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# Handling time misalignment and rank deficiency in liquid chromatography by multivariate curve resolution: Quantitation of five biogenic amines in fish

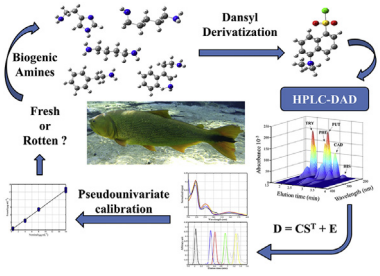
Licarion Pinto[a], César Horacio Díaz Nieto[b], María Alicia Zón[b], Héctor Fernández[b], Mario Cesar Ugulino de Araujo[a,*]

[a] Laboratório de Automação e Instrumentação em Química Analítica e Quimiometria (LAQA), Universidade Federal da Paraíba, CCEN, Departamento de Química, Caixa Postal 5093, CEP 58051-970, João Pessoa, PB, Brazil
[b] Departamento de Química, Facultad de Ciencias Exactas, Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, 5800, Río Cuarto, Argentina

## HIGHLIGHTS

- A fast chromatographic method for selective quantitation of five biogenic amines in fish is presented.
- Temporal misalignment and rank deficiency were handled by icoshift and MCR-ALS spectral augmented.
- Seven times faster and improvement in analytical figures of merit from previous studies.
- Low solvent consumption in accordance with green analytical chemistry principles.
- Low LOQ reaching the established by FAO/WHO and EFSA authorities without a pre-concentration step.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Biogenic amines (BAs) are used for identifying spoilage in food. The most common are tryptamine (TRY), 2-phenylethylamine (PHE), putrescine (PUT), cadaverine (CAD) and histamine (HIS). Due to lack of chromophores, chemical derivatization with dansyl was employed to analyze these BAs using high performance liquid chromatography with a diode array detector (HPLC-DAD). However, the derivatization reaction occurs with any primary or secondary amine, leading to co-elution of analytes and interferents with identical spectral profiles, and thus causing rank deficiency. When the spectral profile is the same and peak misalignment is present on the chromatographic runs, it is not possible to handle the data only with Multivariate Curve Resolution and Alternative Least Square (MCR-ALS), by augmenting the time, or the spectral mode. A way to circumvent this drawback is to receive information from another detector that leads to a selective profile for the analyte. To overcome both problems, (tri-linearity break in time, and spectral mode), this paper proposes a new analytical methodology for fast quantitation of these BAs in fish with HPLC-DAD by using the icoshift algorithm for temporal misalignment correction before MCR-ALS spectral mode augmented treatment. Limits of detection, relative errors of prediction (REP) and average recoveries, ranging from 0.14 to 0.50 μg $mL^{-1}$, 3.5–8.8% and 88.08%–99.68%, respectively. These are outstanding results obtained, reaching quantification limits for the five BAs much lower than those established by the Food and Agriculture Organization of the United Nations and World Health

* Corresponding author.
*E-mail address:* laqa@quimica.ufpb.br (M.C.U. de Araujo).

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Organization (FAO/WHO), and the European Food Safety Authority (EFSA), all without any pre-concentration steps. The concentrations of BAs in fish samples ranged from 7.82 to 29.41 μg $g^{-1}$, 8.68–25.95 μg $g^{-1}$, 4.76–28.54 μg $g^{-1}$, 5.18–39.95 μg $g^{-1}$ and 1.45–52.62 μg $g^{-1}$ for TRY, PHE, PUT, CAD, and HIS, respectively. In addition, the proposed method spends less than 4 min in an isocratic run, consuming less solvent in accordance with the principles of green analytical chemistry.

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## 1. Introduction

Biogenic amines (BAs) are alkaline compounds formed in foodstuffs, mainly through decarboxylation of free amino acids by exogenous decarboxylases of the microorganisms present in food [1,2]. Determination of BAs has received considerable interest, because of their detrimental effects on humans; they cause migraines, hypertension, hypotension, rashes, and digestive problems [1–3]. Many cases of toxemias resulting from ingestion of food containing BAs have been reported worldwide, these usually involve fishes, and fish products [2–7].

The concentration level of these BAs can be used as an indicator of food spoilage [6–10]. For public health protection, the Food and Agriculture Organization of the United Nations and World Health Organization (FAO/WHO) [7], and the European Food Safety Authority (EFSA) [8] have established an acceptable maximum concentration of 50 mg $kg^{-1}$ for histamine (HIS) in foods. Although HIS is the unique among the BAs that have an established limit [6], both the FAO/WHO and the EFSA highlight other BAs such as tryptamine (TRY), 2-phenylethylamine (PHE), putrescine (PUT) and cadaverine (CAD) [7,8]. Therefore, it is of fundamental importance to monitor their presence in foodstuffs, considering their potential effects on human health, and food security, especially since these amines are stable against heat and acids, and they are not destroyed by cooking [4,7,8].

High performance liquid chromatography with a diode array detector (HPLC-DAD), and fluorescence spectroscopy (HPLC-FLU) [2–6] are the most frequently used methods for determination of BAs. Due to the lack of significant fluorescence properties, and/or chromophores, chemical derivatization is usually performed to shift maximum absorption to the UV region (190–400 nm), to increase the retention time, and sensitivity for the BAs [11,12]. The derivatization reagent, dansyl chloride, is one of the most widely used because it forms derivatives with primary and secondary amines resulting in stable products [3,6,11–18]. However, once derived, the analytes increase their retention in the chromatographic column requiring more solvent to its complete elution. This results in long chromatographic runs, higher solvent consumption, and longer analysis time. In order to circumvent this drawback, one can increase the strength of the mobile phase, and/or the flow rate. However there is a risk of overlapping analyte signals, which precludes an univariate analysis.

The use of isocratic HPLC-DAD data coupled to second-order chemometrics tools is an economic alternative to save time and solvents [19–24]. The chemometric literature has keyed the expression “second order advantage” to highlight the interesting feature of overcoming interferences, with second and higher order data and multivariate calibration [19,20,22–28].

It is worth to highlight that in chromatography, the same constituent frequently has distinct retention times in different runs [19,29]. This temporal misalignment makes it unfeasible to use second-order multivariate calibration methods that require data that fulfill the tri-linearity principle [22,25]. Moreover, in spectral mode, different constituents may have identical profiles; this also breaks the tri-linearity of the data, and is known as rank deficiency [19,25].

Multivariate Curve Resolution – Alternating Least Square (MCR-ALS) is a decomposition method capable of suitably dealing with retention time misalignment and rank deficiency when the data is augmented, respectively, on time mode or on spectral mode [19,20,22–30].

Escandar and co-authors [19] proposed a HPLC-DAD method to determine four hormones in river water samples. These four hormones have identical spectral profiles that cause rank deficiency when MCR-ALS is used for simultaneous analyte resolution. To circumvent this problem, Escandar and co-workers [19] developed a method which fully separated these four hormones and solve interference problems caused by other co-eluted constituents, when the interferent presents different spectral profiles. The HPLC-DAD dataset was divided into four regions, each region containing only one hormone. MCR-ALS treatment was then done for each column-wise (time mode) augmented region. In order to fully separate the hormones, the proposed method needed longer chromatographic runs, and thus consuming more solvent. Further, if another constituent of the sample present co-eluted spectral profile identical to those of the hormones in any of the four selected regions, the MCR-ALS model yielded inaccurate results due to rank deficiency. Another way to solve the rank deficiency is to row-wise augment the data with a different detector which provides a selective response to each analyte, having an identical profile at the first detector, and then column-wise augment the data for the different samples [31,32]. In spite of this interesting approach having been occasionally used, a different detector then becomes necessary to provide a selective response to the analyte, and it must be synchronized with the first instrument in order to generate high order data; for instance liquid chromatography. In some laboratories, one may not have a chromatograph equipped with more than one detector. Other strategies have been used for this propose. Culzoni and co-authors overcame this problem with a single detector by augmenting the matrix on spectral mode in an MCR-ALS approach [26,27]. Elcoroaristizabal and co-authors pointed that one should augment each sample matrix, before MCR-ALS treatment, on the more overlapped mode [33,34].

