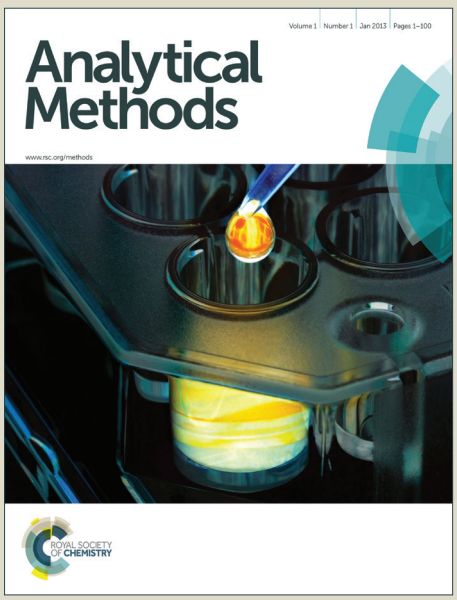
Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

Capillary Column Coated with Graphene Quantum Dots for Gas Chromatographic Separation of Alkanes and Aromatic Isomers

Xueyan Zhang[a], Hongyun Ji[b], Xudong Zhang[b], Zhen Wang[a] and Dan Xiao [a, b, *]

[a] College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China
[b] College of Chemical Engineering, Sichuan University, Chengdu, 610065, P. R. China
*Corresponding author:
E-mail: xiaodan@scu.edu.cn (Dan Xiao)
Tel: +86-28-85415029
Fax: +86-28-85416029

Abstract

Graphene Quantum Dots (GQDs) have potential to be an excellent stationary phase because of its high surface area, adsorption affinities and rich functional groups. The rich functional groups of GQDs can form hydrogen bonding and π-π electrostatic stacking interactions with volatile aromatic compounds or unsaturated organic compounds. Herein GQDs were explored as the stationary phase for gas chromatographic capillary column separation of alkanes and aromatic isomers with 3-aminopropyldiethoxymethyl silane (3-AMDS) as coupling reagent. GQDs coated capillary column exhibits high separation efficiency of ethylbenzene, styrene, xylene, propylbenzene, alkanes, and dichlorobenzene isomers at low temperature. The elution sequence of the analytes follows an increasing order of their boiling points, even for p-dichlorobenzene and m-dichlorobenzene, which have close boiling points (p-dichlorobenzene, 173.4 ^{o}C, m-dichlorobenzene, 173 ^{o}C). The separation behavior of the column upon different organic substances is related to the van der Waals forces or π-π interaction between the tested analytes and GQDs. Compared with the commercial HP-5 and HP-innowax capillary columns, the GQDs allowed fast and efficient separation of the analytes at low temperature without temperature-programming. The relative standard deviations (RSD) of five replicate separations for the tested analytes on GQDs coated capillary column were 0.1-1.6%, 0.7-4.0%, 0.8-8.5%, and 1.2-2.2% for retention time, peak area, peak height, half peak width, respectively.

Keywords: Graphene quantum dots, Stationary phase, Gas chromatography, Isomers, Separation.

Analytical Methods Accepted Manuscript

Introduction

Gas chromatography (GC), which is one of the most important separation methods for volatile compounds, has been under intensive development in recent years. The chromatographic column is the heart of gas chromatographic system. In order to obtain a column with high separation efficiency and good reproducibility, the stationary phases should have the characteristics of narrow size distribution, high surface area and thermal stability. Carbon based materials have long been used for the adsorption and separation of volatile organic compounds [1]. In the field of large carbon materials, carbon nanoparticles have generated tremendous research excitement as gas and liquid stationary phases because these nanoparticles possess a large surface-to-volume ratio, they create unique opportunities for the exploitation of higher performance separation techniques. In order to get the stationary phases which have high resolution and selectivity, chromatographers have explored various carbon based materials such as graphene [2, 3], carbon nanotubes [4-9] and fullerene [10] as the adsorbents in GC. These carbon based materials, especially the carbon nanotubes, have been widely used as stationary phases in gas chromatography because of its exceptional features, namely high surface area, high aspect ratio and the ability to provide π-π electrostatic stacking interaction with aromatic and unsaturated compounds. Carbon nanotubes had been employed on the separation of standard mixtures such as alkanes[11, 12], alcohols[8, 11], aromatic compounds[8, 11, 12] and ketones[11], but bare carbon nanotubes were difficult to handle because they were insoluble in most solvents. In order to optimize the separation effect as GC stationary phase, bare carbon nanotubes should be often modified to get functionalized carbon nanotubes.

Graphene (G) has aroused great interest among the researchers because of its excellent thermal properties, large adsorptivity affinities, ultra high surface area and the large delocalized π-electron system. G has been demonstrated to be a promising material for chromatographic separation [13] and extraction [14-17]. Graphene oxide (GO), a precursor of graphene, contains heavily oxygenated groups. The functional groups of GO can be assembled onto many support surfaces. For example, an octadecylsilane functionalized GO/silica stationary phase had been explored for the separation of alkylbenzenes, amines and phenolic compounds in reversed-phase liquid chromatography [18, 19]. GQDs, which consist of a single atomic layer of nano-sized graphite, possess most of the advantages of graphene and GO. Due to the existence of hydroxyl, epoxy and carboxyl groups, GQDs show nice properties similar to those of GO, such as excellent water solubility and hydrophilicity [20]. What's more, supramolecular interaction (mainly the CH-π interaction), the π-π conjugated network and surface groups offer abundant binding sites for the analytes. In recent years, G and GO had been used for solid-phase microextraction of pyrethroid pesticides [21]. Besides, Qu and Gu had reported that GO could be used for gas chromatography [22]. However, the researches of GQDs had still mainly focused on its quantum confinement , edge effects [23] and its application on photovoltaic devices, biosensing and imaging [24]. To the best of our knowledge, no recent survey showed an available

Analytical Methods Accepted Manuscript

report on the utilization of GQDs as a stationary phase for gas chromatographic separation, even though the high surface area, functional groups were advantageous to the fabrication of GQDs coated capillary column by a dynamic coating method. What's more, reducing the particle size of stationary phase will improve mass transfer in gas chromatography. Herein, we report the application of GQDs as an efficient stationary phase for GC separation. The capillary wall coated with GQDs will increase the column's phase ratio. GQDs were immobilized onto the capillary wall using 3-aminopropyldiethoxymethyl silane as coupling reagent [25-27]. The chromatographic performance of capillary column coated with GQDs was evaluated by alkanes and aromatic isomers.

