DEVELOPMENT OF AND FABRICATION OF HIGH RESOLUTION GAS CHROMATOGRAPHIC CAPILLARY COLUMNS

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Introduction

Gas chromatographic columns which are presently used in the Trace Gas Analyzer (TGA) for the space shuttle are coated with Witconol LA-23, a polyoxyethylene lauryl ether. This stationary phase is of medium polarity and has a temperature limit of 160°C. The object of the present investigation was to evaluate a new polymer for this application which would have an improved thermal stability. Further, the possible use of fused silica capillary columns with specially bonded phases as well as a new introduction system (on-column) was also to be studied.

Evaluation of New Stationary Phase

Pluronic F-68 (Wyandotte Chemical Corp.); polypropylene glycol: polyethylene glycol

Avg. Molecular Weight:	8350
M.P.:	52°C
Polarity:	similar to UCON H 90,000

Preparation of Capillary Column

A 300' x 0.032" O.D. x 0.015" I.D. stainless steel column, Chromat I.D. (Handy and Harmon, Norristown, Pa.) was etched overnight using a solution of 5 g ferric chloride, 15 ml conc. HCl and 60 ml distilled water. The column was blown out, then washed with distilled water, acetone, and methylene chloride.

The dried column was then dynamically coated with a 5% (W/W) Pluronic F-68 solution in methylene chloride. The column was dried in a stream of nitrogen overnight, then conditioned for 24 hours by programming from 50-200°C at 0.5°C/min. The column was now ready for use.

Testing of the Column

Figure 1.

Test Mixture: carbon tetrachloride
chloroform
p-xylene
m-xylene
o-dichlorobenzene

Conditions: T: 85°C isothermal
u: H_2 at 2 cc/min
Chart Speed: 5 mm/min
Instrument: HP 5830 A

Figure 2.

Test Mixture: vinylidene chloride
methylene chloride
benzene
toluene
ethylbenzene
p-xylene
m-xylene
o-xylene
styrene
mesitylene

Conditions: T: 75° isothermal

u: H_2 at 2 cc/min

Chart Speed: 5 mm/min

Instrument: HP 5830 A

Figure 3.

Same as Figure 2 except carrier gas flow rate = 3 cc/min H_2

The new column offers two significant advantages over the previous Witconol LA-23:

1) Thermal stability - The Pluronic F-68 phase can be operated to 200°C without any bleeding (probably to 235° with further conditioning). This will extend the life of the column as well as minimize contamination of the mass spectrometer.
2) The separation characteristics of the new phase are comparable to Witconol LA-23 in polarity. However, the column can be run isothermally at 85°C to give the required separation in one hour. This will eliminate special electronic requirements for temperature programming and also avoid the necessity of cooling the oven after each run.

Considerable progress has been made in the development of efficient thermally stable, insoluble silicone polymeric stationary phases during the past two years. Film stability, low level of bleeding phenomena at elevated temperatures, the ability to handle large volumes of solvent are outstainding advantages of capillary columns. The combination of an on-column injection with bonded phase fused

silica capillary columns is described below.

On-Column Injector for Capillary Gas Chromatography

On-column injection has been consistently demonstrated to be superior to all other sampling techniques utilized in capillary gas chromatography (GC). This is especially evident when the sample components vary widely in volatility (1-3). An on-column injection technique was first investigated in this laboratory in 1963 when Zlatkis and Walker described direct introduction of samples into wide bore capillary columns (4). This work, however, employed heated inlet conditions, the traditional method of assuring sample volatilization, but one which incurs the penalty of sample discrimination. A cold (ambient temperature) direct sample introduction technique has been described by Schomburg et al (5) who sought to avoide the use of a septum as well through the use of a sealed, moving plunger bearing the sample in an inverted capsule. Sample introduction is effected by lowering the plunger until the sample in the capsule contacts the capillary column. Subsequent analysis showed the substantially lowered discrimination effects and excellent quantitation. Grob and Grob (2) have reported on a technique which avoids the use of a septum and introduces the sample syringe through a valve. They rely on the close fit between the syringe needle and the wall of the needle guide to minimize leakage from the system during on-column sample injection. After sample deposition (ambient temperature), the needle

is withdrawn, the valve closed, and the analysis carried out. Low discrimination effects were obtained. These authors (2) also proposed that a relatively wide bore (1 mm I.D.) tube be used for the carrier gas supply, in order to avoid injector pressure drop resulting from even a minute amount of leakage through the injector channel.

