Quantitative Determination of LPG Hydrocarbons by Modified Packed Column Adsorbent of Gas Chromatography Via Full Factorial Design

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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. Optimization of gas chromatography with modified and unmodified columns was investigated by full factorial design. According to the results of proposed design, the temperature, flow rate and carrier gas are known to be important factors affecting performance. 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. Finally, the greatest difference between the response profiles in modified and unmodified column was determined.

Keywords: MWCNTs-SiO₂, Nanocomposite, Sol-Gel process, Gas chromatography, LPG, Hydrocarbon, Alkanes
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INTRODUCTION
Finding the best analytical method for separation of hydrocarbons is the key research at petroleum industry. Alkanes are used as a primary raw material for conversion to other products and also are known as air pollutants. So, analysis of these compounds are so interesting for scientists. Due to same physical and chemical
characters, determination of their mixtures are so difficult and regular GC methods can separate these mixtures partially. There are some different chromatographic techniques for separation of gas mixtures, in respect of their chemical and physical characters. In all techniques, the researchers encounter to similar problems that are related to finding the optimum chromatographic conditions. Most of new researches are focused on preparation of new stationary phases that provide the highest gradient affinity to gases, which can increase signal to noise (S/N), difference of sequence retention time and area of peaks. 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(1). All of these materials have special instrumental conditioning and specific variety of separation.

Silica gel has polar surface that makes it excellent adsorbent for doing separation of polar compounds as stationary phase at micropacked column(2). Although these characters are good for some separations, but this adsorbent does not have enough surface for separate compounds with same polarity specifications. So, fabrication of functionalized silica gel is the best technique for getting better separation of gaseous mixtures(3). Multiwall Carbon Nanotube (MWCNT) has a promising characters and its high affinity to non-polar hydrocarbons can increase retention time of non-polar gases and provides separate peaks. The hydrocarbons have different physical characters on CNT based stationary phase in comparison of polar surface and polar-nonpolar surface can provide proper gradient surface for higher separation. 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(4), (5) and (6).

Sol-Gel technique is a reliable and promising method for fabrication of silica gel and silica gel has polar surface that makes it excellent adsorbent for doing separation of polar compounds. By this method, the size and mesh of granules could be adjusted and at solution step, functionalization can be done (7), (8). High heat resistivity of silica gel is another character of this stationary phase that is so interested for researchers. Based on incredible abilities of MWCNTs and strong bond between C and SiO₂, MWCNT-SiO₂ ceramic can be the best candidate for fabrication of packed column(9).

Experimental design that takes into account to simultaneously investigate the effects of several variables seems to be the most convenient approach to searching the optimal operational conditions in a reasonable number of runs (10, 11). Factors that affected on GC performance were screened and optimized by performing of factorial design. The proposed design was developed for chemometric analysis of complex multi-component chromatographic signals of gas chromatography with modified and unmodified columns, which help to resolve mixtures by determining the greatest difference between their response profiles.

In this research, MWCNT-SiO₂ nanocomposite as a selective adsorbent is fabricated by Sol-Gel technique and separation of alkanes 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.

**EXPERIMENTAL**

**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.

**Sol-Gel process for Synthesis of MWCNT-SiO$_2$ nanocomposite**

Primary compound for silica gel is water glass (Na$_2$SiO$_3$). First of all, a homogeneous mixture of MWCNT in water glass was prepared by adding 5% MWCNT (W/V) and 7.5% water glass (Na$_2$SiO$_3$). 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.

$$\text{Na}_2\text{SiO}_3 + \text{H}^+ \rightarrow [\text{SiO}_2\cdot\text{xH}_2\text{O}] + 2\text{Na}$$

Silica Gel

$$\text{Na}_2\text{SiO}_3 + \text{H}^+ + \text{MWCNTs} \rightarrow [\text{SiO}_2\cdot\text{xH}_2\text{O}, \text{MWCNTs}] + 2\text{NaX CNTs-Silica Gel}$$

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. 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 (3) and due to importance of homogeneous mixing of solution, pH=2.5-3.5 was selected.

