Analytica Chimica Acta 902 (2016) 59–69

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

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

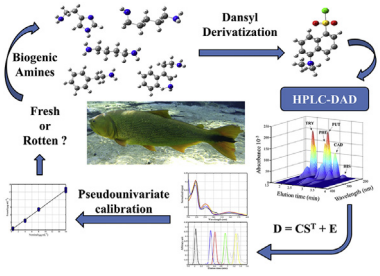
Licarion Pinto[a], César Horacio Díaz Nieto[b], María Alicia Zón[b], Héctor Fernández[b], Mario Cesar Ugulino de Araujo[a,*]

[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



ARTICLE INFO

Article history:
Received 16 May 2015
Received in revised form 27 October 2015
Accepted 28 October 2015
Available online 7 November 2015

Keywords:
Biogenic amines
Dansyl derivatization
Rank deficiency
High performance liquid chromatography
Icoshift
Multivariate Curve Resolution

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).

http://dx.doi.org/10.1016/j.aca.2015.10.043
0003-2670/Published by Elsevier B.V.

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.

Published by Elsevier B.V.

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