Talanta 169 (2017) 189–194

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Multivariate curve resolution applied to kinetic-spectroscopic data matrices: Dye determination in foods by means of enzymatic oxidation

Valeria Boeris, Juan A. Arancibia*, Alejandro C. Olivieri

Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario e Instituto de Química Rosario (IQUIR-CONICET), Suipacha 531, S2002LRK Rosario, Argentina

ARTICLE INFO

Keywords:
Dye quantification
Multivariate curve resolution
Laccase-mediated oxidation
Kinetic-spectroscopic data

ABSTRACT

In this work, the combination of chemometric techniques with kinetic-spectroscopic data allowed quantifying two dyes (tartrazine and carminic acid) in complex matrices as mustard, ketchup, asparagus soup powder, pumpkin soup powder, plum jam and orange-strawberry juice. Quantitative analysis was performed without the use of tedious sample pretreatment, due to the achievement of the second-order advantage. The results obtained showed an improvement in simplicity, speed and cost with respect to usual separation techniques, allowing to properly quantifying these dyes obtaining limits of detection below 0.6 mg L^{-1}. In addition, to the best of our knowledge, is the first time that kinetic-spectroscopic data are obtained from the action of laccase for analytical purposes.

1. Introduction

Food additives are used widely for various purposes, including preservation, coloring and sweetening, being a consequence of industrialization and also of the development of food processing technology. As consumers recognize color as one of the main attributes of food, colorants have been extensively used to give an attractive presentation to food products. However, from the last decades, there is an increasing concern about the health and its relation with feeding, and also a preference toward the natural food, particularly, free of additives.

Tartrazine [trisodium salt of 3-carboxy-5-hydroxy-1 (*p*-sulfophenyl) –4- (sulfophenyl azo) pirazolone] (Fig. 1A) is an artificial yellow dye widely used in different types of food products. This is a particularly controversial dye since it has been implicated as the food additive most often responsible for several negative effects on health [1], accounting from allergic reactions [2], hyperactivity in susceptible children [3], alteration in brain [4], liver and kidney [5] to, without consensus, carcinogenic and mutagenic effects [6–8].

Carmine, based on carminic acid (7β-D-glucopyranosyl-1-methyl-3,5,6,8-tetrahydroxy-9,10-anthraquinone-2-carboxylic acid) (Fig. 1B) is a natural red dye extracted from cochineal insects (*Dactilopius coccus*) and is one of the most used natural colorings. There are some studies that report negative effect of this dye as an oxidant [9] and as allergenic [10,11].

The concentration limits of the compounds used as color additives are subject to regulations [12,13]. Several analytical methods have been applied for the determination of these and other dyes in different food samples, including: planar chromatography [14], liquid chromatography coupled to diode array detection [15,16] and capillary electrophoresis [17]. Although these assays are selective and sensitive, they require expensive equipment and/or toxic solvents. In addition, to provide clean extracts, food samples require a pretreatment, including cleanup processes that are normally tedious and time-consuming [15].

On the other hand, the classical methods used for quantification are based on absorbance measurements at a single wavelength of maximum absorption. However, this methodology cannot be employed in foods containing other absorbing components, either endogenous or exogenous.

Nevertheless, dyes can be determined in complex multicomponent mixtures by means of spectroscopic analysis coupled to chemometrics. Three- or higher-way data arrays can be handled using multi-way methods of analysis, which improves the selectivity. One way to obtain second-order data is to collect visible spectra of a sample as a function of time while a certain reaction occurs [18]. Some authors have reported the use of kinetic – spectroscopic data for analytical purposes [19,20] and also the use of oxidizing enzymes for the quantitative determination of analytes in complex mixtures [21]. The oxidation of dyes has been applied to their degradation by means of the Fenton reaction [22]. However, the latter reaction is too fast and cannot be easily applicable for analytical purposes. In order to carry the oxidation in a reasonable period of time, a promiscuous oxidizing enzyme was used. Laccase, a class of copper-containing oxidase, is produced by

* Corresponding author.
E-mail address: arancibia@iquir-conicet.gov.ar (J.A. Arancibia).

http://dx.doi.org/10.1016/j.talanta.2017.03.079
Received 22 December 2016; Received in revised form 23 March 2017; Accepted 25 March 2017
Available online 29 March 2017

