Journal of Chromatography, 629 (1993) 291–296
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 656

Improvement of continuous counter-current gas–liquid chromatography for practical use

Katsuya Sato

Laboratory of Industrial Analytical Chemistry, Faculty of Technology, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji-shi, Tokyo 192-03 (Japan)

Katsunori Watabe

Central Research Laboratory, Shimadzu Corporation, Kyoto (Japan)

Toshihide Ihara and Toshiyuki Hobo

Laboratory of Industrial Analytical Chemistry, Faculty of Technology, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji-shi, Tokyo 192-03 (Japan)

(First received March 24th, 1992; revised manuscript received July 16th, 1992)

ABSTRACT

Counter-current gas–liquid chromatography, in which samples are processed continuously, is suitable for preparative separations. Following previous work, which made the fundamental aspects clear, a scaled-up instrument was constructed. Several factors that influence the sample separation, such as selection of the liquid phase, separation temperature, gas- and liquid-phase flow ratio, sample feed rate and the structure of separation tower, were evaluated in order to optimize separations on the scaled-up system. Under the optimum operating conditions, a mixture of *cis*- and *trans*-decahydronaphthalene (1:1, w/w) could be introduced at a rate of 7.2 ml/h into the system and a purity of each isomer of more than 95% was obtained continuously for more than 15 h.

INTRODUCTION

In continuous counter-current gas–liquid chromatography (CCGLC), the gas and liquid phases move in opposite directions, which makes continuous sample introduction possible for preparative-scale purification. In a previous paper, we reported a high-temperature continuous CCGLC system and demonstrated some applications [1]. However, the system was not suitable for practical use because the maximum sample feed rate was less than 1 ml/h and further investigations on the operating condition were required. In this work, we designed a larger scale CCGLC system and studied the influences of operating parameters such as liquid phase, separation temperature, gas and liquid flows, maximum sample feed rate and tower structure on a two-component separation. Decahydronaphthalene stereoisomers, the separation of which has been studied previously and found to be difficult [1], were chosen as the test sample in order to evaluate the new system.

EXPERIMENTAL

Instrumentation

The new CCGLC system is similar to the previ-

Correspondence to: Professor Dr. Toshiyuki Hobo, Laboratory of Industrial Analytical Chemistry, Faculty of Technology, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji-shi, Tokyo 192-03, Japan.

0021-9673/93/$06.00

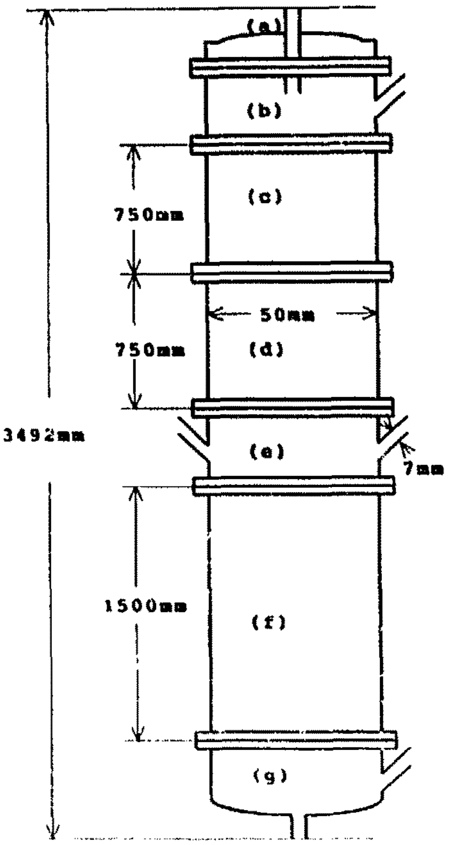

Fig. 1. Separation tower. (a) Liquid-phase inlet unit; (b) top gas-phase outlet unit; (c) upper separating section unit; (d) lower separating section unit; (e) bottom gas-phase outlet unit; (f) stripping section unit; (g) gas-phase inlet and liquid-phase outlet unit.

ous one [1], with the following differences. The tower diameter was enlarged from 17 mm to 50 mm. The tower consisted of seven Pyrex glass units, namely a liquid-phase inlet, a top gas-phase outlet, an upper separating section, a lower separating section and a gas-phase inlet. Stainless-steel nets were placed inside the liquid-phase inlet, gas-phase outlets and gas-phase inlet for fixing the stainless-steel helical-coil packing (Naniwapac). The packing was placed in the hatched area in Fig. 1. Silicone-rubber sheets were inserted between the glass-to-glass interfaces to prevent gas leaks.

