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Chemometric application in foodomics: Nutritional quality parameters evaluation in milk-based infant formula☆

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ABSTRACT

A method to verify the differentiating characteristics of milk-based infant formula is proposed in this work. In order to evaluate a classification of the milks according to their nutritional profile, the concentration of 24 elements were determinated. Supervised methods PCA-LDA, PLS-DA, and SIMCA were contrasted. PCA-LDA and SIMCA provided significantly better results for milk classification of the two studied classes (infant formula and infant formula fortified). As an alternative approach SIMCA was capable to discriminate an overlapped group consisting of baby milks administrated during first 6 months of life. Chemometric methods employed highlight four metal concentrations (Zn, Mn, Cu, and S) which could be associated to relevant nutritional parameters in baby growth. Thus, proposed methodology provides a simpler, faster and more affordable classification for simple study on Foodomics in milk-based infant formula.

1. Introduction

Ensuring food safety and quality is one of the most challenging tasks for food researchers, government, and food industry. *Foodomics* has grown as a discipline that studies food along nutrition through the application and integration of advanced '*omics*' analytical techniques with multivariate data analysis (chemometrics), to reach the main objective: improve human health, well-being, and knowledge; connecting food components with health [1–3].

Milk-based infant formula has been recognized as a very important dairy product regarding food quality and safety [4,5]. There are a large variety of formulas available for children under 1 year, which vary in nutrients, calorie count, taste, ability to be digested and cost. However, as fast as the production and demand for milk have grown international authorities and regulators are challenged to incessantly improve both compliance and safety regulations [6,7]. Thus, is necessary to consider robust and specific methods for nutritional elements determination in milk-based infant formulas to ensure rigorous control of their composition, including elements added routinely in order to satisfy mineral content requirements [8–12].

The promising research on foodomics area requires advanced mass spectrometry technologies, such as inductively coupled plasma mass spectrometry (ICPMS). Advantages include the ability to determine multielemental composition simultaneously with low detection limits, gaining widespread interest for nutritional studies where the identification of compounds containing metals and metalloids that are toxic to human or other organism is of great importance [12]. Therefore, with multielemental determination of milk-based infant formulas by ICPMS a large number of chemical variables data is reached to be used for multivariate statistical analysis.

Foodomics studies normally needs chemometrics tools to handle such large data sets of multivariate analysis and assist to extract qualitative and quantitative relevant chemical information, aiming to improve quality control of food products [13–15]. Chemometric techniques allow construction of models to characterize target samples within previously defined and validated groups. There are three major pattern recognition methods: unsupervised principal component analysis (PCA), hierarchical cluster analysis (HCA), and supervised discriminant analysis (DA) and these provide either cluster plots or dendrogram structures for segregation and discrimination. Recently, soft independent modeling of class analog (SIMCA) has also been extensively employed for different classification purposes [16–20]. SIMCA could

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be used in various foodomics studies, such as food adulteration, food authenticity, food traceability, and food effects on human health.

Regarding foodomics, chemometric models to identify milk-based infant formula were proposed in this work, considering child's nutritional requirements in different stages of growth. A method to discriminate different milk-based infant formula according to their elemental composition is developed employing three supervised techniques: linear discriminant analysis (LDA), partial least square discriminant analysis (PLS-DA), and soft independent modeling of class analogy (SIMCA). Discriminant capacity of each obtained model was evaluated.

2. Materials and methods

2.1. Reagents

Throughout the work water was distilled and de-ionized, with a resistivity of 18.2 MΩ cm, produced by an Easy pure RF system from Barnstead (Dubuque, IA, USA). Concentrated nitric acid (65%v/v) from Sigma-Aldrich (Germany), Dimethylformamide from Acroorganics (New Jersey, USA), were used. Certified multielement standard solutions 2, 3 and 5, and Rh mono-elemental standard solution from Perkin Elmer Pure Plus-Atomic Spectroscopy Standards, (Norwalk, USA) were used for calibration and recovery studies.

