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Analytical Methods

Development of a chromatographic low pressure flow injection system using amperometric detection: Application to the analysis of niacin in coffee

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ABSTRACT

In this work, an analytical flow system able to perform low pressure chromatography with amperometric detection is presented. As case study, the determination of niacin (vitamin B3) in coffee brewed samples was selected. The manifold comprised a 1.0 cm length monolithic column coated with didecyldimethylammonium bromide, a laboratory-made boron doped diamond electrode, and featured in-line ionic strength adjustment of the mobile phase. The figures of merit concerning the selected case study namely, detection limit, 7.90×10^{-7} M, determination rate, ca. 10 samples h^{-1}, mobile phase and ISA solution consumption, ca. 2.6 mL per analysis, and CV, below 5% for retention time and peak height, showed the competitiveness of this analytical strategy comparing to the described HPLC methods for niacin determination. The strategy displays a simple configuration, low cost, fast and easy assembling, foreseeing its use to general purpose applications.

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1. Introduction

Recently, the coupling of short length monolithic columns into usual flow analysis systems (Satinsky, Solich, Chocholous, & Karlicek, 2003) has triggered the development of analytical methodologies based on this approach (González-San Miguel, Fernández, Estela, & Cerdà, 2009; Hartwell, Kehling, Lapanantnoppakhun, & Grudpan, 2013; Paull & Nesterenko, 2005). The main advantage of this strategy is the extra selectivity inherent to chromatographic columns that can now be added to the well-known potentialities of flow analysis systems. From an instrumental point of view, the majority of low pressure chromatographic methodologies use UV–Vis spectrophotometers as detection systems (Connolly, Victory & Paull, 2004; García-Jiménez, Valencia, & Capitán-Vallvey, 2007) and, to a lesser extent, conductimetric (Pelletier & Lucy, 2006; Victory, Nesterenko, & Paull, 2004) and amperometric detectors (Hart & Jordan, 1989). The lack of methodologies based on amperometric detection with chromatographic separation can be due to the main challenges arising from coupling these detectors to the usual non-polar chromatographic columns: the incompatibility of the detectors toward organic solvents, as well as the incompatibility of chromatographic columns toward mobile phase solutions of high ionic content. In this context, the versatility of low pressure flow systems to perform in-line sample/solutions conditioning can contribute to overcome these problems (Trojanowicz, 2011).

In this work, an analytical methodology able to quantify niacin in coffee matrices using a low pressure flow system comprising a short length monolithic column previously coated with a cationic surfactant and an amperometric detection system (using a boron doped diamond (BDD) electrode as working electrode) is presented. The interest over the determination of niacin in coffee is due to two main reasons. Firstly, coffee is a significant source of this vitamin regarding the human uptake (100 mL cup of a medium roasted coffee can supply ca. 20% of the daily Dietary Reference Intake) (Chu, 2012, chap. 2) and secondly, the concentration of this compound has been correlated to the roasting extent of coffee. The analytical methodologies available to perform this determination are scarce due to the low level of this analyte, lower than 3×10^{-4} g/g of dry weight basis (Casal, Oliveira, & Ferreira, 1998; Perrone, Donangelo, & Farah, 2008), within a sample matrix that suffers continuous chemical changes during its roasting process. The determination of niacin in coffee matrices is usually performed by HPLC using ODS columns with gradient elution and molecular absorption spectrophotometry (Alves & Dias, 2006; Casal,

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Oliveira, & Ferreira, 2000; Casal et al., 1998) or mass spectrometry detection (Perrone et al., 2008). The main challenge described in the referred works using spectrophotometric detection is the optimization of the experimental conditions so that it becomes feasible to resolve niacin chromatographic signal from the remaining compounds in the coffee extract, especially trigonelline. With respect to the methodology based on HPLC with mass spectrometry detection, the main handicap is the high equipment cost inherent to this technology.

The analytical approach described in this work aims to illustrate the feasibility of using a low cost, and easy assembling manifold to be applied in the determination of analytes at low levels within complex matrices.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared using deionized water with a specific conductance of less than 0.1 $\mu S\,cm^{-1}$. All reagents were used as purchased without additional purification.

Stock solutions of niacin 1.00×10^{-3} M were prepared weekly through rigorous weighing of the reagent (Sigma Aldrich, N4126, $\geqslant$98%). Standard solutions of niacin were daily prepared by rigorous dilution of the stock solution. Column conditioning solutions were prepared using didecyldimethylammonium bromide (DDAB) (Aldrich, 382310, 98%) and acetonitrile (Merck, 1.00030.5000, gradient grade for liquid chromatography). HCl (Merck, 1.00317.2501, 37%) and NaCl (Merck, 1.06404.1000, $\geqslant$99.5%) were used in the preparation of the mobile phase solution and ionic strength adjustment (ISA) solution.

