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Separation and Quantification of Hydrocarbons of LPG Using Novel MWCNT-Silica Gel Nanocomposite as Packed Column Adsorbent of Gas Chromatography

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Abstract

In this study, a new silica gel based adsorbent was fabricated and its ability in separation and quantification of alkanes mixture was investigated. Silica gel (SiO2) is a polar absorbent which is mainly used to separate polar compounds. Also, the carbon materials such as activated carbon and recently carbon nanotube (CNTs), have been widely used for separation of nonpolar materials. Carbon nanotubes are nanosized carbon-based sorbents that have a high surface area and a large aspect ratio and are known to be stable at high temperatures. It is, therefore, conceivable to use of their unique properties in gas chromatography. In this work, a MWCNT-Silica gel nanocomposite was prepared by Sol-Gel process and it was used as stationary phase in gas chromatography for separation of alkanes mixture. In first part, ability of silica gel adsorbent was studied and then results were compared with new MWCNT-Silica gel nanocomposite. Finally, a quantitative investigation was done on a LPG sample and propane, 2-methylpropane, n-butane, 2,2-dimethylpropane, 2-methylbutane and n-pentane were measured by standard addition.

Keyword: MWCNTs-SiO2, Nanocomposite, Sol-Gel process, Gas Chromatography, LPG, Hydrocarbon, Alkanes

1. Introduction

Hydrocarbons are one the most important raw materials and plays key role in industrial process, from heat production to conversion to new materials. These materials also are known as pollutants environment. Therefore, determination and analysis of these materials need important attention. Based on incredible variety of these materials and different physical and chemical characters, identification and quantification of these materials in different mixture is goal of some separation researches. Isomerization of these materials changes their activity and molecular size and leads to complexity of these mixtures and

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reduces ability of current separation methods (1). In addition of instrumental progression in Gas Chromatography (GC), adsorbents have incredible promotion and some new materials and composites were introduced by researchers. Molecular sieves, Porous polymers (e.g. Porapak), activated carbons, nanocomposites, silica gel and other materials are developed and used for separation and determination of volatile and gaseous mixtures (2). All of these materials have special instrumental conditioning and specific variety of separation. Based on incredible thermal abilities and high polarity of silica gel, this material plays key role as adsorbent in Gas Chromatography packed column. Sol-Gel technique is a applicable method for fabrication of silica gel (3), (4). Silica gel has polar surface that makes it excellent adsorbent for doing separation of polar compounds. Although these characters are good for some separations, but this adsorbent does not have enough surface for separate compounds with same polarity specifications (5). Most of gaseous mixtures have polar and non-polar compounds simultaneously and so all separation must be done in two or three step by polar and non-polar column. Production of column with polar and non-polar characters is the main goal of researchers. Carbon nanotube (CNTs) was shown interesting ability for using as adsorbent for Gas-Solid Chromatography (GSC) in packed and capillary column (6). Polarity or non-polarity of surface (based on its functional groups), good inner hollow cavity, extend outside surface, spaces between nano bundle, active π orbitals on its surface and high temperature resistance make MWCNTs as a good candidate for adsorption composites (7). Based on incredible abilities of MWCNTs (8) and strong bond between C and SiO2 (9), MWCNT-SiO2 ceramic can be the best candidate for fabrication of packed column (10), (11).

In this research, MWCNT-SiO2 nanocomposite as a selective adsorbent is fabricated by Sol-Gel technique and separation of alkans mixture is investigated and then, by standard addition technique and generating of calibration curve, percentage of different alkanes in a sample Liquid Petroleum Gas (LPG) is determined and reproducibility of separations and stability of this adsorbent are tested.

2. Experimental

2.1. Chemicals and Apparatus

All chemicals were in the highest purity and bought from Sigma-Aldrich. For doing sol-gel process, these compounds were provided: glass water (sodium silicate) with NaO:Si ratio of 7.5% and Si-concentration of 14% mol/lit, deionized water, sulfuric acid (96%). The MWCNTs (-COOH derivative) and LPG were produced by Research Institute of Petroleum Industry (RIPI) via CVD process. All pure hydrocarbons were purchased from Mojallali Chemicals in capsules. An equipped Shimadzu 14B Gas chromatograph (GC) with thermal conductivity detector (TCD) was used. High purity helium (99.99%) was employed as carrier gas. All injection was done by especial injection instrument that was designed by RIPI and was embedded between carrier gas and sample injector. All hydrocarbon gases were carried by 5 ml Gas Sampling Bags from Tedlar. Adsorbent was prepared by passing carrier gas in proper column conditions and checking TCD detector. The instrument was conditioned at 200 °C with a He carrier gas flow of 35 ml/min for 3 hours. Important factors are listed at table 1.

