Food Chemistry 214 (2017) 670–677

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

A comprehensive evaluation of three microfluidic chemiluminescence methods for the determination of the total phenolic contents in fruit juices

Buthaina Al Haddabi, Haider A.J. Al Lawati *, FakhrEldin O. Suliman

Department of Chemistry, College of Science, Sultan Qaboos University, Box 36, Al-Khod 123, Oman

ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form 20 July 2016
Accepted 20 July 2016
Available online 21 July 2016

Keywords:
Microfluidics
Chemiluminescence
Potassium permanganate
Rhodamine
Phenolic antioxidants
Interferences

ABSTRACT

Three recently reported microfluidic chemiluminescence (MF-CL) methods (based on reactions with acidic permanganate enhanced by formaldehyde ($KMnO_4$-COH), acidic cerium (IV) and rhodamine B (Ce-RB), and acidic cerium (IV) and rhodamine 6G (Ce-R6G) enhanced by SDS) for the determination of the total phenolic content (TPC) in juices were critically evaluated in terms of their selectivity. The evaluation was carried out using 86 analytes, including 22 phenolic compounds (phenolic acids and polyphenols), 6 known non-phenolic antioxidants, 9 amino acids and a number of proteins, carbohydrates, nucleotide bases, inorganic salts and other compounds. Each method was sensitive toward phenolic compounds (PCs). However, the $KMnO_4$-COH CL system showed a higher sensitivity toward phenolic acids and also responded to non-phenolic antioxidants. The other two systems showed higher sensitivity toward polyphenolic compounds than to phenolic acids and did not responded to all other compounds including non-phenolic antioxidants.

1. Introduction

PCs are of great interest due to their antioxidant activity. The current method for determining the total phenolic content is based on the Folin-Ciocalteu (FC) assay. This assay has been used for many years by the food and agricultural industries to determine the phenolic content of plant products. However, the FC reagent reacts with other compounds besides phenols, such as proteins, thiols and many vitamin derivatives. It is also reactive toward the nucleotide base guanine and the trioses glyceraldehyde and dihydroxyacetone (Everette et al., 2010)

A number of chemiluminescence (CL) methods have been proposed as alternatives for determining the total phenolic content. Flow injection analyses, sequential injection methods of analysis or microfluidics are often used as platforms for the proposed CL methods (Al Haddabi, Al Lawati, & Suliman, 2016; Al Lawati, Al Haddabi, & Suliman, 2014; Costin, Barnett, Lewis, & McGillivery, 2003; Francis et al., 2010; Nalewajko-Sieliwoniuk, Malejko, Święczkowska, & Kowalewska, 2015). Microfluidics use miniaturized platforms that consume minute amounts of chemicals and reduce the cost of analysis. Additionally, microfluidic methods reduce analysis time and increase sample throughput (Al Lawati, 2014; Al Lawati, Al-Azwani, Varma, Suliman, & Al Kindy, 2012; Al Lawati, Al-Azwani, Varma, Suliman, & Shalabi, 2011).

However, several key issues concerning these proposed methods have not been critically investigated. All prior studies generally evaluated only a limited number of PCs, often four to eight standards, despite a wide range of types of phenolic compounds existing in food samples. Additionally, selectivity studies have generally been carried out on a limited number of compounds. This is a critical factor and is considered to be one of the current limitations of the FC method.

Taking these points into consideration, we critically evaluated three methods previously proposed in our research for the determination of TPC in food samples (Al Haddabi et al., 2016; Al Lawati et al., 2014). The three methods are: $KMnO_4$-COH, Ce-RB and Ce-R6G.

We first evaluated and compared the three methods using 22 phenolic antioxidant members of various groups, including *flavonols, flavanols, flavones, isoflavonoids, anthraquinones, phenolic acids, hydroxycinnamic acids* and other natural phenolic compounds (Fig. 1).