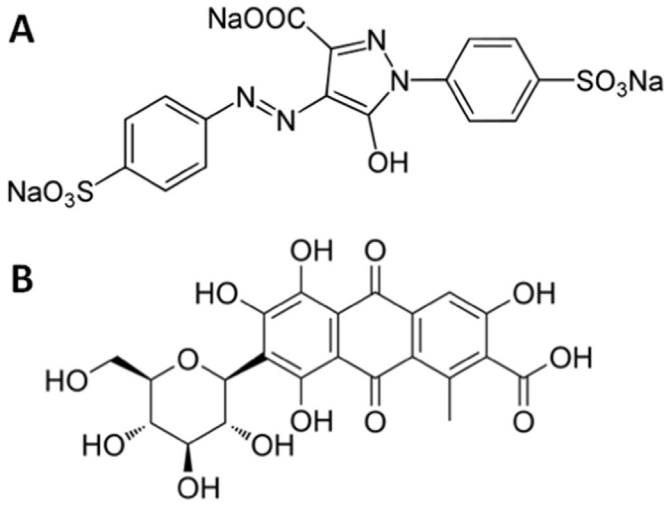

Fig. 1. Chemical structures of the two assayed dyes. (A) Tartrazine. (B) Carminic acid.

plants and fungi [23]. Laccase oxidizes organic substrates in the presence of oxygen, which is reduced to water [24]. The reaction mechanism of the oxidation of different substrates carried out by laccase was previously reported [25,26].

The aim of this work was to develop a method to quantify tartrazine and carminic acid in complex mixtures, using the analytical potential of the second-order advantage. For this purpose, and according to the available data (spectral-kinetic matrices), multivariate curve resolution coupled to alternating least-squares (MCR-ALS) was applied. To the best of our knowledge, there are no analytical studies based on kinetic-spectroscopic data obtained from the action of the oxidizing enzyme laccase. Finally, the viability of determining the above mentioned two dyes in spiked commercial food samples, without performing tedious sample processing, was demonstrated.

2. Theory

The theory of MCR-ALS is now well-known and can be found in the relevant references [27,28]. Nevertheless, the structure of the data used in this work and their interpretation with the MCR model is briefly described. For applying this multivariate algorithm in the so-called extended version, an augmented data matrix is created from the calibration and test sample data matrices. For the presently discussed matrices of size is $J{\times}K$ (J is the number of reaction times and K the number of wavelengths), the columns represent the kinetic mode and the rows the spectral mode. Augmentation can be performed either column-wise or row-wise, depending on the type of experiment being analyzed [27]. The most common way to augment matrices is along the temporal mode, i.e. column-wise, because of the need of modeling potential changes in kinetic profiles from sample to sample.

The bilinear decomposition of the augmented matrix is then performed according to the expression:

$$\mathbf{D} = \mathbf{C}\,\mathbf{S}^{T} + \mathbf{E} \quad (1)$$

where $\mathbf{D}$ [size $J(I_{cal}{+}1){\times}K$] is the augmented matrix of experimental data, containing the signals for (I_{cal}+1) different samples at different times, $\mathbf{C}$ [size $J(I_{cal}{+}1){\times}N$] is the matrix whose columns contain the signal of time profiles of the N components present in the samples, $\mathbf{S}^{T}$ (size $N{\times}$K) is the matrix whose rows describes the component spectra and $\mathbf{E}$ (same size as $\mathbf{D}$) is a matrix collecting the experimental errors and the variance not explained by the bilinear model of Eq. (1).

To achieve decomposition of $\mathbf{D}$ by iterative least-squares minimization, MCR-ALS requires initialization, which is made by resorting to the so-called purest variables [29,30], as well as suitable restrictions, imposed during the least-squares phase, such as non-negativity in both time and spectral profiles.

Finally, after MCR-ALS decomposition of $\mathbf{D}$, concentration information contained in $\mathbf{C}$ can be used for quantitative predictions. First the area under the profile for the ith sample is calculated for the anaylte:

$$a(i, n) = \sum_{j=1+(i-1)J}^{iJ} C(j, n) \quad (2)$$

The values of *a(i,n)* represent the relative concentrations of each component in the training samples, and are used to build a pseudo-univariate calibration graph, predicting the concentration in the unknown sample using a univariate approach. This is done by interpolation of the analyte value in the test sample in the calibration graph.

