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Low pressure ion pair chromatography with amperometric detection for the determination of trigonelline in coffee samples

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ABSTRACT

In this work, the use of ion pair chromatography strategy in low pressure chromatographic flow systems is explored for the first time. The straightforward flow manifold encompassed a peristaltic pump, an injection valve and a 1 cm-length C_{18} monolithic column. The amperometric detection system relied on a boron-doped diamond electrode, used as working electrode. The determination of trigonelline in coffee samples was the case-study selected. This alkaloid is an important quality marker for this commodity and is usually determined using HPLC-UV methodologies. The proposed methodology, based on ion-pair chromatography with amperometric detection, enabled the quantitative resolution of the studied analyte from the matrix compounds by adding to the mobile phase the ion pair reagent, 1-tetradecanosulfonate sodium. The present work, following the recent developments of the low pressure chromatography approach, demonstrates the potentialities of coupling monolithic columns to traditional flow analysis systems for separation and quantification of ionic or ionisable compounds.

1. Introduction

Automatic systems joining low pressure flow manifolds and monolithic columns are a recent analytical approach, that combines the high selectivity inherent of chromatographic columns and the well-recognized potentialities of low pressure flow systems (González-San Miguel, Fernández, Estela, & Cerdà, 2009).

In low pressure flow systems, C_{18} monolithic columns are the ones most frequently used in the development of multi-parameter methodologies for non-ionic compounds (Ballesta Claver, Valencia, & Capitán-Vallvey, 2009; García Jiménez, Valencia, & Cápitan-Vallvey, 2009) and, more recently, for the separation of ionic compounds. In order to achieve this capability, coating of the stationary phase with a surfactant (Chambers, Glenn, & Lucy, 2007) has been the strategy followed. Retention of anions can be achieved using a cationic surfactant as didodecyldimethylammonium bromide (Connolly & Paull, 2002) or cetyltrimethylammonium chloride (Ito, Takayama, Makabe, Mitsui, & Hirokawa, 2005), while cations can be retained using anionic surfactants as dioctyl sulfosuccinate sodium (Connolly, Victory, & Paull, 2004). To this same aim, the use of ion pair reagents (IPR) has not yet been exploited in low pressure flow systems. These reagents are a versatile alternative to control the retention of ionic compounds, supported by the high number of different IPRs available, to impart to the analytical system the desired selectivity toward each analytical challenge. Furthermore, since no permanent coating is involved, coating long term stability (Chambers et al., 2007) is not an issue when using IPRs, if compared to the use of surfactants. A further and recent development upon these low pressure chromatographic systems exploited the use of electrochemical (amperometric) sensors (Santos & Rangel, 2015) instead of the commonly UV–Vis detectors. Despite the usual good sensitivity of the amperometric sensors, their scarce utilization within chromatographic flow systems can be understood due to two main reasons: the low ionic strength of the mobile phases usually employed which impart higher background electrical noise, and; the low repeatability of the solid electrodes' analytical response due to passivation phenomena. With the recent developments of new electrode materials, in addition to the several electrochemical measurement modes available, higher reproducibility and sensitivity can be attained, imparting higher analytical performance to this approach.

Trigonelline is an alkaloid compound that occurs in green coffee at concentration levels within 0.4–1.8% w/w (Campa et al., 2004). This compound is an important precursor of flavoured compounds during coffee roasting (Farah, Monteiro, Calado, Franca, & Trugo, 2006; Franca, Mendonça, & Oliveira, 2005) and correlates with coffee cup quality due to its direct contribution to perceived bitterness (del Campo, Berregi, Caracena, & Zuriarrain, 2010). Trigonelline

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concentration in green coffee depends mainly on the coffee species (Campa et al., 2004), green bean maturation state (Clifford & Kazi, 1987) and post-harvesting processing method (Duarte, Pereira, & Farah, 2010). Defective beans as black or sour beans present less trigonelline concentration (Franca, Oliveira, Mendonça, & Silva, 2005). Furthermore, during the roasting procedure, trigonelline concentration decreases to at least 50% of its initial value (Farah et al., 2006; Franca, Oliveira, et al., 2005). In this process, several compounds are formed, particularly pyrazines, alkyl-pyridines, furans and pyrroles (De Maria, Trugo, Moreira, & Werneck, 1994; Ky et al., 2001), which have been correlated with the sensory profile of coffee beverage. This context highlights the importance of developing simple analytical methodologies to quantify this analyte in coffee samples. The inherent complexity of both green and roasted coffee matrix, the ionic character of trigonelline (positively charged in acidic media and a zwitterion at pH > 4) and the low occurrence of this analyte, especially in roasted coffee, are difficulties to be surpassed in a method development. The majority of methodologies described in the literature for the determination of trigonelline in coffee is based in reverse phase HPLC with UV–Vis detection, as it was reviewed by Jeszka-Skowron, Zgola-Grzeskowiak, and Grzeskowiak (2015): in the referred methodologies one can observe the low retention times for trigonelline in C_{18}-chromatographic columns, and the difficulty upon resolution of this analyte with other less-retained matrix compounds. This feature is a consequence of the low retention ability of these columns toward ionic compounds. Ionic chromatography or ion pair chromatography approaches, by previous coating of the C_{18} column with polybutadiene-maleic acid, PBDMA (Martin, Pablos, Bello, & Gonzalez, 1997), or by adding octanesulfonate to the mobile phase (Arai et al., 2015), respectively, were also exploited.