Alkanes play significant roles in petroleum refining [28], while ethylbenzene (EB), styrene, propylbenzene, dichlorobenzene and xylene isomers are important constituents of raw chemicals in modern industry [29, 30]. For instance, EB is dehydrogenated to styrene for polystyrene, p-xylene is used as the reactant of poly (ethylene terephthalate) (PET), and o-xylene is widely used to produce phthalic anhydride. Propylbenzene and dichlorobenzene isomers are extensively applied as industrial solvents or chemical materials in the production of pesticides, herbicid and deodorant. Alkanes and aromatic isomers are usually separated for analytical purposes on capillary column coated with metal-organic frameworks, which act as a molecular sieve, but the diffusivities of these analytes are very low in the phase. So effective method for the rapid gas chromatographic separation still needs to be optimized. The stationary phases, such as diphenyl-phenyl polysiloxane [31], β-cyclodextrin [32], UIO-66 [33], gold nanoparticles [34], imidazolium ionic polymer[35] and carbon nanotubes [5, 8, 36], have been successfully applied as GC separation, but high temperature [9, 35-37], long analysis time [31, 38] or temperature-programming [6, 8 33, 39] are often needed.

In our work, GQDs were first investigated as a novel stationary phase for gas chromatography separation of alkanes, EB, styrene, propylbenzene, dichlorobenzene and xylene isomers. The capillary column coated with GQDs we prepared achieves a good separation of these isomers, what's more, it only needs short analysis time and the separation temperature was low. The effects of temperature and injected mass of analytes were also investigated.

Experimental

Chemicals and reagents

All chemicals and reagents were of analytical grade or above. Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Graphite powder was bought from Huayi Company (Shanghai, China). Phosphorus pentoxide (P_4O_{10}), hydrogen peroxide (H_2O_2, 30%), sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$, >99.5%), sodium hydroxide (NaOH), hexane, heptane, octane, nonane, decane, acetone, ethylbenzene, styrene and 1, 3, 5-trimethylbenzene were purchased from Kelong Technological Co. (Sichuan, China). Sec-, n-, isopentanol and o-, m-, p-dichlorobenzene were bought from Shanghai Chemical Reagent Co. (Shanghai, China). Potassium peroxydisulfate

Analytical Methods Accepted Manuscript

($K_2S_2O_8$, >99.5%), 2, 4-dimethylhexane and 3-methylheptane were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). n- Propylbenzene, isopropylbenzene, n-butylbenzene, sec-butylbenzene and tert-butylbenzene were bought from Aladdin Chemistry Co. Ltd. (Shanghai, China). o-Xylene, m-xylene and p-xylene were purchased from Tianjin Kermel Chemical Reagent (Tianjin, China). Isooctane was from Tianjin Meilin Industry and Trade Co. (Tianjin, China). All the chemicals were used without further purification. 3-AMDS was purchased from sigma (St. Louis, MO).

Instrumentation

The TEM images were conducted by a Hitachi H-800 electron microscope operating at an acceleration voltage of 200 kV. The thermal gravimetric analysis (TGA) was performed on a TA Q500 thermogravimetric analyzer (TA, USA) from room temperature to 600 ^{o}C at a heating rate of 8 ^{o}C min^{-1} under nitrogen. SEM images were performed by a Hitachi S-4800 ultra-high resolution field emission scanning electron microscope (Tokyo, Japan) to investigate the inner wall of the GQDs coated capillary column. X-ray photoelectron spectroscopy (XPS) spectra of the samples were measured by a Kratos XSAM 800 system for observing chemical composition and dispersion of species with a mono X-ray source Al Kα excitation (1486.6 eV).

All separations were performed on a Fuli model 9790 series GC equipped with a flame ionization detector (FID) (Shanghai, China). The data acquisition and processing were controlled by N3000 chemstation software (Zhejiang University, China). The carrier gas was nitrogen (99.999%). The injector temperature of the gas chromatograph was set to 250 ^{o}C, and the temperature of FID was set to 290 ^{o}C. The split ratio was 16:1. The commercial HP-5 (30 m, 0.32 mm i.d., 0.25 μm film thickness) and HP-innowax (20 m, 0.32 mm i.d., 0.25 μm film thickness) capillary columns from Agilent Technologies were employed for comparison.

Synthesis of GQDs

GO was synthesized from natural graphite powder by a modified Hummers method [40]. In this work, GQDs were prepared according to literature procedure [41]. Briefly, GO (0.5 mg mL^{-1}) was dispersed in deionized water with hydrogen peroxide (0.05 mL) added to the solution, then the mixture was re-oxided for 1 h by ozone which was produced by an OZ-7G Ozone Generator. After these procedures, the mixture was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (50 mL) and heated for 10 h at 200 ^{o}C. The products we got contained orange transparent suspension and black sediments. The suspension was further filtered through a 0.22 μm microporous membrane to remove the large tracts of GO and the greenish yellow fluorescent GQDs were obtained.

Capillary pretreatment and preparation of GQDs coated capillary columns

A fused silica capillary (22 m long × 0.32 mm i.d.) (Yongnian Ruifeng Optic Fiber Plant, Hebei, China) was treated according to the following recipe prior to

Analytical Methods Accepted Manuscript

coating [22, 42]: the capillary was washed sequentially with 1 M NaOH for 2 h, ultrapure water for 30 min, 0.1 M HCl for 2 h, and ultrapure water until the outflow reached pH 7.0. Finally, the capillary was dried with a nitrogen purge at 120 ^{o}C overnight.

After drying with nitrogen, the capillary column was flushed with 3 mL 3-AMDS toluene solution (1 vol%) to modify the inner surface of the capillary column through covalent interaction between hydroxy groups and 3-AMDS. The capillary column was kept at 80 ^{o}C for 12 h and then flushed with nitrogen. The GQDs were coated onto the inner wall of the pretreated capillary by a dynamic coating method as follows: The solution of GQDs in ethanol was filled with a plug into the capillary column under N_2, and then pushed through the column at a velocity of 30 cm·min^{-1}, leaving a wet coating layer on the inner wall of the capillary column. In order to avoid acceleration of solution plug near the end of the column, a 1 m long buffer tube (0.32 mm i.d.) was attached to the capillary column end as a restrictor. After coating, the capillary column was settled for 2 h for conditioning under gaseous N_2. The procedure could be repeated to increase the surface coverage. Further conditioning of the capillary column was carried out by employing a temperature program including three steps: 50 ^{o}C for 180 min, ramp from 50 ^{o}C to 100 ^{o}C at a rate of 1 ^{o}C·min^{-1} and 100 ^{o}C for 600 min.

Determination of McReynolds constants

As the most widely used system for evaluating the classification of novel chromatographic stationary phases, McReynolds constants were commonly employed to characterize the polarity of the stationary phases by choosing five probe compounds, namely benzene, n-butanol, 2-pentanone, nitropropane and pyridine. The respective constants of the five probe compounds were thought to evaluate various interactions between the stationary phase and the analytes in a particular way: X represents benzene, which is related to weak dispersion forces and the polarizability character of the phase. Y is for n-butanol, which indicates the hydrogen-bonding ability of the phase. Z represents 2-pentanone, whose behavior relates to the polarizability and part of the dipolar character of the stationary phase. U refers to nitropropane, which is related to the electron donor, electron acceptor and dipolar character of the phase. S refers to pyridine, a strong proton acceptor and polar molecule, which indicates the acidic character of the phase [43].

