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Effect of efficiency improvement by injecting a sample at a lower carrier gas velocity in isothermal gas–liquid chromatography

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Abstract

The effect of efficiency improvement of chromatographic system by injecting a sample at a lower carrier gas velocity (in comparison with the carrier gas velocity at subsequent separation) was studied experimentally and theoretically in isothermal gas–liquid chromatography. The suggested technique is based on sample introduction in the programmed carrier gas velocity operation mode: the injection is realized at low carrier gas velocity, then the velocity is increased rapidly up to the operation value. The technique can be applied in chromatographic practice. © 2001 Published by Elsevier Science B.V.

Keywords: Efficiency; Injection methods; Carrier gas velocity; Gas chromatography

1. Introduction

Shortening analysis duration and increasing gas chromatograph productivity are of primary importance for modern routine gas chromatography (GC). Hence, chromatographers use the advantages of isothermal GC [1,2] and carry out the separation in the high-speed operation mode [3].

But the high-speed separation usually leads to a considerable decrease of column efficiency [i.e., to the drastic increase of the height equivalent to a theoretical plate (HETP)].

The purpose of the present research was to study a new technique which allows decreasing the HETP value in the high-speed operation mode.

Band broadening of chromatographic zones is determined by two additive processes: (1) by the formation of an initial (wide) zone when sample is being injected into the carrier gas flow in the injector; (2) by the following band-broadening of the initial zone in the column during the separation. In the case where the carrier gas velocity at the moment of sample injection and that during the separation are different, the following expression can be written for the width of the chromatographic zone at the column outlet:

$$\mu_{com} = \mu_{inj}(u_{inj}) + \mu_{col}(u_{col}) \quad (1)$$

where $\mu_{inj}(u_{inj})$ is the initial width of the chromatographic zone that forms when sample is being injected into the chromatographic system at carrier gas velocity u_{inj}; $\mu_{col}(u_{col})$ is the linear width of the chromatographic zone, which is determined by the band broadening in the column at carrier gas velocity u_{col}.

Let us consider the length of the chromatographic

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zone at sample injection (i.e., at sample transfer from a needle to a carrier gas flow in the injector). When neglecting the band broadening due to temperature and transition from liquid state to gas that, an initial linear width of the zone can be given as:

$$\mu_{inj}(u_{inj}) = u_{inj} t_s \quad (2)$$

or

$$\mu_{inj}(u_{col}) = u_{col} t_s \quad (3)$$

Eq. (2) corresponds to a two-stage (by carrier gas velocity) process, but Eq. (3) deals with a single-stage process.

As a rule, in chromatographic practice the u_{inj} value does not differ from the operation value of carrier gas velocity u_{col} (see Eq. (3)), i.e.:

$$u_{inj} = u_{col} \quad (4)$$

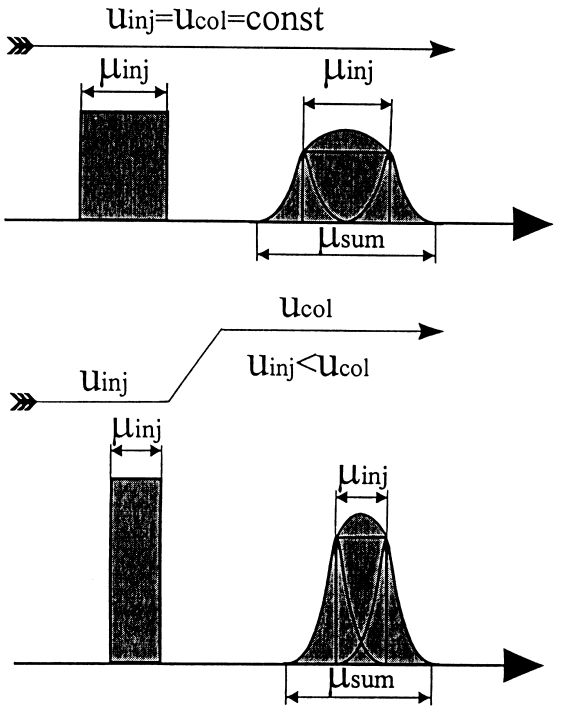

Fig. 1. The scheme of the suggested technique of efficiency improvement by injecting a sample at low carrier gas velocity and by the following increasing of the velocity up to the operating value. The upper scheme illustrates the traditional GC variant without programming of carrier gas velocity, the lower the new variant where carrier gas velocity at the moment of sample injection is lower than that during separation.