2.2. Instrumentation

For multielemental determination, an inductively coupled plasma mass spectrometer from Perkin-Elmer SCIEX, ELAN DRC-e (Thornhill, Canada) was used. The Ar gas with a minimum purity of 99.996% was supplied by Air Liquide (Río IV°-Córdoba, Argentina). An HF-resistant and high performance perfluoracetate (PFA) nebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with internal baffle and drain lines, cooled with PC^3 Peltier inlet system from ESI (Omaha - NE, USA) were used. Tygon black/black 0.76 mm i.d. and 40 cm length peristaltic pump tubing were used. The instrument conditions were: auto lens mode on, peak hopping measurement mode, dwell time of 15 ms, 30 sweeps per reading, 1 reading per replicate and 3 replicates. Nickel sampler and skimmer cones were used. A water bath model HH-S from Arcano (Argentina) was also used for sample pre-treatment with DMF.

2.3. Analytical procedure

Sample introduction was carried out using a PFA high-efficiency microconcentric nebulizer coupled to a baffled cyclonic spray chamber, at −5 °C as desolvating temperature. An optimization for maximum analyte intensity and minimum back-ground was performed in a previous work [21], the conditions adopted were the following: solutions were introduced into the plasma at 700 μL min^{-1}, applying 1100 W of radio frequency power and using 0.7 L min^{-1} nebulizer of argon gas flow rate; samples were triplicate analyzed.

Twenty four analytes were evaluated in this study. For element quantification, each sample was independently treated with DMF as recommended in a previous work [21]: 250 μL of milk was accurately weighed directly in a 15-mL polypropylene flask and then, 2 mL of DMF was added and shaken vigorously. The volume was completed to 10 mL with HNO_3 (1.0%). Matrix matching calibration (added with 20%v/v DMF and 1% nitric acid) was used as calibration method. The analytes concentrations were 1.0; 5.0; 10.0; 20.0; 40.0 and 80.0 μg L^{-1}. Rhodium (10 μg L^{-1}) was added to all solutions as internal standard.

2.4. Samples

Forty five commercial infant formulas products (15 milk formula × 3 box of each one) available in Argentinean local markets were purchased for analysis: 27 baby milk (1–12 life months), and 18 fortified baby milk (0–12 months old). The samples were stored at 5 °C and immediately prepared and analyzed after being opened. The accessible milks are bestowed in Table 1. A Standard Reference Material (SRM) – skim milk powder BCR 063R – from Community Bureau of reference, Geel, Belgium was used for optimization and to assess the trueness and precision of the analytical methods.

2.5. Data analysis

A multivariate analysis to evaluate the ratio between elemental concentration and different milk samples was evaluated. Principal component analysis (PCA) was used as descriptive tool for the data visualization. In order to analyze several supervised pattern recognitions, Linear Discriminant Analysis (LDA), Partial Least Squares Discriminant Analysis (PLS-DA), and Soft Independent Modelling Analysis (SIMCA) were performed using the software Unscrambler × 10.3 (CAMO-ASA, Trondheim, Noruega). The validation step for each of the algorithms was performed using full cross-validation [22].

3. Results and discussion

3.1. Analytical validation and elemental concentrations for milk-based infant formula

Table 2 presents the figures of merit for trace elements determinated in milk-based infant formula: quantification limits ranged between 1,9 (Gd) and 92 (Zn) μg L^{-1}, respectively. Precision calculated as relative standard deviation (RSD%) was better than 7.2. Analytical method was validated through accuracy by a certified reference material: skim milk powder (BCR 063R) from Community Bureau of reference. The certified values and the found values for the analytes Cu, Pb and Zn that are present in the reference material are shown in Table 3. The results were compared through a paired *t*-test and no significant differences were observed ($n = 3$, $p = 0.05$).

The presence of Co, Cu, Mn, Mo, Ni, Rb, S, Sr, V and Zn was evidenced in milk-based infant formula. The remaining analytes were lower than quantification limits. Average concentrations of the analytes found in milk samples and comparison of the obtained results between baby infant formulas and baby fortified infant formulas for the different growth stages - 0 to 6 months (1), 6 to 12 months (2), after 12 months (3) - are shown in Table 2.

3.2. Classification models development

In the development of milk-based infant formula classification models according to nutritional requirements in different growth

Table 1
Milk-based infant formula commercialized in Argentina.