The proposed strategy can only be applied as long as the time range in all experiments is the same. However, the kinetic profiles for a given component in different samples need not be identical, because the potential changes are taken into account by the augmentation strategy employed in MCR-ALS analysis.

3. Experimental

3.1. Reagents

Carminic acid and tartrazine were purchased from Sigma-Aldrich. Milli-Q water (Millipore) was used in all experiments.

3.2. Stock standard solutions and calibration samples

Stock standard solutions of carminic acid (256 mg L^{-1}) and tartrazine (1091 mg L^{-1}) were prepared in 25.00 mL volumetric flasks by dissolving accurately weighed amounts of the dyes in water and completing to the mark.

Calibration samples for univariate analysis containing either pure dye were prepared by proper dilution of the corresponding stock solutions. The concentrations of the calibration samples were set by means of experiments establishing the linear range, after analysis of different solutions covering the interval 0–10 mg L^{-1}.

3.3. Test sample preparation: commercial spiked samples

Some of the food products that may contain the analytes were chosen as test samples. The test samples were spiked with one of the analyte dyes; however, the commercial samples used were naturally colored or contained additional dyes different from those tested in our work. Commercially available mustard, ketchup, asparagus soup powder, pumpkin soup powder, plum jam and orange-strawberry juice were purchased from local supermarkets. Accurately weighted portions of each sample were spiked with the corresponding dye, depending on the color. Tartrazine was spiked to yellowish foodstuff: mustard, asparagus soup powder and pumpkin soup powder. On the other hand, the reddish ketchup, jam and juice were spiked with carminic acid. The dry samples were dissolved in water, jam and dressings were blended with water and juice was diluted with water. Five levels of the corresponding dye were added to each spiked sample.

Therefore, two sets of samples were analyzed: those containing tartrazine (yellow-colored) and those containing carminic acid (red-colored). There are no samples that contain both analytes. Calibration and test samples were prepared for each of these sets. The calibration samples consist in aqueous solutions of the corresponding dye.

3.4. Spectrometric measurements and data treatment

The reactions were monitored using a diode-array spectrophotometer (MultiSpec-1501- Shimadzu, Osaka, Japan) thermostatized at 25 °C with a thermoelectrically temperature controlled cell holder (TCC-240A Shimadzu, Osaka, Japan) for in situ collection of the spectra during the oxidation of the sample. The reaction mixture was

composed by 2.00 mL of a proper dilution of the sample plus 20.0 μL of 5 mol L^{-1} acetic buffer pH 4.5, and the reaction was initiated by adding 5 μL of the enzyme (0.1 U). Spectra in the range 350–650 nm in steps of 1 nm were collected every 6 s during 10 min, generating a matrix composed by 30401 data points (301 wavelengths ×101 time steps). All kinetic experiments were developed in the same time range and with the same interval among consecutive spectra. The time-absorption matrices were transformed to ASCII format for subsequent manipulation.

3.5. Software

The data were handled using the MATLAB computer environment [31]. The calculations involved in the mixture resolution by MCR-ALS have been made using mvc2_gui, a MATLAB graphical interface toolbox which is a new version of that already reported in the literature [32].

4. Results

4.1. Developing the method and analysis of the calibration set

Using pure analyte standards, a kinetic-spectroscopic method was developed, making proper selection of the range of detected wavelengths, the amount of added enzyme, working temperature and medium condition, in order to obtain an overall assay time of ca. 10 min. Both pH and temperature were selected considering previous reports whereas the minimum amount of enzyme that allow a significant change in the spectra was used [33]. Under these conditions, it was possible to obtain a certain degree of oxidation of the analytes, allowing for the addition of the kinetic mode to the spectral data. The spectrum of carminic acid shows that range of largest sensitivity is from 420 nm to 600 nm, thus longer wavelengths were discarded in the analysis. For samples containing tartrazine, the full range (350–650 nm) was used.

The kinetic oxidation profiles of each dye significantly shift from run to run. This effect, combined with the presence of potential interferents in some of the analyzed samples, makes it difficult the alignment of the matrices in the kinetic mode, in order to restore the trilinearity required by some second-order multivariate algorithms. This is the main reason for employing the MCR-ALS algorithm for data processing, and also for the augmentation of the matrices in the time direction. In the analysis, initialization of the multivariate algorithm was performed using spectral estimates obtained from the analysis of the purest variables. Non-negativity restriction was applied in both modes. Spectral profiles were normalized to unit length to avoid ambiguity in the intensity scale.