We then evaluated the three methods using a number of known non-phenolic antioxidants, including vitamin C, uric acid, menthol, α-lipoic acid and zinc acetate. Finally, we studied the effect of the presence of 57 other compounds of various classes, such as amino acids, vitamins, alkaloids, organic acids, alcohols, aldehydes,

* Corresponding author.
E-mail address: haiderl@squ.edu.om (H.A.J. Al Lawati).

http://dx.doi.org/10.1016/j.foodchem.2016.07.119
0308-8146/

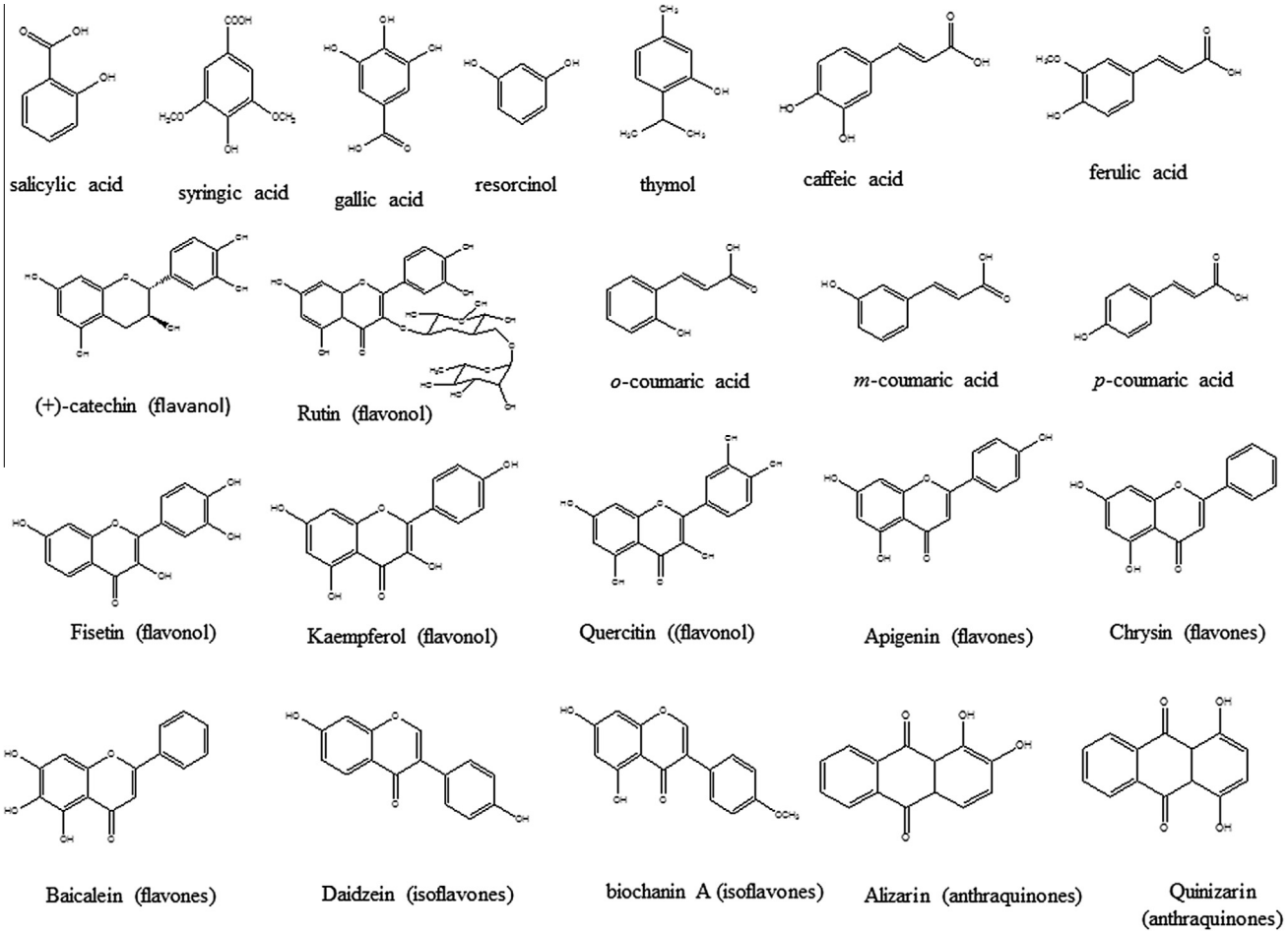

Fig. 1. Chemical structure of phenolic compounds investigated in this study.