Table 1 Parameters of Gas Chromatography for analysis

Columns	Carrier gas	Detector: TCD	injection
Stainless steel columns of 3 m long and 3mm. Column was packed with adsorbent with mesh 60-80 (0.16-0.125 mm)	He with flow rate: 35 ml/min	temperature: 180 ˚C current: 150 mA	sample loop volume:1ml, 2ml

2.2. Sol-Gel process for Synthesis of MWCNT-SiO2 nanocomposite

Primary compound for silica gel is water glass (Na2SiO3). First of all, a homogeneous mixture of MWCNT in water glass was prepared by adding 5% MWCNT (W.V) and 7.5 % water glass (Na2SiO3). For this reason, this solution was mixed and dispersed using ultrasonic bath. After preparing a homogeneous dark solution, the mixture was added slowly to sulfuric acid solution to reach pH = 2.5-3.5. The following reactions were occurred based on type of primary materials.

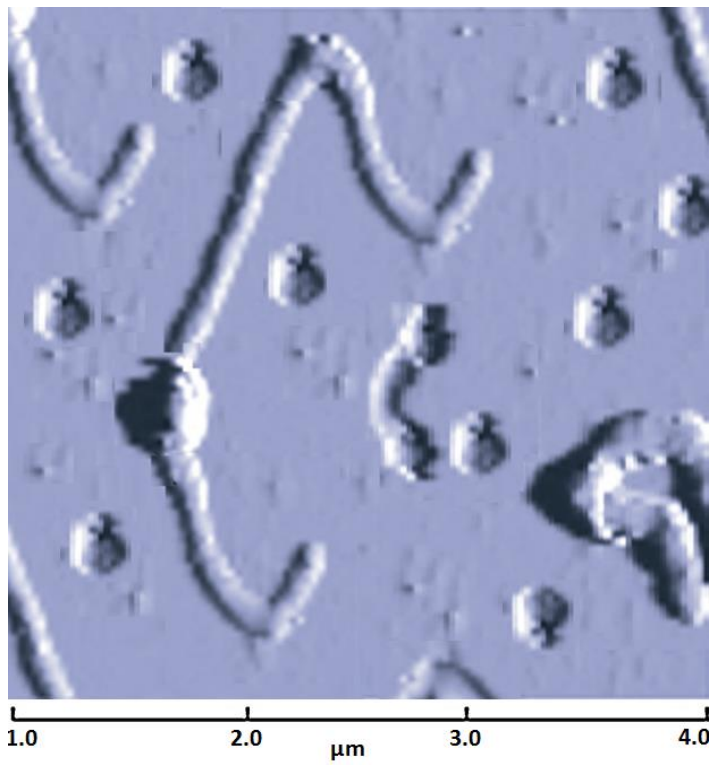

Figure 1: The AFM images of MWCNT-Silica gel gas chromatography adsorbent.

$$Na_2SiO_3 + H^+ \rightarrow [SiO_2.xH_2O] + 2NaX$$
Silica Gel

$$Na_2SiO_3 + H^{++} MWCNTs \rightarrow [SiO_2.xH_2O, MWCNTs] + 2NaX$$
CNTs-Silica Gel

In next step, for making suitable mesh, spraying the solution with high pressure into the hot oil was done by oil drop method. Washing MWCNT- SiO_2 mixture by water and organic solvents was the next step for removing oil and other impurities. Then by blowing warm air, solvent was evaporated. Fixing of mixture was done by calcination of the mixture at 200˚C in oven. Meshing process was the final step (60-80). After that, adsorbent got ready for packing in suitable GC packed column. Figure 1 shows AFM (Atomic force microscopy) image of this new adsorbent. The AFM images were obtained with CSM instrument. For the analysis of samples, firstly sample were speeded in dimethylformamide (0.1 mg/mL) by sonication for at least 1 h, then 5 µL of that was scattered onto a mica sheet and scans were carried out with a scan rate of 1.0 Hz.

pH is the most important factor in gelation time. Based on this factor, pH must be tuned for getting best mesh and highest quality, because an aggregation may takes place and desired mesh cannot be produced after oil drop method (12). The lowest gel forming was occurred at pH=2 and fastest gelation time is at pH=6 (13) and due to importance of homogeneous mixing of solution, pH=2.5-3.5 was selected.

