



# Graphitic carbon nitride as high-resolution stationary phase for gas chromatographic separations



Yunzhong Zheng, Meiling Qi\*, Ruonong Fu

Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials and School of Chemistry, Beijing Institute of Technology, Beijing 100081, China

## ARTICLE INFO

### Article history:

Received 31 March 2016  
Received in revised form 15 May 2016  
Accepted 22 May 2016  
Available online 24 May 2016

### Keywords:

Graphitic carbon nitride  
Gas chromatography  
Stationary phase  
Separation

## ABSTRACT

This work presents the first example of utilization of graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) as stationary phase for capillary gas chromatographic (GC) separations. The statically coated  $g\text{-C}_3\text{N}_4$  column showed the column efficiencies of 3760 plates/m and weak polarity. Its resolving capability and retention behaviours were investigated by using the Grob test mixture, and mixtures of diverse types of analytes, and structural and positional isomers. The results showed superior separation performance of the  $g\text{-C}_3\text{N}_4$  stationary phase for some critical analytes and preferential retention for aromatic analytes. Specifically, it exhibited high-resolution capability for aromatic and aliphatic isomers such as methylnaphthalenes and dimethylnaphthalenes, phenanthrene and anthracene and alkane isomers. In addition,  $g\text{-C}_3\text{N}_4$  column showed excellent thermal stability up to 280 °C and good repeatability with relative standard deviation (RSD) values less than 0.09% for intra-day, below 0.23% for inter-day and in the range of 1.9–8.4% for between-column, respectively. The advantageous separation performance shows the potential of  $g\text{-C}_3\text{N}_4$  and related materials as stationary phase in GC and other separation technologies.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Polymeric graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ , Fig. 1), an analogue of graphite, has a stacked two-dimensional conjugated structure formed by tri-*s*-triazine connected via tertiary amines, and is mainly composed of carbon, nitrogen and minor hydrogen [1].  $g\text{-C}_3\text{N}_4$  has been regarded as the promising candidate to complement carbon-based materials. It can be easily synthesized by thermal condensation of certain nitrogen-rich precursors (e.g., melamine, cyanamide or urea, etc.) at high temperatures. It inherently shows high thermal stability up to about 600 °C in both nitrogen and air [2], and high chemical stability with high inertness to oxygen and water [1]. In the past years, its intrinsic electron-rich and photoelectrochemical properties has attracted growing attention as a metal-free catalyst for a broad variety of reactions [1–4], and as a chemical sensor for selective detection of metal ions [5], trinitrophenol [6], and acid/basic molecules [7] and so forth. Recently,  $g\text{-C}_3\text{N}_4$  was reported as the enrichment material for solid-phase microextraction of organic analytes [8], and as the sorbent for solid-

phase extraction of phthalate esters [9] and polycyclic aromatic hydrocarbons [10] in water samples, showing good extraction ability for the aliphatic and aromatic analytes. Its unique structure, high selectivity and physicochemical stability inspired us to explore its potential as stationary phase for gas chromatographic (GC) separations. Up to date, there is no report on using  $g\text{-C}_3\text{N}_4$  as stationary phase in GC and other chromatographic technologies.

Carbon-based materials such as carbon nanotubes and fullerene [11,12] and graphene [13,14] were reported for GC separations of various types of organic analytes.  $g\text{-C}_3\text{N}_4$  is similar to graphene in the perspective of having a planar electron-rich carbon-based structure. But  $g\text{-C}_3\text{N}_4$  differs from graphene in its high in-plane nitrogen content and much higher physicochemical stability. Hence,  $g\text{-C}_3\text{N}_4$  as GC stationary phase may exhibit different selectivity and retention behaviour from the aforementioned carbon-based materials. Additionally, its high inertness to oxygen [1] also show advantages over the conventional GC stationary phases such as typical polysiloxanes and polyethylene glycol, which are vulnerable to trace oxygen in carrier gas and in the system. Thus, it would be interesting and valuable to investigate its GC separation performance and retention behaviours.

Herein, we report the first example of utilizing  $g\text{-C}_3\text{N}_4$  as stationary phase for GC separations. After statically coated onto a

\* Corresponding author.  
E-mail address: [mlqi@bit.edu.cn](mailto:mlqi@bit.edu.cn) (M. Qi).

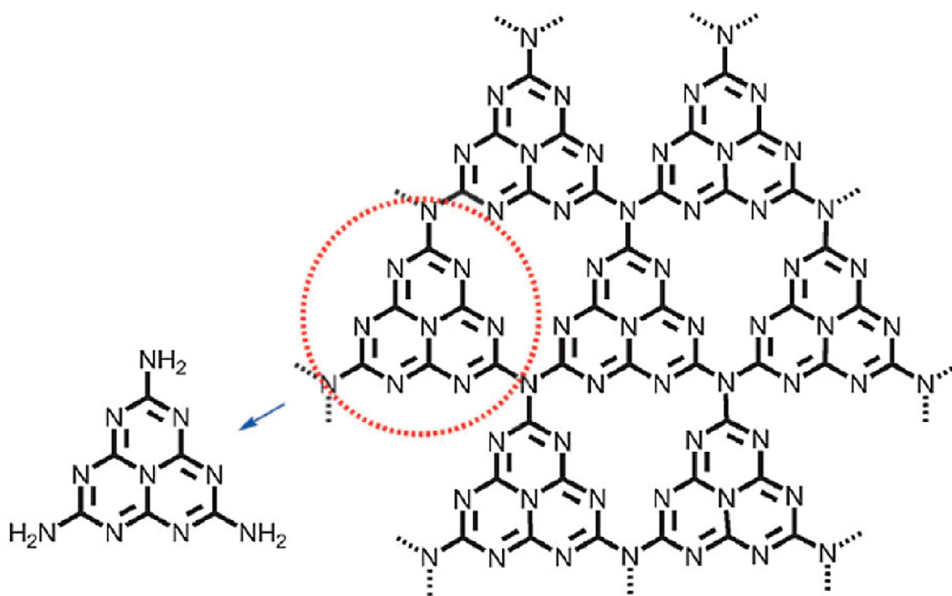


Fig 1. The proposed structure of  $g\text{-C}_3\text{N}_4$ .