This paper presents a fast chromatographic method using HPLC-DAD and MCR-ALS for quantitation of five BAs; (TRY, PHE, PUT, CAD, and HIS) in fish samples. Due to the lack of chromophores, chemical derivatization with dansyl chloride is needed for the analysis. A problem is that the reaction occurs with any primary or secondary amine, so it is non-selective for the five target amines since both analytes and interferents co-elute and may present identical spectra profiles, leading to a system with rank deficiency. Moreover, the chromatographic system also presents peak misalignment. MCR-ALS can handle time misalignment or rank deficiency by augmenting the data on time mode [19,20,23,29] or on spectral mode [26,27], respectively, but not both simultaneously if a different detector is not used, as would be the case with a row and column-wise augmented matrix [31,32].

In the data from the present study, there are two constituents generating identical spectral profiles, therefore each sample matrix was augmented on spectral mode, but it is important to highlight that if the data is augmented on spectral mode, the time mode should not have time shift [27]. In this work, to overcome both

time misalignment and rank deficiency, the HPLC-DAD dataset was augmented on spectral mode, while the temporal misalignments (frequently present in chromatographic runs) were corrected using the icoshift algorithm [35,36], before MCR-ALS treatment. The predictive capacity of the calibration models built with the BAs individual standard solutions were tested in two ways: (1) with synthetic mixtures of the five BAs, each one in four concentration levels; and (2) with recovery tests in three concentration levels for the fish samples.

## 2. Theory

### 2.1. Multivariate Curve Resolution – Alternating Least Squares

MCR-ALS is explained in detail by Tauler and Blanchet [23,29,30]; here, only a brief description will be presented. MCR-ALS is a bilinear decomposition method that assumes additivity of the recorded signal. It can be mathematically represented as in Eq. (1).

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

Where **D** is an individual matrix of size $j \times k$. For LC-DAD data $j$ corresponding to the elution times, and $k$ to the wavelengths, **C** is the matrix containing the concentration profiles; of size $j \times n$, $\mathbf{S}^{\mathbf{T}}$ is the matrix containing the spectral profiles of size $n \times k$, $n$ is the number of factors for the MCR model, previously informed by the analyst. Commonly, initial estimates of $n$ are obtained by inspection of the significant eigenvalues of **D**. The matrix **E** contains the data not modeled by MCR-ALS; of size $j \times k$. After choosing the number of components, MCR-ALS requires booting of the **C** or $\mathbf{S}^{\mathbf{T}}$ matrix. This estimate can be made based on a pure variables detection such as SIMPLe to use Interactive Self modeling Mixture Analysis (SIMPLISMA) method [30,37], or Evolving factor analysis (EFA) [29,38–40].

Assuming the initial estimates of $\mathbf{S}^{\mathbf{T}}$ are available, **C** is estimated using least squares. The estimated **C** likewise calculates a new $\mathbf{S}^{\mathbf{T}}$ matrix. This updating procedure of **C** and $\mathbf{S}^{\mathbf{T}}$ (alternately employing least squares) is only interrupted when the maximum number of iterations is hit, when the convergence criterion of ALS is reached, (≤0.1% of relative change in fit for successive interactions), or when diverging from the convergence criterion 20 times in a row. At the end of the ALS procedure, (in case of convergence), **C** and $\mathbf{S}^{\mathbf{T}}$ contain the optimal concentration and spectral profiles, respectively.

When i+1 samples are analyzed, i+1 LC-DAD matrices of j × k size are generated, and the simultaneous analyses of the i+1 matrices are done using extended MCR-ALS, where i is the calibration sample, and 1 is the sample with the unexpected constituent. The $i$+1 matrices are arranged in an augmented matrix **Daug** obtained by arranging the LC-DAD matrices one below the other (column-wise of size $(i+1)j \times k$), or side by side (row-wise of size $j \times (i+1)k$). The **D** matrix should always be augmented in the

**Table 1**
Test set containing the five amines at four concentration levels (μg mL$^{-1}$).

| Exp. | TRY | PHE | PUT | CAD | HIS |
|---|---|---|---|---|---|
| 1 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| 2 | 4 | 4 | 4 | 4 | 0.4 |
| 3 | 8 | 8 | 8 | 8 | 0.4 |
| 4 | 16 | 16 | 16 | 16 | 0.4 |
| 5 | 16 | 8 | 0.4 | 4 | 4 |
| 6 | 8 | 16 | 4 | 0.4 | 4 |
| 7 | 4 | 0.4 | 8 | 16 | 4 |
| 8 | 0.4 | 4 | 16 | 8 | 4 |
| 9 | 4 | 16 | 0.4 | 8 | 8 |
| 10 | 0.4 | 8 | 4 | 16 | 8 |
| 11 | 16 | 4 | 8 | 0.4 | 8 |
| 12 | 8 | 0.4 | 16 | 4 | 8 |
| 13 | 8 | 4 | 0.4 | 16 | 16 |
| 14 | 16 | 0.4 | 4 | 8 | 16 |
| 15 | 0.4 | 16 | 8 | 4 | 16 |
| 16 | 4 | 8 | 16 | 0.4 | 16 |