2.2. Column coating and conditioning

The procedure for column coating with DDAB was based on the experimental protocol described by Hatsis and Lucy (2003). It consisted in propelling sequentially the following solutions, at a flow rate of 0.5 $mL\,min^{-1}$: (a) acetonitrile, water, 50/50, v/v (40 min); (b) acetonitrile, water, 5/95, v/v (5 min); (c) acetonitrile, water, 5/95, v/v, 1 mM DDAB (1 h); and finally, (d) HCl 0.0025 M (1 day). The last step aimed to wash thoroughly the monolithic column until the excess of DDAB was purged, since the leaching of this compound reduced the sensitivity of the BDD electrode.

The column coating was stable for at least one month, operating on a daily basis. The column performance was evaluated on a routine basis through injection of niacin standard solutions. The column coating procedure was performed either when resolution significantly decreased or the flow system backpressure increased, the latter indicated by observing higher retention times for niacin.

At the end of each working day, the column was kept in HCl 0.0025 M.

2.3. Apparatus

2.3.1. Electrochemical detection system

The electrochemical system was composed of a BDD electrode (Windsor Scientific, 3 mm Ø, one-side polished, DIAFILM PE R0030-0500P1) as working electrode, an Ag/AgCl double junction electrode (Metrohm, 6.0728.000) as reference electrode and a glassy carbon rod electrode (Metrohm, 6.1247.000) as auxiliary electrode. The working electrode was constructed as follows. A shielded electrical wire was fixed over the non-polished side of the BDD disk using conductive silver resin and metallic silver, as described elsewhere (Santos, Lima, Quinaz, Rodríguez, & Barrado, 2007). After the hardening of the conductive resin, the BDD disk was then fixed with a non-conductive epoxy resin at the top of a PMMA cylinder with 7 mm e.d., 4 mm i.d., with the BDD polished side facing the outer part of the PMMA cylinder.

Electrochemical measurements, namely cyclic voltammetry and multiple pulse amperometry, were performed using an Autolab system (EcoChemie model PStat 10) controlled by GPES 4.8 software for Windows. Peak height measurements of the chromatographic peaks were performed using GPES 4.8 software.

2.3.2. Flow manifold

A low pressure chromatographic flow system similar to the one previously evaluated in a recent work was assembled (Santos & Rangel, 2012). The flow system included a peristaltic pump (Gilson, Minipuls 3), an injection valve (Rheodyne 5020), a 1.0 cm length C18 reversed phase monolithic column (Chromolith RP-18E, Merck, 1.51471.0001), and the electrochemical system as mentioned above. This manifold configuration enables a maximum flow rate of ca. 2.5 $mL\,min^{-1}$ at pressures below 5 bar. The coupling of the working electrode at the end of the monolithic column, through a wall-jet configuration, was achieved with a laboratory-made confluence made of non-conductive epoxy resin.

Furthermore, the confluence was aimed to allow a tight fit of the monolithic column and to enable the on-line adjustment of the ionic strength of the eluate. The confluence presented three channels of 0.8 mm i.d., namely for inlet of ISA solution, inlet of eluate, and exit of the resulting mixture toward the reference and auxiliary electrodes.

Tygon tubing of 0.89 mm i.d. and of 0.38 mm i.d. were used to propel the mobile phase and ISA solutions, respectively. PTFE tubing of 0.8 mm i.d. was used for the remaining flow connections.

The distance between the injection valve and the working electrode surface was as short as possible (6 cm). Fig. 1 depicts schematically the flow assembly.

The operation of the flow system was as follows. Initially, the mobile phase solution (propelled through the monolithic column) and the ionic strength adjustment solution were continuously propelled and merged at the confluence toward the detector until a stable baseline was achieved. Thereafter, for sample analysis, the loop of the injection valve was loaded and the content injected toward the column, where the chromatographic separation took place. Finally, as already mentioned, the ionic strength of the eluate was adjusted with the ISA solution at the confluence, heading toward the surface of the BDD electrode, where the electrochemical detection occurred.

2.4. Sample analysis procedure

2.4.1. Coffee samples

Niacin analysis was performed in coffee samples during the roasting process and in commercially roasted samples. For roasting trial purposes, two non-defective green coffee sample varieties respectively, *arabica* (from Colombia) and *robusta*, (from Indonesia) were purchased from local stores. Commercially available roasted coffee samples were randomly selected to encompass the usually consumed coffee-based beverages, i.e. soluble coffee, decaffeinated coffee, insoluble coffee (dark and light roast) and coffee cereals mixture.

2.4.2. Green coffee samples roasting

Roasting was performed for each sample at four different periods, respectively, 8.0, 12.0, 25.0 and 45.0 min in a preheated oven at 200 °C. The roasting experimental conditions intended to provide a light, medium, dark and very dark roasting profile, respectively (Farah, Monteiro, Calado, Franca, & Trugo, 2006). Then, ca.

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