The number of MCR-ALS components was estimating by principal component analysis of the augmented data matrix for each studied system. The explained variance by each successive component was analyzed, but special attention was focused to the residual fit of the reconstruction of the augmented data matrix by adding successive principal components. The stabilization of the residual fit was indicative that the optimum number of components was reached. The estimated number of components was two in both cases, with an explained variance greater than 99% and an associated Sfit value of 0.001. This can be justified taking into account the presence of two different signals (corresponding to carminic acid or tartrazine and a background signal). The resolution of calibration samples provided the temporal oxidation profiles and pure spectra for each analyte, and an additional signal corresponding to the background. The second profile was assigned to a background signal, since only one chemical component is present in each calibration sample (corresponding to the main dye profile), thus the second component was labeled as background. This second profile may include some turbidity as well as the native spectrum of the enzyme. After MCR-ALS resolution of the augmented calibration matrix, a pseudo-univariate calibration was carried out for each compound. The parameters corresponding to the linear regression of the relative concentrations (Eq. (2)) vs. the corresponding nominal concentrations are shown in Table 1. Linear relationships between relative concentrations obtained by MCR-ALS and nominal concentrations were found in all cases, using the rigorous test recommended by the International Union of Pure and Applied Chemistry (IUPAC) [34]. Sensitivities were estimated as discussed in the literature [35]. The IUPAC-consistent limits of detection (LOD) were computed taking into account the presence of both type I and II errors (false positives and false negatives) and also the uncertainty propagation from the slope and intercept [36].

Table 1
Calibration parameters for both analytes from MCR-ALS analysis of calibration data matrices.

	Tartrazine	Carminic acid
Slope (SD)	35 (1)	5.00 (0.05)
Intercept (SD)	2 (3)	−2.3 (0.2)
r^2	0.996	0.999
$s_{y/x}$	4.47	0.48
Linear range (mg L^{-1})	0–5	0–7.2
p value for linearity test	0.64	0.18
SEN (mAU L^{-1} mg)	34.8	5.0
LOD (mg L^{-1})	0.59	0.38
Number of calibration samples	5	8

SD = standard deviation, r^2 = correlation coefficient, $s_{y/x}$ = standard deviation of regression residuals, SEN = sensitivity, mAU = milliabsorbance units, LOD = limit of detection.

4.2. Analysis of spiked real samples

Real food products were spiked with each of the two studied dyes and were subjected to the analytical protocol discussed above, and individually resolved by MCR. The estimated number of components was larger than those in the calibration set (in both cases 3 components, with an explained variance greater than 99% and an associated Sfit value of 0.001), meaning that there are additional components in the test samples, in comparison to the calibration samples. Therefore, the analysis of these samples confirms that there are interfering species, and those may be a complex mixture or a combination of compounds.

Fig. 2A shows the three-dimensional plot, Fig. 2C the MCR-ALS recovered spectra, and Fig. 2E the retrieved augmented kinetic profiles corresponding to asparagus soup powder, a yellow sample spiked with tartrazine. Analogous plots are shown in Figs. 2B, D and F for plum jam, a red sample, spiked with carminic acid. As can be seen, the spectra corresponding to the interfering species were different than those corresponding to the dyes, allowing their resolution. Notice in Figs. 2E and F that the interferents (dashed lines in both cases) are present in the test sample under study (the first time sub-profile) and absent in the calibration samples (the next time sub-profiles).

The recovery results corresponding to different levels of each analyte in three samples of each color are collected in Fig. 3. As can be appreciated, the analyte predictions are in good agreement with the nominal values, indicated in the abscissa of Fig. 3. If the elliptical joint confidence region is analyzed for the slope and intercept of the plot of predicted vs. nominal concentrations, we conclude that the ellipse includes the theoretically expected values of (1,0), indicating the accuracy of the used methodology (Fig. 4). Indeed, a paired t-test indicates significant differences between the nominal concentrations and the predicted ones using the presently proposed methodology. The p values, the root mean square error of prediction (RMSEP) and the relative errors of prediction (REP), computed with respect to the mean calibration concentration of each analyte are listed in Table 2. These results strongly suggest that the present methodology is useful for the

