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Acrylamide-modified graphene for online micro-solid-phase extraction coupled to high-performance liquid chromatography for sensitive analysis of heterocyclic amines in food samples



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ABSTRACT

Heterocyclic amines (HAs) are considered as potential mutagens and carcinogens, and are found in trace quantities (ng/g level) in food samples. Therefore, it is important to develop a selective and effective method to determine trace HAs in complex matrices. In this study, acrylamide-modified graphene (AMG) was successfully synthesised and showed good stability and permeability in aqueous and organic phases. AMG was used as an efficient adsorbent in the online micro-solid-phase extraction (μ -SPE) of trace HAs. The enrichment factors of the AMG μ -SPE column were determined as 78–166 for six HAs. An online method based on AMG μ -SPE coupled to high-performance liquid chromatography was developed. The limits of detection ranged from 0.70 to 2.5 ng/L. Trace HAs in spicy salted duck, baked fish, and fried chicken samples were determined and the concentrations of 2-amino-3-methylimidazo[4,5-f]quinoxaline, 2-amino-3,4-dimethylimidazo[4,5-f]quinoxaline, and 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline in these samples were 4.7–37.3, 8.1–15.4, and 43.3–109 ng/g, respectively. The recoveries for the six HAs ranged from 65.9% to 118%, and the relative standard deviation (RSDs) were less than 10.8%. The proposed online method was sensitive, reliable, and convenient for the analysis of trace HAs in food samples.

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1. Introduction

Heterocyclic amines (HAs), found in cooked meat products, are considered as highly potential mutagens and carcinogens [1,2]. They are formed mainly during the frying, baking, grilling, roasting, and smoking of meat and fish, which are cooked at 150–250 °C [3]. The food safety issues of HAs are receiving increasingly more attention. To date, chromatographic techniques, including high-performance liquid chromatography (HPLC) with various detectors [4–12], gas chromatography–mass spectrometry [13,14] and capillary liquid chromatography [15–17], have been commonly used to identify and quantify HAs in different matrices. However, the concentration of HAs is normally in the relatively low ng/g range in complex matrices and a large number of matrix interferences can be present [18,19]. Efficient sample pretreatment and a sensitive analytical method are very important in HAs analysis. To date, several sample preparation techniques have been employed to preconcentrate HAs in different matrices such as

liquid–liquid extraction [20], dispersive liquid–liquid microextraction [4], solid-phase extraction (SPE) [21], hollow-fibre supported liquid membrane extraction [22], solid-phase microextraction (SPME) [23,24], supercritical fluid extraction [25], and tandem SPE [13,15,26]. However, the above methods were operated in the off-line mode; consequently, they are labour-intensive, tedious, and time-consuming. Online sample preparation techniques were improved in recent years, through miniaturisation and automation. These techniques show better sensitivity with good reproducibility, less solvent and sample consumption, and fewer analytical errors [27,28]. Micro-solid-phase extraction (μ -SPE), reported by Basheer and co-workers [29], is a promising alternative to the multi-step μ -SPE method, which is a simple and efficient sample preparation method for complex samples [30–32]. Thus, the implementation of suitable extraction media and online SPE procedures is an important strategy to establish sensitive and environment-friendly methods for complex sample analysis.

Various media were used in the past, such as C₁₈ [3], ionic liquids [4–6], diatomaceous earth [21], carbowax [23], Oasis MCX [33], and a propylsulphonyl silica gel [34]. Although some conventional sorbents, or a coupling of different eluents in tandem were successfully used for the analysis of HAs, the sorbent is critical for improving the enrichment performance. Thus,

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developing an effective sorbent remains a great challenge for HAs analysis in meat samples. Graphene has received increasing interest and has become one of the most prominent topics of research over the last decade. As the graphene is a one-atom-thick planar sheet of sp^2 -bonded carbon atoms densely packed in a honeycomb crystal lattice, graphene exhibits a high theoretical surface area of close to $2630 \text{ m}^2/\text{g}$ [35]. The surface area is the characteristic that makes graphene a promising material for use in sample pretreatment [36], including matrix solid-phase dispersion [37], SPME [38], and SPE [39,40]. As a low-polarity material, graphene is incompetent to polar HAs extraction in the aqueous phase. Therefore, functional graphene sheets are crucial. Recently, ammonia, hydrazine hydrate, *n*-butyl amine [41], polydopamine [42], and benzylamine [43]-modified graphene have been used as sorbents in SPE for the effective enrichment of pesticides, phosphopeptide, pentachlorophenol, bisphenol A, and polyfluorinated analytes in different matrices.

In the present work, acrylamide-modified graphene (AMG) was successfully synthesized and used as an efficient adsorbent in a μ -SPE column to enable the online enrichment of trace HAs. Moreover, a novel analytical methodology based on AMG μ -SPE online coupled to HPLC was developed for the trace analysis of six HAs, namely IQ, IQX, MeIQ, MeIQX, 4,8-DiMeIQx, and 4,7,8-TriMeIQx, in spicy salted duck, baked fish, and fried chicken samples.