carbohydrates and others, on the CL signal intensity of gallic acid and quercetin solutions (1 mg L^{-1}), respectively (Table 1).

It is worth mentioning here that conducting such a comprehensive investigation was facilitated by the versatility and robustness of on-chip CL systems.

2. Material and methods

2.1. Reagents and solutions

All reagents were of analytical grade, and dilutions were performed using deionized water (Millipore, MilliQ water system). SDS was purchased from Kanto (Japan). The Folin-Ciocalteu reagent and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma (USA). Gallic acid, caffeic acid, *o*-coumaric acid, *m*-coumaric acid, *p*-coumaric acid, syringic acid, ferulic acid, salicylic acid, quercetin, kaempferol, apigenin, daidzein, catechin, rutin, baicalein, chrysin, alizarin, quinizarin, biochanin A, fisetin, thymol, ascorbic acid, uric acid, menthol, α-lipoic acid, β-citrolenol, zinc acetate, resorcinol, β-D-(+)-glucose, sucrose, mannose, maltose, ribose, D-(−)-fructose, leucine, N-acetyl-L-cysteine, glycine, L-valine, DL-alanine, DL-tryptophan, histidine, arginine, hydrated magnesium sulfate, sodium sulfate, potassium chloride, aluminum sulfate hydrate, copper chloride, manganese sulfate hexahydrate, ferrous chloride, calcium chloride, magnesium sulfate, zinc sulfate, caffeine, folic acid (vitamin B_9), thiamine (vitamin B_1), nicotinamide (vitamin B_3), D-biotin, casein, gelatine, starch, bovine albumin, and citric acid were purchased from BDH (Poole, England). Sulfuric acid, *trans*-cinnamic acid, DL-malic acid, palmitic acid, phthalic acid, tartaric acid, butanol, butyraldehyde, dithiol, androstenol, β-estradiol, aminopyrazine, 2,4-dibromopyridine, 4-iodopyridine, thymine, adenine, copper complex, acrylamide, niflumic acid and sodium hydroxide were purchased from Sigma-Aldrich (Germany).

System 1. Potassium permanganate (0.5 mmol L^{-1}) was prepared in 1% w/v sodium polyphosphate. This solution was adjusted to pH 2.5 with *ortho*-phosphoric acid (Ajax) and 2% formaldehyde.

System 2. Ammonium cerium (IV) nitrate (24 mmol L^{-1}) was prepared by dissolving 131.6 mg in 10 mL of 0.05 M sulfuric acid; 0.077 mmol/L rhodamine B was dissolved in water.

System 3. Ammonium cerium (IV) nitrate (10 mmol L^{-1}) was prepared by dissolving 55.0 mg in 10 mL of 0.05 mol L^{-1} sulfuric acid and in 1.5 mol L^{-1} nitric acid; 10 mmol L^{-1} rhodamine 6G was dissolved in 0.4% sodium dodecyl sulfate (SDS).

2.2. Sample pre-treatment of orange, pomegranate and lemon juices

Fifteen commercially available juices (four orange, four lemon and four pomegranate juices) were purchased from local markets, and three fresh juices (one of each type) were squeezed from the fruits for comparison. The juices were selected because of the high ascorbic content and were prepared by dissolving 2.5 ml of juice in 100 mL of a hot 0.1 mmol L^{-1} NaOH solution while stirring the sample, followed by filtering prior to use. All juice samples were stored in a fridge below 8 °C before use.