3. Result and Discussion

3.1 Separation of linear and branched alkanes by Silica gel adsorbent

In first step of experiments, an unmodified silica gel packed column was employed on Shimadzu and stabilization was achieved after 4 h at 200 °C with a carrier flow rate 50 ml/min. Other instrument conditions were listed at table 1. After that, 1 ml of hydrocarbons mixture, includes equal value of

propane, 2-methylpropane, n-butane, 2,2-dimethylpropane, 2-methylbutane and n-pentane were injected and gas chromatogram of this mixture at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min was obtained (figure 2). As shown in figure 2, based on nature of silica gel and polarity of this adsorbent, elution of all compounds was done after applying temperature program and asymmetric and tailed peaks were obtained. 2-methylpropane and n-butane have same molecular mass and so were co-eluted at close retention time. Except 2,2-dimethylpropane (due to its space shape), two other C5 hydrocarbons (2-methylbutane and n-pentane) were co-eluted at near retention time and their peaks were tailed and silica gel could not apply proper gradient adsorption on this mixture of compounds.

3.2 Separation of linear and branched alkanes by modified MWCNT-Silica gel adsorbent

In next step and the same column conditions, ability of modified MWCNT-silica gel adsorbent was tested by injection of hydrocarbons mixture. As shown in figure 3, six incredible symmetric peaks were appeared and hydrocarbons were eluted in longer time and separation at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min was done completely.

There are some reasons for interpretation of this good separation. The first reason is increasing of active surface due to characters of MWCNT. Functional MWCNTs are open-ended tubes and have extended surface in and out of tubes. These holes on surface of adsorbent increase active surface for interaction with analytes and based on Van de Waals forces and entropy, interaction of non-polar molecules are different on surface of adsorbent.

On the other hand, strength of the interaction is related to length of hydrocarbon, surface area and hydrophobicity of surface. This statement is the main reason for separation of linear hydrocarbons. On the other side, branched hydrocarbons are affected by entropy effect and they cannot have strong interaction with surface as well as slender molecules and so, their rate of exit is increased. The second reason for this good sieving is that branched hydrocarbons cannot pass interstices of MWCNT or between of them.

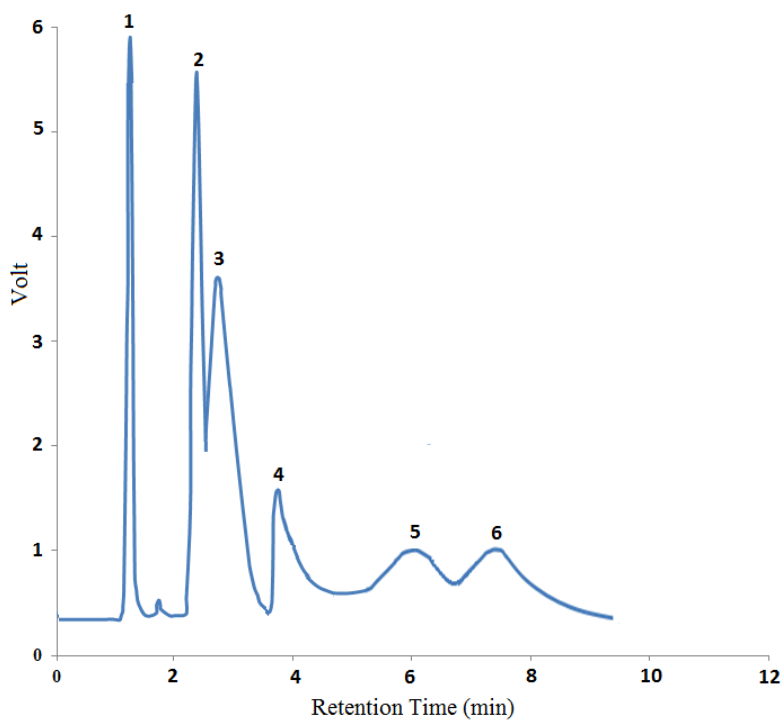

Figure 2: Chromatogram collected of a alkanes mixture sample with equal value on unmodified silica gel, at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min. propane (1), 2-methylpropane (2), n-butane (3), 2,2-dimethylpropane (4), 2-methylbutane (5) and n-pentane (6).

Jiang et al. found out that branched hydrocarbons cannot fit between SWCNT bundles and based on this effect, a molecular sieving was occurred on surface of adsorbent (14). Last effect is applying of programmed temperature on column. Different molecular shape causes a variety of Wan der Waals interaction between adsorbent and analytes and based on correlation of Wan der Waals interaction and temperature, adsorption and desorption processes were done completely.