Commercially available on-column injectors, while avoiding the use of a septum, can be susceptible to a drop in pressure at the amount of injection. No single, commercial on-column injector is capable of being adapted to the wide variety of gas chromatographic equipment on the market (6).

With the commercial availability of syringes with small diameter needles (32 gauge and smaller), we have been able to apply on-column injection to small bore capillary columns. This report describes an injection mechanism which, although utilizing a septum to avoid pressure changes during injection, substantially minimizes the deleterious effects commonly associated with septum usage. Furthermore, the device is readily adaptable to any standard GC equipment.

Experimental

The work described in this report was carried out in an HP 5830A GC unit equipped with a flame ionization detector. The injector heater block was removed and a cooling coil added around the

injection port to maintain the septum at a low temperature (see Figure 5) regardless of oven temperature.

Figures 4 and 5 illustrate the principal elements and operation of the injection device. The mechanism utilizes the point of a 25 gauge, syringe needle to effect the actual septum penetration and to act also as the protective guide for the finer 32 gauge sampling needle (Hamilton 701 SN, 10 cm. in length), which is subsequently inserted. Referring to Figure 4, the GC (Hewlett Packard 5830 A) injector nut (A) has two guide rods (B) soldered to it. Syringe needle guide (C) consists of a BD 25 gauge, ½" regular stainless steel needle, held in place in the base of the movable platform (D) by means of two set screws (Figure 5, R). Spring (F) serves to return the movable platform (D) to its original position, which is set by the adjustable stop (G). The syringe holder (H), which centers the sampling syringe (I) over the needle guide (C), is adjusted and fixed in the required vertical position through the use of a set of screws (E).

In operation, the needle guide (C) is first lowered onto the septum (Figure 5, M) until its tip indents the septum slightly, then stop (G) is lowered and locked in place. This arrangement assures that septum penetration takes place through the same hole in successive penetration-retraction cycles. This eliminated random septum cutting and greatly reduces particle contamination. During sample introduction, the filled syringe (I) is placed in

its holder (H) and lowered until its needle passes through the guide (C) to just contact the septum surface. The syringe (I) is now clamped in this position by a set screw (Figure 5, N). The movable platform (D) with its needle guide (C) is now lowered to puncture the septum (Figure 5, M) and is held in this position manually or by a latching device. The syringe (I) is lowered until it meets stop (G). This results in the sampling syringe needle entering to a depth of about half an inch below the oven wall (see Figure 5). The movable platform (D) is now released to allow spring (F) to raise the needle guide (C) out of the septum by the prearranged amount noted earlier. This leaves the sampling syringe needle inserted in the septum which closes around it. The sample is injected, the syringe is raised gently, and the GC program is activated. In order to be certain that the sampling syringe needle enters the capillary column, a glass guide (Figure 5, K) is utilized. This consists of a length of glass tubing necked down in hour-glass fashion, inserted in the injector port below the septum, and resting on the end of the capillary column (see Figure 5). As the sampling needle is lowered, it is guided by this tubing through the necked portion and into the capillary column itself. An extra benefit of this arrangement is that any septum particles which may be picked up by the needle are generally deposited on the side of this glass guide prior to its entry into the capillary column. A domed tip needle may also be used in conjunction with a prepunctured septum in order to avoid cutting the septum (7).

Results and Discussion

Figure 6 shows chromatograms obtained by injecting samples of 1 µl, 5 µl, and 10 µl, using the on-column injection device described. The solvent was hexane containing equal amounts of toluene, ethylbenzene, and ortho, meta, and para xylenes. The column employed was a 40 meter x 0.32 mm I.D. DB-5 fused silica capillary (J & W Scientific, Inc., Rancho Cordova, California, U.S.A.). Injection was carried out with the column at 60°C, and after four minutes the temperature was programmed at the rate of 2°C/min. In all cases the output peaks were symmetrical. Some band broadening may occur with sample volumes in excess of 5 µl.

Figure 7 compares chromatograms obtained with a 1 µl sample injection, using three isothermal column conditions: 60°C, 80°C, and 100°C. The solvent hexane, which boils at 69°C (760 torr) is thus exposed to a temperature near, and at two temperatures above its boiling point. A distinct narrowing of the solvent peak is observed at 80°C and 100°C compared to the 60°C result. Our tentative interpretation of this is that this is due to the higher degree of volatilitization achieved at 80°C and 100°C (i.e., hence lowered dilution by carrier gas).

