Supplementary Information

**Figures S1.** For the validation of the analytical method, three best reproducible spectra were chosen for each milk species and, a dendrogram reference was produced (Panels a). CM/DM mixtures, in volume ratios 0.3/99.7, 0.4/99.6, 0.7/99.3, 1.5/98.5, 9/91, 15/85, 40/60 were prepared and a blinded investigator analyzed them. Panels a–h, shows a hierarchical clustering analysis, producing dendrograms. Figures S1 shows clearly the high performance of the analytical method in the identification of all the adulteration levels (from 0.3% to 40% of CM addition) for all the test samples prepared.
Figure S1. Cont.

PCA Dendrogram

(c) PCA Dendrogram

(d) PCA Dendrogram
Figure S1. Cont.

PCA Dendrogram

(e)

PCA Dendrogram

(f)
Figure S1. Cont.

PCA Dendrogram

Spectra

Distance Level

0
1.5
0.5

CM GM EM BM DM 40/60 (v/v) CM/DM

Spectra

Distance Level

0
1.5
0.5

CM GM EM BM DM 15/85 (v/v) CM/DM

(h)
Figures S2. For the validation of the analytical method, three best reproducible spectra were chosen for each milk species and, a PCA analysis reference was produced (Panels a). CM/DM mixtures, in volume ratios 0.3/99.7, 0.4/99.6, 0.7/99.3, 1.5/98.5, 9/91, 15/85, 40/60 were prepared and a blinded investigator analyzed them. Panels a–h shows the respective PCA analysis, producing 3D scatter plot images. Figure S2 shows clearly the high performance of the analytical method in the identification of all the adulteration levels (from 0.3% to 40% of CM addition) for all the test samples prepared.
Figure S2. Cont.

(c) (d)
Figure S2. Cont.
Figure S2. Cont.

(g) 15/85 (v/v) CM/DM

(h) 40/60 (v/v) CM/DM
Figures S3. Three best reproducible spectra were chosen for each level of adulteration, producing a reference dendrogram (Panel a). CM/DM mixtures, in volume ratios 0.3/99.7, 0.4/99.6, 0.7/99.3, 1.5/98.5, 9/91, 15/85, 40/60 were prepared and a blinded investigator analyzed them (Panels b–h). The figure shows a hierarchical clustering analysis, producing dendrograms. The figure shows the low performance of the analytical method in the quantitative analysis.
Figure S3. Cont.

(c) PCA Dendrogram

(d) PCA Dendrogram
Figure S3. Cont.

**PCA Dendrogram**

Distance Level

0 0.4 1.4

Spectra

5% 0.5% DM 2% 1.5% 0.2% 1% 10% COW 50% 30%

16 17 18 7 9 13 14 15 1 2 3 4 5 6 19 21 20 10 11 12 22 23 24 30 28 29 25 26 27 28 30 29

(e) PCA Dendrogram

(f)
Figure S3. Cont.

(g) PCA Dendrogram

(h) PCA Dendrogram
Figures S4. Hierarchical clustering and dendrograms and PCA 3D scatter plots of the first three principle components for the three mixtures in volume ratios 0.2/99.8, 10/90, and 50/50 of the simulated adulteration of the pasteurized DM and GM by CM (Panels a–p). All milk adulterations grouped inside the correct clade and cluster.
Figure S4. Cont.

(c) Spectra

(d) PCA Plot
Figure S4. Cont.

(e)

PCA Dendrogram

Distance Level

BM EM CM GM DM 10/90 (v/v) CM/DM

Spectra

(f)

PC1 PC2 PC3
Figure S4. Cont.

(g) Spectra

(h) PCA Dendrogram
Figure S4. Cont.

(i) PCA Dendrogram

(ii) Spectra

EM  DM  GM  0.2/99.8 (v/v) CM/GM  BM  CM

Distance Level

PC1  PC2  PC3
Figure S4. Cont.

PCA Dendrogram

Distance Level

Spectra (m)

(n)
Figure S4. Cont.

PCA Dendrogram

Spectra

(o)

(p)
Figures S5. Hierarchical clustering and dendrograms and PCA 3D scatter plots of the first three principle components for the three mixtures in volume ratios 0.2/99.8, 10/90, and 50/50 of the simulated adulteration of the UHT DM and GM by CM. All milk adulterations grouped inside the correct clade and cluster (Panel a–n); Panel o illustrates the comparison between DM and pasteurized and UHT DM mass spectra. The circle shows the modulation of mass peaks between spectra; Panel p illustrates the comparison between GM and pasteurized and UHT GM mass spectra. The circle and the arrows shows the modulation of mass peaks between spectra.
Figure S5. Cont.

(c) Spectra

(d) 3D PCA plot

Distance Level

PC1

PC2

PC3

0 4 0 4 0 4

0 6 0 6 0 6

BM EM GM CM CM/DM DM 10/90 (v/v)

0

0.4

1.4
Figure S5. Cont.

(e) PCA Dendrogram

(f) Spectra
Figure S5. Cont.

PCA Dendrogram

Spectra

(g)

(h)
Figure S5. Cont.

PCA Dendrogram

Distance Level

Spectra

(i)

PC1

PC2

PC3

10/90 (v/v) CM/GM

CM/GM

CM

GM

DM

BM

(ii)
Figure S5. Cont.