Generally speaking, observance of condition (4) is not obligatory. To improve the separation efficiency it seems reasonable to decrease the initial width of the chromatographic zone $\mu_{col}(u_{col})$. According to Eq. (2), it is necessary to decrease the carrier gas velocity of sample introduction into a chromatographic system. This leads to a decrease of the initial linear length. Then it is expedient to increase immediately the carrier gas velocity up to the optimal operating value. The maximum carrier gas velocity providing the best separation is considered to be the optimal one. Thus, in order to improve the separation efficiency it makes sense to carry out a two-stage analysis: the sample is injected at a low carrier gas velocity u_{injopt}, the separation is performed at the optimal carrier gas velocity u_{col}. Note, that:

$$u_{injopt} < u_{col} \quad (5)$$

and

$$\mu_{injopt}(u_{inopt}) = u_{opt} t_s \quad (6)$$

From Eqs. (3) and (6) we write:

$$\frac{\mu_{inj}(u_{col})}{\mu_{injopt}(u_{injopt})} = \frac{u_{col}}{u_{injopt}} \quad (7)$$

or

$$\mu_{injopt}(u_{injopt}) = \mu_{inj}(u_{col}) \cdot \frac{u_{injopt}}{u_{col}} \quad (8)$$

From Eq. (5), the following expression can be obtained:

$$\frac{\mu_{inj}(u_{injopt})}{\mu_{inj}(u_{inj})} < 1 \quad (9)$$

or

$$\mu_{injopt}(u_{injopt}) < \mu_{inj}(u_{col}) \quad (10)$$

Thus, application of low carrier gas velocities for sample introduction allows decrease of the initial width of the zone (and, therefore, the general final width of zone). This means improvement of separation.

The scheme of the two-stage chromatographic separation with various carrier gas velocities is listed in Fig. 1.

In the discussed new chromatographic variant let

us consider the separation number (SN) as a value characterizing the efficiency of the chromatographic system [1]:

$$SN = \frac{t_{n+1} - t_n}{\mu_{com}} = \frac{\Delta t}{\mu_{com}} \quad (11)$$

$$\Delta t = t_{n+1} - t_n \quad (12)$$

where t_n and t_{n+1} are retention times of two consecutive organic compounds with n and $(n+1)$ carbon atoms in their molecules, respectively; μ_{com} is the general width of zone after separation.

The following relationship is valid for the reciprocal of separation number:

$$\frac{1}{SN} = \frac{\mu_{inj}(u_{inj}) + \mu_{col}(u_{col})}{\Delta t} = \frac{\mu_{inj}(u_{inj})}{\Delta t} + \frac{\mu_{col}(u_{col})}{\Delta t} \quad (13)$$

Therefore, the purpose of the present study was to develop a new approach for efficiency improvement, which is based on the use of two various carrier gas velocities for the sample introduction and the separation.

2. Experimental

Chromatographic measurements were made using a Trace 2000 gas chromatograph (Thermo Separation/CE Instruments, USA) equipped with an electronic pressure control, an autosampler AS 2000 and a flame ionization detection (FID) system. Chromatographic separations were performed on a 30 m×0.32 mm I.D. column (Hewlett-Packard, USA) coated with liquid stationary phase (SLP) HP-5 (cross-linked 5% phenylmethylsilixane) (film thickness: 0.25 μm). Test compounds (*n*-alkanes C_{14}–C_{16}) were used as a 0.0033% solution in hexane (Hewlett-Packard). Nitrogen was used as carrier gas. The carrier gas velocities were: at sample introduction from 18 cm/s up to 103 cm/s (for 0.5 min), then with an increase of 20 ml/min^2 up to the operation value of 47.6 cm/s or 91.1 cm/s. The split ratio was 1:50 for all experiments. Programming of carrier gas velocity and the split ratio were operated by the electronic pressure control. Injection technique: air–sample–air sandwich. Injection speed: pre-injection dwell time 2 s, post-injection dwell time 0 s. Dwell time is that of needle with air to be kept in injector. The technique of sample introduction is described in detail in Chrom. Quest Manual for Trace 2000 gas chromatograph. The speed of sample introduction was 30 μl/s. Standard cylindrical liner without packing for the Trace 2000 split/splitless injector for 1 μl sample was used. Column position in the liner was 40 mm from the column end to ferule (according to manufacturer's recommendations for split sample injection). Inlet pressures: at 120°C – 47.6 cm/s (1.11 bar), 91.1 cm/s (2.21 bar); at 150°C – 10.0 cm/s (0.237 bar), 100.0 cm/s (2.61 bar). Septum purge 3.5 ml/min, constant. Oven temperature was 120°C. The detector temperature was 220°C. Flow-rates in detector were: air 350 ml/min, hydrogen 50 ml/min, make-up gas (nitrogen) 35 ml/min. The injector temperature was 200°C. The sample was introduced with a 1 μl microsyringe. The speed of microsyringe's rod movement corresponds to a sample introduction speed of 30 μl/s.

