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Chemometrics-enhanced high performance liquid chromatography-diode array detection strategy for simultaneous determination of eight co-eluted compounds in ten kinds of Chinese teas using second-order calibration method based on alternating trilinear decomposition algorithm

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ABSTRACT

In this work, an attractive chemometrics-enhanced high performance liquid chromatography-diode array detection (HPLC-DAD) strategy was proposed for simultaneous and fast determination of eight co-eluted compounds including gallic acid, caffeine and six catechins in ten kinds of Chinese teas by using second-order calibration method based on alternating trilinear decomposition (ATLD) algorithm. This new strategy proved to be a useful tool for handling the co-eluted peaks, uncalibrated interferences and baseline drifts existing in the process of chromatographic separation, which benefited from the "second-order advantages", making the determination of gallic acid, caffeine and six catechins in tea infusions within 8 min under a simple mobile phase condition. The average recoveries of the analytes on two selected tea samples ranged from 91.7 to 103.1% with standard deviations (SD) ranged from 1.9 to 11.9%. Figures of merit including sensitivity (SEN), selectivity (SEL), root-mean-square error of prediction (RMSEP) and limit of detection (LOD) have been calculated to validate the accuracy of the proposed method. To further confirm the reliability of the method, a multiple reaction monitoring (MRM) method based on LC–MS/MS was employed for comparison and the obtained results of both methods were consistent with each other. Furthermore, as a universal strategy, this new proposed analytical method was applied for the determination of gallic acid, caffeine and catechins in several other kinds of Chinese teas, including different levels and varieties. Finally, based on the quantitative results, principal component analysis (PCA) was used to conduct a cluster analysis for these Chinese teas. The green tea, Oolong tea and Pu-erh raw tea samples were classified successfully. All results demonstrated that the proposed method is accurate, sensitive, fast, universal and ideal for the rapid, routine analysis and discrimination of gallic acid, caffeine and catechins in Chinese tea samples.

1. Introduction

Tea, firstly discovered in China and grown in about 30 countries, is one of the most widely consumed beverages in the world [1–3]. Numerous studies have reported the biological functions of tea, for example, anti-oxidant, anti-inflammation, anti-carcinoma, anti-obesity, anti-atherosclerotic and anti-viral properties, etc. [4–8]. These beneficial effects have been attributed mainly to the presence of polyphenols and purine alkaloids in tea [9]. There are already growing epidemiological and preclinical evidences showing that tea polyphenols can reduce the risks of cardiovascular diseases and a variety of other cancers (such as oral cavity, esophagus, stomach, liver, small and large intestine, and mammary gland) in humans [10,11]. The major functional components in tea are gallic acid (GA) and tea catechins, mainly (+)-catechin (C), (−)-epicatechin (EC), (−)-epigallocatechin(EGC), (−)-epicatechin gallate (ECG), (−)-epigallocatechin gallate (EGCG) and (−)-gallocatechin-gallate (GCG). In addition, caffeine (CAF), the major alkaloid, is responsible for the stimulating effect [12]. Among them, EGCG is the most abundant catechin and may represent up to 50% of the catechins by weight. The structures of gallic acid, caffeine and various catechin monomers are shown in