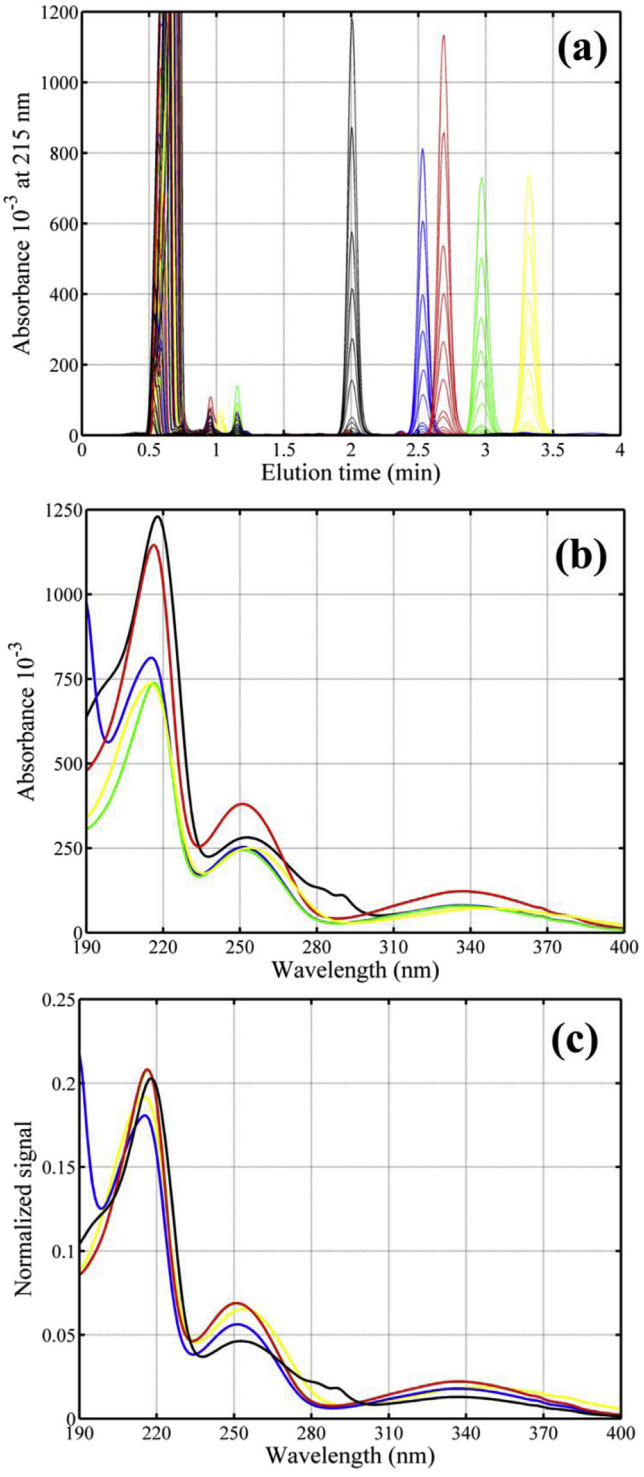


**Fig. 1.** (a) Chromatograms recorded at 215 nm for the individual calibration standards of TRY (■), PHE (■), PUT (■), CAD (■), and HIS (■); (b) Spectra at the retention time for the calibration standards of all five BAs with the higher concentration (c) Normalized spectrum of all five BAs.

tri-linearity breaking mode, so the time augmented matrix should be used when the tri-linearity breaking occurs in the elution mode, and spectral augmented when it is in the spectral mode. In cases where the **Daug** is column-wise, the **Daug** matrix is decomposed by MCR-ALS into **Caug**, $\mathbf{S}^T$, and **Eaug** matrices. Otherwise, when it is row-wise, it is decomposed into **C**, $\mathbf{S}^T$**aug**, and **Eaug** matrices. If it is column and row-wise augmented, it will be decomposed into **Caug**, $\mathbf{S}^T$**aug**, and **Eaug** matrices.

When the objective is to employ the MCR-ALS for the purpose of predicting the concentration of a chemical species (construction of a calibration model), the matrix **Daug** is composed of $i$ calibration standards (with the known analyte concentration), and the unknown sample, all of size $j \times k$. Finally, to make the prediction of the unknown sample, the profile obtained from the **Caug** matrix is employed, and the analyte scores defined as the area under the recovered curve for $i$+1 samples. A linear fit is built between the $i$ scores of the calibration standards and their nominal concentrations. The procedure is known as a pseudo-univariate calibration curve [19,20,25,40], and the unknown sample concentration value is obtained by interpolation.

## 3. Materials and methods

### 3.1. Reagents

Dansyl chloride, Tryptamine hydrochloride (TRY), Putrescine dihydrochloride (PUT), 2-Pheylethylamine hydrochloride (PHE), Cadaverine dihydrochloride (CAD), and Histamine dihydrochloride (HIS) were all purchased from Sigma Aldrich. Acetonitrile (HPLC grade) was purchased from J. T. Baker. Ammonium hydroxide (p.a. grade), and sodium bicarbonate (p.a. grade) were purchased from Vetec. Perchloric acid (p.a. grade), acetone (p.a. grade), and sodium hydroxide (p.a grade), were purchased from Dinámica Química Contemporánea Ltda. Milli-Q water (Millipore) was used in all experiments.

### 3.2. Chromatographic runs

Chromatographic runs were performed on an Ultimate 3000 Dionex chromatograph, consisting of a quaternary pump, a manual injector fitted with a 20 uL fixed loop, and a UV–visible diode array detector. An Acclaim™ 120 C18 column of 150 mm × 4.6 mm, 5 μm particle sizes, and 120 Å pore size was employed. An isocratic mode with a binary mixture of Acetonitrile:Water (73:27) was used, with a flow rate of 2 mL $min^{-1}$, and column temperature of 30 °C. The total elution time was 4 min. The data were collected using the software Chromeleon, Version 6.80 with a frequency of 2 Hz.

### 3.3. Software

The data were handled using the MATLAB computer environment. The calculations involving MCR-ALS were made using mvc2 [40], a MATLAB graphical user interface available at www.iquir-conicet.gov.ar/descargas/mvc2.rar.

### 3.4. Derivatization

The derivatization of amines with dansyl chloride was performed according to Hwi-Chang Chen's method [41], with some modifications. To one milliliter of the mixed amines solution were added, 0.2 mL of 2 M sodium hydroxide, and 0.3 mL of saturated sodium bicarbonate solution. To the solution was added 2 mL of 1% dansyl chloride solution, dissolved in acetone, mixed, and held at 40 °C for 45 min. After the reaction, 100 μL of ammonia was added, and held for 30 min. Acetonitrile was added to a final volume of 5 ml, the solution was filtrated through a 0.22 μm filter, and then used for chromatographic analyses. The calibration, test, and real sample were derivatized before being run in the chromatographic system.

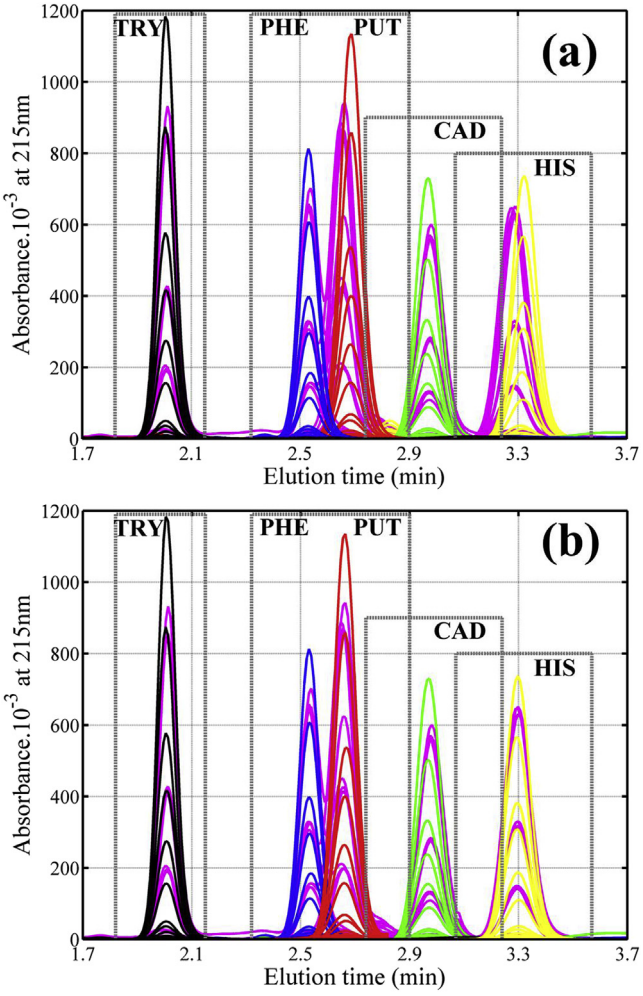


**Fig. 2.** Chromatograms recorded at 215 nm for calibration standards before (a), and after (b) the peak alignment using the icoshift algorithm TRY (▬), PHE (▬), PUT (▬), CAD (▬), and HIS (▬); and for the synthetic test samples (▬). Dashed gray lines indicate elution time and wavelength ranges.

