

Separation of Some Benzene Derivatives by Gas – liquid Chromatography

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(Received on 12 / 6/2005) (Accepted for publication on 29 / 4 /2006)

Abstract

Using chromatographic column of glass beads coated with solid lithium nitrate and modified by water vapor in the Helium carrier gas can be used at room temperature give a highly efficient separation, in a reasonable time of range (10-40) min., mixture containing different types of xylene and some benzene derivatives. The column glass beads used were (40 / 50) mesh . Its high separation efficiency was obtained compared with conventional gas – liquid chromatography.

(40-10)

(40 / 50)

Introduction

Advantages of gas liquid chromatography arise from the high selectivities possible with solid substrates and the stability of such substrates at high temperatures⁽¹⁻⁴⁾. It's principal disadvantage is the

nonlinearity of the absorption isotherms usually found for gas – solid interactions. This problem can often be solved by modifying the surface with a suitable chemical substance⁽⁵⁻⁸⁾ another disadvantage coefficient found for arises from the

large distribution adsorption. To achieve reasonable retention times, high column temperatures must be used and the analyses restricted to low boiling mixtures.

We have constructed a column for which this latter disadvantage has been eliminated. It consists of glass beads coated with solid LiNO_3 . This salt was chosen because of its ability to complex with benzene or Xylene by modifying this surface with water vapor⁽⁴⁻⁸⁾, we produced a highly efficient column that could analyze in a reasonable time at room temperature aromatic hydrocarbons with boiling points as high as 165°C . The study describes how the column was made and how it compares in efficiency with two conventional gas-liquid chromatographic columns, di-n-propyl tetra chlorophthalate (DPTP) and 7,8-benzoquinoline (BQ).

Experimental

Columns

The glass beads used in the (40-50) mesh range. They were washed two times with (0.5 N) nitric acid and seven times with distilled water.

A known amount of (0.4 M) Lithium nitrate was dissolved in distilled water and a mixture of (beads and water) evaporated until the beads were dry at (105°C). The column packed in the usual manner. The carrier gas of dry helium was

passed through the column at 120°C to further dry the packing. Column dimensions were $160\text{ cm} \times 0.9\text{ mm}$.

Apparatus and Materials

The column sat in a water bath whose temperature was controlled to $(80 \pm 0.05)^\circ\text{C}$. Upstream from the column was a water saturated in a constant temperature bath $(80 \pm 0.05)^\circ\text{C}$. To prevent Lithium nitrate from going into solution, the partial pressure of the water vapor in the carrier gas was kept lower than the partial pressure of saturated LiNO_3 solution at the column temperature. In line with the saturator was a valve which directed the helium either through the saturator or directly into the column. The effluent was monitored by a hydrogen flame detector. The sample was composed of 7 component mixture of aromatic hydrocarbons and was injected on to the column with $10\ \mu\text{l}$ gas syringe.

Results and discussion

Column Properties

The retention volume of benzene derivative solute was found to be dependent upon the partial pressure of the water vapor in the helium carrier gas, at a fixed column temperature. In increasing the partial pressure resulted in smaller retention volumes while dry helium caused the solute to be retained completely. The

relative retention volumes were independent of the partial pressure of the water vapor but dependent on the column temperature.

A column packed with 40 / 50 mesh LiNO₃ gave identical results but was much less efficient. For columns containing the same amounts of glass bead but with different LiNO₃ coverage (0.2, 0.3, 0.4, 0.5, 0.7 % w / w) gave approximately the same retention volumes for the ar-



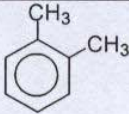

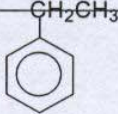
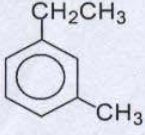
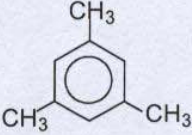
omatic solutes at a given column temperature and water vapor concentration. The columns had the same number of theoretical plates (4×10^3 calculated for O-xylene)

Comparison with other columns

Halasz⁽⁶⁾ has derived the following equation for calculating the number of theoretical plates (N_{req}) required to separate two peaks.

$$N_{req} = 36 \left(\frac{S}{S-1} \right)^2 \frac{V_r}{V_r - V_d}$$

Table (1): Comparative for the Retention of benzene derivative by several columns

No.	Benzene derivatives		Separation factor			Boiling Point °C
	Structure	Name	LiNO ₃	DPTP	BQ	
1-		Benzene	—	—	—	80°C
2-		Toluene	3.09	2.10	1.92	111 °C
3-		O – xylene	1.42	1.33	1.25	144 °C
4-		P-xylene	1.11	1.08	1.10	138 °C
5-		Ethyl benzene	1.61	1.26	1.37	136 °C
6-		1- methyl 3-ethyl –benzene	1.18	1.04	1.06	163 °C
7-		1, 3, 5 – Trimethyl benzene	1.40	1.31	1.27	165 °C

Where S is the separation factor, V_r is the retention volume of the compound eluted later, V_d is the dead volume of the columns. When S is near unity, N_{req} can be greatly reduced, if S can be increased even slightly by changing the nature of the substrate. However, S is not the sole quantity to consider in judging column performance, the factor involving V_d and V_r can also be important, par-

ticularly for early peaks where the ratio V_d / V_r can be large⁽⁵⁾.

