Potentiality of Optical Diffraction Grating Technology in the Fabrication of Miniaturized Multicapillary Chromatographic and Electrophoresis Columns

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Abstract

A possible way of fabricating miniaturized multicapillary columns for gas and liquid chromatographs or electrophoresis devices containing many thousands of identical channels with a width (or depth) of approximately 1–30 µm by means of industrial technology for the production of optical plane reflecting diffraction gratings is proposed.

Introduction

The miniaturization of sample-analysis instrumentation and especially separation systems such as gas and liquid capillary chromatographs or capillary electrophoresis devices will generally result in improved performance characteristics and reduced production and analysis costs. In this regard, the miniaturized separation systems provide a more effective system design that results in an increased speed of analysis, lower solvent and gas consumption, and the possibility of increased detection efficiency. The small dimension, low electricity consumption, and high speed of analysis will make it possible to use miniaturized chromatographs in field conditions, such as for the detection of explosives or the in situ study of physicochemical transformations of aerosols and gaseous impurities in the atmosphere.

A miniaturized gas chromatograph requires a capillary column that must be much shorter than those 20- to 100-m long with a 200- to 500-µm i.d. that are applied in conventional capillary chromatographs. Nevertheless, such a short column (e.g., approximately 5- to 100-cm long) must possess the resolution power comparable with the efficiency of long columns. For this purpose, the miniaturized column must have an internal diameter of approximately 5- to 40-µm to provide high separation efficiency. The diminution of the capillary diameter will however result in a sharp decrease in sample capacity, and perhaps this decreased sample will be insensible in the detection system. In order to overcome contradiction between column resolution and sample capacity, multicapillary columns have been proposed (1). In this case, several tens or hundreds of small-diameter capillaries are united in a bundle and all capillary inlets are joined together as well as the outlets. A relatively large sample is injected into the joint inlet, and the carrier gas–sample flow is distributed among all of the capillary channels so that a partial substance quantity in every channel does not exceed a permissible sample size. A resolved sample component, which must simultaneously elute from all of the channels, collects in the joint outlet and passes to a detector.

Multicapillary columns are usually fabricated from a low-melting glass, fused silica, or metal. For instance, a bundle of wide-bore glass capillary tubes is heated to the melting point, the tubes are drawn, and thus narrow-bore capillaries (i.e., approximately 30- to 40-µm i.d. and 20 to 100 cm in length) are obtained. Such bundled columns having 900–1100 capillary channels have been effectively applied (2–5) and used in Ekho gas chromatographs (6,7). The method for the preparation of the column using a bundle of metallic wires has been described (8) and the slits between the wires were proposed for use as capillary channels. The designs of metallic disk-like and conical (9) or cylindrical columns (10), which could potentially be transformed to a multicapillary system, are also known, and in these cases the channels of various forms (e.g., triangular and helicoidal) were threaded, ground, or cast on the face surfaces of the previously mentioned objects.

The necessity for making multicapillary columns (and also the greatest difficulty) is to prepare many hundreds of channels that must be identical to each other, particularly in their diameters. Other difficulties are the liquid-phase coating and stationary phase bonding on the inner walls of the capillaries. It should be noted that all of these problems will be greatly enhanced by attempting to make a column with channel widths of 5–10 µm and smaller. Such columns (5- to 20-cm long) would be necessary for designing miniaturized gas and liquid chromatographs or electrophoresis systems. In this case, the performance of every channel must be very accurate within a small fraction of a micrometer. It should also be taken into account that such a column must contain many thousands of channels in order to allow the column to retain large sample capacity. It seems

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unlikely to fabricate 5000–10,000 identical channels that are 5- to 10-µm wide and smaller using the previously mentioned methods for producing glass or metallic columns.

This study relates to a possible way of fabricating miniaturized multicapillary columns containing many thousands of identical channels with a width (or depth) of approximately 1–30 µm (or somewhat smaller or larger) by using the technology for the production of the optical plane reflecting diffraction gratings (11).

