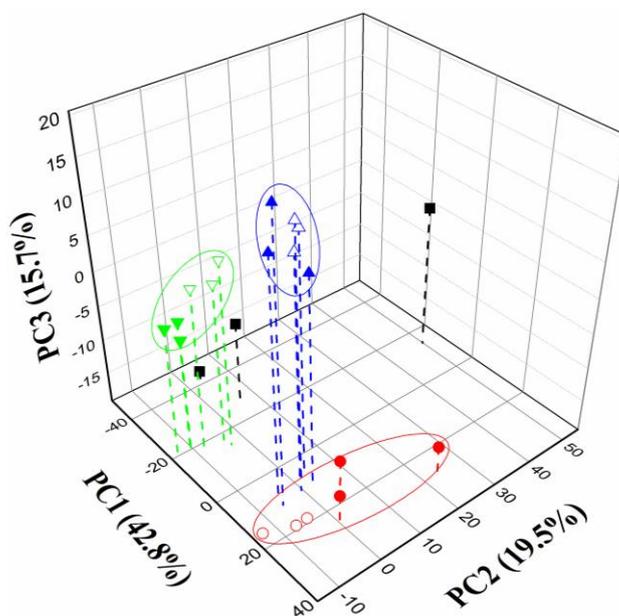
**Figure S9.** PCA 3D plots of commercial (Elegê®) (BRF S.A. – Entrepósito Usina, Teutônia, RS, Brazil) whole milk samples: unadulterated samples (black squares), and samples adulterated with  $100 \text{ mmol L}^{-1}$  of formaldehyde (red circles),  $9.5 \text{ mmol L}^{-1}$  of melamine (blue up triangles), and  $41.6 \text{ mmol L}^{-1}$  of urea (green down triangles). Samples were analysed in triplicate.



**Figure S10.** PCA 3D plots of commercial (Elegê®) (BRF S.A.–Entrepósito Usina, Teutônia, RS, Brazil) whole milk sample: unadulterated samples (black squares), and samples adulterated with  $10 \text{ mmol L}^{-1}$  (red circles) and  $100 \text{ mmol L}^{-1}$  (open red circles) of formaldehyde;  $0.95 \text{ mmol L}^{-1}$  (blue up triangles) and  $9.5 \text{ mmol L}^{-1}$  (open blue up triangles) of melamine; and  $4.16 \text{ mmol L}^{-1}$  (green down triangles) and  $41.6 \text{ mmol L}^{-1}$  (open green down triangles) of urea. Samples were analysed in triplicate.



**Figure S11.** PCA 3D plots of commercial (Eleg<sup>®</sup>) (BRF S.A.–Entrepoto Usina, Teutônia, RS, Brazil) whole milk samples: unadulterated samples (black squares), and samples adulterated with 10 mmol L<sup>-1</sup> (red circles) and 100 mmol L<sup>-1</sup> (open red circles) of formaldehyde; 0.95 mmol L<sup>-1</sup> (blue up triangles) and 9.5 mmol L<sup>-1</sup> (open blue up triangles) of melamine; and 4.16 mmol L<sup>-1</sup> (green down triangles) and 41.6 mmol L<sup>-1</sup> (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.



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