3. Results and discussion

Dependence of efficiency (in SN units) on the carrier gas velocity at the moment of sample injection is shown in Fig. 2. As seen the carrier gas velocity has an influence on the efficiency. The obtained results confirm the possible improvement of the efficiency by injecting a sample at a low carrier gas velocity and then increasing the velocity up to the operating value.

As expected, the dependence of the reciprocal of SN on the ratio of the carrier gas velocities during the injection and the following separation is practically linear (see Fig. 3). This allows simplification of separation evaluation and its optimization.

The separation of a mixture of organic compounds at the constant carrier gas velocity of 100 cm/s during analysis and that under the conditions of low carrier gas velocity of 10 cm/s at the moment of sample injection and its subsequent increase up to 100 cm/s are presented in Fig. 4. As seen, the improvement of separation is observed for the fol-

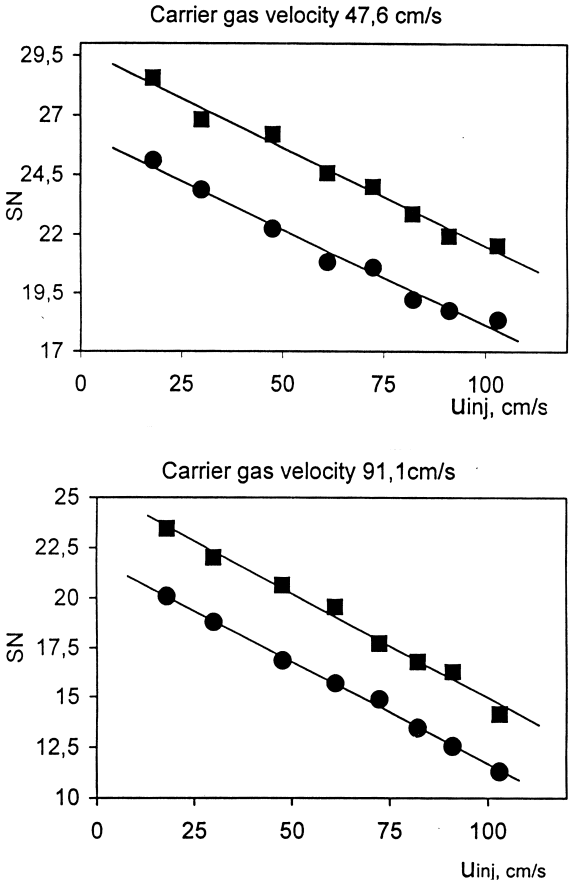

Fig. 2. Dependence of SN on carrier gas velocity during injection with carrier gas velocity during separation of 47.6 cm/s (upper curve) and of 91.1 cm/s (lower curve). Experimental conditions: column 30 m×0.32 mm coated with HP-5 (SLP) (film thickness 0.25 μm), nitrogen as carrier gas, 120°C, sample size 1 μl. Solutes: ● *n*-C_{15}/*n*-C_{14}, ■ *n*-C_{16}/*n*-C_{15}.

