Separation of light hydrocarbons by gas chromatography using serpentine as stationary phase

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The application of serpentine ore (brownish colour) as a stationary phase for the separation of hydrocarbons by gas-solid chromatography has been tested. Separation of methane, ethane, propane, n-butane, iso-butane and acetylene has been accomplished at room temperature (25°C). The separated components were detected with a flame ionization detector. The peaks of isobutane and n-butane were rather broad, unsymmetrical and poorly resolved at room temperature but the resolution improved and the peaks were sharper and symmetrical when the separation was carried out at a higher temperature (50°C). The variation of retention time and peak shape have been studied as a function of flow rate and temperature of separation. Light hydrocarbons (C1-C4) could be separated at 25°C on a stainless steel column (2.8 M long and 2.3 mm i.d.) packed with 60-100 mesh particles using nitrogen as carrier gas flowing at 8 mL/min. The separation of hydrocarbons on serpentine column has been successfully applied to the determination of dissolved hydrocarbon gases in transformer oil. The results of the analysis agree well with those obtained using silica gel column.

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Gas chromatography is a very useful technique for the determination of lower hydrocarbons in various samples. It has been applied to the determination of dissolved hydrocarbon gases in high voltage transformer oil\(^1\), petroleum products and in environmental samples\(^2\). Analysis of light hydrocarbons has played an important role in the space missions\(^3\) where traces of these gases are determined in the presence of large amount of nitrogen and argon. Gas-solid chromatography has been applied to the separation of mixtures of permanent gases and light hydrocarbons\(^4\). Porous layered open tubular and conventional GC columns provide efficient analysis of light hydrocarbon gases\(^5\). Micropacked columns are considered to be a better alternative because of their high sample capacity, low flow rate and small resistance to mass transfer\(^6\). The analysis of dissolved hydrocarbon gases plays a very important role in electrical industry. The malfunctioning of high-voltage transformers results in the chemical decomposition of mineral oil and cellulose insulation due to arcing, overheating or partial discharges. Due to chemical degradation several gases such as H\(_2\), CH\(_4\), CO, CO\(_2\), C\(_2\)H\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_6\) and C\(_3\)H\(_6\) are produced and these gases are totally or partially dissolved in the oil. The concentration of these gases is a measure of the extent of damage caused to the transformers. It is possible to detect the fault at an early stage of development and take preventive measure before the failure takes place, if the concentrations of these gases are periodically monitored. The gas chromatographic method has been successfully implemented in various laboratories\(^12,13\) for the analysis of dissolved gases in mineral insulating liquid.

Silica based normal columns and capillary columns have generally been used for the gas chromatographic separation and determination of the hydrocarbon gases. However, the separation of these gases on other stationary phases has not been thoroughly investigated. In the present study, separation of several light hydrocarbon gases has been studied using serpentine as stationary phase.

Serpentine is a group of common rock forming minerals exhibiting various colours and compositions. The mineral has the general formula\(^14,15\) (Mg, Fe\(_x\))Si\(_3\)O\(_4\)(OH)\(_4\). These are secondary minerals derived from magnesium rich silicate minerals and are found in both igneous and metamorphic rocks. The

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minerals are generally compact, tough and crystallize in the monoclinic system. There is a great deal of similarity in the chemical composition and physical properties of the material with Keolinite and Bentonite which have been successfully used as stationary phases for the separation of permanent gases and hydrocarbons. It was, therefore, of interest to study the behaviour of serpentine as a stationary phase for the separation of hydrocarbons. In the present study, the suitability of serpentine as a stationary phase in the separation of various synthetic mixtures of hydrocarbon gases has been examined. The separation method has been applied for the determination of dissolved hydrocarbon gases in transformer oil. The results obtained agree well with those obtained by using a silica gel column, commonly used for the analysis.

**Experimental Procedure**

**Serpentine**

Serpentine mineral (brownish colour) was obtained from Reactor Processing Division of Bhabha Atomic Research Centre, Mumbai and was used as such. The mineral was characterized by X-ray, thermal studies and chemical analysis.

**Standards**

Standard mixtures of hydrocarbon gases were procured from Indian Oxygen Ltd., Mumbai and the hydrocarbon gases of purity >99.9% were obtained from Chemtron Science Laboratory, Navi Mumbai, India.

**Carrier gases**

Pure nitrogen, hydrogen and zero air gas were obtained from Hydrogas Ltd., Mumbai. Nitrogen used as carrier gas was >99% pure. It was dried by passing through a column of ascarite before allowing it to flow through the column.

**Instrument**

A simple gas chromatograph fabricated in the laboratory was used for the separation studies. The instrument was equipped with a flame ionization detector (FID) for detecting the eluted components. The output of the detector was fed to a strip chart recorder (Rikadinki, Japan) for recording the chromatogram and measuring the concentration of the eluted compounds.

**Columns**

The analytical columns (2.8 M long and 2.3 mm i.d) were made from stainless tubes. The stationary phase of appropriate particle size was prepared from the mineral after drying it at 110°C and grinding them in a mechanical stone grinder and sheaving to a desired mesh size. The columns were packed with the stationary phase material of two different mesh size. The column A contained the stationary phase having 50-100 mesh while the column B was packed with particles of 60-100 mesh. The columns were prepared by plugging one of the open ends with glass wool and pouring the solid phase through the other end using a small funnel fitted with a rubber tubing sleeve. It was then packed by tapping gently down its length while the material was being added. Finally an open space of about 1/8 inch was was left out and the empty space was packed with glass wool. The column was bent to proper shape, connected to the flow line with suitable connecting device and was placed inside a horizontal furnace with proper shielding with glass wool. The inside temperature of the furnace was measured with a pyrometer calibrated with an accuracy of ±1°C. A flow meter connected to the gas stream (nitrogen) was used for the measurement of flow of the carrier gas. Both the columns were conditioned at 100°C for 4 h by passing nitrogen at a rate of 20 mL per min. This conditioning was essential for obtaining the proper efficiency of the column.

