

EVALUATION OF GLC SYSTEM PERFORMANCE: COLUMN EVALUATION

(This experiment was devised by Prof. Wolfgang Bertsch, and later modified by Manop Sittidech)

NOTE: Please study the synopsis on "Column testing in gas chromatography".

INTRODUCTION

The Grob test is a very widely used procedure for evaluating four important aspects of the quality of open tubular columns: (i) separation efficiency, (ii) adsorptive activity, (iii) acidity/basicity and (iv) stationary phase film thickness. In this experiment, we shall limit our evaluation to the first three phenomena. The experimental conditions are actually optimized for the measurement of the separation efficiency of columns, with film thicknesses in the range 0.08 - 0.40 μm and internal diameters 0.25 -0.35 mm, but for convenience, the same conditions are used for all column types.

In Table 1 is given the composition of the Grob test mixture. All the components are present in equal amounts. Nonanal, a compound in the Grob test mixture for aldehyde adsorption, has been omitted, because upon storage it tends to form a Schiff's base derivative with 2,6-dimethylaniline.

Table 1. Components of the Grob Test Mixture

Substance	Abbrv
2,3-Butanediol	D
n-Decane	10
Dicyclohexylamine	am
2,6-Dimethylaniline	A
2,6-Dimethylphenol	P
n-Dodecane	12
2-Ethylhexanoic acid	S
Methyl decanoate	E10
Methyl dodecanoate	E12
Methyl undecanoate	E11
Nonanal	al
1-Octanol	ol

PROCEDURE

The instrument will be set up with an apolar column (100% methyl or 95% methyl/5% phenylpolysiloxane). Your instructor will tell you something about the film thickness and column ID. You should adjust the instrument to run the Grob test, according to the conditions stated in the synopsis ("Column Testing ...). We will follow these general conditions, but will change the temperature program rate to save time.

1. Instrument startup and verification (methane test).
 - (i) Check the instrument settings (primarily temperature readouts).
 - (ii) Ignite the FID and verify that the flame is on.
 - (iii) Determine the approximate column length (to $\pm 15\%$).
 - (iv) Set the carrier gas pressure to 15 psi.
 - (v) Set the split flow to 30 ml/min (± 10 ml/min) and inject methane. Determine its retention time. The measurement should be done at room temperature.
 - (vi) Adjust carrier gas velocity by changing inlet pressure so that methane moves through the column at 30 cm/s (± 5 cm/s). This may take several injections. The amount of methane injected is not critical.

2. Production of Grob test chromatogram.
 - (i) Set the temperature program as follows:

starting temp.	50°C
time 1	2 min
rate	10°C/min
temp 2	220°C
time 2	0 min

 - (ii) Adjust the split ratio to 1:20 ($\pm 20\%$)
(You need to calculate the approximate column flow rate from the methane holdup time and the column dimensions.) Choose an attenuation of 4 or 5 and inject 1 μ L of the concentrated standard. Start the program.
 - (iii) Observe the chromatographic development. After the solvent (and some of its impurities) comes out, adjust attenuation such that the peaks are between 20% and 80% full scale. This requires some guesswork but it is OK for the survey run.
 - (iv) Produce a "good chromatogram" by reinjecting the standard under the appropriate attenuation. You can omit this step if the chromatogram from (iii) is satisfactory.
 - (v) Inject a standard of C8-C12 n-alkanes under the same chromatographic conditions. There is no need to adjust attenuation.

$$TZ = [t_R(z+1) - t_R(z)] / [W_h(z) + W_h(z+1)]$$

Using the chromatogram of the standard alkanes, identify the peaks due to decane and dodecane in your chromatogram of the Grob mixture. You should now be in a position to *deduce* which three-peaks in the chromatogram of the Grob mixture are due to the methyl esters. Draw the "100 % line" over the two alkanes and the three esters. Tabulate the height of the remaining peaks in the chromatogram (does evaluation of tailing help you in this respect?). Determine two values for the separation number (or Trennzahl, TZ) using the following formula, where t_R is the retention time, W_h the width at half-height, z and $z + 1$ are sequential members of a homologous series. Quote the mean result and comment on the likely error.

QUESTIONS

- (i) Of what practical value is knowledge of the separation number? What other measure of column efficiency could be used?
- (ii) To the experienced observer, the shape of the peaks in the Grob test mixture chromatogram, especially that of the 1-octanol, are indicative of column performance. Are your chromatographic peaks as expected? Why are there more than 2 peaks at the beginning of the chromatogram?
- (iii) Does the column appear to be particularly acidic, or basic? Explain.
- (iv) Are there any peaks "missing" from the chromatogram? Are there "additional" peaks? If so, explain this observation.
- (v) Originally, n-undecane was one of the two alkane components in the test mixture (look at the chromatogram of the original mixture). It has now been replaced by n-dodecane. With reference to your data, explain why this is the case.
- (vii) To what do you attribute the rising baseline at the end of your chromatograms?
- (viii) Explain why some peaks are tailing but others are not.
- (ix) What is the value of the "methane test"?

REFERENCES

K. Grob, Jr., G. Grob and K. Grob, J. Chromatog. 156: 1-20 (1978).

C. F. Poole and S. K. Poole, in "Chromatography Today" (Elsevier, 1991) pp. 158-169.