Figure 8 shows the influence of column inlet pressure on solvent peak tailing in the same column. Here 1 µl of diethyl ether (b.p. 34.6°C) was injected in one second at a column temperature

of 70°C, i.e., where rapid volatilization would occur. With the column inlet pressure at 5 psi, severe solvent tailing occurred. However, when a 10 psi pressure was applied momentarily to the inlet (through an auxiliary line) then released, and followed by injection, the tailing effect did not occur. We believe this to be due to the substantial pressure pulse produced by the rapid volatilization and retrograde movement of ether vapor into the inlet portion, which competes easily with a 5 psi condition, but not as well at a 10 psi condition.

Figure 9 shows the chromatogram obtained by injection of 10 µl of natural gas (laboratory gas line) at room temperature using a 60 meter x 0.32 mm I.D. DB-1 fused silica capillary column. Once again, excellent peak shape was observed. This demonstrates the feasibility of utilizing on-column injection of gaseous samples with satisfactory results.

Using on-column injection at a column temperature above the boiling point of the sample solvent, the solvent peak is narrower compared to that obtained below the solvent boiling point. We would expect discrimination effects to be smaller with this procedure than with the use of splitting or the splitless modes of sample production (8).

It should be possible to apply higher temperature, on-column injection for non-bonded stationary phase capillary columns.

Conclusions

1. Conventional capillary columns using a stationary phase of polypropylene glycol: polyethylene glycol will extend the operating range of the columns to 200°C. Although this high temperature is not used during the separation, lower temperatures provice less bleeding and therefore less contamination in the mass spectrometer.

2. Fused silica capillary columns which contain a non-extractable stationary phase offer several advantages in a TGA system.

(a) Temperature range is up to 320°, therefore bleeding is non-existent.

(b) Flexibility and lack of fragility make these columns suitable for the TGA. The end of the column can be fed directly into the ion source of a mass spectrometer.

(c) Separations are as good as or better than conventional capillary columns.

(d) These columns lead themselves to trace analysis with a high capacity for solvents.

(e) An on-column injector which has been developed permits injections at ambient or higher temperatures. Large liquid samples (10 µl) can be injected without any tailing effects.

(f) Trace analysis at the ppm and ppb level are possible using these techniques in combination with selective detectors.

LITERATURE CITED

(1) Schomburg, G. "Capillary Chromatography", Fourth International Symposium, May 3-7, 1981, Hindelang, West Germany, ed. by R. E. Kaiser, Institute of Chromatography, Bad Durkheim, West Germany, 1981; 371-404.

(2) Grob, K.; Grob, K., Jr. J. Chromatogr. 1978, 151, 311-320.

(3) Grob, K., Jr.; Neukom, H. P. HRC and CC 1979, 2, 15-21.

(4) Zlatkis, A.; Walker, J. Q. J. Gas Chromatogr. 1963, 1, May, 9-11.

(5) Schomburg, G.; Behlau, H.; Dielmann, R.; Weeke, F.; Husmann, H. J. Chromatogr. 1977, 142, 87-102.

(6) Rinderknecht, F.; Wenger, B. HRC and CC 1981, 4, 295-296.

(7) Dawes, E. F., Private communication.

(8) Wang, F.-S.; Shanfield, H.; Zlatkis, A. Manuscript in preparation.

Figure 4: The Comparison of Solvent Peak Widths at Different Isothermal Oven Temperatures

A. 60^0C
B. 80^0C
C. 100^0C

On-Column Injection:

Solvent: 1 µl hexane
Sample: 1. toluene
2. ethylbenzene
3. m,p-xylene
4. o-xylene
Column: 40 m x 0.32 mm I.D. DB-5 fused silica capillary
Attenuation: 2^6

Figure 5: The Influence of Column Inlet Pressure on Solvent Peak Tailing

A. Inlet pressure, 5 psi
B. Inlet pressure increased to 10 psi momentarily through an auxiliary line, prior to sample injection

On-Column Injection:

Sample: 1 µl ethyl ether
Oven Temperature: 70^0C (twice as high as the b.p. of ethyl ether)
Attenuation: 2^6
Column: 40 m x 0.32 mm I.D. DB-5 fused silica capillary

Figure 6: 10 µl Natural Gas
Isothermal at Room Temperature

Attenuation: 2^5, 2^3 after 7.3 minutes
Chart Speed: 0.5 cm/min
Column: 60 m x 0.32 mm I.D. DB-1 fused silica capillary

FIGURE CAPTIONS

Figure 1: Analysis of Test Mixture Containing:
carbon tetrachloride, chloroform, p-xylene,
m-xylene and o-dichlorobenzene
Operating conditions as on page 2.