3.3 Determination of hydrocarbons in a LPG sample by modified MWCNT-Silica gel adsorbent

Based on column performance on separation of alkanes mixture, a certified LPG sample was injected and figure 4 at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min was obtained. As figure 4 shown, gas chromatogram of LPG shows propane, 2-methylpropane, n-butane, 2,2-dimethylpropane, 2-methylbutane and n-pentane. For quantification of alkanes in LPG, standard addition was used and propane and 2,2-dimethylpropane were selected for standard addition and five different syringes (5 µL, 10 µL, 25 µL, 50 µL and 100 µL) was used and five point calibration curve for propane and 2,2-dimethylpropane was generated (figure 5 and 6). The linear regression equations and the correlation coefficients (R2) for propane and 2,2-dimethylpropane were obtained.

Base on signals and calibration curve, this sample was involved: 33% 2-methylpropane, 30% n-butane, 18% propane, 10% 2,2-dimethylpropane, 5% 2-methylbutane, 3% n-pentane and 1% other compounds. RSD% is from 8 to 13% for determinations.

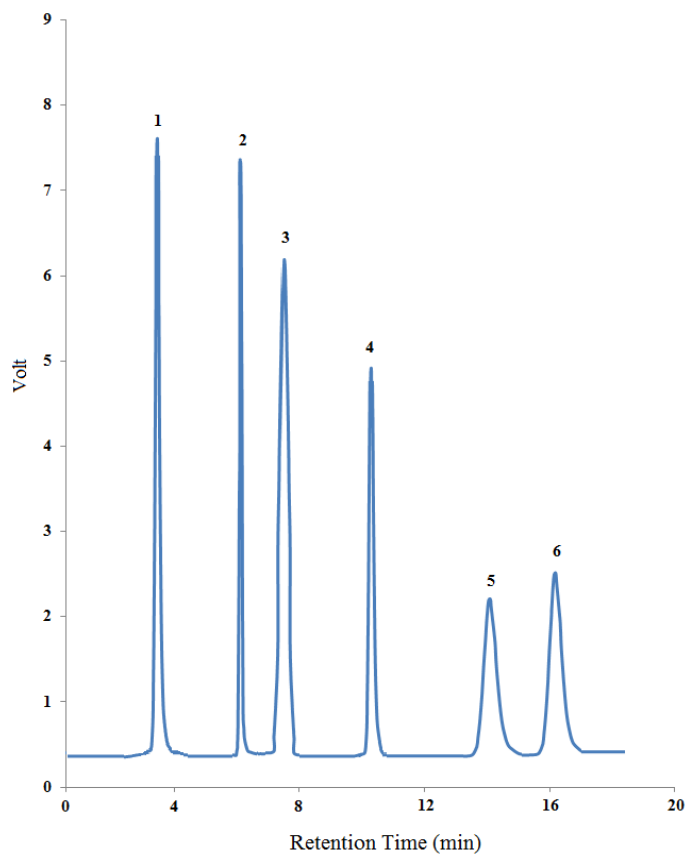

Figure 3: Chromatogram collected of a alkanes mixture sample with equal value on MWCNT-Silica gel, at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min. propane (1), 2-methylpropane (2), n-butane (3), 2,2-dimethylpropane (4), 2-methylbutane (5) and n-pentane (6).

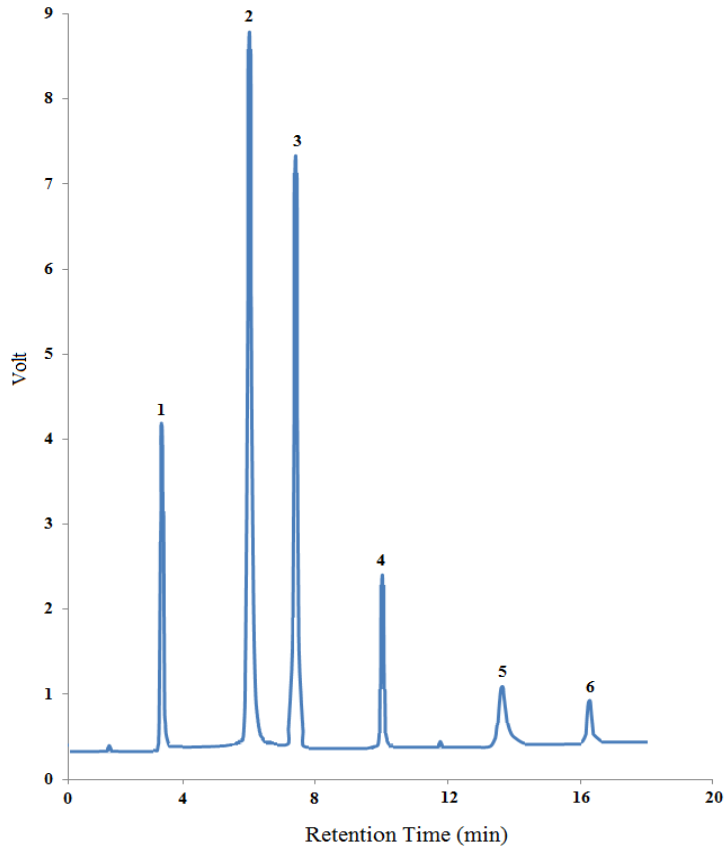

Figure 4: Gas chromatogram of LPG sample on MWCNT-Silica gel adsorbent at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min. propane (1), 2-methylpropane (2), n-butane (3), 2,2-dimethylpropane (4), 2-methylbutane (5), n-pentane (6).