Optical plane reflecting diffraction gratings

Optical plane reflecting diffraction gratings are widely used in optical devices such as infrared and UV–vis spectrographs, monochromators, and lasers, and they are produced by the optics industry (12–15). A schematic view of a standard diffraction grating with 100 grooves per millimeter is shown in Figure 1. Usually, it is a rectangular or square flat plate (i.e., 100 × 100 mm and approximately 10 mm in thickness and made from metal or glass). On the face surface of a plate, the strictly parallel and identical triangular-formed grooves are ruled with the help of a special ruling machine using a diamond edge that is ground to the desired shape as a ruling point. Various dimension types are standardized in the optics industry. Plate sizes vary from approximately 50 to 300 mm, but the line ruling areas are somewhat smaller. The line rulings are performed within approximately 40–3000 grooves/mm so that the grating spacing (i.e., the groove width) is within approximately 0.3–25 µm. Gratings with a spacing of approximately 50–500 µm (2–20 grooves/mm) are also produced. The plates can be made of either aluminum, an aluminum alloy (Al–Mg–Zn), or other metals (i.e., nickel, Invar, bronze, or stainless steel). The usual practice is also to rule the grooves on aluminum, gold, or other metal layers deposited on glass flat plates. Also, the grooves with a very small spacing (approximately 3000 grooves/mm) are ruled sometimes directly on the surface of a glass plate. Because a grating of good quality is difficult to produce, replicas of original rulings are often used. These are obtained by using a pressing or molding from the original ruled master grating (proper plastics are used for the pressing or molding). The replicas are much lower in price than the original gratings and are more suitable for serial production.

Conceptual design of the multicapillary grating column

The perfect grating has grooves of identical form and size, because this is necessary for good spectral resolution power. The groove nonidentity is much less than 1%, at least for the infrared gratings with a spacing of approximately 1–2 µm and coarser (12–15). The identity of many grooves seems very promising for diffraction gratings to be used for fabricating miniaturized multicapillary columns. The variety of groove widths (within approximately 1–30 µm), lengths (approximately 5–30 cm), and materials (i.e., metal, glass, or plastic) could provide the required working characteristics for chromatographic or electrophoresis columns. It would also be possible to modify the material of grooves (i.e., that of future capillary channels) by depositing a proper "chromatographic" material onto the open grating surface by means of either metal evaporation under vacuum, chemical polymerization, or oxygenation. It would be easier to perform and control the liquid-phase coating and phase bonding directly on the open surface of the grooves.

A hypothetical design of a multicapillary column is shown in Figure 2. It consists of a standard diffraction grating and another matching (but flat) plate that cover the face side of the grating in order to form numerous capillary channels. Two transversal channels were ruled additionally on the working side of the matching or grating plates (or both) near the beginning and the

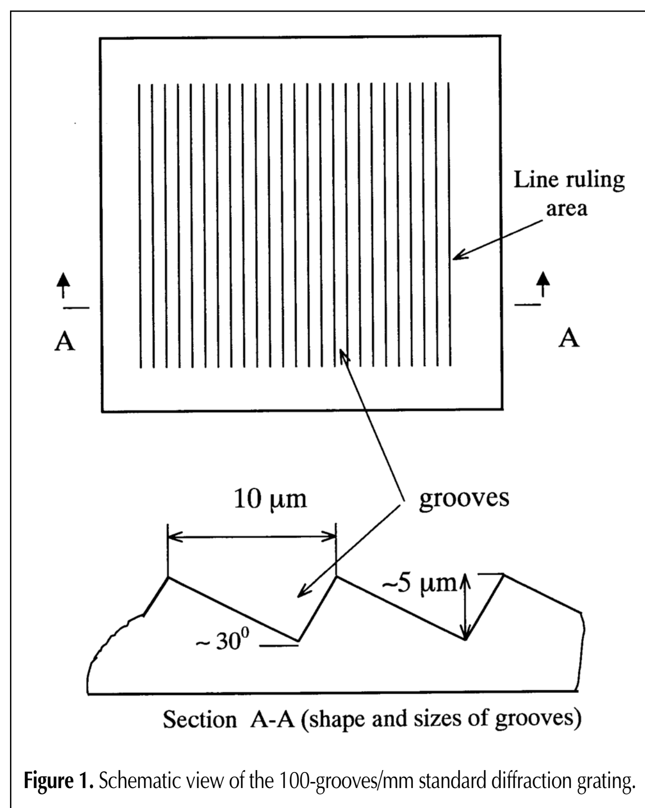

Figure 1. Schematic view of the 100-grooves/mm standard diffraction grating.