Milk-based infant formula		Growth stages
A1	Baby 1	0–6 months
A2	Baby 2	6–12 months
A3	Baby 3	1–3 years
B1	Baby 1	0–6 months
B2	Baby 2	6–12 months
B3	Baby 3	1–3 years
C1	Baby 1	0–6 months
C2	Baby 2	6–12 months
C3	Baby 3	1–3 years
AP1	Baby Premium 1	0–6 months
AP2	Baby Premium 2	6–12 months
AP3	Baby Premium 3	1–3 years
BP1	Baby Premium 1	0–6 months
BP2	Baby Premium 2	6–12 months
BP3	Baby Premium 3	1–3 years

Table 2
Concentration range comparison of analytes in milk-based infant formulas and milk-based fortified infant formulas for different growth stages - 0 to 6 months (1), 6 to 12 months (2), after 12 months (3).

Analyte	Milk based infant formula			Milk based infant formula fortified					
range	1	2	3	1P	2P	3P	Isotope (u.m.a.)	LOQ	RSD %
[μg L^{-1}]								[μg L^{-1}]	[20 μg L^{-1}]
Co	3.5 ± 2	5 ± 2.7	6.3 ± 1.5	4.2 ± 0.3	4.3 ± 1.9	3.8 ± 0.1	59	3.2	6.6
Cu	367 ± 24	370 ± 306	167 ± 120	400 ± 2	268 ± 350	27 ± 0.4	63	3.1	2.9
Mn	433 ± 464	262 ± 387	230 ± 219	313 ± 132	47 ± 11	38 ± 1	55	5.4	2.9
Mo	13.3 ± 7	20.5 ± 10.6	23.7 ± 3.8	11.8 ± 0.8	11.9 ± 0.4	23.9 ± 10.7	98	8.2	0.5
Ni	40 ± 14	93 ± 35	129 ± 25	65 ± 2	93 ± 52	66 ± 6	60	12	7.2
Rb	282 ± 105	412 ± 51	532 ± 62	157 ± 47	354 ± 48	479 ± 0.23	85	2.8	3.4
S[a]	1395 ± 496	2496 ± 314	2963 ± 224	1219 ± 151	2552 ± 76	3203 ± 62	48	78	2.4
Sr	368 ± 72	743 ± 290	720 ± 63	382 ± 7	993 ± 76	1330 ± 19	88	4.7	1.5
V	7.5 ± 2.2	9.8 ± 3.1	9.8 ± 1.2	16.9 ± 1.6	6.4 ± 0.7	6.9 ± 0.8	51	4.4	2.1
Zn	5031 ± 325	4705 ± 992	4701 ± 454	7543 ± 488	8239 ± 468	10,125 ± 33	66	92	7.4

Analytes lower than Quantification Limits [units in μg L^{-1}].
As < 4.0; Cd < 4.3; Eu < 2.5; Ga < 7.9; Gd < 1.9; Ge < 7.4; Nb < 2.4; Nd < 3.5; Pb < 2.4; Pr < 3.1; Sm < 2.6; Ta < 3.1; Tb < 2.0; Zr < 2.3.
[a] Measured as $^{32}S^{16}O^{+}$.

stages, from data modeling viewpoint, three approaches were used: (a) data modeling employing LDA coupled to PCA for selecting a subset of variables; (b) full data modeling using PLS-DA; and (c) full data modeling making use of SIMCA.

Supervised classification methods process consists of two stages, namely: the training stage, in which the individual models of the data classes are developed, and the testing stage, in which new samples (not used in the training stage) are classified within the established class models to evaluate their efficiency [23,24]. Construction of the multivariate classification models was performed using a training set (32 milk samples). Each model was validated using the leave-one-out cross-validation technique. A test set (13 milk samples) was then used for final data evaluation and comparison to the classification models. The performance of the models was evaluated by accuracy, which is defined using the ratio of samples in the test set correctly assigned into their respective classes [25].