PCA Dendrogram

Spectra

(m)
Figure S5. Cont.

(o) DM

(P) GM

PASTEURIZ. DM

UHT DM

PASTEUR. GM

UHT GM
**Figure S6.** Pseudo-gel like and MS proteomic profiling of the simulated adulteration of (a) DM by BM; (b) DM by EM; (c) GM by BM; and (d) GM by EM. The colour bar, reported on the $Y$ axis, indicated the relationship between the colour and the pick intensity and was expressed by arbitrary units (a.u. $\times$1000), while the mass values ($m/z$) were reported on the $X$ axis.
Figure S6. Cont.

Spectra

(c)

(d)
Figure S7. Mathematical analysis of all spectra replica datasets for the eight mixtures (from 50% to 0.2%) of the simulated adulteration of DM by BM and EM. Hierarchical clustering analysis, producing dendrograms and PCA analysis, producing 3D scatter plot image of DM by BM (a–h) and DM by EM (i–r); Pearson’s correlation analysis, producing correlation matrix of DM by BM (s) and DM by EM (t). The similarity index in the correlation matrix was reported by a scale ranging from 0 to 1 and represented by blue and yellow colours, respectively.
Figure S7. Cont.

PCA Dendrogram

Spectra

(b)
Figure S7. Cont.

PCA Dendrogram

Spectra

(c)
Figure S7. Cont.

PCA Dendrogram

Distance Level

BM
GM
EM
CM
DM
S/95 (v/v)
BM/DM

Spectra

PC1
PC2
PC3
BM
EM
CM
GM
S/95 (v/v)
BM/DM
DM

(d)
Figure S7. Cont.

PCA Dendrogram

Spectra
Figure S7. Cont.

PCA Dendrogram

Distance Level

0
0.4
1.4

CM
BM
EM
GM

1/99 (v/v)
BM/DM

PC1
PC2
PC3

Spectra

CM
BM
EM
DM
1/99 (v/v)
BM/DM
Figure S7. Cont.

PCA Dendrogram

Distance Level

Spectra

PC3

PC2

PC1

0.5/99.5 (v/v) BM/DM

CM

GM

EM

BM

DM

0.5/99.5 (v/v)
Figure S7. Cont.

PCA Dendrogram

Distance Level

CM  GM  EM  BM  DM

0.2/99.8 (v/v) BM/DM

Spectra

PC1  PC2  PC3

CM  GM  EM  BM  DM

0.2/99.8 (v/v) BM/DM
Figure S7. Cont.

PCA Dendrogram

Spectra

(i)
Figure S7. Cont.

PCA Dendrogram

Spectra

(l)
Figure S7. Cont.

PCA Dendrogram

Distance Level

BM   CM   GM   EM   DM   10/90 (v/v) EM/DM

Spectra

PC1   PC2   PC3

(m)
Figure S7. Cont.

PCA Dendrogram

Spectra
Figure S7. Cont.

PCA Dendrogram

Distance Level

BM
CM
EM
GM
EM/DM
DM
2/98 (v/v)

Spectra

PC1
PC2

BM
CM
EM
GM
2/98 (v/v)
EM/DM

DM
Figure S7. Cont.

PCA Dendrogram

Distance Level

Spectra

PC1

PC2

EM

CM

BM
Figure S7. Cont.

PCA Dendrogram

Spectra

(q)
Figure S7. Cont.

PCA Dendrogram

Spectra

CM  EM  GM  0.2/99.8 (v/v)
EM/DM  BM
0.2/99.8 (v/v)
EM/DM

PC1  PC2  PC3

0  0  0

0  0  0
Figure S8. Mathematical analysis of all spectra replica datasets for the eight mixtures (from 50% to 0.2%) of the simulated adulteration of GM by BM and EM. Hierarchical clustering analysis, producing dendrograms and PCA analysis, producing 3D scatter plot image of GM by BM (a–h) and GM by EM (i–q); Pearson’s correlation analysis, producing correlation matrix of GM by BM (r) and GM by EM (s). The similarity index in the correlation matrix was reported by a scale ranging from 0 to 1 and represented by blue and yellow colours, respectively.
Figure S8. Cont.

(a) PCA Dendrogram

PC1

PC2

PC3

Distance Level

Spectra

BM

30/70 (v/v)

BM/GM

DM

EM

GM

CM

50/50 (v/v)

BM/GM
Figure S8. Cont.

(b) PCA Dendrogram
Figure S8. Cont. (c)

PCA Dendrogram
Figure S8. Cont.

(d) PCA Dendrogram
Figure S8. Cont.

PC2

PCA Dendrogram

Spectra
Figure S8. Cont.

PCA Dendrogram

Spectra
Figure S8. Cont.

PCA Dendrogram

Spectra
Figure S8. Cont.

(h)

PCA Dendrogram

Distance Level

Spectra

BM
DM

50/50 (v/v)

EM/GM

EM

CM
Figure S8. Cont.

(i)

PCA Dendrogram

Spectra
Figure S8. Cont.

PCA Dendrogram

Spectra
Figure S8. Cont.
Figure S8. Cont.
Figure S8. Cont.
Figure S8. Cont.
Figure S8. Cont.

(q)  

(r)  

(s)