The gas flow system is shown in Fig. 2. Two nitrogen cylinders (B grade, Nippon Sanso) were connected to the flow system and used alternately because the system consumed more nitrogen than the previous system. Trace amounts of oxygen in the nitrogen were removed by the heated purifiers (300 mm × 6 mm I.D. stainless-steel tubes) packed with reduced copper beads (1–2 mm diameter). Two purifiers were used alternately and reactivated by passage of hydrogen at 300°C when not being used. The nitrogen was fed after heating to the temperature of the tower using heaters inserted in the gas line.

The liquid phase was pumped into the top of the tower by a constant-flow pump (Shibata Model SPC-200 micro pump). The temperatures of the pump, liquid phase tank and flow line were kept at 60, 100 and 70°C, respectively. Samples were fed to the middle of the tower using a constant-flow pump (Senshu Kagaku Model 3100S) through a syringe needle. The whole sample flow line was heated to keep the viscosity of samples low.

One of the two components eluted from the tower was trapped in the collector (volume 25 ml) after cooling by a water-jacketed cooler, as shown in Fig. 3. Nine mantle heaters were placed around the tower and the temperatures were controlled independently. The temperature was monitored using thermister thermometers (Takara Kogyo A600 and D226) and a thermosensor (Takara Kogyo BXK-67).

Sample

A decahydronaphthalene stereoisomer mixture, which was not sufficiently separated with the previous system [1], was used as the test sample. *trans*-Decahydronaphthalene (b.p. 187.2°C) and *cis*-decahydronaphthalene (b.p. 195.7°C) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan) and a 1:1 mixture was prepared.

Measurement of partition coefficients

The partition coefficients were calculated from the gas chromatographic retention times. A Shimadzu Model GC-8A gas chromatograph equipped with a flame ionization detector was used. Samples were injected onto a 2 m × 3.0 mm I.D. column packed with 20% Apiezon C on Chromosorb W AW DMCS (80–100 mesh).

Measurement of the purity of the eluates

The collected product was dissolved in 2–3 ml of dichloromethane and 1 μl was injected into a gas

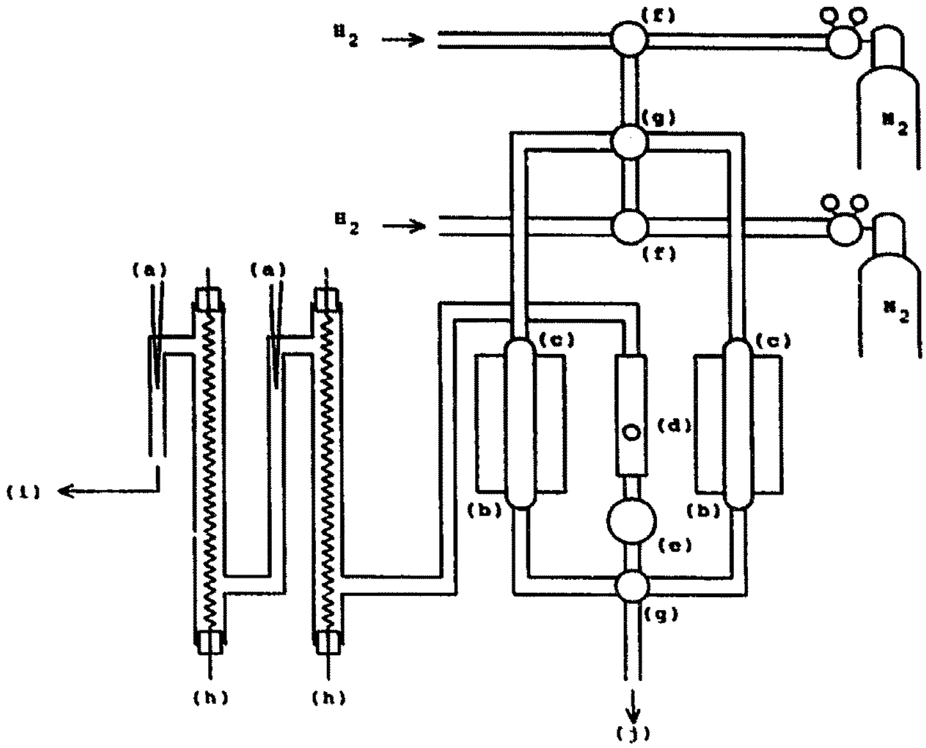

Fig. 2. Gas flow system. (a) Thermocouple; (b) electrical furnace; (c) reactor packed with reduced copper beads; (d) flow meter; (e) control valve; (f) three-way valve; (g) four-way valve; (h) heaters; (i) to separation tower; (j) to vent.

chromatograph. A 2 m × 3.0 mm I.D. column packed with 20% Apiezon C on Chromosorb W AW DMCS (80—100 mesh) was used at 130°C.