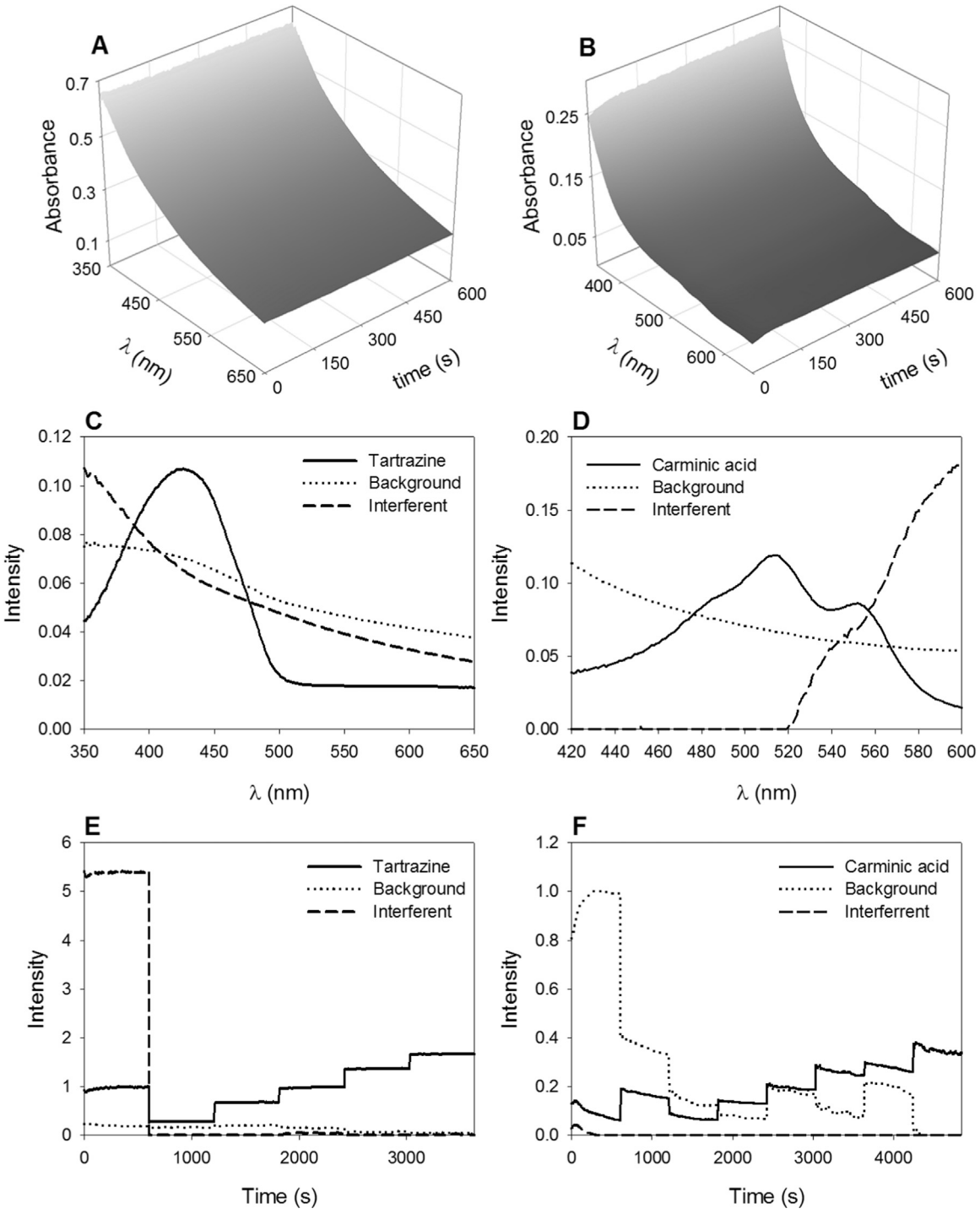

Fig. 2. Results for the analysis of food samples. (A) and (B) Three-dimensional surface plot of: (A) asparagus soup powder sample spiked with tartrazine. (B) plum jam sample spiked with carminic acid. (C) and (D) Spectral profiles retrieved by MCR–ALS analysis (C: asparagus soup powder sample and D: plum jam sample). E and F) MCR–ALS resolved kinetic profiles (E: asparagus soup powder sample and F: plum jam sample).

analysis of these analytes, its versatility make it useful for potential applications in the determination of other analytes in different types of samples.