Results and discussion

Characterization of the synthesized GQDs and capillary column coated with GQDs

Fig. 1A showed the TEM image of GQDs, and the inset in Fig. 1A was the representative image of individual GQDs, which was high crystallinity. To investigate the chemical composition variation of the GO before and after the treatment of ozone and hydrothermal reaction, The XPS spectra were acquired. From Fig. 2A, we can see that the four C1s peaks can be assigned to C=C/C-C, C-O, C=O, and O-C=O, respectively. It was obvious that GQDs were functionalized with hydroxyl, carbonyl, epoxy, and carboxylic acid groups, while the GO only contained C=C and C-O before

Analytical Methods Accepted Manuscript

treatment. The TGA curve revealed that the GQDs were stable up to 100 ^{o}C (Fig. 1B). Although it showed poor thermostability, we could still obtain good separation of aromatic isomers under low temperature. Fig. S1 showed SEM images of the bare fused silica capillary column. We could see that the inner surface of the bare silica capillary column was smooth after the treatment of 1 M NaOH. After coating, the inner surface of the fabricated open tubular column became roughened (Fig. 2B), it also indicated that GQDs were successfully immobilized onto the capillary column. But the GQDs on the capillary wall were not evenly distributed. The column was coated with GQDs in a thin film with an average thick of $\approx$50 nm.

Performance of GQDs coated capillary column for gas chromatographic separation of alkanes, EB, styrene, xylene, propylbenzene, dichlorobenzene isomers

In order to investigate the separation capability of GQDs coated capillary column, we chose alkanes, EB, styrene, xylene, propylbenzene, dichlorobenzene isomers as the tested analytes. The GQDs coated capillary column also exhibited good separation with good precision (0.1-1.6%, 0.7-4.0%, 0.8-8.5%, and 1.2-2.2% ((RSD, n=5) for retention time, peak area, peak height, and half peak width, respectively) (Table 1**)**.

The gas chromatographic separation effect of GQDs coated capillary column were examined by alkanes with a wide range of boiling points, because alkanes play an important role in petroleum refining. We chose linear alkanes with the number of carbon atoms over 6 (Fig. 3A) to evaluate the potential application of GQDs coated capillary column. We successfully separated five alkanes within 5 min at low temperature. The elution sequence of alkanes on GQDs capillary column followed the order of boiling points, which was similar to the traditional stationary phase such as (5%-phenyl)-methylpolysiloxane. The relatively stronger van der Waals interaction between alkanes and the framework of GQDs made linear alkanes well separated from each other.

Fig. 3B showed the separation of isooctane, n-octane, 3-methylheptane, and 2, 4-dimethylhexane on GQDs column at 40 ^{o}C. The column could efficiently separate 2, 4-dimethylhexane from 3-methylheptane at 40 ^{o}C. The elution sequence of the octane isomers on GQDs coated capillary column followed the order of boiling points (2,4-dimethylhexane, 109 ^{o}C, 3-methylheptane, 118 ^{o}C, n-octane, 125.8 ^{o}C). The retention of alkanes on the capillary column mainly depended on their van der Waals interactions with GQDs. The 2,4-dimethylhexane molecule, which had shorter linear chain, had a weaker van der Waals interaction with GQDs, so it eluted faster than 3-methylheptane. The same trend was observed for 3-methylheptane and n-octane.

Our GQDs coated capillary column also exhibited high selectivity for the separation of EB and styrene. Their separation was also achieved on GQDs coated capillary column (Fig. 4A). EB and styrene were baseline separated with a selectivity of 1.8 , indicating that the π-π interaction between the styrene and aromatic framework walls of GQDs served an important function in the good separation. Besides, we could also find the same elution order of EB and styrene on HP-5 (Fig.

Analytical Methods Accepted Manuscript

S2) and HP-innowax (Fig. S3). On commercial HP-5 column, the selectivity of EB and styrene was 1.3, lower than 1.8, which was obtained on GQDs coated capillary column at 40 °C. In addition, compared with HP-5, the analysis time was greatly shortened, so the GQDs column provided us an efficient approach to lower the analysis time without sacrificing selectivity.

EB and xylene isomers play significant roles in air monitoring[44] and blood analysis[45]. However, the separation of EB and xylene isomers was a technical challenge due to the similarity of their boiling points and dimensions [28]. In recent years, they had been triumphantly separated by MIL-53(Al)[46]. Here, EB and xylene isomers were also chosen to test the feasibility of GQDs coated capillary column in gas chromatography. The chromatograms obtained on GQDs capillary column under chromatographic conditions were shown in Fig. 4B and Fig. S4, indicating that the p-xylene and m-xylene were eluted at equal retention time. The capillary column coated with GQDs was also investigated for gas chromatographic separation of dichlorobenzene, propylbenzene (Fig. 4C and 4D), butylbenzene and pentanol isomers (Fig. 5). The column offered good separation for these isomers. The peak symmetry of pentanol isomers was poor, indicating that pentanols showed strong hydrogen bond interaction with GQDs.

Dichlorobenzene isomers showed stronger retention than propylbenzene, EB, and xylene isomers, indicating that dichlorobenzene isomers had stronger interaction with GQDs because of the polar character contributed by hydroxyl and carboxyl groups, which enhanced the ability of polar affinity. The easier elution of p-xylene could be attributed to its lower dipole moment compared to o-xylene. What's more, o-xylene had the strongest van der Waals interaction and the highest polarity (dipole moment 0.54 D) among its four isomers. The dipole-induced hydrogen-bonding provided by the interaction of acid sites and o-xylene also made contribution to the good separation, so o-xylene was more strongly retained than EB and p-xylene. The elution order of EB, xylene, propylbenzene and dichlorobenzene isomers is the same for the commercial HP-5 (Fig. S2) and HP-innowax (Fig. S3) capillary columns. Besides, the elution order of EB and xylene isomers on GQDs coated capillary column follows the order of boiling points while MIL-101[47] is not. On MIL-101 column, p-xylene, whose boiling point is higher than EB, elutes earlier than EB. The reason of this phenomenon may be that pore-filling effect plays significant roles on MIL-101 column while van der Waals makes great contribution on GQDs coated capillary column.