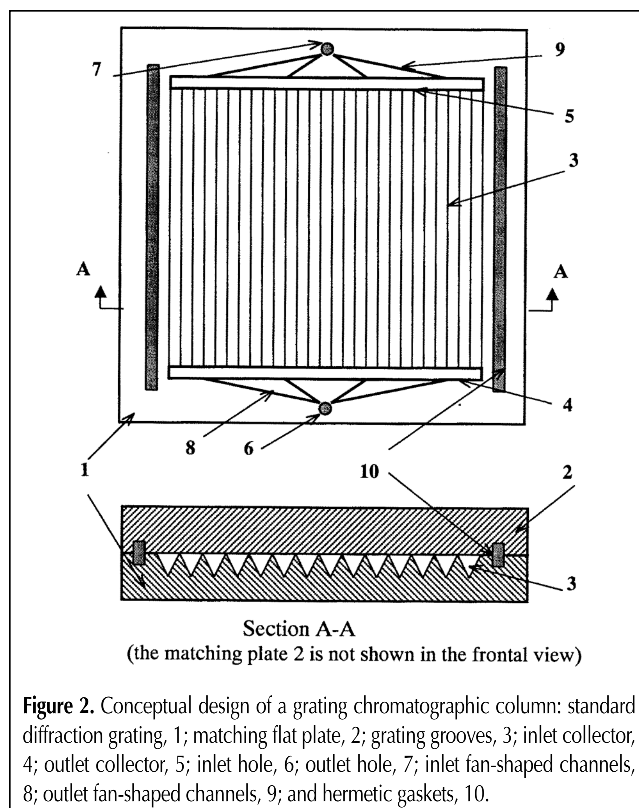

Figure 2. Conceptual design of a grating chromatographic column: standard diffraction grating, 1; matching flat plate, 2; grating grooves, 3; inlet collector, 4; outlet collector, 5; inlet hole, 6; outlet hole, 7; inlet fan-shaped channels, 8; outlet fan-shaped channels, 9; and hermetic gaskets, 10.

end of the grooves. These formed the inlet and outlet collectors, respectively, in order to distribute the gas–sample mixture among the capillaries and join again the capillary flows. Through the appropriately arranged inlet hole and fan-shaped channels, the gas–sample mixture flowed into the inlet collector and thereafter eluted the column through the outlet collector, the outlet hole, and the outlet fan-shaped channels (numbered in Figure 2 as 5, 7, and 9). All of the channels are shown in Figure 2 as the individual ones assuming that the groove tops are hermetically sealed with the matching plate. Actually, this would be unnecessary because of the high identity of the channels, the spatial distributions of the gas pressure, and the sample components along the column that must be the same in every channel. Therefore, the possible nonhermetic joints of the groove tops and plate should not cause cross-flows of the carrier gas and sample components from one groove to another. In addition, it would be even desirable to cut the groove tops to form a single quasi-flat slit, because a chromatographic column with a slit-like cross-section is known to have the best separation efficiency (16,18). Also, because of the technological feature of grating production, it would appear that the groove tops of standard gratings are located somewhat below the overall face plane so that the above slit-like channel would form in itself. Thus, the hermetic gaskets in the hypothetical column (numbered as 10 in Figure 2) must be arranged only along the edges of the line ruling area on the matching or grating plates (or both).

Figure 3 shows other column designs with twin or triple gratings. Either parallel or serial commutations of the inlet/outlet collectors of both gratings (Figure 3A) may result in the doubling of either a number of channels (i.e., double sample capacity) or channel length (i.e., an increase in resolution power), respectively. It should be noted that in the first case the gratings must have identical grooves, but in the second case the gratings may be either equal or different. In the designs shown in Figures 3B, 3C, and 3D, one of the gratings serve as a matching plate, thus the different forms of resulting slits could be obtained. The third grating (Figure 3E) may also be matched to the previously mentioned twin gratings, thus the serial commutations of collectors must increase the column resolution.