In this work, a low pressure ion pair chromatographic flow system with amperometric detection is exploited. As case-study, trigonelline determination in coffee was assayed. The study of the mobile phase composition for trigonelline peak resolution, and the experimental conditions, in terms of electrochemical measurement mode and supporting electrolyte medium, to achieve a good sensitivity and repeatability in the electrochemical signal are discussed.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with deionized (specific conductance of < 0.1 μS cm^{-1}) and filtered (0.45 μm) water. Reagents were used as purchased without further purification. Trigonelline hydrochloride (Sigma-Aldrich, T5509, ≥97.5%) 1.00×10^{-3} mol L^{-1} stock solutions were prepared weekly, after rigorous weighing of the reagent. Standard solutions of trigonelline were prepared daily by rigorous dilution of the stock solution.

Niacin (Sigma-Aldrich, N4126, ≥98%), caffeine (Fluka, 27,600, ≥99%), chlorogenic acid (Aldrich, C3878, ≥ 95%) and caffeic acid (Sigma, C0625, ≥98%) were used for interferences studies. Benzoic acid (Merck, 8.22257.1000, ≥99%) was used for electrochemical studies.

Mobile phases were prepared using acetonitrile, (Fisher Chemical, A/0627/17, HPLC gradient grade, 99.99%) and orthophosphoric acid (Fisher Chemical, O/0515/PB08, HPLC electrochemical grade, > 85%).

Tetrabutylammonium phosphate monobasic (Sigma-Aldrich, 86,833, ≥99.0%), sodium 1-octanesulfonate monohydrate (Sigma-Aldrich, 74,882, for ion pair chromatography, ≥99.0%) and sodium 1-tetradecanesulfonate (Sigma-Aldrich, 87,191, for ion pair chromatography, ≥99.0%) were used as ion pair reagents.

The ionic strength adjustment (ISA) solutions were prepared using HCl (Fisher Chemical, H/1200/PB17, 35.9%) and NaCl (Sigma-Aldrich, 31,434, ≥99.8%).

All solutions were kept at room temperature.

2.2. Flow system

A low pressure chromatographic flow manifold with amperometric detection, similar to the one referred in a previous work (Santos & Rangel, 2015) was assembled. Likewise, the flow system comprised a peristaltic pump (Gilson, Minipuls 3) to propel the mobile phase (tygon tubing of 1.02 mm i.d. - Gilson, Inc., F117938) and ISA solutions (tygon tubing of 0.38 mm i.d. - Gilson, Inc., F117933), a low pressure injection valve – (Rheodyne, 5020–34 μL loop), a 1-cm length monolithic column (Merck, Chromolith RP-18e) housed in a column holder (Merck, 1.51471.0001), and a laboratory-made confluence of poly(methyl methacrylate) which enabled the coupling of the working electrode within a wall-jet configuration and, the in-line mixture of the eluate with the ISA solution before detection.

The differences were as follows: with respect to the electrochemical system, the working electrode was a boron doped diamond electrode housed in a PEEK body (Windsor Scientific, 3 mm Ø, 3MMDIAM.BDD.PEEK). The electrochemical signals were measured using a potentiostat μAutolab Type II, controlled through GPES 4.9 software (EcoChemie B.V., Utrecht, The Netherlands). With respect to the flow network, the following change was performed: a nylon syringe filter, 25 mm Ø, 1.0 μm (Whatman, 6750-2510), was placed in the mobile phase line between the peristaltic pump and the injection valve in order to extend the monolithic column lifetime. This filter was replaced after each 5 working days.

The flow system respected all previously referred cautions (Santos & Rangel, 2015), particularly short length distances (< 2 cm) between the injection valve and the monolithic column as well as between the column-end and the working electrode were kept to minimize band broadening.

2.3. Low pressure chromatographic system operation

Each mobile phase and ISA solutions prepared were previously deaerated by means of an ultrasounds bath, before being used. Next, the selected mobile phase and ISA solutions were simultaneously propelled by the peristaltic pump at 7.50 rpm (flow rates were 0.71 mL min^{-1} and 0.14 mL min^{-1} for mobile phase and ISA solution respectively). At this point, column equilibration with the ion pair mobile phase solutions takes place and, at the column end, in the confluence, the eluate is mixed with the ISA solution immediately before this mixture reaches the working electrode, enabling the stabilization of the electrode response.

This is an important procedure to be accomplished before beginning sample analysis since column equilibration period with IPRs depends of the IPR concentration used. Column equilibration period is longer when IPRs are present in the mobile phase than under traditional partition chromatography conditions, as complete equilibria of the IPR with the stationary phase needs to be previously established. Considering a mobile phase composition of sodium 1-tetradecanesulfonate, 0.25 mmol L^{-1}, acetonitrile, 10% v/v, H_3PO_4 1% w/w and a flow rate of ca. 0.85 mL min^{-1}, a conditioning period of 90 min was typically necessary. Analysis were carried out when stable intensity of current baseline was reached (Δi < 0.5 μA/ 5 min^{-1}). For so, the sample loop (34 μL) was loaded with the sample and thereafter injected toward the monolithic column where the chromatographic separation takes place. As previously mentioned, the eluted analytes were automatically mixed with the ISA solution at the column-end, immediately before being analysed.

At the end of each working day, the column was conditioned in acetonitrile. This experimental procedure enabled to extend the performance of the monolithic column for several months.

All samples were previously filtered through syringe filters of regenerated cellulose 0.45 μm (Sartorius, ref. 17,765) before being analysed.