5. Conclusions

In this work, the combination of chemometric techniques with kinetic-spectroscopic data allowed quantifying dyes in complex matrices. It is necessary to emphasize that, thanks to the achievement of the second-order advantage; quantitative analysis was performed without the use of tedious sample pretreatment. The results obtained showed an improvement in simplicity, speed and cost with respect to usual separation techniques.

Moreover, the present one is an additional case where the capacity of MCR-ALS algorithm to process and predict non-trilinear data where bilinearity is preserved has been demonstrated. Finally, as mentioned earlier, although many kinetic measurements by following the time evolution of absorption spectra have been reported in literature, to the best of our knowledge, kinetic-spectroscopy data from the action of laccase enzyme were not obtained.

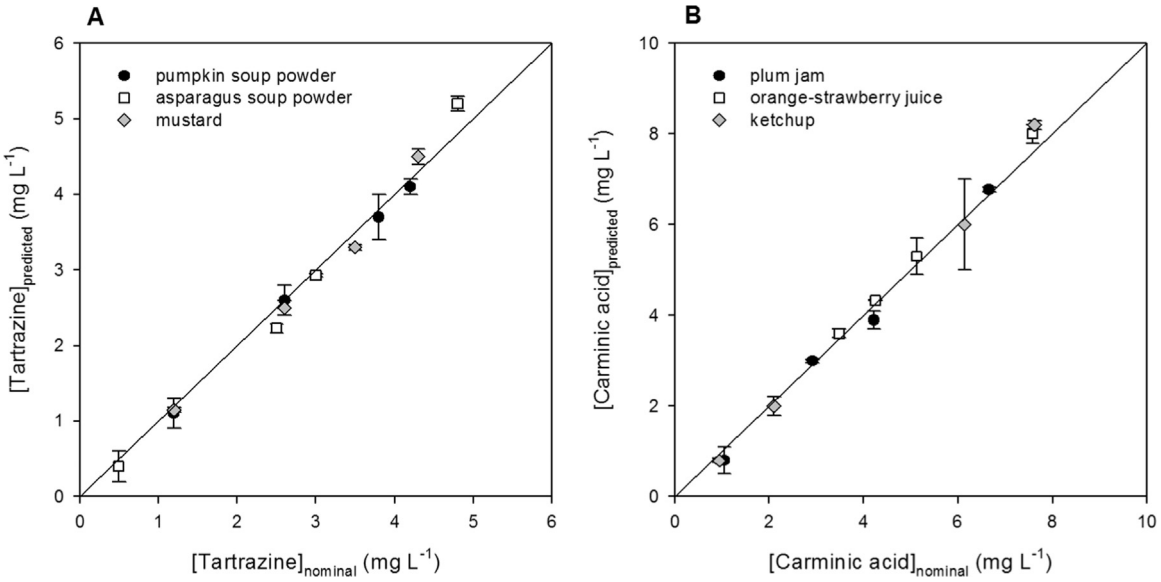

Fig. 3. Recovery results corresponding to different levels of each analyte: (A) Samples spiked with tartrazine and (B) Samples spiked with carminic acid.

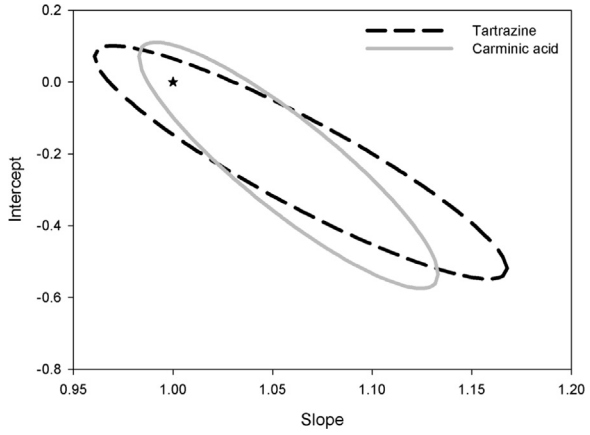

Fig. 4. Elliptic joint confidence regions for the slope and intercept for the accuracy study. The star represents the point (1, 0).

Table 2
Statistical analysis of the agreement between nominal and predicted values.