silica-fused capillary column, the  $g\text{-C}_3\text{N}_4$  stationary phase was investigated in terms of column efficiency, polarity, separation capability and retention behaviors, column repeatability and thermal stability. In this work, multiple mixtures were employed, namely the Grob test mixture, and mixtures of diverse types of analytes, and structural and positional isomers that are difficult to be separated owing to their high resemblance in physicochemical features. Meanwhile, a commercial column with close polarity, i.e., HP-5MS column, was also employed as reference to evaluate the separation performance of the  $g\text{-C}_3\text{N}_4$  stationary phase.

## 2. Experimental

### 2.1. Materials and equipment

All the analytes used in this work were of analytical grade. 2,3-Butanediol, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tetradecane, *n*-pentadecane, *n*-hexadecane, 1-butanol, *n*-nonanal, 1-octanol, 2,6-dimethylphenol, 2,6-dimethylaniline, 2-ethylhexanoic acid, methyl octanoate, methyl decanoate, methyl undecanoate, methyl dodecanoate and dicyclohexylamine were purchased from TCI (Osaka, Japan). Melamine, 2-pentanone, 1-nitropropane, pyridine, benzene, *sec*-butylbenzene, 1,4-dichlorobenzene, nitrobenzene, naphthalene, 1,2,3-trichlorobenzene, biphenyl, acenaphthene and fluorine were purchased from Aladdin Industrial (Shanghai, China). The rest of the chemicals were purchased from Beijing Chemical Reagent Company (Beijing, China).

Untreated fused-silica capillary tubing (0.25 mm, i.d.) was purchased from Yongnian Optic Fiber Plant (Hebei, China). A HP-5MS capillary column (10 m  $\times$  0.25 mm, i.d., 0.25  $\mu\text{m}$  film thickness, 5% phenylmethylpolysiloxane) was purchased from Agilent Technologies. An Agilent 7890A gas chromatograph equipped with a split/splitless injector, a flame ionization detector (FID) and an autosampler was used in GC separations. Nitrogen (99.999%) were used as the carrier gas. The injection port temperature was set at 250  $^\circ\text{C}$  and the detector temperature was 300  $^\circ\text{C}$ . The X-ray diffraction (XRD) pattern was recorded on XRD-6000 (Shimadzu, Japan) with Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Fourier transform infrared spectroscopy (FT-IR) spectra were obtained (as KBr pellets) using a Nicolet 170SXFT-IR spectrometer. Thermogravimetric analysis

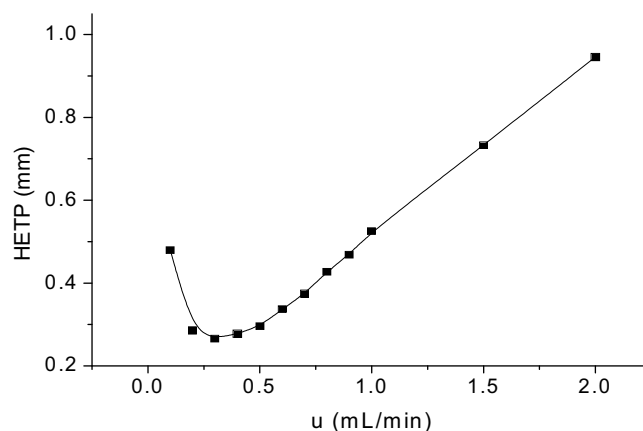


Fig. 2. The Golay plot of  $g\text{-C}_3\text{N}_4$  capillary column determined by *n*-dodecane at 120  $^\circ\text{C}$ .

(TGA) was performed on a DTG-60AH Thermogravimetric Analyzer (Shimadzu, Japan) from 30  $^\circ\text{C}$  to 800  $^\circ\text{C}$  at a ramp rate of 10  $^\circ\text{C}/\text{min}$  in air.

### 2.2. Synthesis and characterization of $g\text{-C}_3\text{N}_4$

The bulk  $g\text{-C}_3\text{N}_4$  used in this work was prepared by directly heating the melamine in a semiclosed system with two-step heat treatment as described in the literature [15]. Briefly, 10 g of melamine powder was put into an alumina crucible with a cover and heated to 500  $^\circ\text{C}$  in a muffle furnace for 2 h at 20  $^\circ\text{C}/\text{min}$  and then to 550  $^\circ\text{C}$  for 2 h, respectively. The obtained  $g\text{-C}_3\text{N}_4$  product was confirmed by XRD and FT-IR. Specifically, the XRD pattern showed the strong diffraction peak at 27.4 $^\circ$  ( $d_{002} = 0.325 \text{ nm}$ ) corresponding to the interlayer stacking peak of conjugated aromatic systems, and the small peak at 13.1 $^\circ$  ( $d_{100} = 0.676 \text{ nm}$ ) from the in-plane structural packing. The FT-IR spectrum showed the adsorption of 801  $\text{cm}^{-1}$  attributed to the vibration of the triazine ring, the adsorptions of 1200–1600  $\text{cm}^{-1}$  from the C–N stretching modes, and the broad adsorption of around 3000  $\text{cm}^{-1}$  correspond-

Download English Version:

<https://daneshyari.com/en/article/1200191>

Download Persian Version:

<https://daneshyari.com/article/1200191>

[Daneshyari.com](https://daneshyari.com)