RESULTS AND DISCUSSION

Theoretical approach to the optimum separation

Liquid phase. For the liquid phase, silicone KF-54 (Shinetsu Kagaku) and Apiezon C were tested. Packed columns with both liquid phases were prepared and the partition coefficients were obtained. The values on KF-54 (162 for the *trans* and 208 for the *cis* form at 140°C) were smaller than those on Apiezon C (358 and 464, respectively, at 142°C). The ratios of the partition coefficients (separation factor), however, were almost the same (1.284 with KF-54 at 140°C and 1.296 with Apiezon C at 142°C). Although both liquid phases had similar separation properties, Apiezon C was chosen because its better stability in long-term operation.

Partition coefficients. The logarithm of the partition coefficient is linearly related to the reciprocal of the separation temperature. From the partition coefficient data at 121, 142, 162 and 183°C, the following empirical equations were derived by approximation:

$$\ln K_t = 4.72(1/T) \cdot 10^3 - 5.48$$

$$\ln K_c = 4.87(1/T) \cdot 10^3 - 5.60$$

where K_t and K_c are the partition coefficients of the *trans* and *cis* forms, respectively, and T (K) is the separation temperature. The correlation coefficient was 1.

Optimum flow ratios and separation temperature. The gas- and liquid-flow ratio (G/L) in the separation section should be between the two partition coefficients in CCGLC. When the separation is low, partition coefficient becomes large, then G/L also becomes large. This means that a high gas flow-rate should be used. As the trapping efficiency becomes low at high gas flow-rates, a high separation tem-

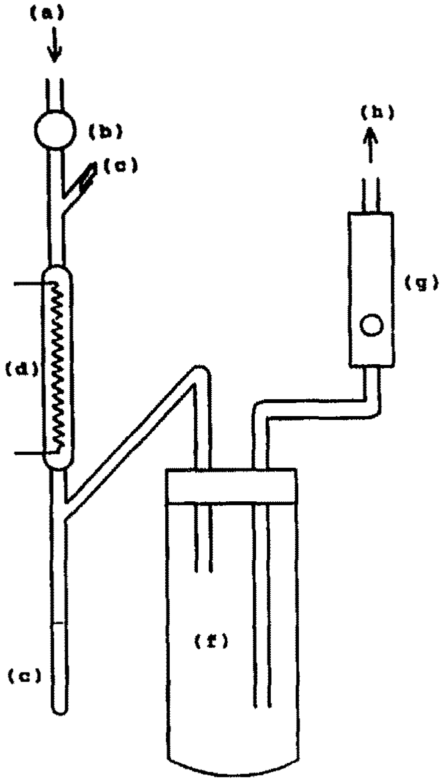

Fig. 3. Trap system. (a) From separation tower; (b) needle valve; (c) sampling port; (d) water jacket; (e) collector; (f) trap, (g) flow meter; (h) to vent.