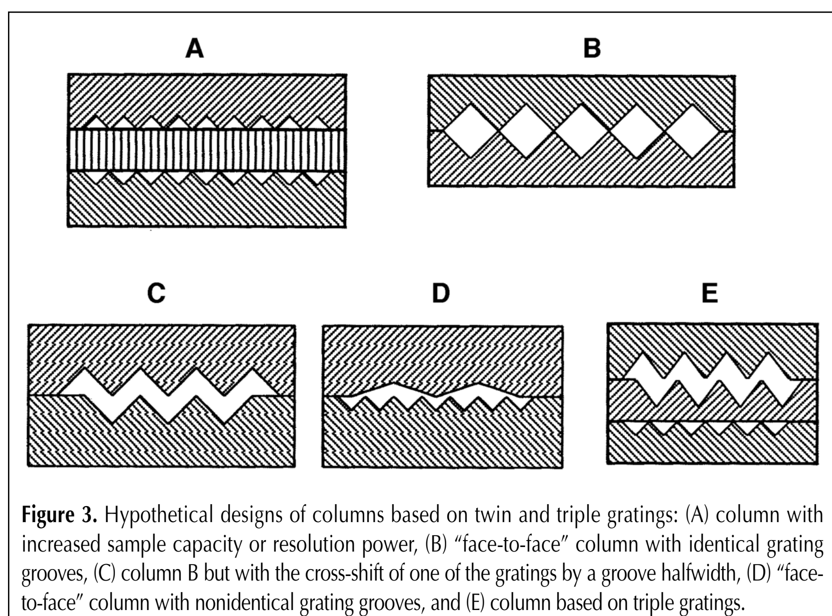

Figure 3. Hypothetical designs of columns based on twin and triple gratings: (A) column with increased sample capacity or resolution power, (B) "face-to-face" column with identical grating grooves, (C) column B but with the cross-shift of one of the gratings by a groove halfwidth, (D) "face-to-face" column with nonidentical grating grooves, and (E) column based on triple gratings.

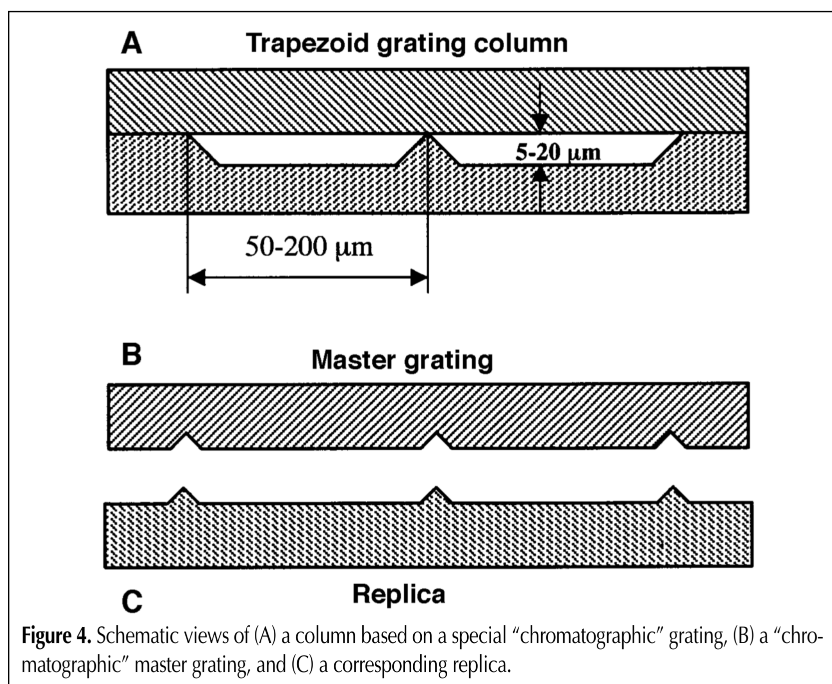

Figure 4. Schematic views of (A) a column based on a special "chromatographic" grating, (B) a "chromatographic" master grating, and (C) a corresponding replica.

The standard optical gratings with triangular grooves are assumed to be used in the columns, but the production of special "chromatographic" gratings would also be possible. These could be prepared with the help of grating equipment (i.e., ruling machine and diamond chisel), but chisels ground to the rectangular or trapezoid shape should be used to rule the relatively wide rectangular or trapezoid slits (i.e., having a width of 50 to 200 μm and a depth of 5 to 20 μm) (Figure 4A). As was pointed out earlier, the channels of such cross-sections should demonstrate better efficiencies when compared with the channels of round or triangular forms. It should be emphasized that in this case the slit depth will affect the intrachannel diffusion rate and thus characterize chromatographic separation.