**Table 2**
MCR-ALS results for HPLC-DAD synthetic samples.

| Synthetic sample | TRY (1) | PHE (2) | PUT (2) | CAD (2) | HIS (2) |
|---|---|---|---|---|---|
| SEL | 1.00 | 0.97 | 0.93 | 0.90 | 0.86 |
| $\gamma$ (mL $\mu g^{-1}$) | 92.00 | 65.00 | 68.00 | 62.00 | 120.00 |
| LOD ($\mu g$ $mL^{-1}$) | 0.19 | 0.14 | 0.21 | 0.50 | 0.30 |
| LOQ ($\mu g$ $mL^{-1}$) | 0.57 | 0.41 | 0.65 | 1.50 | 0.91 |
| RMSEP ($\mu g$ $mL^{-1}$) | 0.75 | 0.41 | 0.86 | 0.44 | 0.34 |
| REP (%) | 7.69 | 4.20 | 8.84 | 4.47 | 3.50 |

In parentheses are the number of estimated constituents. *SEL*: selectivity; $\boldsymbol{\gamma}$: analytical sensitivity; *LOD*: Limit of detection; *LOQ*: Limit of quantification; *RMSEP*: Root mean square error of prediction; *REP* Relative error of prediction. All figures of merit are calculated according to Olivieri and coauthors [25,44,45], using the graphical user interface MVC2 [40].

### 3.5. Calibration and test samples

A 1000 μg $mL^{-1}$stock solution was prepared by weighing an appropriated amount of each amine to a volumetric flask, and brought to the mark with 0.1 M HCl. The standard solutions were stored at 4 °C until the use. Each stock solution was used to prepare the calibration and test set which were then derivatized.

For the calibration set, all BAs were individually prepared at 12 concentration levels, 0.05, 0.10, 0.30, 0.50, 0.75, 1.00, 3.00, 5.00, 7.50, 10.00, 15.00, and 20.00 μg $mL^{-1}$. For the test set, 16 samples were prepared following Taguchi's experimental design [42,43], containing five BAs in four levels. The different concentration levels chosen for Taguchi's design were 0.4, 4.0, 8.0, and 16.0 μg $mL^{-1}$, as shown at Table 1.

### 3.6. Sample pretreatment

Three fish samples were purchased at the local fish markets, from João Pessoa, Paraíba, Brazil. The selected fish species corresponded to locally typical fishes; *Salminus maxillosus*, *Scomber scombrus*, and *Seriola dumerili*.

Each fish sample was ground in a food processor for 3 min. Five grams of the grounded samples were transferred to 50 mL

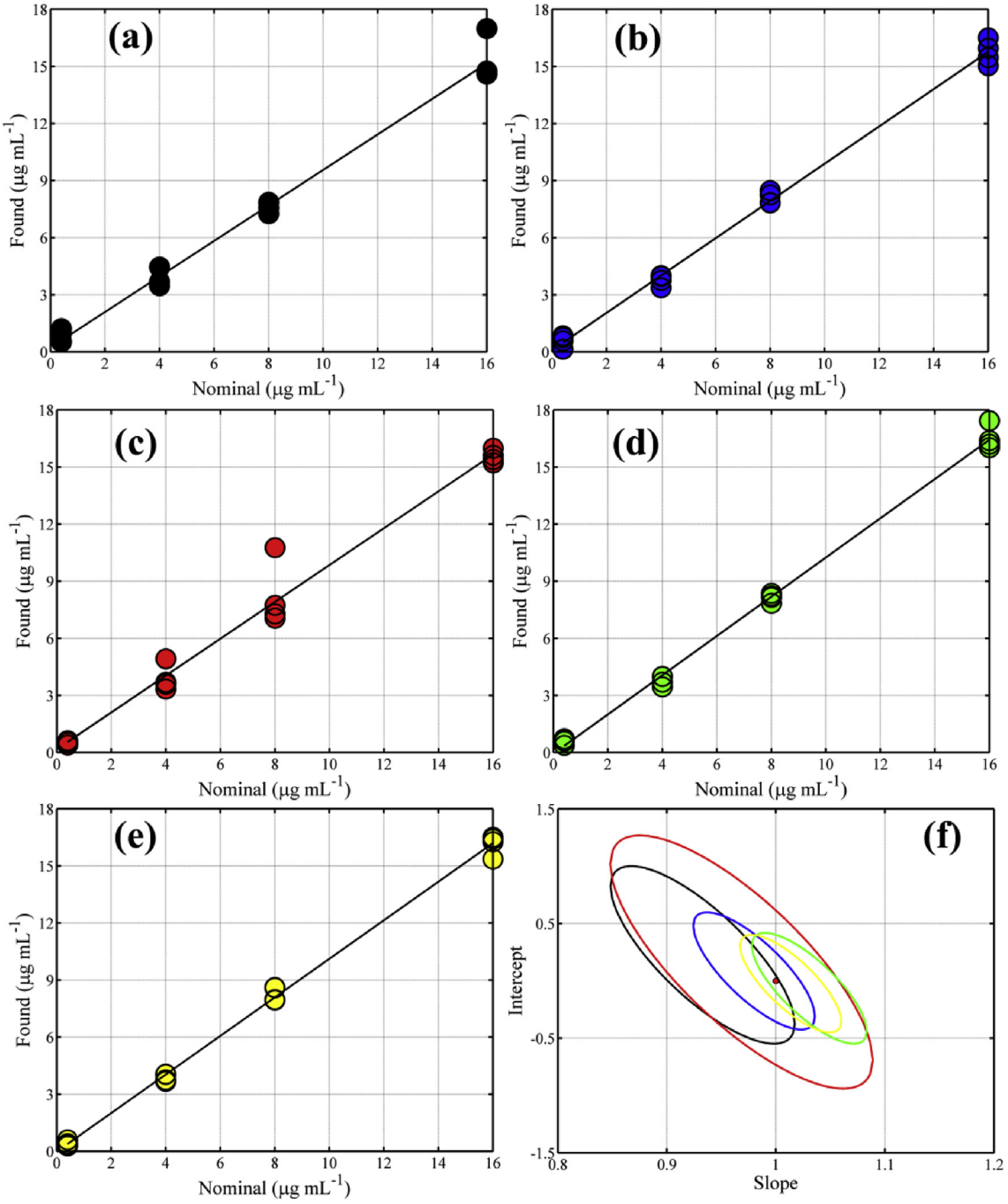


**Fig. 3.** Predict versus nominal plots for (a) TRY, (b) PHE, (c) PUT, (d) CAD, (e) HIS; (f) Elliptical joint confidence region for TRY (▬), PHE (▬), PUT (▬), CAD (▬), and HIS (▬).

beaker and homogenized with 30 mL of 0.6 M perchloric acid for 15 min with a magnetic stirrer. The homogenates were filtered through No. 2 filter paper (Whatman, Maidstone, England). The filtrates were then placed in volumetric flasks, and brought to a final volume of 50 mL with the 0.6 M perchloric acid. One milliliter aliquots of the fish extracts were than derivatized with dansyl chloride as explained before.