In addition, the polarity of the column was expressed by McReynolds constants at 100 °C. The values for the stationary phase of GQDs were obtained in the study while the data for OV-22 and DB-5 were taken from the literature with the purpose of making comparison[48]. The average polarity of the stationary phases was listed in **Table 2**. It was found that the polarity of GQDs coated capillary column was 161， higher than DB-5 (64) but lower than OV-22 (215), so the polarity of GQDs stationary phase was moderate. The McReynolds constant for proton donor (Y,

Analytical Methods Accepted Manuscript

n-butanol) was higher than others, indicating that the hydrogen bond interaction is strong between the stationary phase and analytes.

The good resolution, precision, and selectivity for the separation of alkanes, EB, styrene, xylene, propylbenzene and dichlorobenzene isomers made the GQDs a promising candidate of GC stationary phase. An increase in analyte mass resulted in a linear increase of the chromatographic peak areas of aromatic isomers (Fig. 6), but almost no change occurred in retention time (Fig. S5). The features of the GQDs coated capillary column offered us its potential application in the aromatic isomers' qualitative and quantitative analysis.

HP-5 capillary column is an excellent nonpolar column which is coated with (5%-phenyl)-methylpolysiloxane. In our work, the commercial HP-5 capillary column is employed for comparison to demonstate the separation performance of GQDs coated capillary column. The elution time of alkanes and aromatic isomers on HP-5 capillary column is long, 57 min for EB, and 42 min for o-dichlorobenzene (Fig.S2C and S2F). But on GQDs coated capillary column, they only need a short time within 9 min (Fig. 4) to obtain a good separation. Besides, the isothermal separation is done at a temperature of no higher than 60 ^{o}C, far below the boiling points of the higher boiling analytes in the mixture, while high temperature is often needed on commercial HP-5 capillary column. What's more, because of the existence of epoxy, hydroxyl, carboxyl groups, GQDs column shows some characteristics of polar column, the commercial HP-innowax column is also used for comparison. In Fig.S3, it is found that the elution sequence of alkanes and aromatic isomers on HP-innowax is the same as the GQDs and HP-5 capillary columns, but high temperature and long analysis time are also inevitable. The above results show that GQDs coated capillary column offers us an other way to separate alkanes and aromatic isomers in a short analysis time without the process of temperature-programming.

In order to further explore the thermodynamics of the separation, a temperature range of 40-90 ^{o}C was measured to investigate the separation of xylene, propylbenzene, dichlorobenzene, styrene and EB isomers. When the column temperature increased, the retention time of analytes on GQDs coated capillary column gradually decreased (Fig. 7). The phenomenon indicated that the separation processes were exothermic[49]. Besides, the selectivity and resolution followed the same trends as the plots of retention time against the increase of temperature (Fig. 8 and Fig. S6).

The good linearity of the van't Hoff plots for the separation of substituted aromatics (Fig. 9) demonstrated that interaction mechanism remained unchanged in the studied temperature range. The values of ΔH and ΔS obtained from the van't Hoff plots were summed up in Table 3. More negative ΔH and more positive ΔS should be beneficial to the transfer of the solute from the mobile phase to the stationary phase, resulting in stronger retention of the analytes. Thus, we could come to the conclusion that the separation of isomers was a complex balance of thermodynamic and kinetic factors.

Analytical Methods Accepted Manuscript

Conclusion

In conclusion, we have not only demonstrated the feasibility of GQDs as a promising stationary phase for the GC separation of styrene, EB and xylene, propylbenzene and dichlorobenzene isomers with high resolution, good selectivity and reproducibility, but also offered excellent feature for the separation of linear and branched alkanes. They can be separated within 9 min at low temperature without the process of temperature-programming. Compared with the separation of these analytes on commercial HP-5 and HP-innowax capillary columns, the GQDs coated capillary column offered us a fast separation method at low temperature. 3-Aminopropyldiethoxymethyl silane, the coupling reagent between GQDs and the fused silica capillary column, makes GQDs firmly immobilized onto the inner surface of the capillary column. The presence of aromatic rings, rich functional groups and high surface areas makes GQDs very promising for effective application and separation in high-resolution capillary gas chromatography.

Acknowledgments

The authors are grateful to the Natural Science Foundation of China (Grant 21177090, 21275104) for supporting this work.

References

1. E. Matisova and S. Skrabakova, *J. Chromatogr. A*, 1995, 707, 145-179.
2. V. K. Ponnusamy and J.-F. Jen, *J. Chromatogr. A*, 2011, 1218, 6861-6868.
3. H. Zhang and H. K. Lee, *Anal. Chim. Acta*, 2012, 742, 67-73.
4. A. Safavi, N. Maleki and M. M. Doroodmand, *Anal. Chim. Acta*, 2010, 675, 207-212.
5. C. Saridara and S. Mitra, *Anal. Chem.*, 2005, 77, 7094-7097.
6. M. Karwa and S. Mitra, *Anal. Chem.*, 2006, 78, 2064-2070.
7. L.-M. Yuan, C.-X. Ren, L. Li, P. Ai, Z.-H. Yan, M. Zi and Z.-Y. Li, *Anal. Chem.*, 2006, 78, 6384-6390.
8. C. M. Hussain, C. Saridara and S. Mitra, *Anal. Chem.*, 2010, 82, 5184-5188.
9. Q. Li and D. Yuan, *J. Chromatogr. A*, 2003, 1003, 203-209.
10. P. F. Fang, Z. R. Zeng, J. H. Fan and Y. Y. Chen, *J. Chromatogr. A*, 2000, 867, 177-185.
11. A. Speltini, D. Merli, D. Dondi, G. Paganini and A. Profumo, *Anal.Bioanal. Chem.*, 2012, 403, 1157-1165.
12. A. Speltini, D. Merli, E. Quartarone and A. Profumo, *J.Chromatogr. A*, 2010, 1217, 2918-2924.
13. M.-M. Wang and X.-P. Yan, *Anal. Chem.*, 2011, 84, 39-44.
14. W. Zhang, J. Zhang, T. Bao, W. Zhou, J. Meng and Z. Chen, *Anal. Chem.*, 2013, 85, 6846-6854.
15. M. Sun, R. Tang, Q. Wu, C. Wang and Z. Wang, *Anal. Methods*, 2013, 5, 5694-5700.