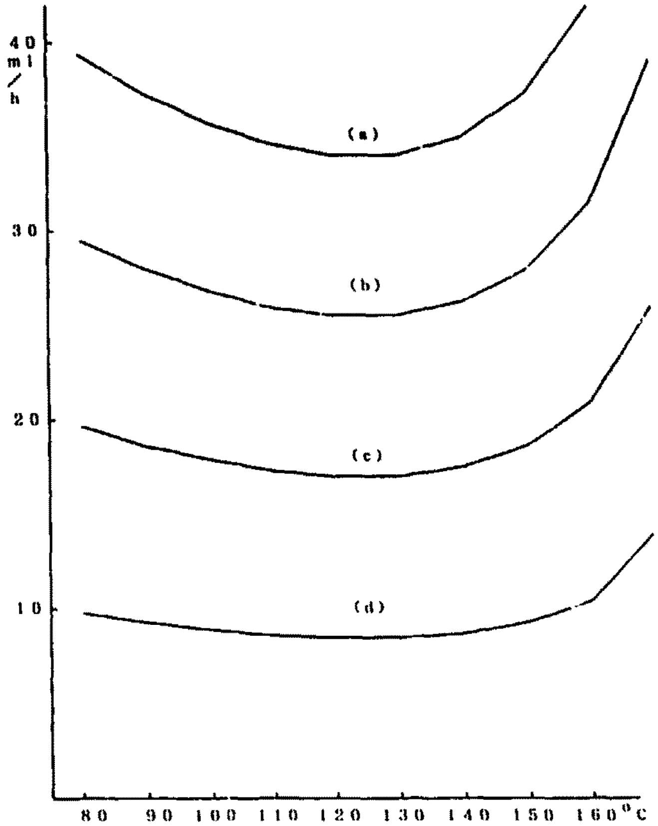

Fig. 4. Calculated maximum sample feed rate *vs.* separation temperature. Sample, decahydronaphthalene isomer mixture (1:1, w/w); liquid phase, Apiezon C; liqund phase flow-rate, (a) 0.4, (b) 0.3, (c) 0.2 and (d) 0.1 l/h.

perature is to be preferred. However, at low temperatures, the separation efficiency becomes high as the separation factor increases. Therefore, to determine the optimum separation temperature, those factors should be taken into consideration.

Maximum sample feed rate. The maximum sample feed rate, F_{max}, is calculated by the following equation:

$$F_{max} = \frac{tK_cP_t(G - LK_t) + cK_tP_c(LK_c - G)}{tK_c(760 - P_t) + cK_t(760 - P_c)} \cdot \frac{273}{273 + T'} \cdot \frac{1}{22400} \text{ (mol/min)}$$

where t and c are the contents of the *trans* and *cis* forms, respectively ($t + c = 100$). K_t and K_c are the partition coefficients of the *trans* and *cis* forms, P_t and P_c (mmHg) are the vapour pressures of the *trans* and *cis* forms, G and L (ml/h) are the flow-rates of the gas and liquid phases, respectively, and T' (°C) is the separation temperature.

The calculated maximum feed rates of the decahydronaphthalene sample are plotted against temperature in Fig. 4. The calculated maximum feed rates were lowest at *ca.* 125°C. The maximum sample feed rate is also proportional to the liquid flow-rate. Considering the limitation of the liquid flow-rate and the structure of the system, the sample feed rates were set from 7.2 to 14.7 ml/h. Better results were obtained at lower sample feed rates.

Tower structure

Tower construction. In the previous work [1], the separation tower was made from a single glass tube. However, the newly constructed tower was made from seven units, which made possible the insertion of the thermosensors in several locations. This structure was also convenient for fixing the stain-

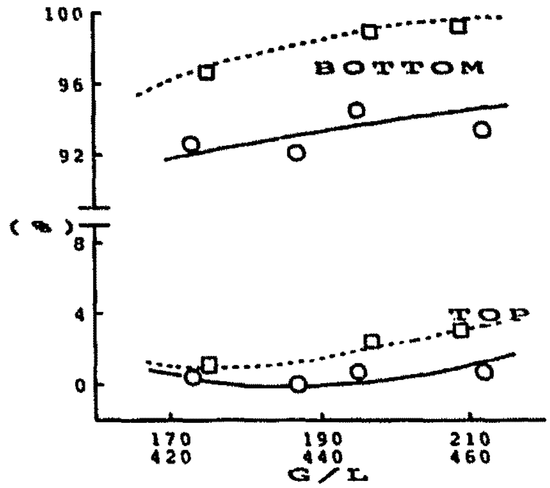

Fig. 5. Content of *cis*-decahydronaphthalene in the bottom and top recovered fractions: comparison of separation efficiency according to separation tower diameter. Tower diameter: = 17 mm; = 50 mm.

less-steel net inside the tower. No influence on the separation efficiency was observed when these connected sections were used.