	Tartrazine	Carminic acid
RMSEP (mg L^{-1})	0.18	0.26
REP (%)	5.9	6.8
p value for paired *t*-test	0.44	0.52

RMSEP = $[(1/I)\sum_1^I (c_{act} - c_{pred})^2]^{1/2}$ where I is the number of calibration samples. REP = $(100 \times \text{RMSEP}/\overline{C})$ where $\overline{C}$ is average concentration of the component for the calibration samples

Acknowledgements

Financial support provided by the University of Rosario, CONICET (PIP 0163) and ANPCyT (Project No. PICT 2013-0136) is appreciated. Valeria Boeris is grateful to CONICET for her scholarship.

References

[1] D.D. Stevenson, R.A. Simon, W.R. Lumry, D.A. Mathison, Adverse reactions to tartrazine, J. Allergy Clin. Immunol. 78 (1, Part 2) (1986) 182–191.
[2] J. Devlin, T.J. David, Tartrazine in atopic eczema, Arch. Dis. Child. 67 (1992) 709–711.
[3] N.I. Ward, K.A. Soulsbury, V.H. Zettel, I.D. Colquhoun, S. Bunday, B. Barnes, The influence of the chemical additive tartrazine on the zinc status of hyperactive children—a double-blind placebo-controlled study, J. Nutr. Environ. Med. 1 (1990) 51–57.
[4] Y. Gao, C. Li, J. Shen, H. Yin, X. An, H. Jin, Effect of food azo dye tartrazine on learning and memory functions in mice and rats, and the possible mechanisms involved, J. Food Sci. 76 (2011) T125–T129.
[5] K.A. Amin, H. Abdel Hameid II, A.H. Abd Elsttar, Effect of food azo dyes tartrazine and carmoisine on biochemical parameters related to renal, hepatic function and oxidative stress biomarkers in young male rats, Food Chem. Toxicol. 48 (2010) 2994–2999.
[6] A. Maekawa, C. Matsuoka, H. Onodera, H. Tanigawa, K. Furuta, J. Kanno, J.J. Jang, Y. Hayashi, T. Ogiu, Lack of carcinogenicity of tartrazine (FD & C Yellow No. 5) in the F344 rat, Food Chem. Toxicol. 25 (1987) 891–896.
[7] I. Moutinho, L. Bertges, R. Assis, Prolonged use of the food dye tartrazine (FD & C yellow n° 5) and its effects on the gastric mucosa of Wistar rats, Braz. J. Biol. 67 (2007) 141–145.
[8] R. Münzner, J. Wever, Mutagenic activity of the feces of rats following oral administration of tartrazine, Arch. Toxicol. 60 (1987) 328–330.
[9] J.M.C. Gutteridge, G.J. Quinlan, Carminic acid-promoted oxygen radical damage to lipid and carbohydrate, Food Addit. Contam. 3 (1986) 289–293.
[10] S. Voltolini, S. Pellegrini, M. Contatore, D. Bignardi, P. Minale, New risks from ancient food dyes: cochineal red allergy, Eur. Ann. Allergy Clin. Immunol. 46 (2014) 232–233.
[11] B. Wüthrich, M.K. Kägi, W. Stücker, Anaphylactic reactions to ingested carmine (E120), Allergy 52 (11) (1997) 1133–1137.
[12] Código Alimentario Argentino. ⟨http://www.anmat.gov.ar/alimentos/codigoa/CAPITULO_XVIII.pdf⟩.
[13] Color Additive Regulations. ⟨http://www.fda.gov/ForIndustry/ColorAdditives/GuidanceComplianceRegulatoryInformation/ColorAdditiveListingRegulations/default.htm⟩.
[14] G.E. Morlock, C. Oellig, Rapid planar chromatographic analysis of 25 water-soluble dyes used as food additives, J. AOAC Int. 92 (2009) 745–756.
[15] M. González, M. Gallego, M. Valcárcel, Liquid chromatographic determination of natural and synthetic colorants in lyophilized foods using an automatic solid-phase extraction system, J. Agr. Food Chem. 51 (2003) 2121–2129.
[16] H.S. Lim, J.C. Choi, S.B. Song, M. Kim, Quantitative determination of carmine in foods by high-performance liquid chromatography, Food Chem. 158 (2014) 521–526.
[17] M.A. Prado, L.F.V. Boas, M.R. Bronze, H.T. Godoy, Validation of methodology for simultaneous determination of synthetic dyes in alcoholic beverages by capillary electrophoresis, J. Chromatogr. A 1136 (2006) 231–236.
[18] P.H. Março, R.J. Poppi, I.S. Scarminio, R. Tauler, Investigation of the pH effect and UV radiation on kinetic degradation of anthocyanin mixtures extracted from Hibiscus acetosella, Food Chem. 125 (2011) 1020–1027.
[19] M. Shariati-Rad, M. Irandoust, S. Mohammadi, Determination of nitrite in food samples by kinetic spectrophotometric data and multivariate curve resolution-alternating least squares (MCR-ALS), Food Anal. Methods 10 (2017) 694–703.
[20] Y. Wang, J. Hu, Q. Zhuang, Y. Ni, Enhancing sensitivity and selectivity in a label-free colorimetric sensor for detection of Iron(II) ions with luminescent molybdenum disulfide nanosheet-based peroxidase mimetics, Biosens. Bioelectron. 80 (2016) 111–117.
[21] J.M. Amigo, A. de Juan, J. Coello, S. Maspoch, A mixed hard- and soft-modelling approach for the quantitative determination of oxipurines and uricacid in human urine, Anal. Chem. Acta 567 (2006) 236–244.
[22] H. Song, C. Chen, H. Zhang, J. Huang, Rapid decolorization of dyes in heterogeneous Fenton-like oxidation catalyzed by Fe-incorporated Ti-HMS molecular sieves, J. Environ. Chem. Eng. 4 (2016) 460–467.

