Analytica Chimica Acta 936 (2016) 91–96

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Enhanced electrochemical detection of quercetin by Natural Deep Eutectic Solvents

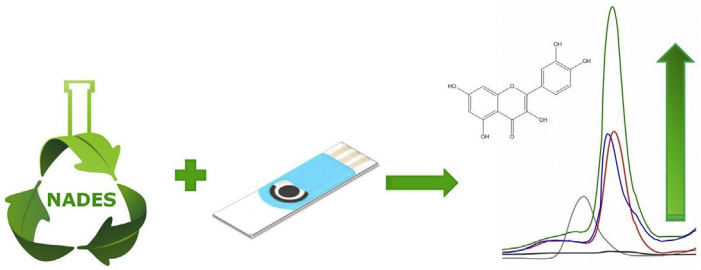
Federico José Vicente Gomez [a], Magdalena Espino [b], María de los Angeles Fernandez [b], Julio Raba [a], María Fernanda Silva [b,*]

[a] Instituto de Química San Luis (INQUISAL- CONICET), Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina
[b] Instituto de Biología Agrícola de Mendoza (IBAM-CONICET), Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo, Mendoza, Argentina

HIGHLIGHTS

- Natural Deep Eutectic Solvents are enhancers of electrochemical detection for phenolic compounds.
- The methodology fully represents the principles of green analytical chemistry.
- The approach was successfully applied for the determination of QR in complex plant matrices.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
14 July 2016
Accepted 19 July 2016
Available online 25 July 2016

Keywords:
Quercetin
NADES
Enhanced electrochemical detection
Onions
Polyphenols

ABSTRACT

New trends in analytical chemistry encourage the development of smart techniques and methods aligned with Green Chemistry. In this sense, Natural Deep Eutectic Solvents represents an excellent opportunity as a new generation of green solvents. In this work a new application for them has been proposed and demonstrated. These solvents were synthesized by combinations of inexpensive and natural components like, Glucose, Fructose, Citric acid and Lactic acid. The different natural solvents were easily prepared and added to buffer solution in different concentrations, allowing the enhancement of electrochemical detection of an important representative antioxidant like quercetin (QR) with improved signal up to 380%. QR is a ubiquitous flavonoid widespread in plants and food of plant origin. The proposed method using phosphate buffer with a eutectic mixture of Citric acid, Glucose and water in combination with carbon screen printed electrodes exhibited a good analytical performance. Detection and quantification limits were of 7.97 and 26.3 nM respectively; and repeatability with %RSDs of 1.41 and 7.49 for peak potential and intensity respectively. In addition, it has proved to be faster, greener and cheaper than other sensors and chromatographic methods available with the additional advantage of being completely portable. Furthermore, the obtained results demonstrated that the proposed method is able for the determination of QR in complex food samples.

1. Introduction

In the last decades, the concept “green” acquired a new significance in chemistry. The definition of sustainable development and green chemistry changed the way of thinking processes and

* Corresponding author.
E-mail address: msilva@fca.uncu.edu.ar (M.F. Silva).

http://dx.doi.org/10.1016/j.aca.2016.07.022
0003-2670/

methods. A critical issue is to look for an alternative to traditional organic solvents due to their low biodegradability, high toxicity and cost. After years of intense research, trying different mixtures with diverse compounds, a spark of light emerged from nature: in 2011 Choi et al. [1] coined the term Natural Deep Eutectic Solvents (NADES) for mixtures that are liquid supermolecules made of natural metabolites bound together by inter-molecular interactions, particularly hydrogen bonding [2]. They have several advantages over synthetic ionic liquids, e.g. their low costs, biodegradability, nontoxicity, sustainability, and simple preparation methods [3]. NADES offer endless opportunities at method development showing very good physicochemical properties as solvents: negligible volatility, liquid state even far below 0 °C, adjustable viscosity, sustainability, biodegradability combined with acceptable toxicity profiles, and high solubilization power of both polar and non-polar compounds [3,4].

The components of NADES are natural metabolites, e.g. sugars, alcohols, organic acids, amino acids and amines, which have several hydroxyl groups, carboxyl groups, or amino groups [1]. Those groups give rise to hydrogen bonding interactions, leading to highly structured liquids [5]. Such liquids can, in turn, form additional hydrogen bonds with solutes, increasing their solubilization ability, e.g. of phenolic compounds [6]. Thus considering the challenge of Analytical Chemistry to develop new techniques and methods aligned with Green Chemistry, NADES represents an excellent opportunity as a new generation of green solvents with many possible applications due to the features can be tailored by changing the nature and molar ratio of their hydrogen-bonding components.

