

## Low Pressure Performances and Applications of Gas Chromatography Using Manganese Sulfate Crystal Hydrate as Stationary Phase

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Combining of low pressure technology with manganese sulfate crystal hydrate as stationary phase in gas chromatography was realized. Experiments results showed that the performances of chromatography column in low pressure are greatly improved than that in standard atmospheric pressure. The maximum plate number of 2465 exists in the optimal pressure of  $0.8 \times 10^5$  Pa. Under this pressure, the retention time decreases 18 % compared to standard atmospheric pressure. The theoretical height of plate is 0.74 mm, which much lower than the 0.90 mm. The efficiency of chromatography column is also improved under low pressure. The chromatography column still maintains its stability after the successive analysis of 60 d. The relative error and average recoveries of toluene are 2.22 % and 100.93 % when the column is applied to the analysis of toluene in xylene.

**Key Words:** Gas chromatography, Low pressure performances, Manganese sulfate crystal hydrate, Stationary phase, Industrial

### INTRODUCTION

Gas chromatography has been widely used in many fields due to its advantages of wide application range, high sensitivity, fast speed and high selectivity. However, problems will arise due to its high column temperature when it is applied to the analysis of thermal unstable, easily decomposition and high boiling point organic substances.

Low pressure gas chromatography has been developed on the basis of the standard atmospheric pressure gas chromatography<sup>1,2</sup>. It can decrease the experimental time, increase the column efficiency, improve the peak shape and lower the column temperature. Therefore, it has great potential in the analysis of high boiling point and easy decomposition substances<sup>3,4</sup>. Recently, low pressure gas chromatography has been applied for the fast analysis of various pollutants in different environmental and food matrices by connecting with mass spectrometry<sup>5-11</sup>. It can increase sample throughput and enhance the signal-to-noise ratio to improve the detection limits.

Inorganic crystal hydrates, such as  $\text{LiNO}_3 \cdot \text{H}_2\text{O}$ <sup>12</sup>,  $\text{KF} \cdot 2\text{H}_2\text{O}$ <sup>13</sup>,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ <sup>14</sup>, have been used as stationary phase of gas chromatography in that it can improve selectivity, increase column efficiency and enhance separation characteristic. However, the column temperature can not be higher than 100 °C due to its hydrate is easy to lose<sup>15</sup>.

However, researches combining with low pressure gas chromatography and stationary are very few. In present study,

the low pressure technology and the chromatography using manganese crystal hydrate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) as stationary phase are combining together. The column performances of gas chromatography under normal and low pressure are systematically investigated. Furthermore, the column is employed to the analysis of toluene in industrial xylene.

### EXPERIMENTAL

A fix amount of deionized water was used to dissolve  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (A.R.). Then, the red 6201 carrier (60-80 mesh) was added slowly to the solution. The mass ratio of carrier to  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  was kept at 10 %. The beaker was shook until the carriers were all below the solution surface. Next, the solution was heated to remove the solvents and the stationary phase was introduced into the stainless steel column to prepare the chromatography column. 0.05 g hexanedioic dhydrocholesteryl ester was added in it to stabilize the column. Hydrogen gas was introduced to the column to 150 °C for 8-12 h before use.

**Detection method:** The outlet of thermal conduction detector was connected to a vacuum pump. Different low pressure was achieved by adjusting the flowmeter of the outlet. The gas chromatography conditions were showed as following: temperature of vapourization: 150 °C, temperature of detector: 150 °C, temperature of column: 70 °C, bridge current: 125 mA, sample size: 0.2  $\mu\text{L}$ . After samples ( $n\text{-C}_6\text{H}_{14}$ ,  $n\text{-C}_7\text{H}_{16}$  or  $n\text{-C}_8\text{H}_{18}$ ) were injected into the SP-502 gas chromatography (Lunan chemical instrument factory, China), retention time

( $t_R$ ) and half width of peak obtained were used to calculate different parameters. The regression equation, precision and recovery analysis of toluene in the industrial xylene were analyzed in the optimum conditions of  $MnSO_4 \cdot H_2O$  as stationary phase under the selected low pressure.