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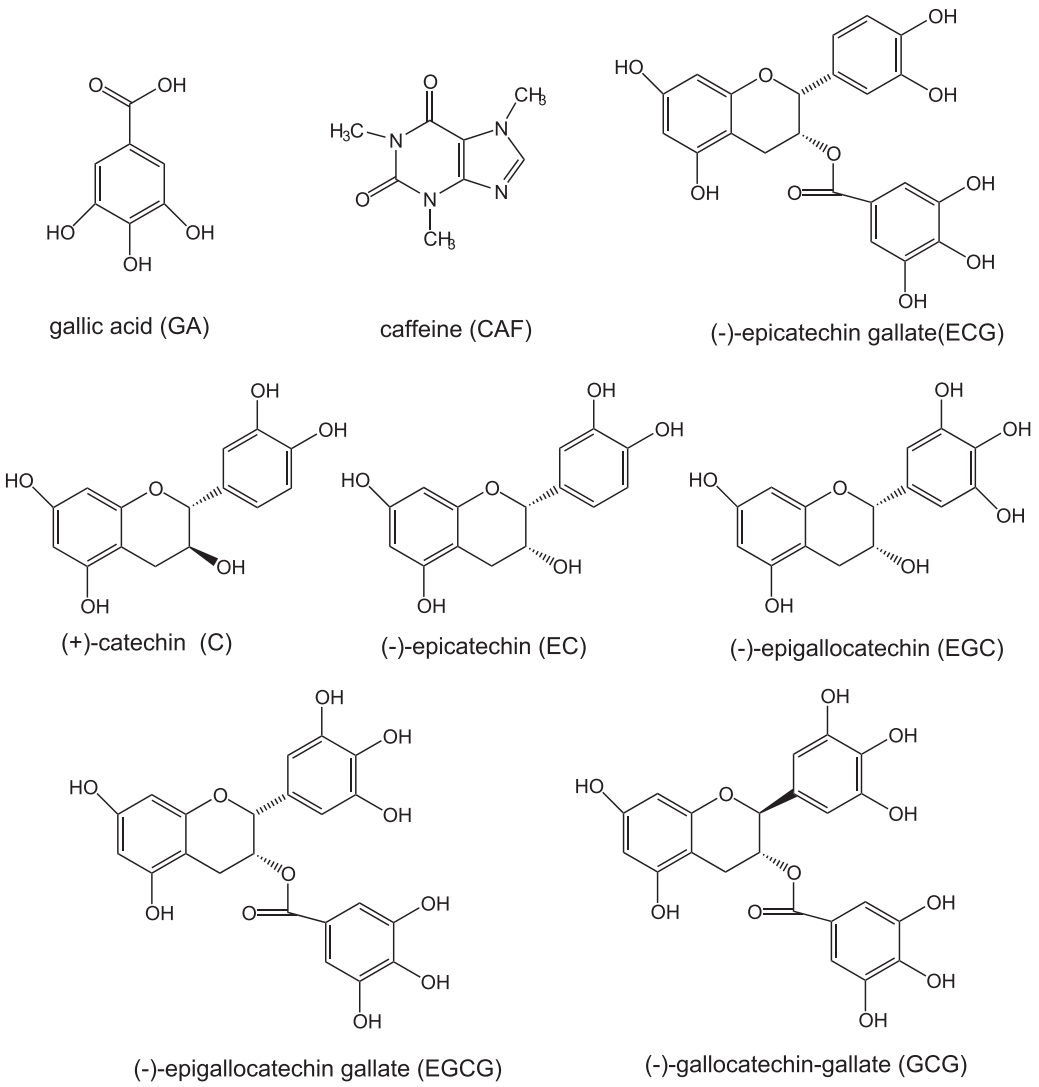

Fig. 1. Chemical structures of gallic acid, caffeine and six catechins.

Fig. 1. Considering these potential therapeutic effects and the great consumption of the tea worldwide, further investigation of the health-promoting function, the quality control and safety of tea have gained increasing attention. The function and quality of tea are closely related to its chemical constituents. Indeed the contents of gallic acid, caffeine and catechins greatly vary depending on the tea species, age of the leaves and environmental conditions of their production sites [13]. It is therefore essential to establish an effective and convenient analytical method for the identification and determination of polyphenols and alkaloids in various tea samples.

The analytical methods used for determination of gallic acid, caffeine and catechins in teas and other biological matrices include capillary electrophoresis (CE) [1], Fourier transform near infrared spectrometry [14], liquid chromatography (LC) techniques including high-performance thin layer chromatography (HPTLC) [15], monolith column, ultrahigh-pressure liquid chromatography (UHPLC) and high-performance liquid chromatography (HPLC) coupled with UV or diode array detector (UV/DAD), electrochemical or mass spectrometry detection [16–22]. Among these analytical methods, HPLC coupled with UV/DAD is by far the most popular method for the analysis of functional components in tea due to its advantages of excellent separations, high reproducibility, sufficient low detection limit, low cost and thus can be applied for the identification and quantification of gallic acid, purine alkaloids and catechins.

However, there are still some drawbacks that should be pointed out. Firstly, almost all published HPLC separation methods require 20–90 min for per run analysis, with the average being 20–40 min, resulting in relatively low efficiency [23,24]. Secondly, because of the existence of the complex matrices and cis-trans isomers, complex chromatographic conditions and large solvents consumption are unavoidable [25]. Thirdly, owing to the different conditions of laboratories in practical applications, the reversed-phase LC methods referred to above may fail to provide satisfactory separation for the analytes from each other and/or from other compounds existing in the samples and thus quantification of gallic acid, purine alkaloids and catechins in real samples may become ambiguous and lack of universality. Finally, other problems such as baseline drifts, changes of the peaks shape as well as shifts in the elution time may also decrease the quality of the final results of the analysis.

Accordingly, a simple, accurate, universal, fast and environmental-friendly approach with shorter HPLC analysis time is required to facilitate larger and more extensive studies with large sample sets. Chemometrics has been widely applied in chromatography in recent 30 years, offering robust and reliable data analytical alternatives to handle the problems derived from the instability of the chromatographic systems (baseline/background