### 3.7. Recovery

In order to evaluate the recovery of the proposed methodology and if there is any matrix effect, spikes of each amine at three concentration levels (40, 90, and 170 $\mu g\ g^{-1}$) directly in the processed fish samples were made. Each sample was extracted and derivatized with dansyl chloride using the same procedure as for the non-spiked real samples.

## 4. Results and discussion

### 4.1. Calibration set

With the conditions reported in the *Chromatographic runs* section, the linear range was defined for each BA. Twelve concentration levels were chosen to cover the linear range of each amine. All analytes were calibrated in the linear range from 0.05 to 20:00 $\mu g\ mL^{-1}$. Each concentration was run in triplicate and their average used in data processing.

Two spectra per second were recorded in the 190–400 nm range (with 1 nm of resolution), the chromatographic run was 4 min. As can be seen in Fig. 1a, the TRY, PHE, PUT, CAD, and HIS derivatized analytes eluted at 2.00 2.53, 2.69, 2.97 and 3.32 min, respectively. Others sub-products eluted in less than 1.5 min. All analytes were completely eluted at about 3.50 min, resulting in a short isocratic run, with partial separations between them. Neither misalignment nor shape change was perceived in the chromatograms for the calibration set prepared with each individual standard solution.

The degree of overlap among the analyte spectral profiles is remarkable, especially for PUT and CAD, as shown in Fig. 1b (where the spectra shown were registered at each respective retention time for the calibration standard with the highest concentration) and in Fig. 1c (the normalized spectra). In the normalized spectra one can see that the PUT and CAD spectra profiles are identical. This occurs due to the dansyl derivatization process and the structural similarities between PUT and CAD, which brings the spectral selectivity close to zero, causing rank deficiency whenever a mixture of these two constituents are present in the LC-DAD matrix [25].

### 4.2. Synthetic samples, peak alignment and MCR-ALS treatment

Sixteen synthetic test samples containing the mixture of the five BAs in four concentration levels were prepared as described in the *Calibration and test samples* section, to assess the second-order advantage of HPLC-DAD data. Chromatograms for the test and calibration samples are shown in Fig. 2a.

Since two BAs have identical spectral profiles (Fig. 1b and c), it was not possible to augment the matrix in chromatographic mode, neither it was possible to augment in the spectral mode due to the temporal misalignment (Fig. 2a) without any treatment.

PUT and CAD are partially overlapped, which in this case leads to rank deficiency. To solve this problem, the strategy was first divide the chromatograms into regions, each region was then aligned with the icoshift algorithm [35,36]. The selected regions were chosen based on their elution profiles (Fig. 2), and on the signal to noise ratio of each individual analyte's spectra (Fig. 1b, 190–290 nm). As can be seen in Fig. 2b, it was possible to align PUT, and maintain the good alignment of the coeluted PHE since this algorithm aligns the chromatographic peaks by intervals.

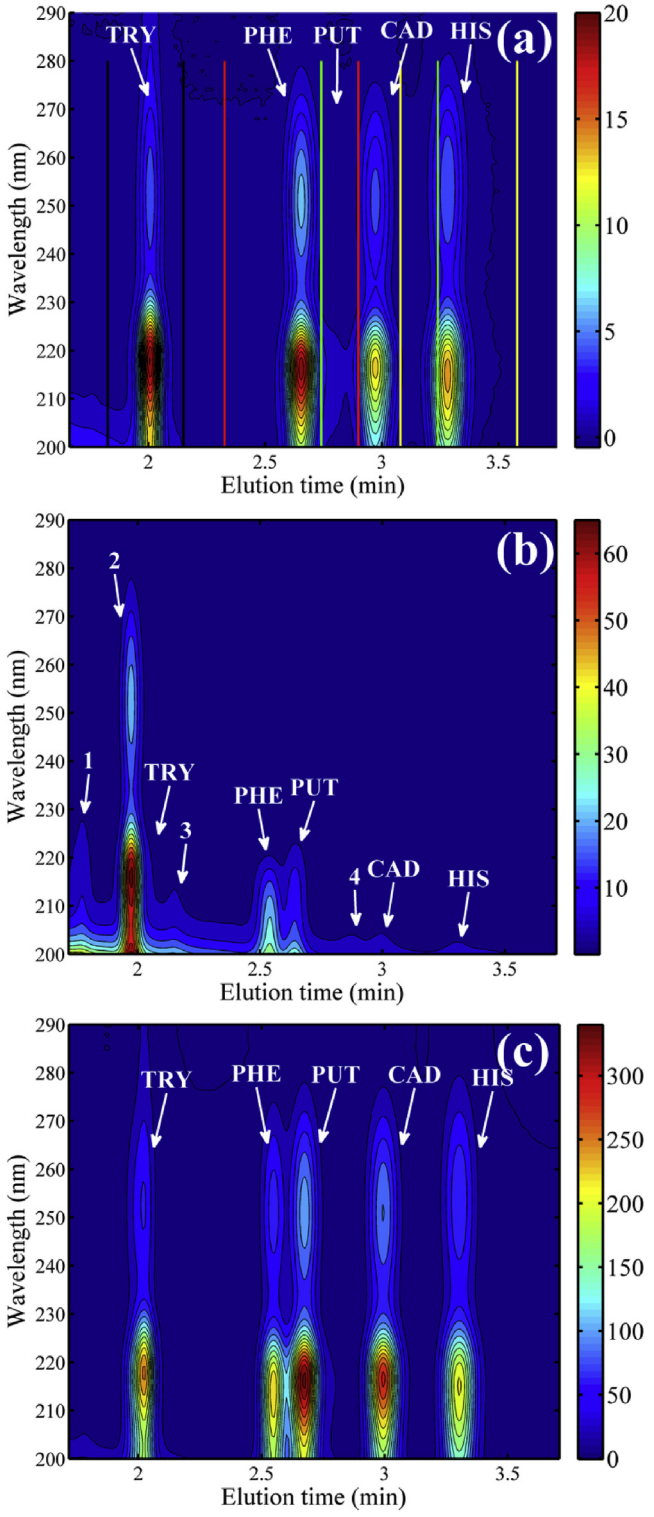


**Fig. 4.** The surface contours for the test sample 1 (a), real sample 2 un-spiked (b), and spiked with 40 $\mu g\ g^{-1}$ for all analytes (c). The vertical lines indicate elution time and wavelength ranges for TRY (■), PHE and PUT (■), CAD (■), and HIS (■). The analytes and interferents (1–4) are pointed out by arrows at the contour surface.