3.2.1. Principal component analysis-linear discriminant analysis (PCA-LDA)

LDA classification methods employ linear decision boundaries (hyperplanes), which are defined in order to maximize between-class separability while minimizing within-class variability [26]. For this purpose, the number of objects in the training set must be larger than the number of variables included in the LDA model. Thus, a reduction in variables can be carried out by PCA. When the entire elemental concentrations were used, samples were misclassified. For this reason, the optimal variables were previously selected from PCA and using full cross validation. Thus, a matrix formed by the multielemental concentrations corresponding to milk samples was built from the autoscaled data. Two first principal components (PCs) were extracted, explaining 98% of the accumulated variance. Score biplot in the plane defined by PC1 and PC2 is shown in Fig. 1, displaying the group discrimination through their nutritional parameters, and verifying variables that had more influence in the formation of each group for the milk samples. Scores biplot depicted the formation of two clusters discriminating milk-based infant formula fortified and no fortified. This discrimination was obtained from the first two PCs, thus four variables were selected (S, Zn, Mn y Cu) presenting a higher influence in the data differentiation. Subsequently, LDA was applied to a matrix formed by 32 milk samples and the four selected variables through PCA with two categorical variables –milk-based infant formula (A-B-C) and fortified infant formula (AP-BP).

Table 3
Certified and experimental concentrations determined in skim milk powder, BCR 063R (n = 3).

Skim milk powder BCR 063R		
Analytes	Certified values	Experimental values
	[μg g^{-1}]	[μg g^{-1}]
Cu	0.602 ± 0.019	0.60 ± 0.05
Pb	18.5 ± 4.7	14.4 ± 3.7
Zn	42.3 ± 2.6	42 ± 3

3.2.2. Partial least squares discriminant analysis (PLS-DA)

PLS-DA is a modification of Partial Least Squares Algorithm for classification purposes. It is a linear regression supervised method based on the combination of a data matrix X and a qualitative values matrix Y (defined for the training set) formed for a vector set containing integer numbers in which encoding for the class in the samples were defined, being a vector for each class. The new object is then assigned to the class with the maximum value in the Y vector or, alternatively, a threshold between zero and one is determined for each class [11]. PLS-DA model was developed using all variables than were above quantification limit (10 elemental concentrations). Optimal PLS-DA model was obtained using 3 PLS components, which explained a 74% of information from the original variables.

3.2.3. Soft independent modeling of class analogy (SIMCA)

SIMCA is a class modeling technique based on principal component analysis (PCA) because each class is defined by an independent PCA taking into account the optimal number of PCs for each class [27,28]. The distance of a sample to the class model is calculated utilizing the orthogonal distance of the sample to the model space and the distance of the sample to the scores space. Then unknown samples are compared to the class models, and assigned to classes according to their analogy to training samples [20].

In this study, it is important to highlight that in the scores plot (Fig. 1) a clear separation of baby milk from the age of 0 to 6 months (1) to the other baby milks could be observed. Taking into account that ideally infant formula should be feed with breast milk for at least the first 6 months of life, it is very important for considering this group samples as a new class for discriminating. However, the samples are overlapped with the other studied classes. The choice of the SIMCA technique in contrast to other supervised pattern recognition techniques is based on the modeling properties of SIMCA, which provides approaches more versatile than those obtained using discriminant techniques. The classification of a sample in one or several classes, or in none of them, is possible with SIMCA, while discriminant techniques only permit to classify a sample in a unique class.

In order to construct the SIMCA model three models were considered: milk-based infant formula (class 1), fortified infant formula (class 2), and infant formula and fortified infant formula from 0 to 6 months (class 3). Initially, a model of PCA (on training