Analytical Methods Accepted Manuscript

16. G. Zhao, S. Song, C. Wang, Q. Wu and Z. Wang, *Anal. Methods*, 2011, 3, 2929-2935.
17. J. Feng, H. Qiu, X. Liu, S. Jiang , *TrAC Trends Anal Chem*, 2013, 46, 44-58.
18. X. Liang, S. Wang, S. Liu, X. Liu and S. Jiang, *J. Sep. Sci.*, 2012, 35, 2003-2009.
19. M. Zhang and H. Qiu, *TrAC Trends Anal. Chem.*, 2015, 65, 107-121.
20. G. I. Titelman, V. Gelman, S. Bron, R. L. Khalfin, Y. Cohen and H. Bianco-Peled, *Carbon*, 2005, 43, 641-649.
21. J. M. Chen, J. Zou, J. B. Zeng, X. H. Song, J. J. Ji, Y. R. Wang, J. Ha and X. Chen, *Anal. Chim. Acta*, 2010, 678, 44-49.
22. Q. S. Qu, Y. Q. Shen, C. H. Gu, Z. L. Gu, Q. Gu, C. Y. Wang and X. Y. Hu, *Anal. Chim. Acta*, 2012, 757, 83-87.
23. L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov and A. K. Geim, *Science*, 2008, 320, 356-358.
24. Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou and L. Qu, *Adv. Mater.*, 2011, 23, 776-780.
25. D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, 39, 228-240.
26. Q. Liu, J. Shi, J. Sun, T. Wang, L. Zeng and G. Jiang, *Angew. Chem. Int. Ed.* 2011, 50, 5913-5917.
27. S. Song, R. Chu, J. Zhou, S. Yang and J. Zhang, *J.Phys. Chem. C*, 2008, 112, 3805-3810.
28. L. I. Devriese, L. Cools, A. Aerts, J. A. Martens, G. V. Baron and J. F. M. Denayer, *Adv. Funct. Mater.*, 2007, 17, 3911-3917.
29. L. Alaerts, M. Maes, P. A. Jacobs, J. F. M. Denayer and D. E. De Vos, *Phys. Chem. Chem. Phys.*, 2008, 10, 2979-2985.
30. C.-X. Yang, S.-S. Liu, H.-F. Wang, S.-W. Wang and X.-P. Yan, *Analyst*, 2012, 137, 133-139.
31. p. Zhao, S. Teng, M. Yu, N. Niu, X. He and B. Wu, *Anal. Methods*, 2014, DOI: 10.1039/C4AY01928H.
32. Y.-M. Liu, P. Gordon, S. Green and J. V. Sweedler, *Anal. Chim. Acta*, 2000, 420, 81-88.
33. N. Chang and X.-P. Yan, *J. Chromatogr. A*, 2012, 1257, 116-124.
34. G. M. Gross, D. A. Nelson, J. W. Grate and R. E. Synovec, *Anal. Chem.*, 2003, 75, 4558-4564.
35. W.-Y. Ho, Y.-N. Hsieh, W.-C. Lin, C. L. Kao, P.-C. Huang, C.-F. Yeh, C.-Y. Pan and C.-H. Kuei, *Anal. Methods*, 2010, 2, 455-457.
36. D. Merli, A. Speltini, D. Ravelli, E. Quartarone, L. Costa and A. Profumo, *J. Chromatogr. A*, 2010, 1217, 7275-7281.
37. Z. Y. Gu and X. P. Yan, *Angew. Chem. Int. Ed.*, 2010, 49, 1477-1480.
38. A. V. Herrera-Herrera, M. Á. González-Curbelo, J. Hernández-Borges and M. Á. Rodríguez-Delgado, *Anal. Chim. Acta*, 2012, 734, 1-30.

Analytical Methods Accepted Manuscript

39. P. Zhao, L. Liu, M. Yu, N. Niu, B. Wu and G. Wang, *Anal. Methods*, 2014, 6, 6278-6284.
40. L.-L. Li, K.-P. Liu, G.-H. Yang, C.-M. Wang, J.-R. Zhang and J.-J. Zhu, *Adv. Funct. Mater.*, 2011, 21, 869-878.
41. F. Yang, M. Zhao, B. Zheng, D. Xiao, L. Wu and Y. Guo, *J. Mater. Chem.*, 2012, 22, 25471-25479.
42. Q. Qu, C. Gu and X. Hu, *Anal. Chem.*, 2012, 84, 8880-8890.
43. A. Berthod, E. Y. Zhou, K. Le and D. W. Armstrong, *Anal. Chem.*, 1995, 67, 849-857.
44. N. Yassaa, E. Brancaleoni, M. Frattoni and P. Ciccioli, *Chemosphere*, 2006, 63, 502-508.
45. H. Hattori, M. Iwai, S. Kurono, T. Yamada, K. Watanabe-Suzuki, A. Ishii, H. Seno and O. Suzuki, *J.Chromatogr. B,* 1998, 718, 285-289.
46. W. De Malsche, S. Van der Perre, S. Silverans, M. Maes, D. E. De Vos, F. Lynen and J. F. Denayer, *Micropor. Mesopor. Mat.*, 2012, 162, 1-5.
47. Z.-Y. Gu and X.-P. Yan, *Angew. Chem. Int. Ed.,* 2010, 49, 1477-1480.
48. W. McReynolds, *J. Chromatogr. Sci.*, 1970, 8, 685-691.
49. Z.-L. Fang, S.-R. Zheng, J.-B. Tan, S.-L. Cai, J. Fan, X. Yan and W.-G. Zhang, *J.Chromatogr. A*, 2013, 1285, 132-138.

Analyte	RSD (%) (n=5)			
	Retention time	Peak area	Peak height	$W_{1/2}$
EB	1.3	1.5	1.8	2.1
Styrene	1.6	2.4	1.1	2.2
EB	0.7	1.4	1.1	2.1
p-Xylene	0.8	1.3	0.8	1.7
o-Xylene	0.8	2.4	0.9	1.8
Isopropylbenzene	0.2	1.4	6.0	1.2
n-Propylbenzene	0.1	1.2	7.0	1.2
1,3,5-Trimethylbenzene	0.1	0.9	8.5	1.7
m-Dichlorobenzene	1.3	0.7	2.3	1.8
p-Dichlorobenzene	1.3	3.1	1.0	1.5
o-Dichlorobenzene	1.2	4.0	3.3	1.6

Table 1 Precision for five replicate separation of aromatic isomers on the GQDs coated capillary column.

Analytical Methods Accepted Manuscript

Columns	X	Y	Z	U	S	Average
Squalane	0	0	0	0	0	0
DB-5(ref.48)	27	66	71	93	63	64
GQDs	29	274	97	191	216	161
OV-22(ref.48)	160	188	191	283	253	215

Table 2 McReynolds constants and average polarity of GQDs and other kinds of columns at 100 ^{o}C.

Analyte	-ΔH (kJ mol^{-1})	-ΔS (J mol^{-1}K^{-1})	R^2
EB	37.9 ± 0.1	92.3 ± 0.4	0.99986
Styrene	40.1 ± 0.2	94.4 ± 0.5	0.99984
EB	37.6 ± 0.2	91.3 ± 0.5	0.99990
p-Xylene	38.4 ± 0.2	93.0 ± 0.5	0.99988
o-Xylene	39.1 ± 0.1	93.0 ± 0.4	0.99992
Isopropylbenzene	40.6 ± 0.3	95.8 ± 0.8	0.99978
n-Propylbenzene	42.0 ± 0.3	97.5 ± 0.9	0.99978
1,3,5-Trimethyl benzene	43.4 ± 0.2	99.5 ± 0.7	0.99974
m-Dichlorobenzene	44.5 ± 0.3	99.0 ± 0.9	0.99980
p-Dichlorobenzene	45.0 ± 0.3	99.9 ± 0.8	0.99984
o-Dichlorobenzene	45.7 ± 0.3	99.8 ± 1.0	0.99978

Table 3 Values of ΔH, ΔS and R^2 for EB, styrene, and xylene, propylbenzene, dichlorobenzene isomers.

