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Analytical Methods

On-cartridge derivatisation using a calixarene solid-phase extraction sorbent for facile, sensitive and fast determination of formaldehyde in beer

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ABSTRACT

This work demonstrates the successful application of an on-cartridge derivatisation procedure for facile, fast and sensitive determination of formaldehyde in beer by HPLC-UV. The derivatisation and solid-phase extraction (SPE) were integrated into a novel calixarene SPE sorbent: tetraazacalix[2]arene[2]triazine bonded silica gel. Specifically, 2,4-dinitrophenylhydrazine was adsorbed onto the sorbent in advance, based on the charge-transfer interaction between the macrocyclic molecule and nitrobenzenes. The method was optimised and validated: under the optimal conditions of derivatisation, SPE and HPLC separation, good linearity was obtained in the range of 0.080–3.2 μg mL^{-1} with a correlation coefficient of 0.9939, the limit of detection was 3.0 ng mL^{-1} (S/N = 3), the limit of quantification was 10 ng mL^{-1} (S/N = 10), and the recovery level using this method was desirable at 75–84%. The developed method was successfully applied to determine formaldehyde content in real beer samples; the results were in the range of 0.11–1.1 μg mL^{-1}.

1. Introduction

Formaldehyde (FA) is the smallest carbonyl compound, has a low boiling point (−19.5 °C) and is widely present in water, the atmospheric environment and foodstuffs. As a hazardous air pollutant (Michoud et al., 2012), FA has been of great concern to human health for a long time. FA generates adverse effects on humans who are chronically exposed to it, such as a higher risk of DNA damage (at a mean level of FA exposure of 0.38 mg L^{-1}) (Costa et al., 2015) and cancer (Zhou, Li, Huijbregts, & Mumtaz, 2015).

Recently, animal feeding experiments have demonstrated that FA may also be carcinogenic after ingestion (Baan et al., 2009). As a consequence, FA has been listed as one of the 15 known and suspected carcinogens in alcoholic beverages (Lachenmeier, Przybylski, & Rehm, 2012). For this reason, monitoring the content of FA in food, especially alcoholic beverages, is significant for human safety and production. The concentration of FA in food has been limited by some organisations: it cannot exceed the World Health Organization threshold of 0.90 mg L^{-1} in drinking water; the daily intake of FA should be controlled in 0.20 mg kg^{-1} body weight set by the US Environmental Protection Agency; FA

Abbreviations: FA, formaldehyde; HPLC, high performance liquid chromatography; UV, ultroviolet; DNPH, 2,4-dinitrophenylhydrazine; SPE, solid-phase extraction; NCS, tetraazacalix[2]arene[2]triazine bonded silica gel; DCM, dichloromethane; MeOH, methanol; ACN, acetonitrile.

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produced from the process of beer fermentation cannot exceed 2.0 mg L^{-1} set by GB 2758-2005 of China. However, relatively high concentrations of FA have been found in alcoholic beverages (maximum content reached 10.9 mg L^{-1}) (Monakhova, Jendral, & Lachenmeier, 2012). Natural production during fermentation or artificial addition may account for the presence of FA.

Detecting FA in beer has always been a challenge due to the coexisting status of FA with the complicated matrix (Zgherea, Stoian, & Peretz, 2011). Three strategies have been commonly used for determination of FA in beer. Firstly, in the state standard method of China (GB/T 5009.49-2008), FA was separated from beer matrices by steam distillation, then the aqueous distillate containing FA was derivatised with acetylacetone prior to determination by visible spectrophotometry. For fast and high throughput analysis, the biggest limitations of this method are that it is time consuming (>1 h) and uses inconvenient operation devices. Secondly, FA was derived with an additional derivatisation reagent in the complex matrix, then the derivatives were extracted by a solid-phase extraction (SPE) column (Zhang & Ou, 2013), cloud point extraction (T. Wang, Gao, Tong, & Chen, 2012) or liquid-liquid microextraction (Xu et al., 2011), etc., and analysed by high performance liquid chromatography (HPLC). Great improvement was obtained in the speed of the analysis, while a multi-step process is still inevitable; Thirdly, FA was extracted directly with a magnetic resin modified with derivatisation reagent (H. Wang et al., 2012). Similar methods, such as using 2,4-dinitrophenylhydrazine (DNPH)-coated silica cartridges, are just as commonly applied in gaseous FA analysis (Herrington & Hays, 2012; Ueta et al., 2015). Such methods are attractive and advantageous in rapid analysis, while choosing a selective sorbent is foremost for sensitive and accurate determination.