For chromatographic purposes, it would also be desirable to make replicas by using a special master grating with triangular grooves (e.g., approximately 5–20 μm in width and depth) that should be ruled infrequently (i.e., every other 50–200 μm or more) (Figure 4B). However, the replica obtained will have trapezoid grooves that are 50- to 200-μm wide and 5- to 20-μm deep (Figure 4C). As mentioned previously, the replicas are low in price and thus the reduced production cost will be very important for the serial fabrication of multichannel columns. Of course, the replicas must be made from plastics or other materials with good chromatographic characteristics, particularly stability at a higher temperature (i.e., 50°C, 100°C, or 200°C). For instance,

such materials could be either Teflon (or probably other polyfluorinated plastics), ceramic clay, epoxy, polyimide, or even polyamide plastics, taking into account in the latter case that not too high of a temperature must be applied in a short small-diameter column. Depending on the mutual imbalance of the epoxy resin and other ingredients in the starting liquid epoxy compound, the final hardened epoxy plastic and consequently the walls of channels must contain some quantity of unlinked substance that could serve as a liquid-phase coating. The plastics and ceramics could probably be used for producing the "chromatographic" gratings (Figure 4A) as either the base plates or thin layers linked on glass or metallic plates (thus allowing for the original "chromatographic" grooves to be ruled directly on the plastic or ceramic surfaces).

It should also be noted that it would sometimes be expedient to rule the grooves of different depths on the different sections of one plate, perform there the different liquid-phase or adsorbing coatings, or both. The separate outlet collectors and detectors could be arranged on these plate sections, thus the multiposition column would be realized. In regards to the inlet collectors, they must be either separate collectors or a single common collector. In the latter case, the sample will simultaneously be analyzed by a few different columns and detectors. It would also be advantageous to arrange these tiny elements (i.e., inlet, outlet, injector, and detector) either on the backsides or in the bodies of the matching or grating plates (or both).

Estimations of resolution power and operating pressure for a grating column

We used Golay's equation for a round capillary even though the grating columns contained channels of triangular, rectangular, or trapezoid forms:

$$\mathrm{HETP} = \frac{2D_g}{u} + \frac{1 + 6k + 11k^2}{96\cdot(1 + k)^2}\cdot\frac{d_c^2}{D_g}\cdot u + \frac{2}{3}\cdot\frac{k}{(1 + k)^2}\cdot\frac{d_f^2}{D_f}\cdot u \qquad \text{Eq. 1}$$

where *HETP* is the height equivalent to a theoretical plate; d_c is the capillary diameter; d_f is the thickness of the liquid-phase film; u is the average linear velocity of the carrier gas; D_g and D_f are the diffusivities of a sample substance in carrier gas and liquid film, respectively; and k is the retention factor. For a conventional capillary tube of approximately 200 µm and wider, the third term on the right side of equation 1 is usually ignored because its value is small when compared with the others, but for the small-diameter capillaries this term must be taken into account. Expressions (omitted here) for the optimal data on the gas velocity (u_o) at the column outlet (i.e., under the pressure of p_0 = 1 atm) and the optimal ($HETP_{opt}$) were derived from equation 1 by the known algorithm (16–18). These data are presented in Table I for different capillary diameters and lengths, and the concrete values of diffusivities (D_g = 0.07 and D_f = 0.00002 cm²/s), film thickness (d_f = 0.2 µm), and retention factor (k = 20) were used in the calculations. The velocities obtained were used to calculate the distributions of gas pressure *P(x)* and velocity *u(x)* along the capillary:

$$P(x) = \sqrt{p_o^2 + \frac{64\mu\cdot p_0\cdot u_o\cdot(L - x)}{d_c^2}} \qquad \text{Eq. 2}$$

and

$$u(x) = u_o\cdot\frac{P_0}{P(x)} \qquad \text{Eq. 3}$$

where x is the distance from the capillary inlet, L is the capillary length, and µ is the dynamic viscosity of the carrier gas He. As can be seen from Table I, the operating entry pressures were relatively high, especially for the small-diameter channels. The inequality of pressures along the capillary must have resulted in an additional widening of chromatographic peaks owing to the expandability of the carrier gas. In order to minimize the latter effect, an increased pressure (e.g., approximately 10 atm) can be maintained forcibly at the 5-cm × 5-µm capillary outlet, and in this case the ratio between the new inlet (approximately 17 atm) and outlet (10 atm) pressures would be much smaller than the previous one (10.6:1, Table I). Therefore, the influence of gas expandability would be slight. Among other things, the small sizes of the grating column and other parts of a hypothetical miniaturized chromatograph could simplify operating conditions at a higher gas pressure.