Fig. 1 (A) TEM images of the as-prepared GQDs, the inset is the HRTEM image of GQDs; (B) TGA curve of the prepared GQDs.

Fig. 2 (A) XPS spectra of C1s of the original graphene oxide film (a) and XPS spectra of C1s of the as-produced GQDs (b); (B) (a). SEM image of the GQDs deposited on the inner wall of the capillary column; (b) the SEM image of the GQDs coated capillary column, (c) SEM image of the cross section view of the inlet of GQDs coated capillary column.

Fig. 3 Gas chromatograms on the GQDs coated capillary column (22 m long × 0.32 mm i.d.) at a N_2 flow rate of 0.7 mL min^{-1} for the separation of (A) hexane, heptane, octane, nonane, decane using a temperature program of 40 ^{o}C for 2 min, and then 20 ^{o}C min^{-1} to 90 ^{o}C; (B) isooctane, 2,4-dimethylhexane, 3-methylheptane, n-octane at 40 ^{o}C.

Analytical Methods Accepted Manuscript

Fig. 4 Gas chromatograms on the GQDs coated capillary column (22 m long × 0.32 mm i.d.) for fast separation of (A) EB and styrene under a N_2 flow rate of 0.7 mL min^{-1} at 40 ^oC; (B) EB, p-xylene and o-xylene under a N_2 flow rate of 0.7 mL min^{-1} at 50 ^oC; (C) isopropylbenzene, n-propylbenzene and 1,3,5-trimethylbenzene under a N_2 flow rate of 0.7 mL min^{-1} at 60 ^oC; (D) m-dichlorobenzene, p-dichlorobenzene, o-dichlorobenzene under a N_2 flow rate of 0.7 mL min^{-1} at 50 ^oC.

Fig. 5 Chromatograms on the GQDs coated capillary (22 m × 0.32 mm i.d.) for GC separation of (A) n-pentanol and its branched isomers under a N_2 flow of 0.7 mL min^{-1} using a temperature program (40 ℃ for 2 min, then 20 ℃ min^{-1} to 90 ℃); (B) tert-, sec-, n-butylbenzene under a N_2 flow of 0.7 mL min^{-1} at 50 ℃.

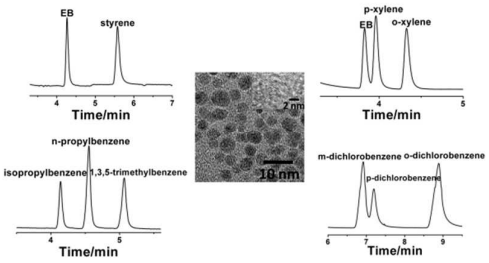
Fig. 6 Effect of analyte mass on the peak area response: (A) EB and styrene; (B) EB, p-xylene and o-xylene; (C) propylbenzene isomers; (D) dichlorobenzene isomers.

Fig. 7 Effect of temperature on the chromatograms on the GQDs coated capillary column (22 m long ×0.32 mm i.d.) for the separation of: (A) EB and styrene; (B) EB, p-xylene and o-xylene; (C) propylbenzene isomers; (D) dichlorobenzene isomers.

Fig. 8 Effect of temperature on selectivity for the separation of: (A) EB and styrene; (B) EB, p-xylene and o-xylene; (C) propylbenzene isomers; (D) dichlorobenzene isomers.

Fig. 9 Van't Hoff plots for (A) EB and styrene; (B) EB and xylene isomers; (C) propylbenzene isomers; (D) dichlorobenzene isomers on the capillary column coated with GQDs.

Analytical Methods Accepted Manuscript



GQDs column was firstly employed for successfully separation of alkanes and aromatic isomers at low temperature in a short time.