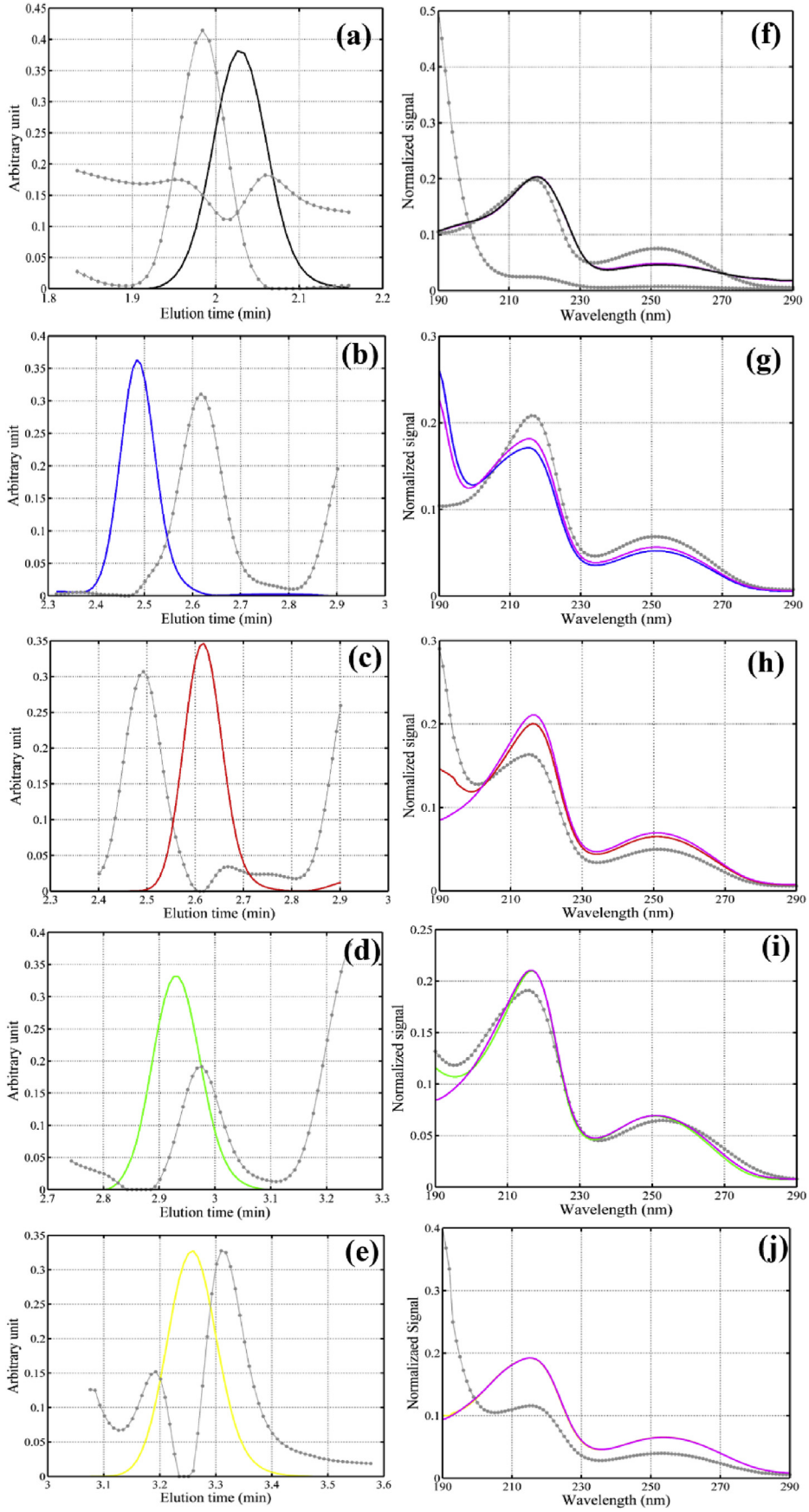


**Fig. 5.** Chromatographic (a, b, c, d, e) and spectral (f, g, h, i, j) profiles retrieved from sample *Seriola dumerili* for TRY (■), PHE (■), PUT (■), CAD (■), and HIS (■); and for the interferents (●). For comparison purposes, the spectral profile of the individual calibration standards was overlapped (■).

The selected regions reduced the interference between PUT and CAD. However, at certain concentration levels the quality of the retrieved profiles was affected. Therefore, in addition another strategy using a set of pure calibration standards and the correspondence among species was adopted [33,34]. This constraint strategy input on calculations that there is only a single constituent in the calibration set, so it is used to restrict the rotational ambiguity. This constrain is automatically used in mvc2 [40] graphical user interface when the user inputs which initial estimate profile is the analyte, and which is the interferent.

To perform MCR-ALS treatment, each individual sample and the calibration matrix was augmented on spectral mode and submitted to a SVD analysis to estimate the number of constituents. The spectral augmented matrix was used due to the overlap degree of this profile [27]. Then, the initial profiles of each constituent (analyte, interferent(s), and/or baseline) were calculated using a pure variable selection algorithm based on SIMPLISMA [29,37] with 10% of permitted noise. In order to guide the calculated profiles to an interpretable chemical result, an ALS optimization was applied to all matrices with the following restrictions: (a) non-negativity for the chromatographic and spectral modes, (b) uni-modality for analyte chromatographic profiles, and the (c) correspondence among species. The convergence was achieved with less than 40 iterations for all of the synthetic samples. A different model is obtained for each individual sample and the figure of merit shown at Table 2 is the mean value of the one obtained for each sample. As the time mode is normalized on this case, the quantitation and the figure of merit calculations were carried out with the area under the spectra profiles [27]. Table 2 shows the results of the MCR-ALS modeling for sixteen synthetic test samples. The low limits of detection (LOD) and quantification (LOQ) values, calculated as described by Olivieri and co-workers [44,45] using the mvc2 [40], show that a pre-concentration step was not necessary to achieve limits much lower as those established by FAO/WHO, and EFSA [7,8]. The relative error of prediction (REP) value below 10% for all predictions of the sixteen samples indicates a good accuracy for the proposed methodology [44,45].

The predictions for the sixteen samples were in agreement with the nominal values, as shown in Fig. 3a–e. Five elliptical joint confidence regions (EJCR) obtained, (based on a linear regression between nominal and predicted concentration) are presented in Fig. 3f. All EJCRs contain the ideal point for intercept and slope (0,1), indicating that the built models predicted the five analyzed BAs without significant bias at a 95% confidence level [46–48].

### 4.3. Real fish sample analysis

Three fish samples, goldfish (*S. maxillosus*), mackerel (*S. scombrus*), and Arabaiana (*S. dumerili*) were analyzed in order to evaluate the efficiency of the proposed methodology. The fresh fish samples were acquired at the local market and processed as described in the *Sample pretreatment* section, and then injected into the chromatographic system.

The contour surface for test sample 1 presents the expected five BAs (Fig. 4a), while the un-spiked real sample 2 (Fig. 4b) shows the four other constituents (indicated by numbered arrows) that coeluted with the analytes. Due to the scale factor, these four interferents cannot be seen in real sample 2 spiked with 40 $\mu g\ g^{-1}$of five BAs (Fig. 4c).

As can be seen in Fig. 5, interferences associated with non-calibrated constituents or with the baseline profile were identified for all BAs. The retrieved MCR-ALS profiles of the real sample *S. dumerili* for chromatographic and spectral modes are presented in Fig. 5a–e and Fig. 5f–j, respectively. It is worth to note that the retrieved spectral profiles are very similar to those acquired from each calibration standard (see Fig. 5f–j). This similarity is confirmed by $S_{12}$ estimated by Eq. (2) [26], whose obtained values were 0.9999, 0.9965, 0.9907, 0.9981 and 0.9999 for TRY, PHE, PUT, CAD, and HIS, respectively. The absent of rotational ambiguity in the retrieved MCR-ALS profile is shown in Table 1S, in the supplementary materials, where the difference between the fmax and fmin values are close to zero for all the studied biogenic amines [30,39]. In Table 1S the differences between fmax and fmin values for the models made with and without the trilinearity constrain are compared; and Table 2S shows the adjustments between these models [39].