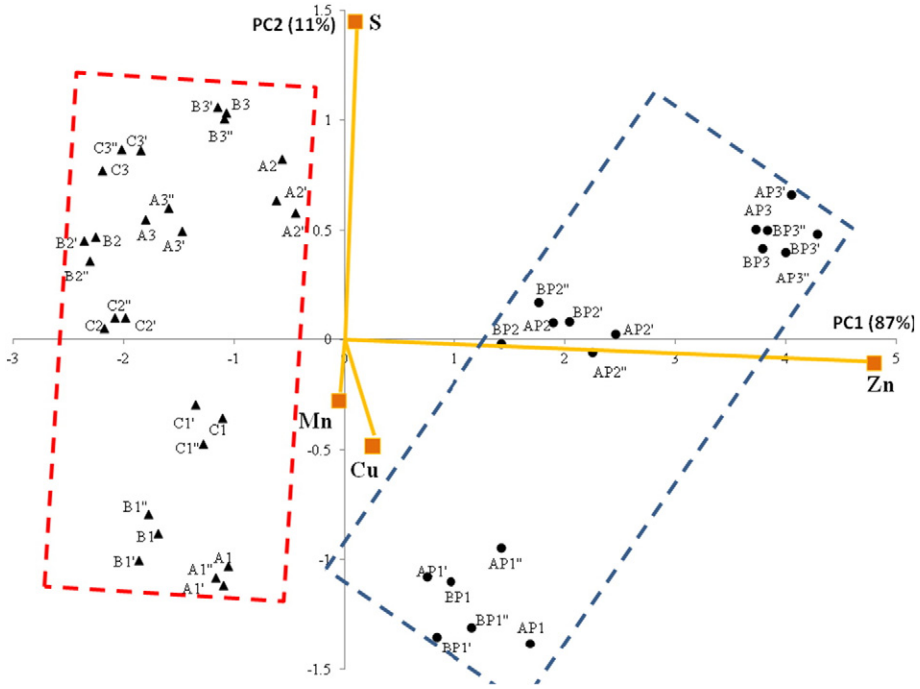

Fig. 1. PCA and loadings plot exhibiting the discrimination of groups through their nutritional requirements in different stages of growth, verifying variables that had more influence in each group formation for milk-based infant formula.

samples) for each class was performed. Thus, the number of principal components necessary to explain the data variance, and the number of variables that explain the model were determined. The optimal SIMCA principal components for defining each class were 2, 4 and 3, respectively. An explained variance higher than 97% using full cross validation was obtained.

Coomans graphics showing the discrimination of two classes are presented in this analysis (Fig. 2). Model distance for a class 1 is represented versus the model distance for a class 2. Thus, the graphic is divided in two axes which is corresponding to critical distance of the models in four quadrant, namely: a right lower quadrant in which the samples from first class are clustered, a left top quadrant in which the samples that pertain to second class are found, a confusion region in the left lower quadrant in which both classes are overlapped, and a zone in the right top quadrant including outliers or samples that do not belong to these classes [29].

In Fig. 2 Coomans graphics depict the samples distance of the model 3 with respect to model 1, with a significance level of 5%. Critical distances are represented with red axes. Model distance and modeling power were analyzed. Modeling power establish amount of variables

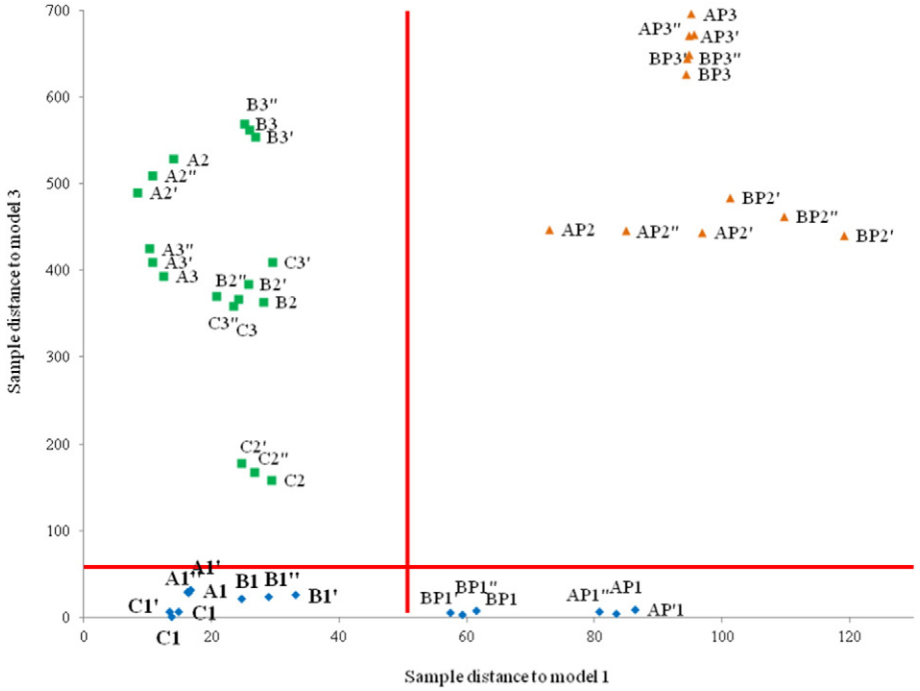

Fig. 2. Coomans graphic depicting samples distance of the model 3 with respect to model 1, with a significance level of 5%.