Analytical Methods Accepted Manuscript

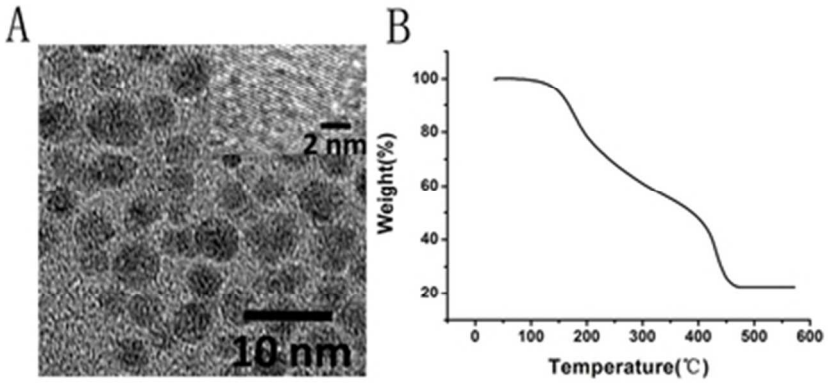


Fig .1
37x17mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

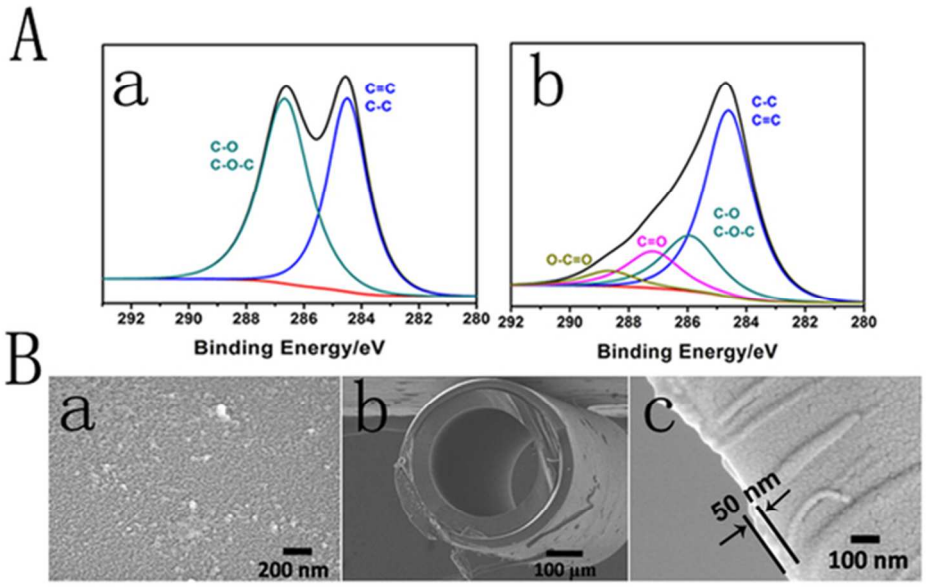


Fig.2
52x33mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

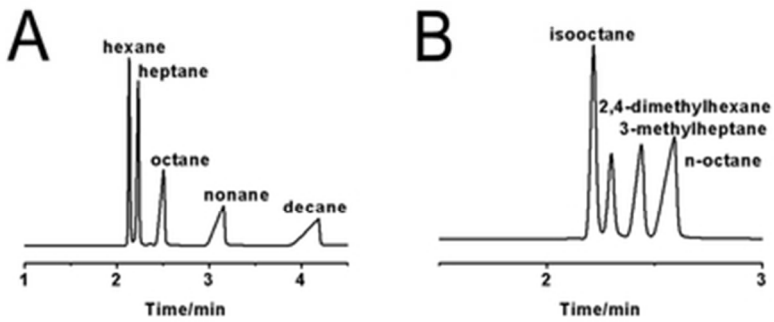


Fig. 3
35x15mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

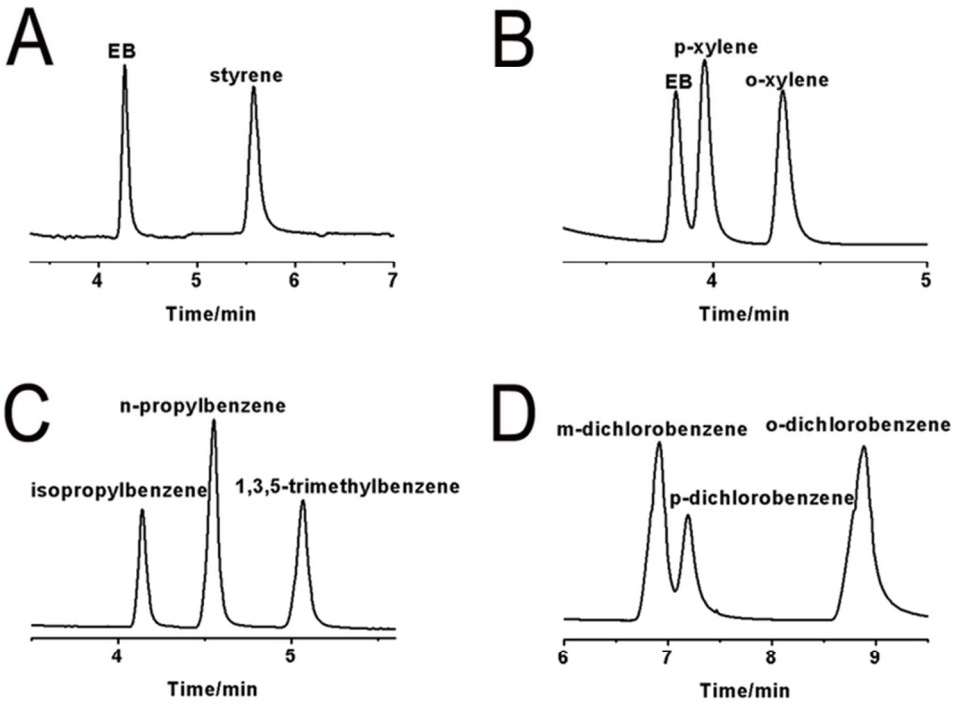


Fig. 4
64x50mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

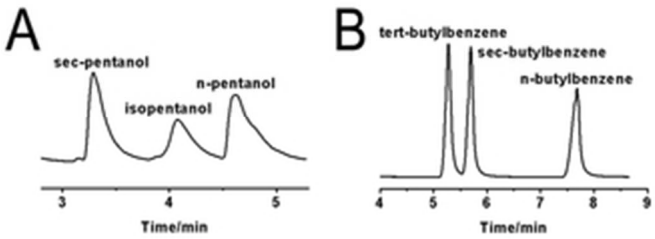