In regards to the $HETP_{opt}$ values calculated either from equation 1 and the pressure and velocity distributions (equations 2 and 3) or by equation 1 modified by Giddings (17), they were approximately the same along the capillary despite the inequality of gas velocities (Table I). This was a result of the fact that the lower velocities near the capillary inlet were accompanied by higher pressures and thus the lower diffusion coefficients of a sample component in the carrier gas. It is shown in Table I that the $HETP_{opt}$ was approximately equal to the value of the capillary diameter, thus the 5-cm × 5-µm capillary should have approximately 7000 theoretical plates. As

Table I. Optimal and Operating Characteristics of Grating Columns

Capillary diameter (µm) / length (cm)	5/5	10/10	20/20	30/30
Optimal outlet gas velocity (m/s) and optimal height equivalent to a theoretical plate for the capillary diameter (µm): u_o / $HETP_{opt}$	3.77 / 1.5	2.56 / 1.1	1.44 / 0.9	0.99 / 0.9

Distributions of gas pressure (atm) and velocity (m/s) along the capillary

x (cm)	P(x)	u(x)	x (cm)	P(x)	u(x)	x (cm)	P(x)	u(x)	x (cm)	P(x)	u(x)
0	10.6	0.36	0	6.2	0.41	0	3.4	0.42	0	2.4	0.41
1.5	8.9	0.42	3	5.2	0.49	6	2.9	0.5	9	2.1	0.48
3	6.7	0.56	6	4	0.64	12	2.3	0.63	18	1.7	0.58
4.5	3.5	1.08	9	2.2	1.17	18	1.4	1.00	27	1.2	0.81
5	1	3.77	10	1	2.56	20	1	1.44	30	1	0.99

was pointed out earlier, the relative inaccuracy of the "diameters" of the grating channels ($\Delta d/d_c$) was much less than 1%, thus the additional widening ($\Delta HETP \approx L(\Delta d/d_c)^2$) can be neglected. Unfortunately, such high resolution cannot be realized in practice, because the very small linear sample size (i.e., the short injection time) was assumed in the theoretical calculation. In reality, the slower transfer of the sample from the injector into the column cuts down the theoretical resolution power. Taking into account this unavoidable obstacle, we may initially apply a nonoptimum gas velocity (i.e., ten times reduced), thus the essentially decreased operating pressures will be required in this case. At the same time, with a 10-fold reduction in gas velocity the *HETP* will increase only approximately 5 times, and thus the 5-cm × 5-µm column will have approximately 1500 plates. It should be underlined that the main goal of the application of a miniaturized chromatograph in field conditions should be the high-speed analysis of the samples with a relatively simple composition (2–5 or somewhat more components) rather than the analysis of samples containing many substances in which conventional long capillaries with 100–200,000 plates must be used. Thus, the hypothetical miniaturized 5-cm × 5-µm column with 1000–2000 plates seems to be compromised for the claimed goal.

In a very thin capillary, coefficient k would be large (≥ 10), because with other factors it is inversely proportional to the capillary diameter. In this regard, a large k value should be advantageous only for short small-diameter columns because in this case the retention times would be suitable (approximately 1–100 s), even at $k \approx 10$–100. However, it may well be that the previously mentioned "fast injection" problem (approximately 10^{-4} s) will be found technically too difficult to use the 5-µm columns. In this case, the wider grooves (10- to 30-µm wide and 10- to 30-cm long) would be suitable for the fabrication of gas columns.