**Method**

When the column was ready after proper conditioning, 10-50 μL of a standard hydrocarbon mixture was injected into the system. The peaks were generally sharp and symmetrical. Standard calibration plots for the peak heights versus concentrations of the individual gas injected were obtained at a given temperature. Chromatograms of gas mixtures were also recorded at different flow rates and at different temperatures.

**Results and Discussion**

Serpentine used in this study had a light brown colour. It had ≈ 9% moisture and low Fe₂O₃ (<1%). The material could be ground to prepare stationary phase of desired mesh size. However, another form of serpentine having light green colour was also tried as stationary phase for the separation of hydrocarbons. It was observed from the preliminary experiments that the preparation of stationary phase of desired mesh size from this type of serpentine was difficult and the separation of hydrocarbons was also poor. Hence, all further experiments were carried out using the brown
variety of serpentine. Flame ionization detector (FID) was used for the detection of the separated hydrocarbons. Separation behaviour of light hydrocarbons (C$_1$-C$_4$) was studied at various temperatures using columns with stationary phases of two different mesh sizes. Most of the hydrocarbon gases could be separated at room temperature (25°C) on a column packed with particles of 50-100 mesh (column A) but resolution of peaks was not satisfactory for a mixture of hydrocarbons. A much better separation could be accomplished using a column with stationary phase of smaller mesh size of 60-100 (column B). Hence, all further studies were carried using column B. The components of the mixture of methane, ethane, propane, isobutane and normal butane could be readily separated at room temperature but the resolution between the peaks of isobutane and n-butane was rather poor. However, at higher temperature (50°C), the isobutene peak was much sharper and symmetrical. The chromatogram of a set of mixture containing both saturated and unsaturated hydrocarbons is shown in Fig. 1. Although the resolution of the peaks for ethylene and ethane are not satisfactory, the other components are clearly separated. This conclusively demonstrates that the serpentine could be successfully used for the separation of both saturated and unsaturated hydrocarbons in a mixture. The effect of flow rate and temperature on the separation of hydrocarbons has been studied. The retention times of various hydrocarbons under different experimental conditions are shown in Table 1. Near baseline separation between two adjacent peaks could be obtained when the chromatogram was obtained at room temperature and a flow rate of 8mL/min.

Table 1—Retention times (min) for hydrocarbons on serpentine ore column B (60-100 mesh) at different temperatures and flow rates.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Flow (6mL/min)</th>
<th>Flow (8mL/min)</th>
<th>Flow (20mL/min)</th>
<th>Flow (30mL/min)</th>
<th>Flow (32mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>1.75</td>
<td>1.67</td>
<td>1.33</td>
<td>1.33</td>
<td>0.92</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>2.50</td>
<td>2.08</td>
<td>1.92</td>
<td>1.75</td>
<td>1.33</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>2.83</td>
<td>2.25</td>
<td>2.25</td>
<td>1.83</td>
<td>1.58</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>7.17</td>
<td>4.33</td>
<td>5.33</td>
<td>3.00</td>
<td>3.67</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>13.20</td>
<td>7.08</td>
<td>10.00</td>
<td>4.50</td>
<td>6.83</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>27.0</td>
<td>12.30</td>
<td>20.30</td>
<td>7.20</td>
<td>14.00</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>37.0</td>
<td>19.25</td>
<td>32.0</td>
<td>10.00</td>
<td>22.00</td>
</tr>
</tbody>
</table>

Fig. 1—Separation of a mixture of saturated and unsaturated hydrocarbons on column B. Temperature – 25°C, Flow rate – 8mL/min, Injection volume – 50 μL; 1 – Methane, 2 – Ethane, 3 – Ethylene, 4 – Propane, 5 – Acetylene.
Analysis of transformer oil

The separation of the dissolved gases in the transformer oil has been carried out using the serpentine columns. Normally, silica gel columns are used for the analysis of dissolved hydrocarbon gases in transformer oil. In order to demonstrate the applicability of the serpentine columns to the determination of dissolved gases in the transformer oil, the gases were collected by a recommended procedure and injected into the column. The concentrations of the dissolved gases were measured from the peak heights. The concentrations of methane, ethane, ethylene, propane and acetylene determined by using serpentine packed columns are given in Table 2. The corresponding values determined by using silica gel column are also given in the table for comparison. It can be seen that the values agree well within the experimental error suggesting the possible application of serpentine as a possible alternative to the silica gel as stationary phase in the chromatographic separation and determination of dissolved hydrocarbons in the transformer oil. Although, serpentine could be used as an alternative to silica gel as stationary phase, the resolution of hydrocarbon peaks is better in the case of silica gel.

Conclusion

Serpentine ore can be used as a stationary phase for the separation of hydrocarbons (C1-C4). The separation on a 60-100 mesh stationary phase was found to be highly satisfactory at room temperature at flow rate of 8 mL/min. The separation method could be successfully applied to the determination of dissolved hydrocarbon gases in transformer oil. This suggests that serpentine could serve as an alternative to silica gel as stationary phase for the analysis of dissolved gases in transformer oil.

References