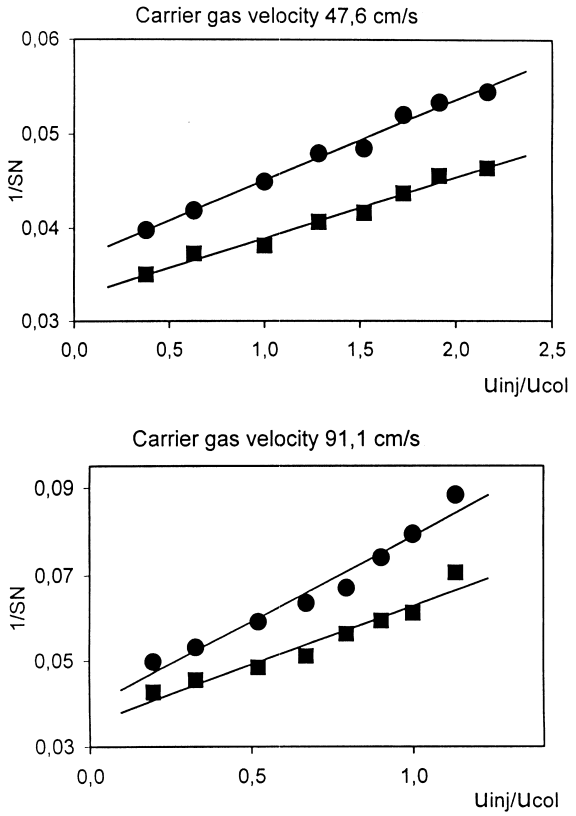

Fig. 3. Dependence of the reciprocal of SN on the ratio of carrier gas velocities during injection and separation [47.6 cm/s (upper curve) and 91.1 cm/s (lower curve)]. Experimental conditions: column 30 m×0.32 mm coated with HP-5 (SLP) (film thickness 0.25 μm), nitrogen as carrier gas, 120°C, sample size 1 μl. Solutes: ● *n*-C_{15}/*n*-C_{14}, ■ *n*-C_{16}/*n*-C_{15}.

lowing pairs: *n*-dodecane/naphthalene and *n*-tridecane/(methyldecanate) under these conditions.

It is evident that the observed effect is of most importance when injecting a sample occupying the whole syringe (needle inclusive). This is not the case for sandwich type injection when a needle is not filled with a sample but the sample is located between two air bubbles. In the case when a sample occupies the whole syringe, evaporation of the sample starts as soon as the needle is placed into the injector. Also it can occur after injection if the needle is removed with delay. These effects lead to an additional increase in time of sample transfer into the injector and a decrease in efficiency.

It seems reasonable to apply the suggested technique to high-speed isothermal gas–liquid chromatography because the maximum effect would be observed at the maximum difference in velocity during injection and that during separation. As seen from Fig. 3 the increase of SN to 50% allows shortening of analysis duration due to the realization of better chromatographic conditions (for example, increase of oven temperature and decrease of column length).

Note that programming of carrier gas velocity from the low value up to the operating one leads to

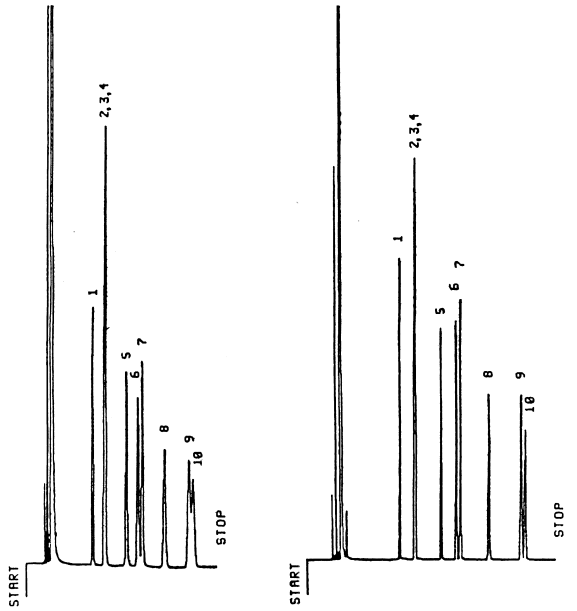

Fig. 4. Separation of mixture at conventional operation mode (A) and at carrier gas velocity programming (B) [sample was injected at carrier gas velocity of 10 cm/s (10 s), then programming of carrier gas velocity to 100 cm/s with 20 ml/min^2]. Experimental conditions: column 20 m×0.15 mm coated with CP-Sil 5 CB (SLP) (film thickness 2.00 μm), helium as carrier gas, 150°C, sample size 1 μl. Peaks: 1=octanol-1, 2=2,6-dimethylphenol, 3=*n*-undecane, 4=methyloctanate, 5=2,6-dimethylaniline, 6=*n*-dodecane, 7=naphthalene, 8=decanol-1, 9=*n*-tridecane, 10=methyldecanate.

some losses in time (for the data presented in Fig. 3, the loss was approx. 1 min). This can be attributed to the fact that the sample is eluted for a while at the low carrier gas velocity. Thus, the suggested technique for sample injection can be recommended for cases when analysis takes a long time at high carrier gas velocities.

Saving of carrier gas as a result of a decrease in carrier gas consumption in the split operation mode is an additional advantage of the suggested technique. This is of great importance for high-speed operation mode and high split ratios as well.

The suggested technique can be easily realized on a modern chromatograph equipped with electronic pressure control.

4. Conclusion

A new chromatographic variant was suggested and studied. In the given variant a sample is injected at a low carrier gas velocity. Examples indicating the expediency of the new technique application are listed. The suggested technique is of general importance and can be also used in liquid chromatography.

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