Figure 2: Analysis of Test Mixture Containing:
vinylidene chloride, methylene chloride, benzene,
toluene, ethylbenzene, p-xylene, m-xylene,
o-xylene, styrene and mesitylene
Operating conditions as on page 2.

Figure 3: Analysis of Test Mixture Containing:
vinylidene chloride, methylene chloride, benzene,
toluene, ethylbenzenem, p-xylene, m-xylene,
o-xylene, styrene and mesitylene
Operating conditions as on page 3.

Figure Captions:

Figure 7: On-Column Injection System (Front View: actual size)

A. Inlet system nut
B. Guide rods
C. Needle guide (BD 25 gauge ½" regular point, SS needle)
D. Sliding platform
E. Set screws (4-40)
F. Spring
G. Adjustable stop
H. Syringe body guide
I. Syringe with 10 cm 32 gauge needle

Figure 8: On-Column Injection System (Side View)

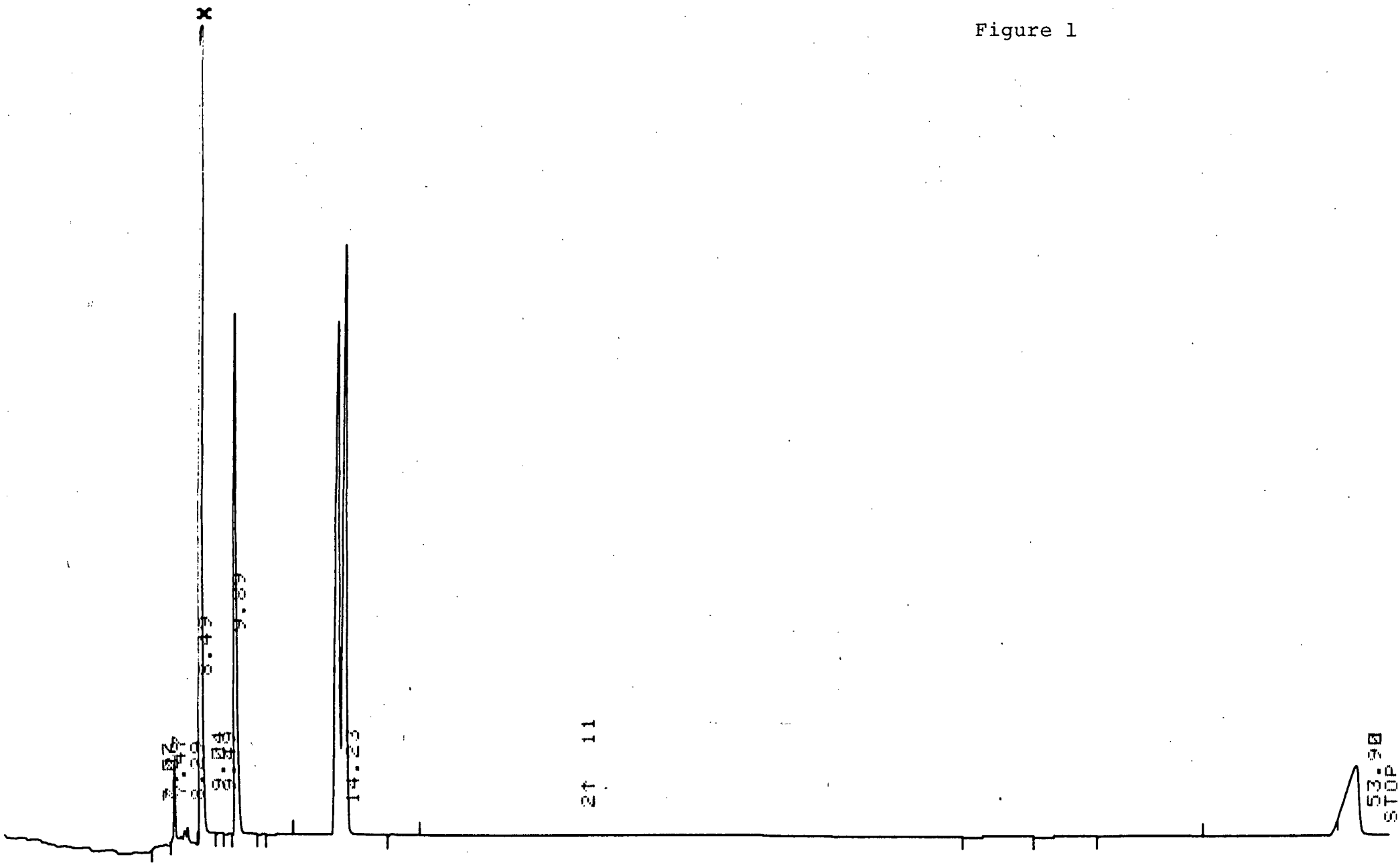
A. Inlet system nut
D. Sliding platform
G. Adjustable stop
H. Syringe body guide
I. Syringe with 10 cm 32 gauge needle
J. Oven wall
K. Glass guide
L. Injector body
M. Septum
N. Set screw
P. Capillary column
Q. Cooling coil
R. Set screw