## RESULTS AND DISCUSSION

### Performances of chromatography column

**Optimal low pressure:** The relationship between the plate number and pressure using Sample  $n-C_7H_{16}$  is shown in Fig. 1. As can be seen from the figure, the plate number rapidly increases with the decrease of pressure. The plate number reaches its maximum value when the pressure is  $0.8 \times 10^5$  Pa. The plate number at this pressure is 2465 which is 57 % larger than that of normal pressure. The plate number declines gradually when the pressure drops. Therefore, the pressure of  $0.8 \times 10^5$  Pa is the optimum low pressure. The normal and low pressures in the following discussions refer to  $1.0 \times 10^5$  Pa and  $0.8 \times 10^5$  Pa, respectively.

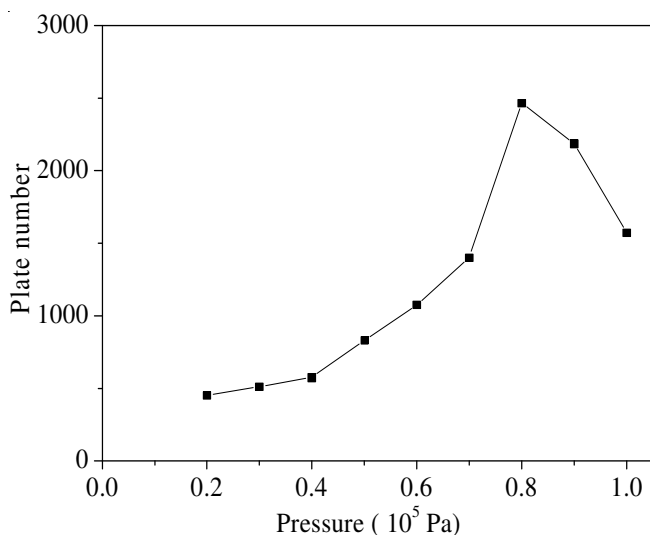


Fig. 1. Effect of pressure on plate number using  $n-C_7H_{16}$  as analysis sample

**Influence of low pressure on retention time:** The retention time of sample  $n-C_7H_{16}$  at the column temperature of  $70^\circ C$  was obtained by alternating the velocity of carrier gas. Fig. 2 gives the relationships between the retention time and the velocity of carrier gas under different pressures. Fig. 2 shows that the retention time of sample under low pressure is obviously smaller than that of standard atmospheric pressure at low velocity. With the increase of velocity, the differences between retention time and pressure decrease and the retention time is coming nearer and nearer. Therefore, it can be concluded that the low pressure help to decrease the analytical time.

**Best linear velocity of carrier gas:** Fig. 3 presents the Van-Deemeter curve at the standard atmospheric pressure and low pressure. It can be seen from figure that the plate height of low pressure is lower than that of standard atmospheric pressure at certain velocity. The best velocity of carrier gas at low pressure is  $10 \text{ cm s}^{-1}$  which is 25 % bigger than the  $8 \text{ cm s}^{-1}$  of standard atmospheric pressure. The curve at low pressure

moves to the direction of increasing speed. The theoretical height of plate is at low pressure is  $0.74 \text{ mm}$  and is 21 % lower than that of standard atmospheric pressure ( $0.90 \text{ mm}$ ). It can be concluded that the low pressure can improve the separating performance.

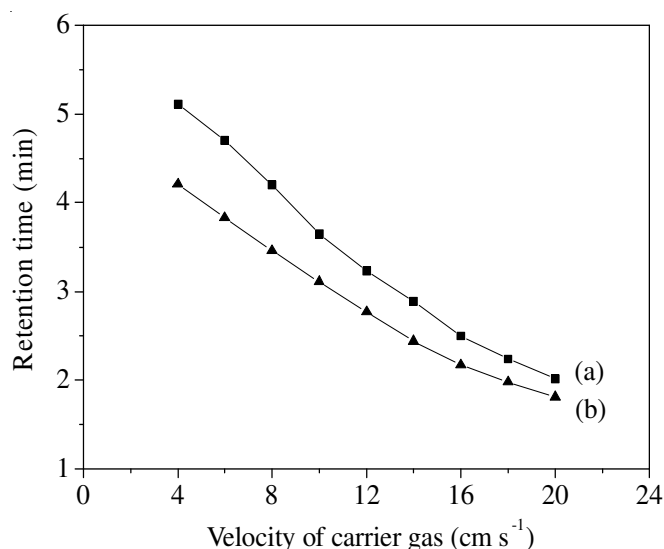


Fig. 2. Effect of velocity of carrier gas on retention time under the pressure of  $1.0 \times 10^5$  Pa (a) and  $0.8 \times 10^5$  Pa (b)