Flavonoids are natural products widely distributed in the plant kingdom and generally present in the common human diet. Quercetin (QR, 3,3′,4′,5,7-penta hydroxyl flavones) is the most common flavonoid widespread in plants and food of plant origin [7]. Onions ranked highest in QR content in a survey of 28 vegetables and nine fruits [8]. The amount of QR in onions varies depending on bulb color and type, being distributed mostly in the outer skin and rings [9]. Most of the studies have revealed various beneficial effects on human health, including anti-viral, anti-cancer, anti-inflammatory and anti-tumor activity [10,11].

Traditional methods for determination of QR include spectrophotometry [12], gas chromatography combined with mass spectrometry [13], high performance liquid chromatography with UV detection [14], or spectrophotometric and coulometric detection [15]. These techniques often require complicated and time consuming pretreatments and/or expensive experimental equipments. Therefore, simpler electrochemical approaches have been developed for QR determination in a wide range of matrices. These methods usually applied modifications of the electrode with graphene [11,16–19], carbon nanotubes [18,20–22], nanoparticles [16,17,19,22,23], alumina microfibers [24] and several combinations of the foregoing [16–19,22]. Electrochemical methods involving modified electrodes are simpler than traditional but they are relatively expensive and time consuming; the modification of the electrode itself decreases sample throughput significantly.

In this sense the development of smart methodologies avoiding unnecessary steps that allow polyphenols determination with similar features are necessary. NADES application in electrochemistry allows the possibility of employing unmodified electrodes. Considering the very recent discovery of these natural solvents, no information can be found concerning the study of detection enhancement provided by them. Thus, the main purpose of this work was to explore the skills of selected NADES as enhancers of electrochemical detection for a representative phenolic compound (QR). NADES were synthesized by different combinations of glucose, fructose, citric acid and lactic acid. Phosphate buffer solutions were prepared with different amounts of NADES to test their effect on the sensitivity in differential pulse voltammetry. Thus, a methodology that fully represents the principles of green analytical chemistry was developed. Indeed, the proposed methodology was applied for the determination of QR in onion samples. The overall profile of the analytical methodology; including extraction and determination was achieved using NADES as solvents for all steps. Afterwards, results were contrasted against HPLC-MWD with satisfactory results.

2. Experimental section

2.1. Chemicals

QR was purchased from Sigma Chemical (St. Louis, MO, USA). D (−) Fructose, D (−) Glucose, Lactic acid and Citric acid were obtained from Biopack (Buenos Aires, Argentina). Sodium hydrogen phosphate was purchased from Carlos Erba Reagents (Milano, Italy). Phosphate buffer 5 mM was prepared by dissolving appropriate amounts of sodium hydrogen phosphate. Ultrapure water (18 MΩ cm) was obtained from Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Equipment

All electrochemical measurements were performed, at room temperature, on an USB-based portable electrochemical station μ-Stat 200 Bipotentiostat (Dropsens, Oviedo, Spain) controlled by DropView 200 software. The electrodes used in this work were carbon screen-printed electrodes (CSPE), which integrates a three-electrode system based on carbon as counter electrode, carbon working electrode of 4 mm diameter and a silver reference electrode (Dropsens, Oviedo, Spain).

The HPLC instrument was a Dionex Ultimate 3000 (Dionex Softron GmbH, Thermo Fisher Scientific Inc., Germering, Germany) consisting of vacuum degasser unit, autosampler, quaternary pump and chromatographic oven. The detector was a Dionex MWD-3000 (RS) model. The working wavelength was fixed at 370 nm. The Chromeleon 7.1 software was used to control all the acquisition parameters of the HPLC-MWD system and also to process the obtained data. A Zorbax SB-Aq column (4.6 mm × 150 mm, 5 μm) Agilent Technologies was used. Ultrapure water with 0.1% Formic acid (A) and Acetonitrile (B) were used as mobile phases. The following gradient was used: 0–2.7 min, 5% B; 2.7–10.7 min, 30% B; 10.7–11 min, 35% B; 11–15 min, 50% B; 15–15.5 min, 50% B: 15.5–16 min 30% B; 16–16.5 min 5% B; 16.5–17 min 5% B. The mobile phase flow was 1 mL/min. The column temperature was held at 20 °C and the injection volume was 5 μL.

2.3. NADES synthesis

NADES synthesis were carried out easily following the heating and stirring method described by Dai et al. [6]. Three different NADES were prepared using inexpensive and natural components, in the following combinations and ratios: Citric acid, Glucose and H_2O (CGH, 1:1:2); Lactic acid, Glucose and H_2O (LGH, 5:1:3); Citric acid, Fructose and H_2O (CFH, 1:1:2). The two-component mixture with calculated amounts of water were placed in a bottle with a stirring bar and cap and heated in a water bath below 80 °C with agitation till a clear liquid is formed (60 min). The stability of synthesized NADES was tested, and they were stable for at least 2 months after its preparation.

2.4. Sample extraction

Red, green and yellow onions were obtained from local market.