Diameter of the tower. It is generally considered that the separation efficiency decreases as the diameter increases. In this experiment, however, the data obtained with a diameter of 50 mm was better than that with 17 mm. The concentration of impurity at the top of the 17 mm diameter tower was lower than that with the 50 mm diameter tower, but at the bottom that of the 50 mm diameter tower was much higher than that of the 17 mm diameter tower, as shown in Fig. 5. Both towers had same length and were operated under optimum conditions and the sample feed rates were about half of the calculated values. Different liquid phases, namely silicone KF-54 and Apiezon C, were used in the 17 and 50 mm diameter towers, but the ratios between the partition coefficients and *G/L* values were similar. Hence the poor purity at the bottom of the 17 mm diameter tower might be due to the tower being overloaded and the excess component fell to the bottom of the tower, which suggests that the effective amount of liquid phase was small. It is assumed that thick-film flow might have occurred at the glass wall and the effective depth of the liquid film depth decreased.

Packing. Direct feeding of liquid phase into the new tower did not seem to make a uniform liquid film on the packing. It was considered that the viscosity of the liquid at room temperature was too low to disperse the liquid phase uniformly. Therefore, the liquid was diluted with chloroform (1:1, v/v) and an aliquot of the mixture was fed into the tower to coat the packing surface. The chloroform was then removed by raising the temperature of the tower. The condition of the helical wire packing and the standing angle of the tower were critical for obtaining a uniform coating.

Gas preheating

When the gas was introduced directly from the high-pressure cylinder through the purifier, fluctuation of the liquid flow at the bottom of the tower was observed. It was considered that the direct flow from the cylinder partially cooled the liquid phase, which made liquid phase viscous and caused turbulent flow. On preheating the gas to the temperature of the stripping section, no fluctuation in flow occurred.

The inner diameter of the gas outlet at the midpoint of the tower was so narrow (7 mm) compared with the diameter of the tower (50 mm) that the liquid phase flowed out with the gas steam and liquid phase flooding occurred. To prevent this flooding, an additional outlet was added on the opposite side to the first one.

Liquid-phase flow

To keep the liquid flow smooth, the viscosity of the liquid phase should be sufficiently low. From the test experiment, it was found necessary to heat the liquid phase to >60°C. Further, the liquid phase at the entrance of the tower should be heated to the temperature of the tower so as not to change the separating conditions, because a cold liquid phase lowered the temperature. The stainless-steel wire net at the top of the tower was confirmed to work as a distributor and a uniform flow of the liquid phase resulted.

Optimization of operating conditions

The gas-phase flow-rates were within the range 63.7–139.2 l/h. Above 100 l/h, poor trapping efficiency resulted. The liquid flow-rates were from 0.195 to 0.376 l/h, which were determined from the gas flow-rates and *G/L* values. The experiments were carried out at tower temperatures of 140 and 150°C. Three sample feed rates were chosen for the different liquid flow-rates: 7.2 ml/h at a liquid flow-rate of 0.195 l/h, 12.0 ml/h at 0.294 l/h and 14.1 ml/h at 0.376 l/h. Each feed rate was determined by considering a safer running and was lower than the calculated maximum feed rate.

The optimum operating conditions at 150°C were studied by changing the gas flow-rates. At around G/L = 383, 93% *trans* form and 89% *cis* form were obtained. The difference between the actual and theoretical optimum G/L values was about 18%. It was assumed that the actual temperature was 3–4°C lower than the measured temperature. The optimum operating conditions at 140°C were also studied by changing the gas flow-rates. At G/L = 460, 97.5% *trans* form and 98.8% *cis* form were obtained. At 140°C, the difference between actual and theoretical optimum G/L was about 7.7%. The same reason for the difference was assumed, but it became smaller. The partition coefficient at 150°C was small and therefore the consumption of gas phase could be small. However, higher purities of products were obtained at 140°C than at 150°C. The separation factor seemed more effective.

Separation of decahydronaphthalene stereoisomers

The mixture of *trans*- and *cis*-decahydronaphthalene (1:1, w/w) was separated by long-term operation under the optimum conditions. For more than 15 h, steady results of >95% purity for both isomers were achieved.

CONCLUSIONS

For preparative purposes, a scaled-up CCGLC system was constructed and the optimum operating conditions were investigated. Separation of a decahydronaphthalene stereoisomer mixture was attempted and 97.5% pure *trans* form from the top and 98.8% pure *cis* form from the bottom of the separating tower at 140°C were achieved. The purity of the *cis* form in the eluate from the bottom of the tower (98.8%) was much improved compared with the result (92.1%) in the previous study [1].

REFERENCE

1 K. Watabe, H. Kanda, K. Sato and T. Hobo, *J. Chromatogr.*, 590 (1992) 289.