Figure 9: Chromatograms of Different Sample Sizes

A. 1 µl, attenuation 2^7
B. 5 µl, attenuation 2^9
C. 10 µl, attenuation 2^{10}

On-Column Injection:
Solvent: hexane
Sample: 1. toluene
2. ethyl benzene
3. m,p-xylene
4. o-xylene
Column: 40 m x 0.32 mm I.D. DB-5 fused silica capillary
Temperature program: 60^0C, 4 min., 2^0C/min.

Figure 1



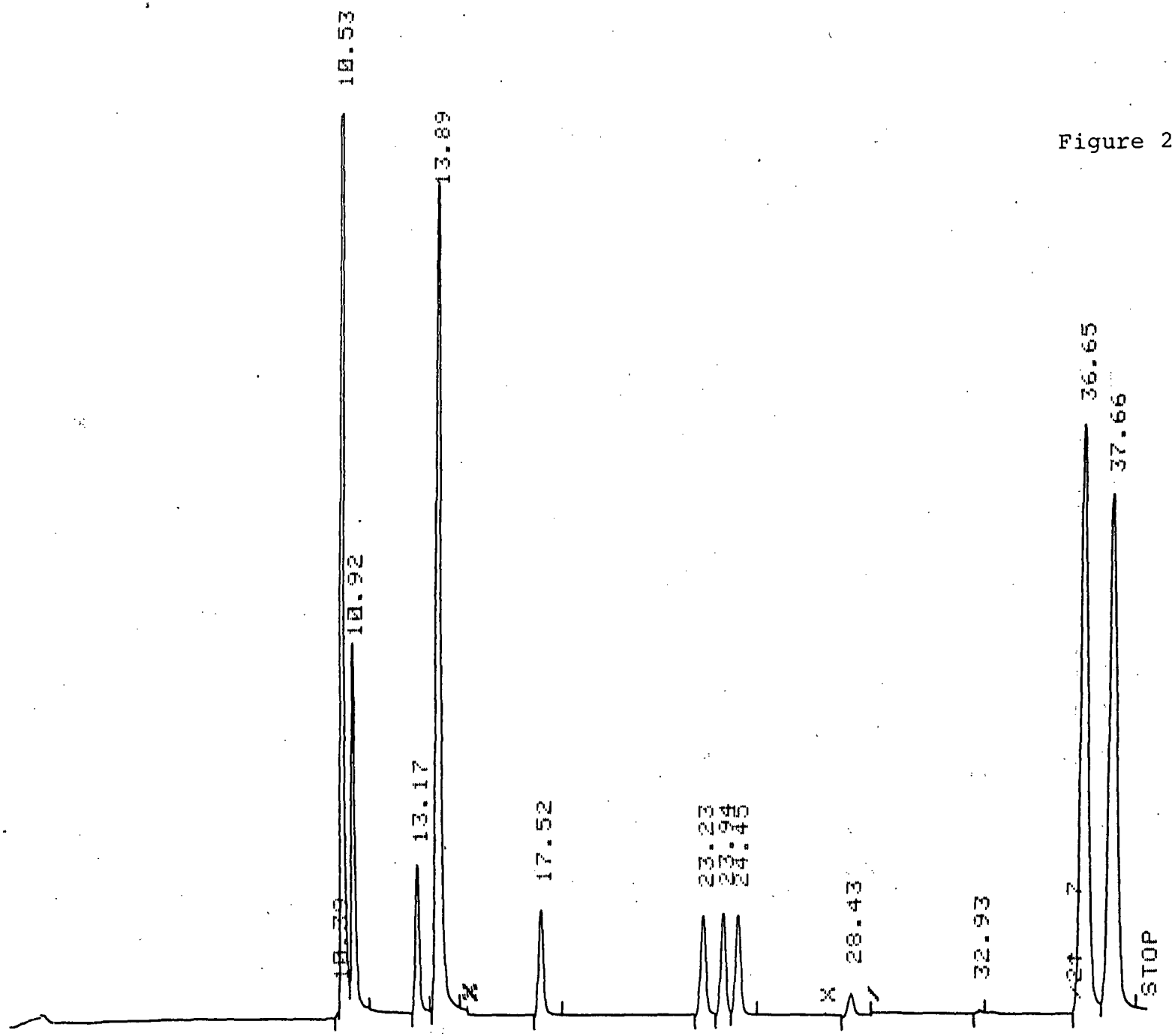

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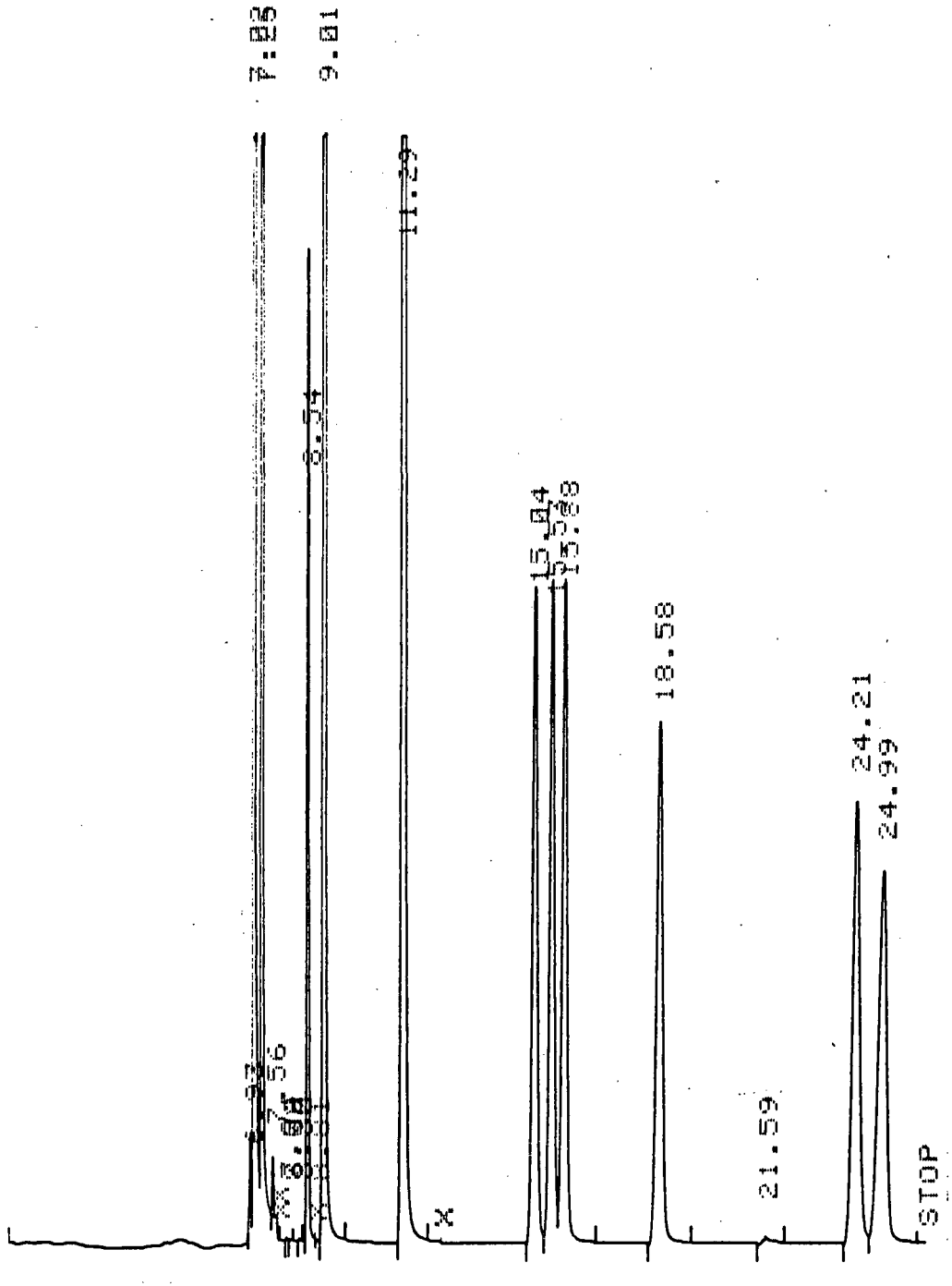
Figure 2



