Comments on Column Characterization: A Sulfur Column

F. Dowell*
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, U.S.A.

G. H. Stewart
Department of Chemistry, Texas Woman's University, Denton, TX 76204, U.S.A.

Key Words
Gas chromatography
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Summary
The McReynolds' constants for liquid sulfur as a stationary phase in gas-liquid chromatography (GLC) are presented. A simple graphical method of pattern analysis is used to indicate the uniqueness of the sulfur column as compared with other stationary liquid phases characterized by McReynolds. The limitations of using a single factor (as polarity) for the basis for the selection of GLC columns is discussed.

Introduction
Stationary liquid phases used in gas-liquid chromatography are frequently characterized by the use of McReynolds' constants, which are calculated from Kováts' retention index numbers.

In the Kováts's retention index system [1], the retention volume of a solute in a stationary liquid phase under given column conditions is expressed relative to the retention volumes of nonpolar standards, the normal alkanes, as solutes in the same stationary liquid phase under the given column conditions. The Kováts' retention index number \( I \) of a solute is defined [2] by

\[
I = 100 \left[ \frac{\ln V_{G(i)} - \ln V_{G(n)}}{\ln V_{G(n+1)} - \ln V_{G(n)}} + n \right]
\]

where \( V_{G(i)} \), \( V_{G(n)} \), and \( V_{G(n+1)} \) are the specific retention volumes of the solute of interest, of the normal alkane eluted from the column immediately preceding the solute, and of the normal alkane eluted immediately following the solute, respectively; and \( n \) is the number of carbon atoms in the normal alkane eluted immediately preceding the solute. Note that the denominator of the first term on the right-hand side of eq. (1) can be shown to be proportional to \( \ln V_g \) for a \( \text{CH}_2 \) group. (The retention index numbers do have a small temperature dependence [2], which is linear over the temperature range with which gas-liquid chromatography is usually concerned [3, 4].)

McReynolds [5] has characterized over two hundred stationary liquid phases at 120 °C. In the McReynolds' characterization system the behaviour of a set of ten solutes in a stationary liquid phase is compared to the behaviour of the set of the same solutes in a nonpolar reference stationary liquid phase, squalane. The McReynolds' constant, \( \Delta I \), for a particular solute is given [5] by

\[
\Delta I = I_a - I_{aq}
\]

where \( I_a \) and \( I_{aq} \) are the Kováts' retention index numbers of the solute in stationary phase \( a \) and in squalane, respectively. The average GLC polarity of a stationary liquid phase is then taken [5] as the sum of the \( \Delta I \) values for the first five compounds (benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine) in the set of solutes.

This paper reports the experimental determination of Kováts' retention index numbers for squalane at 120 °C and for liquid sulfur at 131–132 °C. These measurements were made as a part of a study of the solvent characteristics of molten sulfur [6].

Experimental
A Varian Aerograph 1520 gas chromatograph with a thermal conductivity detector was used with helium as the carrier gas. The injection unit was modified to allow a pre-injection column in the oven to saturate the carrier gas with vapours of the stationary phase.

The injection column inlet pressure was measured at the head of the column to \( \pm 1 \) torr by a mercury manometer; the outlet pressure was measured by a mercury barometer. The flow rate was determined with a soap bubble flow meter.

Solute were injected with a syringe. The standard sample size was 0.2 μl, and several solutes were injected in smaller quantities to verify that the approximation of zero sample size (infinite dilution) was valid.
Pyridine was chromatographed periodically on the sulfur column to verify that column bleeding was insignificant over the period of experimentation. Samples of pyridine, 1-iodobutane, and n-nonane taken before and after passage through the sulfur column were analyzed by IR to verify that there had been no chemical reaction (such as dehydrogenation) between the solutes and the sulfur.

The columns were 2 m in length. The sulfur column was 7 mm o.d. glass tubing, and the squalane column was 0.25 inch o.d. copper tubing. The solid support was Chromosorb W, 60/80 mesh, AW, DMCS. Squalane (Supelco Inc.) was used without further purification. The sulfur column was prepared from sublimed powdered sulfur (Matheson, Coleman and Bell) which was dissolved in carbon disulfide and filtered before use. For both stationary liquid phases, the liquid phase was dissolved in a volatile solvent (carbon disulfide for sulfur and a methylene chloride-chloroform mixture for squalane), the support was coated in this solution, and the solvent was allowed to evaporate. The percentage load was determined by comparing the weights of samples of the coated support before and after heating off the stationary liquid phase on a hot plate and in a vacuum oven. Of the total weight of the coated supports, the stationary liquid phase comprised 15.79% for the sulfur column and 16.72% for the squalane column.