Table 4
Confusion matrix obtained by full cross-validation for training and prediction set.

Model	Class	Training set		Prediction set	
		1 (17*)	2 (10*)	1 (10*)	2 (8*)
LDA	1	17	0	10	0
	2	0	10	0	8
PLS-DA	1	12	5	8	2
	2	2	8	3	5

Model	Class	Training set			Prediction set		
		1 (12*)	2 (10*)	3 (10*)	I (6*)	II (2*)	III (5*)
SIMCA	1	12	0	0	6	0	0
	2	0	10	0	0	2	0
	3	6	4	10	3	2	5

*Number of samples per class.
Grey diagonal contain the correct assignments.

that it contributes to data differentiation. All variables were included in the SIMCA analysis, (Co, Cu, Mn, Mo, Ni, Rb, S, Sr, V, and Zn) exhibiting good modeling power in the discrimination data, being more significant the concentration of Mn and S for classes 1 and 3 differentiation, and Cu and S classes 1 and 3 discrimination.

Table 4 presents the confusion matrices containing the assignation of the test set samples into the studied milk classes using PCA-LDA, PLS-DA, and SIMCA for elemental concentration range. The classification accuracy obtained for each model was 100%, 74%, and 100% respectively.

3.2.4. Prediction of independent samples set

A new object is then assigned by comparing the distances of the class models to the object. Then validated models are used to predict the class of thirteen milk samples by external validation. Further validation was performed using SIMCA and the results of correct classification were calculated and summarized in Table 4. Therefore, the supervised chemometric models, LDA and SIMCA, demonstrated a high recognition rate in the determination of two different milk classes based on nutritional requirement (infant formula and fortified infant formula) being 100% for both LDA and SIMCA models; and presenting a lower rate of 72% for PLS-DA model. In addition, SIMCA was capable to recognize an overlap class corresponding to milk-based infant formula from 0 to 6 months.

3.3. Chemometrics application in foodomics

Human milk is regarded as the best nutrition for infants. However, when breastfeeding is not possible, desirable or sufficient, infant milk formulas serve as an adequate substitute for human milk. They have been designed to provide infants with the required nutrients for optimal growth and development. The obtained models, mainly SIMCA, besides allowing the evaluation of clusters of milk according to their nutritional profile also allowed evidence the elemental composition required by infants not only in different stages of growth but also in special requirements such as fortified milks. The variables that suitable permit differentiations between infant formulas (Cu, Mn, S, and Zn) are also essential trace element for infant nutrition, and their deficiency may be associated with a large variety of clinical disorders [30]. There is a connection between milk and Mn as it is important in brain and central nervous system development. Manganese is required in greater concentration in the first months of infant life; this data is correlated with the obtained results evidencing an outstanding formulation in the studied milks. Zinc deficiency is rare, but low Zn intakes may cause growth stoppage and damages in the immune system. Variations in copper and sulfur concentrations might contribute to fluctuations in biological levels due to formed linkages with proteins.

4. Conclusion

Optimal intakes of individual nutrients and their relative concentrations in complete milk-based infant formulas are areas of active research. Concerning foodomics, chemometric models were capable of recognizing milk-based infant formula, taking into account the range in nutrient concentrations requirements to achieve realistic goals of nutrient accretion and growth. Supervised chemometric models, demonstrated a high recognition rate in the classification of infant formula and fortified infant formula. Furthermore, SIMCA was capable to discriminate the overlapping groups corresponding to early infant period's milk-based formula. When the strongly preferred method of breastfeeding infants is a drawback, the use of milk-based infant formula as nutrient source for full-feeding infants is indicated for their healthy feeding. Thus, chemometric methods developed for classification of milk-based infant formula could be applicable for ensuring safety and nutritional quality monitoring, to be routinely used in food control laboratories or also for underlying new infant formulas.

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