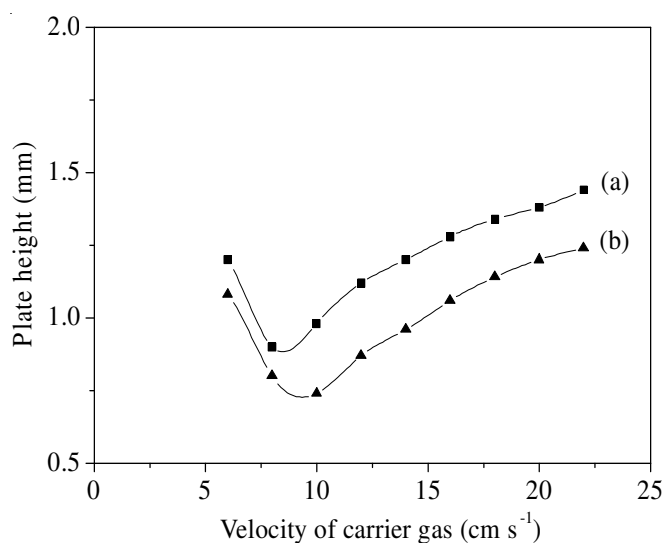


Fig. 3. Van-Deemeter curves under the pressure of  $1.0 \times 10^5$  Pa (a) and  $0.8 \times 10^5$  Pa (b)

**Efficiency of chromatography column:** Due to the limitation of the plate number in the evaluation of column efficiency, the column efficiency can be estimated accurately by the following equation,  $\sigma^2 = \sigma_{cc}^2 + t_M^2 k(k+1)/\gamma$ . Fig. 4 shows the relationship between  $\sigma^2$  and  $k(k+1)$  based on samples  $n-C_6H_{14}$ ,  $n-C_7H_{16}$  and  $n-C_8H_{18}$ . After calculation, we know that the slopes of the two lines under normal and low pressure are  $6.57 \times 10^{-4}$  and  $2.55 \times 10^{-4}$ , respectively. From equation  $\gamma = t_M^2/k$ , we can get the  $\gamma$  values under normal and low pressure are 1210 and 1905, respectively. The more the number of plate is, the lower the height of plate, *i.e.*, the higher the column efficiency will be. The column efficiency of low pressure is much better than that of standard atmospheric pressure.

**Stability of chromatography column:** After the successive experiments performing after 60 d, the retention time of sample  $n\text{-C}_7\text{H}_{16}$  decreases very small and the baseline is also very steady. It shows that the stability of chromatography column using 10 %  $\text{MnSO}_4\cdot\text{H}_2\text{O}$  as stationary phase is very good. From the above analysis, it is concluded that low pressure can improve the performances of column comparing to standard atmospheric pressure.

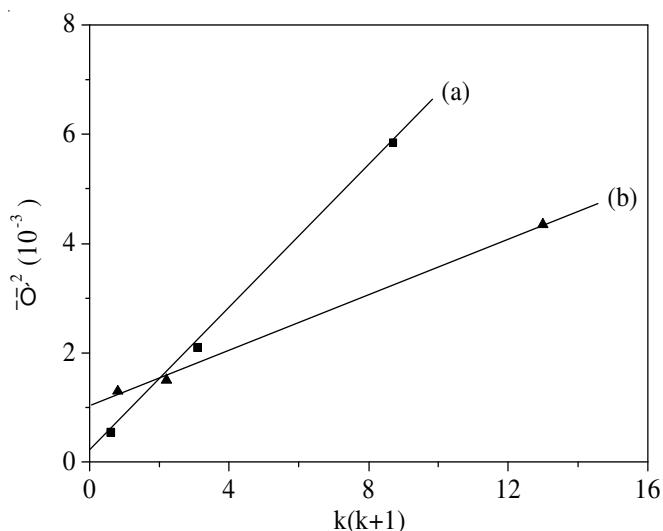


Fig. 4. Effect of  $k(k+1)$  on  $\sigma^2$  under the pressure of  $1.0 \times 10^5$  Pa (a) and  $0.8 \times 10^5$  Pa (b)

**Analysis of toluene in xylene:** Industrial xylene is one kind of important chemical raw materials. It is one distillation of refinery. Its boiling point is about  $140^\circ\text{C}$  (average value of *o*-, *m*- and *p*-xylene). Besides xylene, it also contains toluene. The content of toluene in xylene is an essential quality index. In this paper, the chromatography column containing 10 %  $\text{MnSO}_4\cdot\text{H}_2\text{O}$  stationary phase is applied to the analysis of toluene in xylene at the optimum pressure of  $0.8 \times 10^5$  Pa.