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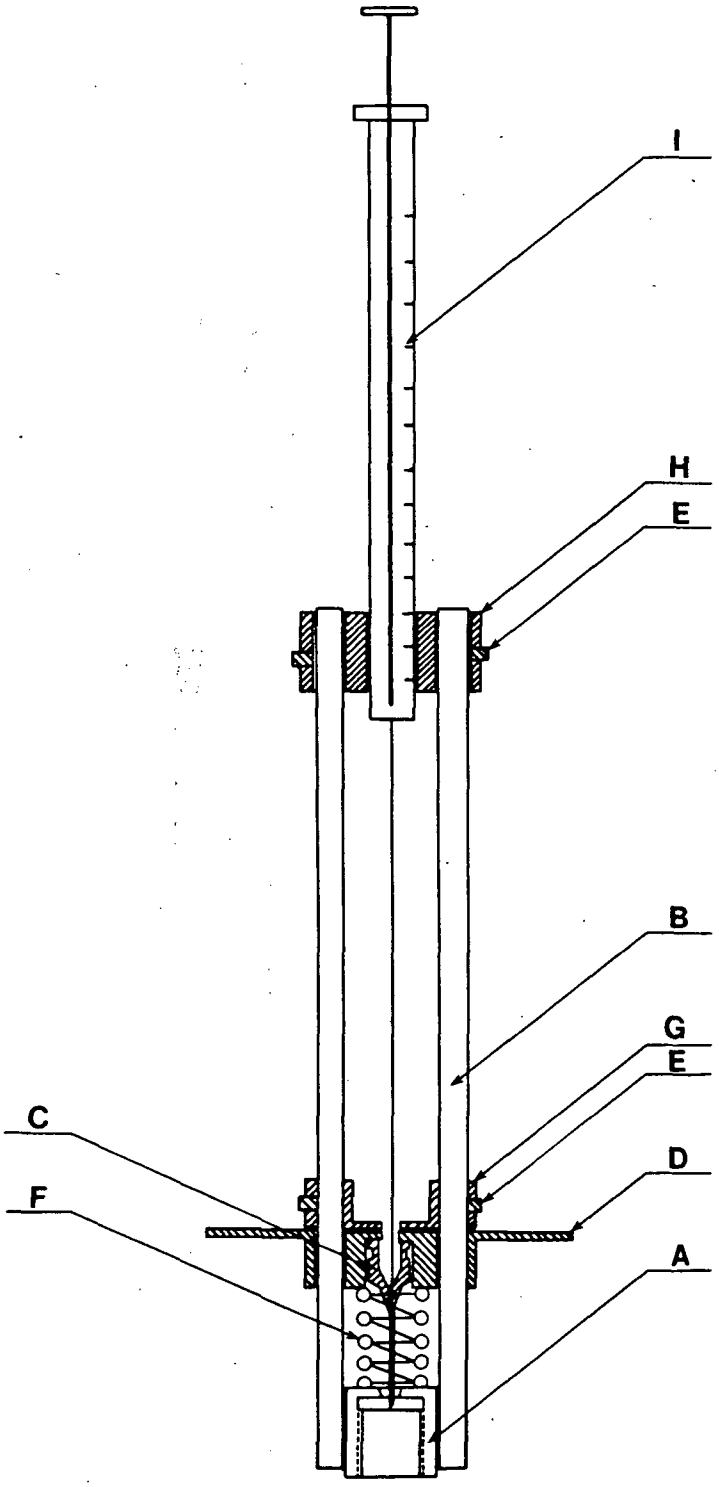