The specific retention volume, \( V_g \), was calculated from the chromatographic data by the following equation:

\[
V_g = \left[ \frac{3}{2} \left( \frac{p_i}{p_o} \right)^2 - 1 \right] \frac{273.16}{T_a} \left( \frac{p_o - p_w}{p_o} \right) \left( \frac{t_R - t_M}{t_R - t_M} \right) \frac{F}{W_L} \]

(3)

where \( p_i \) and \( p_o \) are the column inlet and outlet pressures, \( T_a \) is the ambient (absolute) temperature, \( p_w \) is the vapour pressure of water at \( T_a \), \( F \) is the carrier gas flow rate measured by the soap bubble flow meter, \( t_R \) is the retention time of the solute, \( t_M \) is the gas holdup time ("air peak time"), and \( W_L \) is the weight of the stationary liquid phase in the column.

### Results and Discussion

Plots of \( \ln V_g \) vs carbon number for the \( n \)-alkanes were linear for both squalane and sulfur. From the \( I \) values for squalane and sulfur, values of \( \Delta I \) have been calculated for liquid sulfur and are listed in Table I. According to the convention of McReynolds [5], the average polarity of liquid sulfur is 1527, a value which chromatographically ranks sulfur as a moderately polar solvent when compared with the polarities of the liquid phases characterized by McReynolds. This polarity for sulfur, which is relatively high for a substance with no permanent dipole, is comparable to those for the polyalkylene glycols (as UCON-50-HB-3520 and UCON-50-HB-2000) and for cresyl diphenyl phosphate.

If the GLC polarity of sulfur is to be understood, it should be noted that factor analysis reveals only modest correlation between dipole moment and chromatographic polarity [7]. Novak et al. have defined polarity as a measure of the "reluctance" of a solvent to accept a nonpolar substance, or as the extent to which a polar solute is retained more than a nonpolar one in chromatographic measurements (assuming the pure solutes have the same vapour pressures at a given temperature) [8]. Since the \( n \)-alkanes are the standard reference solutes in the calculation of the \( I \) values and since squalane is the standard reference stationary liquid phase in the calculation of the \( \Delta I \) values, the \( n \)-alkanes and squalane are defined as nonpolar substances in McReynolds' characterization of polarity. (It should be noted that the energy of interaction between a methyl group and a methylene group is almost the same as between two methyl groups or between two methylene groups [9].) The relatively large values of \( \Delta I \) in Table I for benzene, pyridine, 1-iodobutane, 1,4-dioxane, and cis hydridane in the sulfur column are a measure of the reluctance of sulfur (as compared with squalane) to accept \( n \)-alkanes (as compared with aromatic, halogenated, and cyclic compounds).

The McReynolds' constants are designed to give some information about the different kinds of interactions that can exist between solute and solvent, since McReynolds (following the lead of Rohrschneider [10]) chose his particular set of solute probes on the basis of their different functional groups [7]. In Table II, some of the kinds (not extent) of interactions for each solute are listed. In view of the somewhat large overlap of the possible solute-solvent interactions listed for the solute probes in Table II, it is not surprising that various attempts at factor analysis [7, 11], pattern recognition [12], and matrix representation [13] have had limited success in isolating the factors responsible for the retention and selectivity of these solutes in various stationary phases. In general, these studies have found that 97–98% of the solute retention is predictable in terms of a single factor, the GLC polarity [13, 14].

To provide a visual comparison of stationary phase characteristics, Fig. 1 was prepared. It is a simple pattern recognition scheme in which the \( \Delta I \) values for every fifth stationary phase (and the values for the first phase and the last phase) in McReynolds' list [5] have been plotted on the graph as a function of the number (1 to 10) assigned to each of the ten solute probes. Each \( \Delta I \) value for each such stationary phase is connected by a single line linking that \( \Delta I \) value to the next \( \Delta I \) value for that stationary phase; the

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**Table I. Values of \( I \) and \( \Delta I \) for McReynolds' compounds using sulfur as the stationary liquid phase**

<table>
<thead>
<tr>
<th>Solute</th>
<th>( I )</th>
<th>( \Delta I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1010</td>
<td>360</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>819</td>
<td>236</td>
</tr>
<tr>
<td>2-Pentanone</td>
<td>780</td>
<td>156</td>
</tr>
<tr>
<td>1-Nitropropane</td>
<td>941</td>
<td>285</td>
</tr>
<tr>
<td>Pyridine</td>
<td>1190</td>
<td>490</td>
</tr>
<tr>
<td>2-Methyl-2-pentanol</td>
<td>773</td>
<td>81</td>
</tr>
<tr>
<td>1-Iodobutane</td>
<td>1330</td>
<td>510</td>
</tr>
<tr>
<td>2-Octyne</td>
<td>1050</td>
<td>210</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>1010</td>
<td>360</td>
</tr>
<tr>
<td>cis hydridane</td>
<td>1390</td>
<td>390</td>
</tr>
</tbody>
</table>