$\mathbf{S_{12}}$ is the similarity between the two spectra,

$$S_{12} = \frac{\|s_1^T s_2\|}{\|s_1\|\,\|s_2\|} \quad (2)$$

where, $\mathbf{S_1}$ is the normalized spectrum of calibration standard with the higher concentration, $\mathbf{S_2}$ is the normalized MCR-ALS spectral profiles of the real sample. $\mathbf{S_{12}}$ ranges on a scale from 0 to 1, where 0 means that there is no similarity between the compared profiles ($\mathbf{S_1}$ and $\mathbf{S_2}$), and $\mathbf{S_{12}}$ equal to 1 indicates identical profiles.

### 4.4. Recovery test

The performance of the proposed methodology was evaluated by recovery tests done at three concentration levels. The predicted

**Table 3**
Recovery test for biogenic amines on fish samples using the MCR-ALS model.

| Fish type | TRY[a] | | | PHE[a] | | | PUT[a] | | | CAD[a] | | | HIS[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Taken | Found[b] | R[c] | Taken | Found[b] | R[c] | Taken | Found[b] | R[c] | Taken | Found[b] | R[c] | Taken | Found[b] | R[c] |
| *Salminus maxillosus* | – | 10.7(0.8) | | – | 8.7(0.5) | | – | 5.9(0.7) | | – | 5.2(1.6) | | – | 1.5(1.0) | |
| | 40.0 | 49.1(0.6) | | 40.0 | 37.3(0.4) | | 40.0 | 37.0(0.6) | 77.7 | 40.0 | 33.4(1.5) | 70.4 | 40.0 | 41.5(0.8) | |
| | 90.0 | 75.6(0.6) | | 90.0 | 65.5(0.4) | | 90.0 | 64.7(0.5) | 65.3 | 90.0 | 106.4(1.6) | 112.4 | 90.0 | 78.4(0.8) | |
| | 170.0 | 120.4(0.8) | | 170.0 | 135.1(0.6) | | 170.0 | 152.9(1.0) | 86.5 | 170.0 | 188.9(1.4) | 108.1 | 170.0 | 131.8(1.2) | |
| *Scomber scombrus* | – | 7.8(0.8) | | – | 9.4(0.5) | | – | 4.8(0.7) | | – | 5.2(1.6) | | – | 1.7(1.0) | |
| | 40.0 | 47.7(0.6) | 99.7 | 40.0 | 58.7(0.4) | 123.1 | 40.0 | 43.7(0.6) | 97.4 | 40.0 | 50.4(1.3) | 113.0 | 40.0 | 58.2(0.8) | |
| | 90.0 | 93.5(0.7) | 95.2 | 90.0 | 94.4(0.5) | 94.4 | 90.0 | 94.0(0.7) | 99.1 | 90.0 | 94.5(1.5) | 99.2 | 90.0 | 126.3(1.2) | |
| | 170.0 | 173.2(1.3) | 97.3 | 170.0 | 166.9(0.7) | 92.1 | 170.0 | 171.5(1.2) | 98.1 | 170.0 | 168.4(2.5) | 96.0 | 170.0 | 224.7(2.2) | |
| *Seriola dumerili* | – | 14.0(0.7) | | – | 8.9(0.5) | | – | 11.6(0.7) | | – | 15.5(1.5) | | – | 2.3(1.0) | |
| | 40.0 | 44.8(0.6) | 76.9 | 40.0 | 48.5(0.4) | 98.8 | 40.0 | 51.4(0.6) | 99.6 | 40.0 | 57.6(1.3) | 105.5 | 40.0 | 52.0(0.8) | |
| | 90.0 | 82.6(0.7) | 76.2 | 90.0 | 95.6(0.4) | 96.2 | 90.0 | 95.8(0.7) | 93.6 | 90.0 | 101.8(1.5) | 95.9 | 90.0 | 108.6(1.1) | |
| | 170.0 | 155.5(1.1) | 83.2 | 170.0 | 167.9(0.6) | 93.5 | 170.0 | 169.4(1.1) | 92.9 | 170.0 | 170.9(2.5) | 91.4 | 170.0 | 202.0(2.0) | |

[a] Corrected concentration taking in account the extraction procedure in $\mu g\ mL^{-1}$. Recovery (R) is expressed in percentage.
[b] Predicted concentration for real sample with MCR-ALS model. Standard deviation between parentheses.
[c] The recovery value is not shown when the matrix effect is present.

concentration values of the proposed methodology for real and spiked fish samples are shown in Table 3. Good recoveries were obtained for all BAs with average values of 88.08%, 99.68%, 90.01% and 99.10% for TRY, PHE, PUT and CAD, respective.

It worth highlighting that the matrix effect was identified for TRY, PHE and HIS in *S. maxillosus*, and HIS in all the samples. This was statistically confirmed (p-values $< 0.05$) by comparing the slope and intercepts of the pseudo-univariate calibrations between the synthetic samples and the real samples [49]. As can be seen in Table 3 the TRY, PHE and HIS concentration values were underestimated for *S. maxillosus*, while the HIS values are overestimated for the other samples. This phenomena is also shown in Fig. 1S in the supplementary materials. To perform a quantitation in this case, each sample, with and without the standard addition of the studied amines was spectrally augmented, and the areas under the retrieved spectra were correlated with the standard addition concentrations, as is also done for the univariate standard addition method [49,50].

### 4.5. Degradation study

Three samples of fish were left to degrade in the refrigerator at 4 °C for 12 days. Five grams of each sample were collected every two days, and analyzed by the proposed methodology. The degradation evolution is shown in Fig. 6. The predicted concentration ranged from 7.82 to 29.41 μg $g^{-1}$, 4.21–25.94 μg $g^{-1}$, 3.11–28.54 μg $g^{-1}$, 5.19–39.95 μg $g^{-1}$, and 0.36–52.62 μg $g^{-1}$ for TRY, PHE, PUT, CAD, and HIS, respectively. After 12 days of storage at 4 °C, only one sample passed the HIS concentration limit of 50 μg $g^{-1}$ established by FAO/WHO, and EFSA [7,8].

Since the samples were stored at 4 °C, sample spoilage did not rapidly evolve, and the biogenic amine (BA) concentrations did not increase. Moreover, production of BAs depends of the microorganisms present in food. Thus, fluctuation on the concentration levels might be ascribed to the sample heterogeneity and sampling, even though an amount of 5 g of the sample has been collected, as can be seen in Fig. 6a.

### 4.6. Proposed versus others methodologies

Table 4 summarizes various methodologies for quantitation of BAs in fish samples. Almost all methods make use of TCA or $HClO_4$ for the extraction procedure, dansyl-chloride as the derivatizing reagent, and gradient elution. The proposed methodology uses an isocratic elution which is seven times faster, and presents similar analytical figures of merit. Moreover, by employing MCR-ALS, it has the second order advantage that allows circumvention of the presence of unexpected constituents on the real sample, even if these interferents present similar spectral profile.

## 5. Conclusion

This study demonstrated that MCR-ALS is a powerful chemometric tool; developing a fast chromatographic method for selective and sensitive quantitation of five BAs (TRY, PHE, PUT, CAD, and HIS), in fish samples. The proposed method uses chemical derivatization with dansyl, which may lead to co-elution of both expected and unexpected constituents with the same spectral profile, yielding to a system with rank deficiency. Moreover, the chromatographic data also presented peak misalignment. By using peak alignment with icoshift and one MCR-ALS model for each analyte using the spectral augmented matrix, it was possible to handle both temporal misalignment and rank deficiency when proper constrains are applied.