**Regression equation:** A series content of toluene were added to the 50 mL volumetric flask. Then, 0.2 mL benzene was also introduced. In this paper, benzene was used as the inner standard substance. The flask was shaking up after the xylene was added to the scale. Therefore, a series concentration of toluene was prepared. After the analysis, the regression equation obtained is:  $A_i/A_s = 27.00 C' + 0.0560$ . The meaning of  $A_i/A_s$  is the relative peak area of inner standard and sample toluene.  $C'$  is the concentration of toluene ( $\text{g mL}^{-1}$ ) in volumetric flask. And the correlation coefficient  $r$  is 0.9988. It is concluded that the linearity between the concentration of toluene and the relative peak area is good because the correlation coefficient is more than 0.99.

### Precision

The precision of this chromatography under low pressure for the determining of toluene in xylene was evaluated. 0.3 mL of industrial xylene was added to the 50 mL volumetric flask with suction pipette. 0.2 mL benzene was also introduced and xylene was added to the scale. After the flask was shaking up, sample was injected into chromatography column. The areas of peaks were measured and the concentration of toluene in xylene was calculated by the regression equation.  $C$  was the

concentration of toluene in sample xylene. Its concentration in sample xylene can be calculated by the equation:  $C = 50C'/0.3$ . Several times analysis was conducted to perform the precision experiments at the same condition. The average concentration of toluene in xylene is  $0.0860 \text{ g mL}^{-1}$ . The results of precision experiments are shown in Table-1. All the data in table are the average value of three times experiments. Table-1 shows that the relative error is 2.22 % which is much smaller than 5 %. It is concluded that the precision of the chromatography column using  $\text{MnSO}_4\cdot\text{H}_2\text{O}$  as stationary phase is very good.

TABLE-1  
PRECISION EXPERIMENT RESULTS OF  
TOLUENE IN SAMPLE XYLENE

$A_i$	$A_s$	$A_i/A_s$	$C$ ( $\text{g mL}^{-1}$ )	RSDs (%)
249	3559	0.06996	0.0867	2.22
252	3602	0.06996	0.0867	
255	3629	0.07027	0.0883	
250	3592	0.06960	0.0833	
256	3654	0.07006	0.0867	
253	3611	0.07006	0.0867	
252	3623	0.06956	0.0833	

**Recovery:** 0.05 mL of toluene was added to the 50 mL volumetric flask, which contains a series volume of xylene. 0.2 mL benzene was also introduced and xylene was added to the scale. After the flask was shaking up, sample was injected into chromatography column. The areas of peak were determined and the concentration of toluene was calculated by the regression equation. Several times analysis was conducted to perform the recovery experiment at the same condition. The results of recovery experiments were presented in Table-2. All the data in table was the average value of three times experiments. The means of symbol in the table are show as following:  $C'$  is the concentration of toluene in flask;  $m_1$  is the mass of toluene in the flask;  $V$  is the added volume of xylene;  $m_2$  is the added mass of toluene. Table-2 shows that the recoveries of toluene are 101.18 %. Therefore, the recovery experiments of toluene in xylene are in the range of 97.56-104.02 %. The average recovery is 100.93 %.

TABLE-2  
RECOVERIES OF TOLUENE IN SAMPLE XYLENE

$A_i/A_s$	$C'$ ( $\text{g mL}^{-1}$ )	$m_1$ (g)	$V$ (mL)	$m_2$ (g)	Recoveries (%)
0.08421	0.00104	0.05225	0.1	0.0086	104.02
0.08844	0.0012	0.06008	0.2	0.0172	97.56
0.09314	0.00138	0.06878	0.3	0.0258	98.75
0.09859	0.00158	0.07886	0.4	0.0344	103.38

### Conclusion

The performances of chromatography column using 10 %  $\text{MnSO}_4\cdot\text{H}_2\text{O}$  as stationary phase are systematically investigated at various pressures. The column performances is greatly improved under the optimum pressure of  $0.8 \times 10^5$  Pa comparing to standard atmospheric pressure. The prepared chromatography column was applied to the analysis of toluene in industrial xylene. The relative error in the precision experiment is 2.22 % and the recovery of toluene is 100.93 %.

The utilizing of 10 % MnSO<sub>4</sub>·H<sub>2</sub>O as stationary phase in gas chromatography can meet the demands of analysis.

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