[23] S. Rodríguez Couto, J.L. Toca Herrera, Industrial and biotechnological applications of laccases: a review, Biotechnol. Adv. 24 (2006) 500–513.
[24] V. Lettera, C. Pezzella, P. Cicatiello, A. Piscitelli, V.G. Giacobelli, E. Galano, A. Amoresano, G. Sannia, Efficient immobilization of a fungal laccase and its exploitation in fruit juice clarification, Food Chem. 196 (2016) 1272–1278.
[25] Y. Wong, J. Yu, Laccase-catalyzed decolorization of synthetic dyes, Wat. Res. 33 (1999) 3512–3520.
[26] M. Chivukula, V. Renganathan, Phenolic azo dye oxidation by laccase from pyricularia oryzae, Appl. Environ. Microbiol 61 (1995) 4374–4377.
[27] A. De Juan, E. Casassas, R. Tauler, In Encyclopedia of Analytical Chemistry; Myers, RA, Ed, Wiley, Chichester, UK, 2002.
[28] R. Tauler, M. Maeder, A. De Juan, Multiset data analysis: extended multivariate curve resolution|, NOVA The University of Newcastle's ⟨http://hdl.handle.net/1959.13/918333⟩. Accessed 9 October 2016, 2009.
[29] W. Windig, C.E. Heckler, F.A. Agblevor, R.J. Evans, in: Proceedings of the 2nd Scandinavian Symposium on ChemometricsSelf-modeling mixture analysis of categorized pyrolysis mass spectral data with the SIMPLISMA approach, Chemom. Intell. Lab. Syst. *14* 195–207, 1992.
[30] W. Windig, D.A. Stephenson, Self-modeling mixture analysis of second-derivative near-infrared spectral data using the SIMPLISMA approach, Anal. Chem. 64 (1992) 2735–2742.
[31] O.E. Mäkinen, E. Zannini, E.K. Arendt, Modifying the cold gelation properties of quinoa protein isolate: influence of heat-denaturation ph in the alkaline range, Plant Foods Hum. Nutr. (2015) 1–7.
[32] A.C. Olivieri, H.L. Wu, R.Q. Yu, MVC2: a MATLAB graphical interface toolbox for second-order multivariate calibration, Chemom. Intell. Lab. Syst. 96 (2009) 246–251.
[33] J.M. Bollag, A. Leonowicz, Comparative studies of extracellular fungal laccases, Appl. Environ. Microbiol. 48 (1984) 849–854.
[34] K. Danzer, L.A. Currie, Guidelines for calibration in analytical chemistry. Part I. Fundamentals and single component calibration (IUPAC Recommendations 1998), Pure Appl. Chem. 70 (1998) 993–1014.
[35] M.C. Bauza, G.A. Ibañez, R. Tauler, A.C. Olivieri, Sensitivity equation for quantitative analysis with multivariate curve resolution-alternating least-squares: theoretical and experimental approach, Anal. Chem. 84 (2012) 8697–8706.
[36] L.A. Currie, Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC Recommendations 1995), Pure Appl. Chem. 67 (1995) 1699–1723.