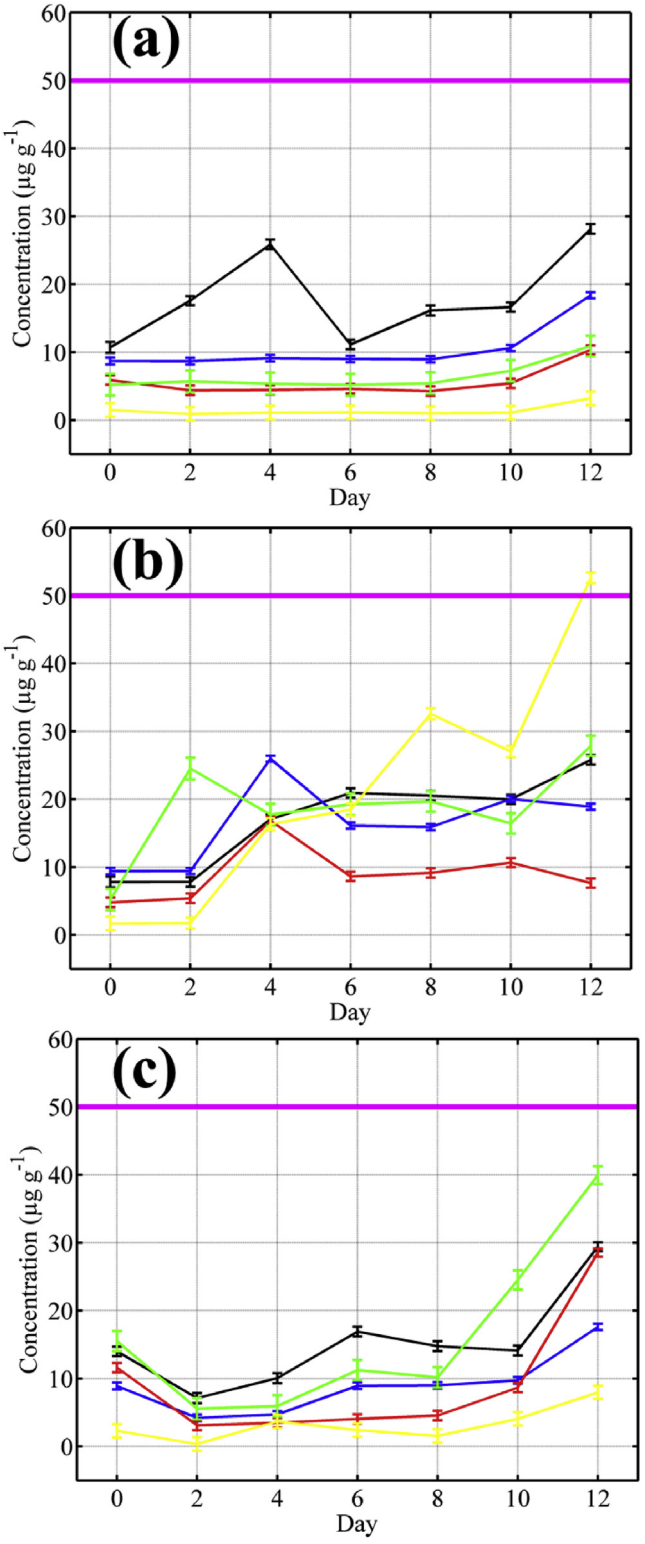


**Fig. 6.** The degradation evolution of (a) *Salminus maxillosus*, (b) *Scomber scombrus*, and (c) *Seriola dumerili* at 4 °C for 12 days. TRY (▬), PHE (▬), PUT (▬), CAD (▬) and HIS (▬) and (▬) the histamine concentration limit of 50 μg $g^{-1}$ established by FAO/WHO, and EFSA [7,8].

The proposed methodology used isocratic elution being seven times faster and presented similar or slightly better analytical figures of merit when compared to previous studies, consuming less solvent in accordance with green analytical chemistry principles. The REP (below 10%), and the average recovery (ranging from 88.08% to 99.68%) are outstanding results achieved by the pro-

**Table 4**
Some chromatographic methodologies reported in the last years for biogenic amine quantitation in fish samples.

| Sample | Sample treatment[a] | Derivatization reagent[b] | Biogenic amine[c] | Method | Range (μg mL$^{-1}$) | Detection | Elution time and mode | LOD (μg mL$^{-1}$) | Recovery (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Tuna fish | 5% TCA | OPA | 5 | HPLC-FLD | 5–100 | Fluorescence Ex: 320 nm Em:523 nm | 14 min (Isocratic) | 1.50 | 95.73–104.78 | [5] |
| Fish and fish products | 5% TCA | D-Cl | 1–6, 12–13 | HPLC-FLD | 1–40 | Fluorescence Ex: 350 nm Em:520 nm | 26 min (Gradient) | 0.02–0.24 | 80.90–97.40 | [13] |
| Fish products | 0.4 M $HClO_4$ | D-Cl | 1–6, 12–13 | HPLC-DAD | 2.5–400 | UV at 254 nm | 20 min (Gradient) | 0.57–1.80 | 68.90–108.70 | [14] |
| Seafood | 0.4 M $HClO_4$ | D-Cl | 1–7, 12–13 | HPLC-DAD | 0.5–100 | UV at 254 nm | 12 min (Gradient) | 0.20–1.20 | 87.00–121.00 | [15] |
| Fish | 5% TCA | D-Cl | 1, 3–6, 12–13 | HPLC-DAD | 0.5–100 | UV at 254 nm | 20 min (Gradient) | 0.02–0.26 | 73.20–107.00 | [16] |
| Fish | 0.6 M $HClO_4$ | OPA | 1–7, 9, 12–15 | UHPLC-FLD | 0.1–50 | Fluorescence Ex: 340 nm Em: 445 nm | 7 min (Gradient) | 0.05–0.3 | 83.68–98.81 | [17] |
| Anchovy | 0.6 M $HClO_4$ | – | 3–6 | UPLC-MS/MS | 0.01–0.75 | MS/MS | 8.5 min (Gradient) | 0.01–0.02 | 71.40–108.40 | [18] |
| Fish cubes | 6% TCA | D-Cl | 1–7, 11–12 | HPLC-DAD | 0–20 | UV at 254 nm | 30 min (Gradient) | 0.05–0.5 | 55.6–113.7 | [39] |
| Fish | 0.6 M $HClO_4$ | D-Cl | 1–5 | HPLC-DAD-MCR-ALS | 0.05–20 | UV from 190 to 290 nm | 3.6 min (Isocratic) | 0.14–0.50 | 88.08–99.68 | [this work] |

[a] Extracted with TCA – trichloroacetic acid or $HClO_4$ – perchloric acid.
[b] OPA – o-phthalaldehyde, D-Cl – Dansyl-chloride.
[c] Tryptamine (1), Phenylethylamine (2), Putrescine (3), Cadaverine (4), Histamine (5), Tyramine (6), Agmatine (7), Methylamine (8), Dopamine (9), Ethylamine (10), Isopentylamine (11), Spermidine (12), Spermine (13), Serotonin (14), Octopamine (15).

posed method. The limits of quantification for the five BAs (without a pre-concentration step) are much lower than those established by FAO/WHO, and EFSA.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.aca.2015.10.043.

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