Fig. 5
29x10mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

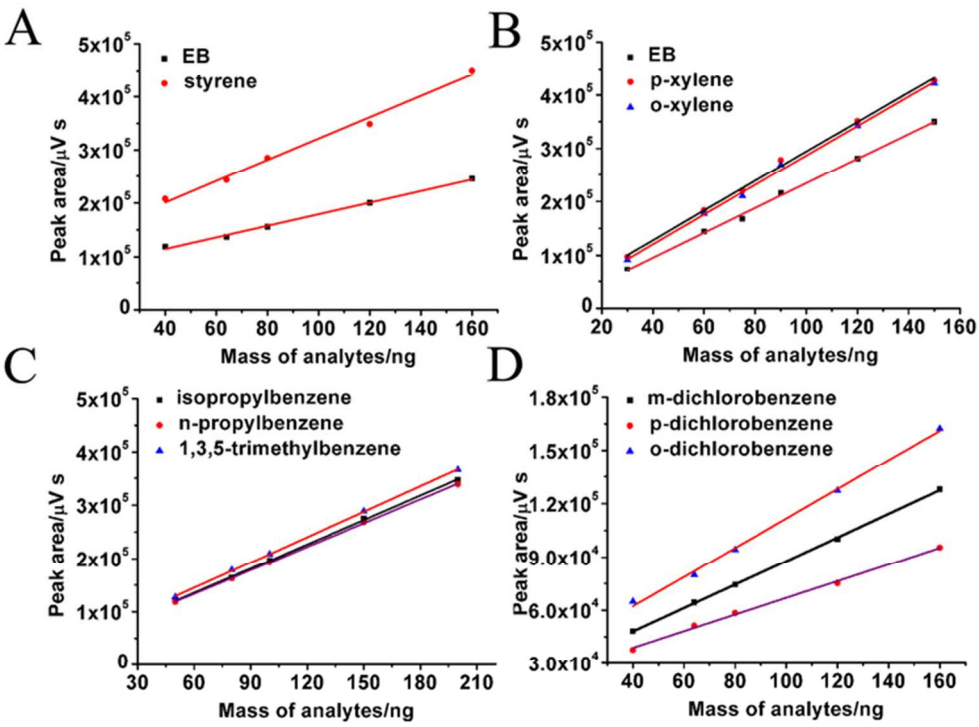


Fig. 6
64x50mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

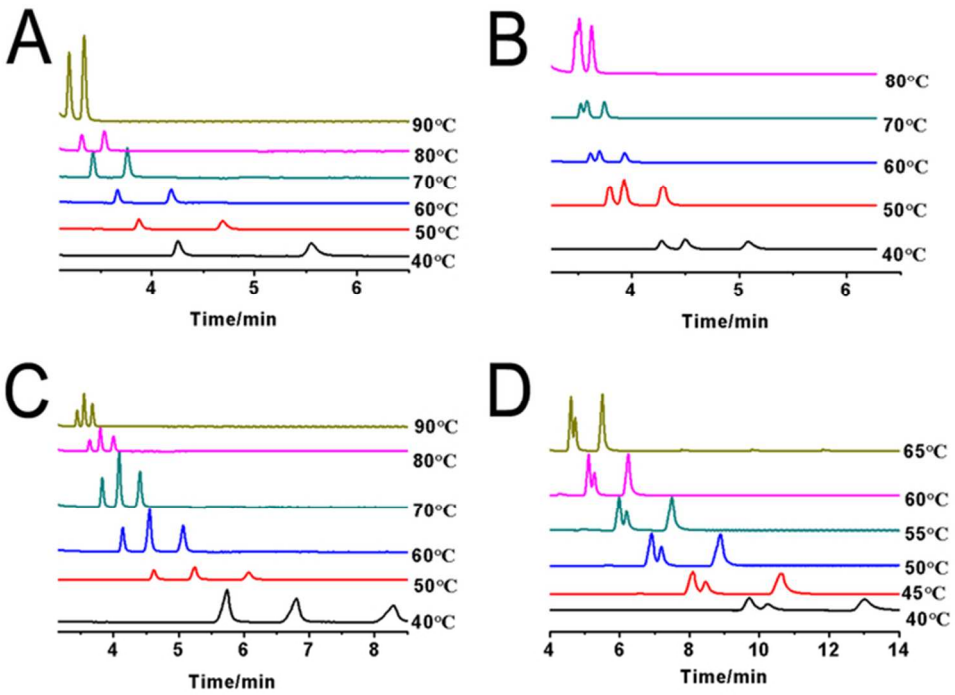


Fig. 7
61x46mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

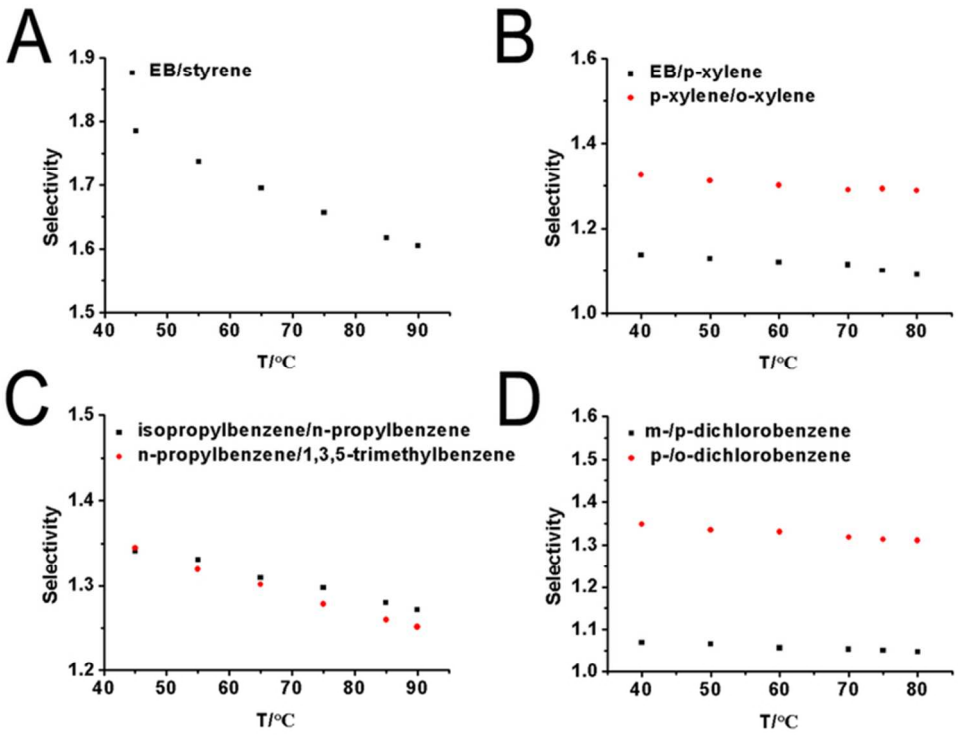


Fig. 8
65x51mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript

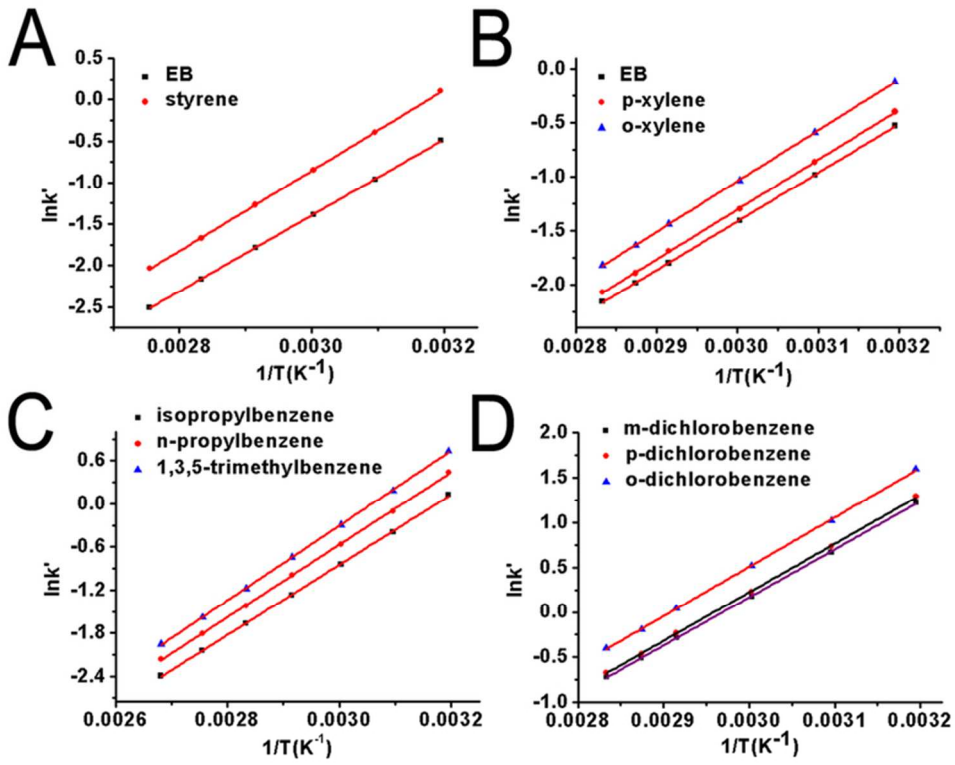


Fig. 9
69x57mm (300 x 300 DPI)

Analytical Methods Accepted Manuscript