2. Experimental

2.1. Chemicals and materials

The compounds studied were as follows: 2-amino-3-methylimidazo[4,5-*f*]quinoine (IQ), 2-amino-3-methylimidazo [4,5-*f*] quinoxaline (IQX), 2-amino-3,4-dimethylimidazo [4,5-*f*] quinoine (MeIQ), 2-amino-3,8-dimethylimidazo [4,5-*f*] quinoxaline (MeIQX), 2-amino-3,4,8-trimethylimidazo [4,5-*f*] quinoxaline (4,8-DiMeIQx), and 2-amino-3,4,7,8-tetramethyl-3*H*-imidazo [4,5-*f*] quinoxaline (4,7,8-TriMeIQx). They were purchased from Toronto Research Chemicals (Toronto, Canada) and their chemical structures are shown in Fig. 1. Stock standard solutions of $100 \mu\text{g}/\text{L}$ in methanol were prepared and used for further dilutions. Acrylamide was purchased from Damao Chemical Reagent Company (Tianjin, China). Thionyl chloride was supplied from Chemical Industry Corporation (Guangzhou, China). Graphite powder (particle size $30 \mu\text{m}$) was purchased from Alfa Aesar. HPLC-grade acetonitrile was used for the mobile phase and

obtained from Dikma (Beijing, China). Ultrapure water was used throughout and was obtained from the MILLI-Q gradient A10 system (Millipore, UK). All the solutions were filtered through a $0.45\text{-}\mu\text{m}$ filter before being injected into the HPLC system. All the other reagents mentioned above were of analytical grade.

2.2. Instruments

An Esca lab 250 spectrometer with an Al $K\alpha$ X-ray source was employed for X-ray photoelectron spectroscopic (XPS) analysis. X-ray diffractometry (XRD) was carried out using a Rigaku diffractometer. Raman spectra were measured with Laser Micro-Raman Spectrometer (Renishaw, UK). Scanning electron microscopy (SEM) images were recorded on a 4300 SEM instrument (Hitachi, Japan). Transmission electron microscopic (TEM) characterization was performed on a Tecnai 10 TEM instrument (Philips, Netherlands). Fourier transform infrared (FT-IR) spectra were measured by Nicolet Avatar 330. All chromatographic measurements were obtained using Shimadzu (Japan) instruments, consisting of two high-pressure gradient pumps (LC-10 ATvp), a SPD-10Avp UV detector, a system controller (SCL-10 A vp), and a CLASS-VP chromatographic workstation.

2.3. Synthesis of AMG

Graphene oxide (GO) was synthesised from natural graphite according to published methods [44,45]. In brief, 3.81 g of graphite powder was treated with a mixture of concentrated 18.5 mL of H_2SO_4 , 3.87 g of P_2O_5 , and 3.88 g of $\text{K}_2\text{S}_2\text{O}_8$ at 80°C . The obtained preoxidized graphite was placed into cold concentrated H_2SO_4 , and KMnO_4 was slowly added. H_2O_2 and distilled water were then added to terminate the reaction. The resulting solution was centrifuged and washed with HCl solution, and finally dried to generate a brown solid. Then, 670 mg of GO was added to 35 mL of a SOCl_2 solution and ultrasonicated for 20 min, followed by stirring and reflux at 69°C for 30 h. Subsequently, the reactant was distilled at 92°C and added to 100 mL of *N,N*-dimethyl formamide (DMF) and 1.82 g of acrylamide under ultrasonication for 20 min. This mixture was stirred at 26°C for 24 h. The product was filtered through a $0.45\text{-}\mu\text{m}$ filter and washed thoroughly with deionised water until its filtrate became neutral. The AMG was dried at 80°C for 24 h in vacuum.

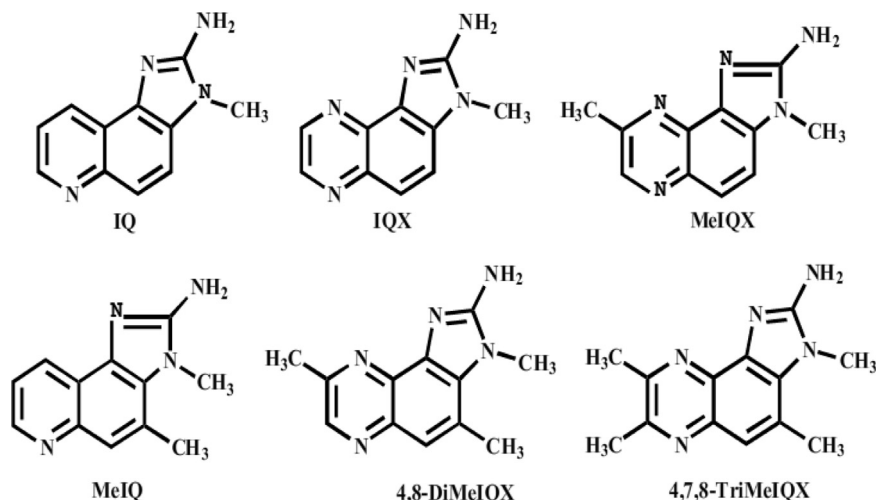


Fig. 1. Molecular structures of HAs compounds.

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