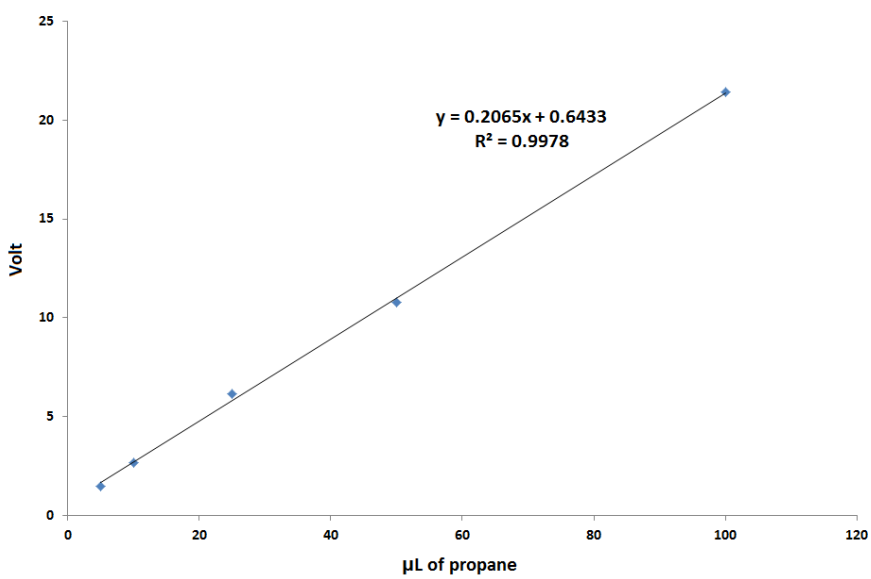

Figure 5: five point calibration curve of standard addition for propane (5 µL, 10 µL, 25 µL, 50 µL and 100 µL).

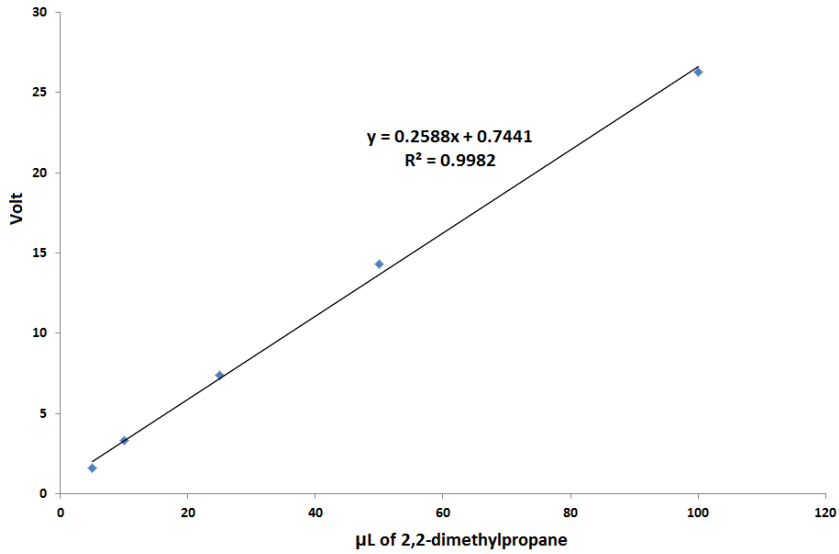

Figure 6: five point calibration curve of standard addition for 2,2-dimethylpropane (5 µL, 10 µL, 25 µL, 50 µL and 100 µL).

4 Conclusions

In this study, a new silica gel based adsorbent was fabricated and its ability in separation and quantification of alkans mixture was investigated. Compared with silica gel adsorbent, MWCNT-silica gel shows some advantages: (1) more surface area and therefore more symmetric peaks, (2) more retention time that cause increase sensitivity and separation ability for mixtures with near boiling points and (3) ability for separation of polar and nonpolar mixture in one injection.

5 Acknowledgements

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