**RESULT AND DISCUSSION**

**Screening design**

To investigate the effects of these factors, a 2$^3$ factorial design was performed on a LPG sample and propane, 2-methylpropane, n-butane, 2,2-dimethylpropane, 2-methylbutane and n-pentane. This design, as a first step, is very useful for doing a few experiments; it is possible to detect the most significant variables. The variables considered, and their levels are shown in Table 2. The temperature, flow rate and carrier gas are known to be important factors affecting performance. The overall design matrix showed 12 runs to be carried out randomly in order to eliminate the effects of uncontrolled variables for each run.

<table>
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<th>Temperature (°C) A</th>
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<tr>
<td>Carrier gas C</td>
<td>Helium and Argon</td>
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Optimization of conditions
Taking into account the results obtained in the preliminary studies described above, a Factorial design was applied with the aim of appropriately optimizing the levels of significant factors affecting the experimental data efficiency, including the temperature, flow rate and carrier gas. The more distance of each two adjacent peaks in the optimum conditions reveals the credibility of obtaining response model. The resulted design for the experiments in the modified and unmodified column had represented in Table 3 and Table 4, respectively.

Table 3. Design matrix and responses for the experiments in the modified column

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<th>No.</th>
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<th>B</th>
<th>C</th>
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<th>3-n-butane-RT(M)</th>
<th>4-2,2-di-methylpropane-RT(M)</th>
<th>5-2-methylbutane-RT(M)</th>
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D21 is the differences of first and second columns of response.
D32 is the differences of second and third columns of response.
D43 is the differences of third and fourth columns of response.
D54 is the differences of fourth and fifth columns of response.
D65 is the differences of fifth and sixth columns of response.

Table 4. Design matrix and responses for the experiments in the unmodified column

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<th>3-n-butane-RT(UM)</th>
<th>4-2,2-di-methylpropane-RT(UM)</th>
<th>5-2-methylbutane-RT(UM)</th>
<th>6-n-pentane-RT(UM)</th>
<th>D21 (UM)</th>
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To investigate the effects of factors and their interactions, the Pareto chart were applied to the results. Figure 1 and figure 2 shows the Pareto chart of standardized effects for this design in the modified and unmodified column, respectively. The vertical line on the plot judges the effects that are statistically significant. The bars, extending beyond the line, correspond to the effects that are statistically significant at the 95% confidence level. Inspections to this figure indicate that several factors were most important, although in some of them, the bars did not pass the vertical line.

According to significances of factors in the modified and unmodified column, it concluded that test condition in unmodified column depends on small changes of factors but after modifying the column, the effect of factors has been minimized. Thus the stability of the process can be concluded.

Fig. 1. Pareto chart of the main effects obtained from design for the modified column.
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 3). As shown in figure 4, 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.

Fig. 3. 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).

Fig. 4. 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).
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 5, 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.

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 (4). 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.

Retention time differences between two consecutive peaks in terms of modified condition is more than unmodified one. The results of this study demonstrate that the gas chromatography using modified condition can generate a suitable separation and better optimization of resolution than unmodified one.

Fig. 5. 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).
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 5 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 6 and 7). 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.

Fig. 6. Five point calibration curve of standard addition for propane (5 µL, 10 µL, 25 µL, 50 µL and 100 µL).

Fig. 7. Five point calibration curve of standard addition for 2,2-dimethylpropane (5 µL, 10 µL, 25 µL, 50 µL and 100 µL).
CONCLUSION

In this study, a new silica gel based adsorbent was fabricated and its ability in separation and quantification of alkanes mixture was investigated by performing of factorial design. The method of gas chromatography has been developed to provide an effective means for simple and rapid quantitative analysis with modified and unmodified columns. The results of factorial analysis indicated that temperature, flow rate and carrier gas were found to be the most significant factors. The results obtained by modified column had a better optimization of resolution than the unmodified one. 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.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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