Figure 1. appear a chromatogram of the seven components of the benzene derivative using column (30% LiNO_3) at 27°C . But table 1 identifies the components and their correspondence to various peaks in Figure 1.

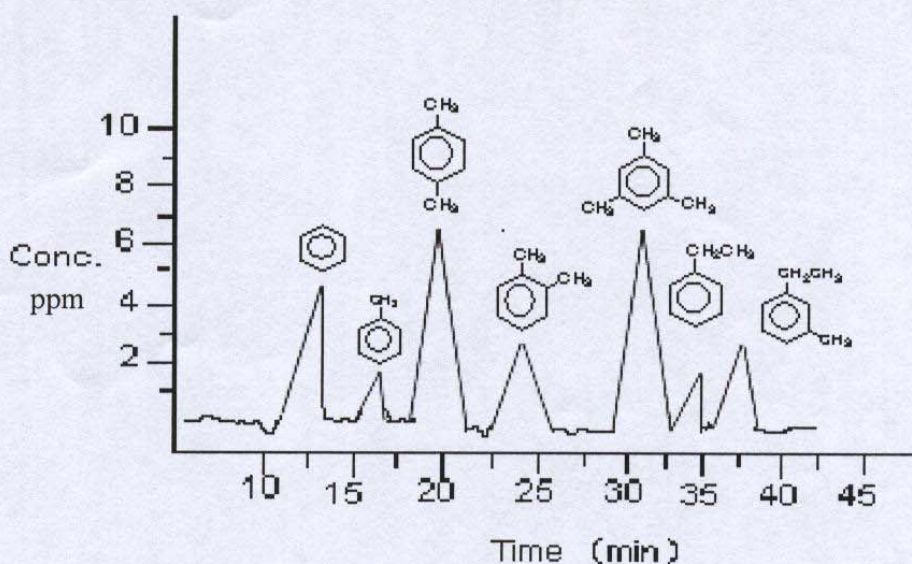

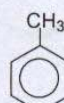

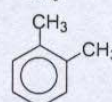
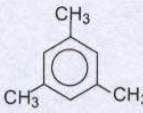
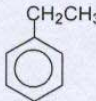
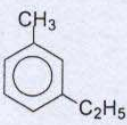


Fig (1) : Separation of benzene derivative on LiNO_3 column

In this study two mixtures used, the first one content (benzene, toluene, *o*-xylene and *p*-xylene). The second mixture content (*o*-xylene,

1,3,5-trimethyl benzene, ethyl benzene and *m*-ethyl toluene).

Table (2) : Comparative data for the Retention time of Benzene derivative on LiON₃ column

No.	Components		Retention time (min)	Conc. Mg / L
	Name	Structure		
1.	Benzene		11.5	5
2.	Toluene		17	2
3.	P - xylene		20.1	6
4.	O-xylene		22.3	3
5.	1,3,5 - trimethyl benzene		31.2	6
6.	Ethyl benzene		35.5	2
7.	3- ethyl - 1- methyl benzene		41.3	3

Values of S for successive Pairs of peaks in order of elution time for three solvents (LiNO₃, BQ and DPTP) and values of N_{req} for the difficult separations.

The retention volumes for the benzene derivative solutes were measured at 100 °C for the DPTP and BQ columns and at 27 °C for LiNO₃ column. The times re-

quired for the three different analysis were approximately the same (shown in table 2). The separation factor values are greater for LiNO_3 column than for the gas-liquid columns. The DPTP column gave a slightly higher value of (S) for this separation. The BQ column compared favorably with the LiNO_3 column for the *o*-xylene / *p*-xylene separation. It had difficulty separating 1-methyl-3-ethyl benzene from ethyl benzene (S value was 1.06), but LiNO_3 column easily made this separation (S value was 1.18). The DPTP column again had difficulty separating 1-methyl-3-methyl benzene from ethyl benzene (S value was 1.04). The advantage of working at lower column temperatures is well known.

Purnell et al.⁽⁹⁾, has shown that the BQ and DPTP Columns would be more efficient at lower temperatures, but to obtain a reasonable analysis time it would be necessary to use very low solvent coverage. Often however, packed columns operating at such low solvent / support ratios require non adsorptive supports and very small sample injections. Another advantage of the LiNO_3 columns comes from the ability one has to change V_r without affecting (S) or V_d by changing the partial pressure of water in the carrier gas. In cases where the ratio V_d

/ V_r is not negligible, Equation 1 shows that the value of N_{req} decrease as V_r is increased. This provides an additional parameter for the analyst to use to achieve desirable separation. The mechanism of aromatic hydrocarbon separation is obscure. Solid LiNO_3 must complex with unsaturated hydrocarbons in the same manner as (Li^+) ion complexes with unsaturated hydrocarbons in solution^(10,11). The effect can be large because benzene derivatives are not eluted by dry carrier gas. Water vapor in the carrier must compete with the hydrocarbons for the active sites on the solid LiNO_3 . Higher partial pressures of water result in fewer available sites for the hydrocarbons and lead to smaller elution times.

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