Since water can elute targets from a polar stationary phase or sorbent, the commonly used DNPH-coated silica cartridge is not suitable for extracting FA from aqueous samples. In order to fabricate a DNPH-coated cartridge, a reversed-phase (RP) sorbent is the optimal choice for DNPH and FA-DNPH adsorption (Fig. 1A). Nowadays, as a complement to the traditional C_{18} RP sorbent, some new and selectively chromatographic media have been developed to recognise nitrobenzene compounds (Ihara et al., 2005; Peng, Zhao, & Feng, 2011). Supramolecular ligands including crown ether, cyclodextrin and calixarene are also widely used as chromatographic stationary phases or SPE sorbents (Barc & Sliwka-Kaszynska, 2009; Deng et al., 2014; Ibrahim, Farhani, Sanagi, & Aboul-Enein, 2010; J. Wang, Zhang, Lawson, & Bartsch, 2009; Li, Zeng, Gao, & Li, 2004; Zeng, Qiu, & Huang, 2001). What has interested us recently is tetraazacalix[2]arene[2]triazine, a typical example of the heterocalixaromatics. Structurally, it is distinct from the conventional calixarenes, in that two benzene rings and two triazines are bridge-linked by nitrogens, forming unique structural features with versatile recognition properties. We therefore prepared a tetraazacalix[2]arene[2]triazine bonded silica gel (NCS) (Fig. 1B) stationary phase (Zhao et al., 2012) and NCS SPE sorbent for the first time (L. Wang et al., 2013).

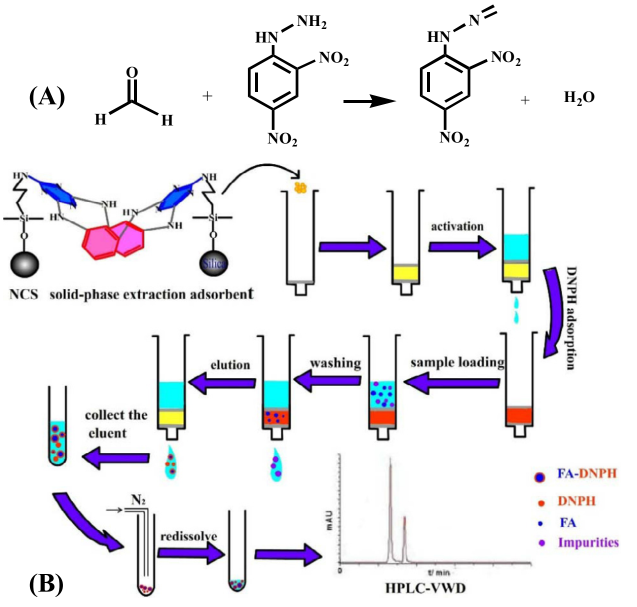

Fig. 1. (A) Reaction equation between FA and DNPH. (B) Scheme of the NCS-DNPH on-cartridge derivatisation.

As the corresponding study showed, NCS featured multi-recognition sites, especially the large π-π conjugated system formed by electron-rich nitrogens associating with the macrocyclic cavity. NCS thus showed strong retention ability for nitrobenzoates via the charge transfer interaction between the host and guest. Therefore, we envisioned NCS sorbent may specifically enrich FA-DNPH from aqueous samples based on charge transfer interaction.

In this present work, a DNPH-adsorbed NCS solid-phase cartridge was fabricated, and an on-cartridge derivatisation procedure for analysis of FA in beer was developed. By using this method, we could accomplish derivatisation, sample purification and preconcentration simultaneously, which greatly shorten the analysis time. The retention behaviour and interaction mechanism between FA-DNPH and NCS were discussed, and the method was optimised and validated. Finally, the developed method was successfully applied to determine FA in different beer samples and compared with other reported methods.

2. Material and methods

2.1. Chemicals, samples and preparation of standard solutions

Unless specified otherwise, all reagents and solvents for sample pretreatment were of analytical grade. Ultra-pure water ($\rho \geqslant 18.2$ MΩ cm) was obtained from a Milli-Q water purification system (Bedford, MA, USA); methanol (MeOH) and acetonitrile (ACN) were HPLC grade and purchased from Fisher Chemicals (Fair Lawn, NJ, USA).

DNPH (⩾99%) was purchased from Beijing Chemical Works. Two standard stock solutions of DNPH (5.0 and 3.0 mg mL^{-1}) were prepared by dissolving 0.2500 and 0.1500 g DNPH in a 50 mL volumetric flask with ACN, respectively. These two standard stock solutions were diluted with ACN to prepare other standard DNPH solutions with different concentrations (2.0, 1.0, 0.50 and 0.10 mg mL^{-1}).

FA standard solution (10 mg mL^{-1}, National Institute of Metrology) was diluted to different desired concentrations with water.

Phosphoric acid was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., and 1%, 0.1% and 0.1‰ phosphoric acid aqueous solutions were obtained by stepwise dilution of phosphoric acid (⩾85%) with water.

The solution for redissolving (RS) solutes is constituently consistent with the derivatisation solution. It consists of 1.00 mL 1‰ phosphoric acid solution, 1.50 mL ACN and 5.00 mL water per 7.50 mL total volume.

In addition, beer samples were purchased from a supermarket in Zhengzhou and stored in a refrigerator at 4 °C.

2.2. Apparatus and materials

An Agilent 1260 HPLC system (Agilent Technologies Inc., USA) equipped with a VWD UV detector and an autosampler was used. A W501 Thermostat water bath (Dawei Science and Education