Similar estimations may be performed for the hypothetical application of grating columns in liquid chromatographs. As can be observed from equation 1, the linear velocities of the liquid mobile phase must be 1000–10,000 times lower than those in gas chromatography, because the diffusivity of sample molecules in a liquid is 1000–10,000 times smaller than that used in the previous case ($D_g \approx 0.07$ cm^2/s). Such a low velocity ($\approx$ 1 mm/s) could be obtained at a relatively low operating pressure, even for the channels of 5-µm width and smaller. The *HETP* values were estimated to be approximately 0.8–0.9 of the capillary diameter. Taking also into account that (*a*) small-diameter and short-length capillaries are usually required in liquid chromatography and (*b*) the previously mentioned injection problem was less difficult than that in the case of gas chromatography, it can be concluded that the diffraction gratings with grooves of approximately 5–10 µm or smaller could be used in multicapillary liquid chromatographs (19) and very likely in electrophoresis devices (20). In addition, the planar structures of grating channels and the outlet collector could essentially extend the light path-length and consequently the sensitivity of the on-column single-pass optical detection technique commonly used in liquid chromatographs and electrophoresis systems.

Conclusion

The present or further technological resources of diffraction grating industry could be applied for designing and fabricating multicapillary columns for miniaturized gas and liquid chromatographs or electrophoresis devices. Such metallic, glass, or plastic columns having many thousands of identical channels (approximately 1–30-µm wide and 5–30-cm long) are unlikely to be produced by another method. At the same time, in order to realize the potential advantages of such unusual columns, it is necessary to design completely new miniaturized gas or liquid chromatographs including the very small sample injector, detection technique, carrier gas, or liquid supply.

References

1. M. Golay. *Chromatographia* **8:** 421 (1975).
2. A. Vlasov, V. Zhdanov, V. Sidelnikov, V. Malakhov, and V. Parmon. Russ. Patent 2,060,498 (1995).
3. V.V. Malakhov, V.N. Sidelnikov, and V.A. Utkin. The possibilities of capillary packet as a chromatographic column. *Dokl. Akad. Nauk* **329:** 749–51 (1993).
4. R. Lobinsky, V. Sidelnikov, Y. Patrushev, I. Rodriguez, and A. Wasik. Multicapillary column gas chromatography with element-selective detection. *Trends Anal. Chem.* **18:** 449–60 (1999).
5. I. Rodriquez, S. Mounicou, R. Lobinski, V. Sidelnikov, Y. Patrushev, and M. Yamanaka. Species-selective analysis by microcolumn multicapillary gas chromatography with inductively coupled plasma mass spectrometric detection. *Anal. Chem.* **71:** 4534–43 (1999).
6. W. Cooke. Multicapillary columns: an idea whose time has come. *Today's Chemist at Work* **5:** 3–6 (1996).
7. V. Soldatov, I. Naumenko, A. Efimenko, V. Vaganov, and A. Chertilina. Russ. Patent 1,651,200 (1991).
8. A. Janik. Multicapillary columns. *J. Chromatogr. Sci.* **14:** 589 (1976).
9. A. Rose and R.E. Kemper. U.S. Patent 3,319,409 (1967).
10. C. Moreaux. Fr. Patent 2,409,786 (1979).
11. Y. Samsonov. Russ. Patent 2,149,397 (2000).
12. I.V. Peysakhson. *Optics of Spectral Devices*. Machinostroenie, Leningrad, U.S.S.R., 1975, pp. 52–64, Appendix 2, Table P2.
13. V.V. Lebedeva. *Techniques for Optical Spectroscopy*. Moscow State University, Moscow, U.S.S.R., 1986, pp. 219–20.
14. M. Born and E. Wolf. *Principles of Optics*, 2nd ed. Pergamon Press, Oxford, U.K., 1964, pp. 407–409.
15. R.W. Ditchburn. *Light*. Blackie & Son, Ltd., London, U.K., 1963, Chapter 6.
16. M. Golay. In *Gas Chromatography*. D.H. Desty, Ed. Butterworths, London, U.K., 1958, p 36.
17. J.C. Giddings. *Dynamics of Chromatography, Part I: Principles and Theory*. Marcel Dekker, New York, NY, 1965.
18. B.A. Rudenko. *Capillary Chromatography*. Nauka, Moscow, U.S.S.R., 1978, Chapter 2.
19. R.F. Meyer, P.B. Champlin, and R.A. Hartwick. Theory of multicapillary columns for HPLC. *J. Chromatogr. Sci.* **21:** 433–38 (1983).
20. P. Kaltenbach, S. Swedberg, K. Witt, F. Bek, and L. Mittelstadt. U.S. Patent 5,804,022 (1998).

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