Figure 4

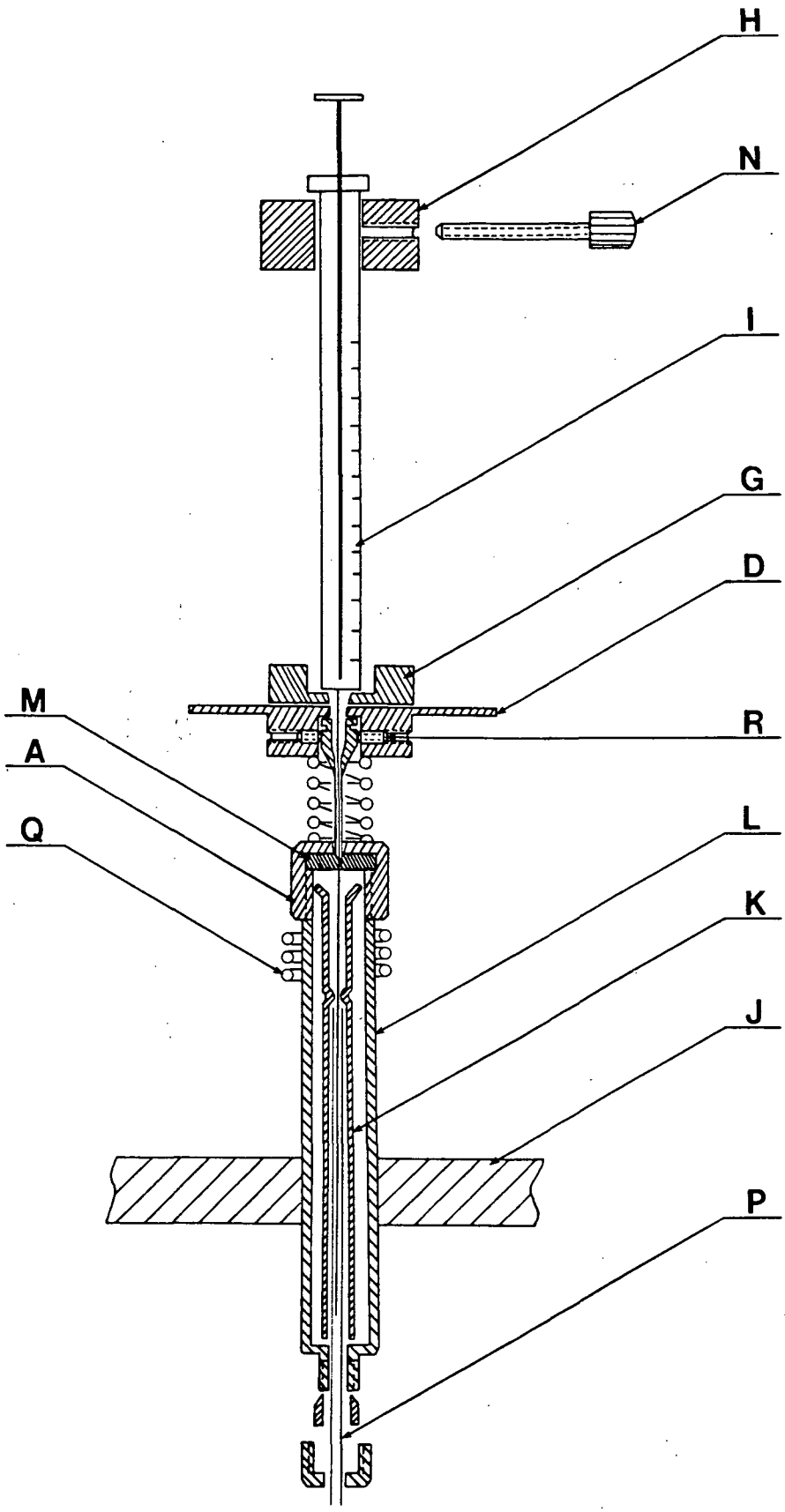

Figure 5

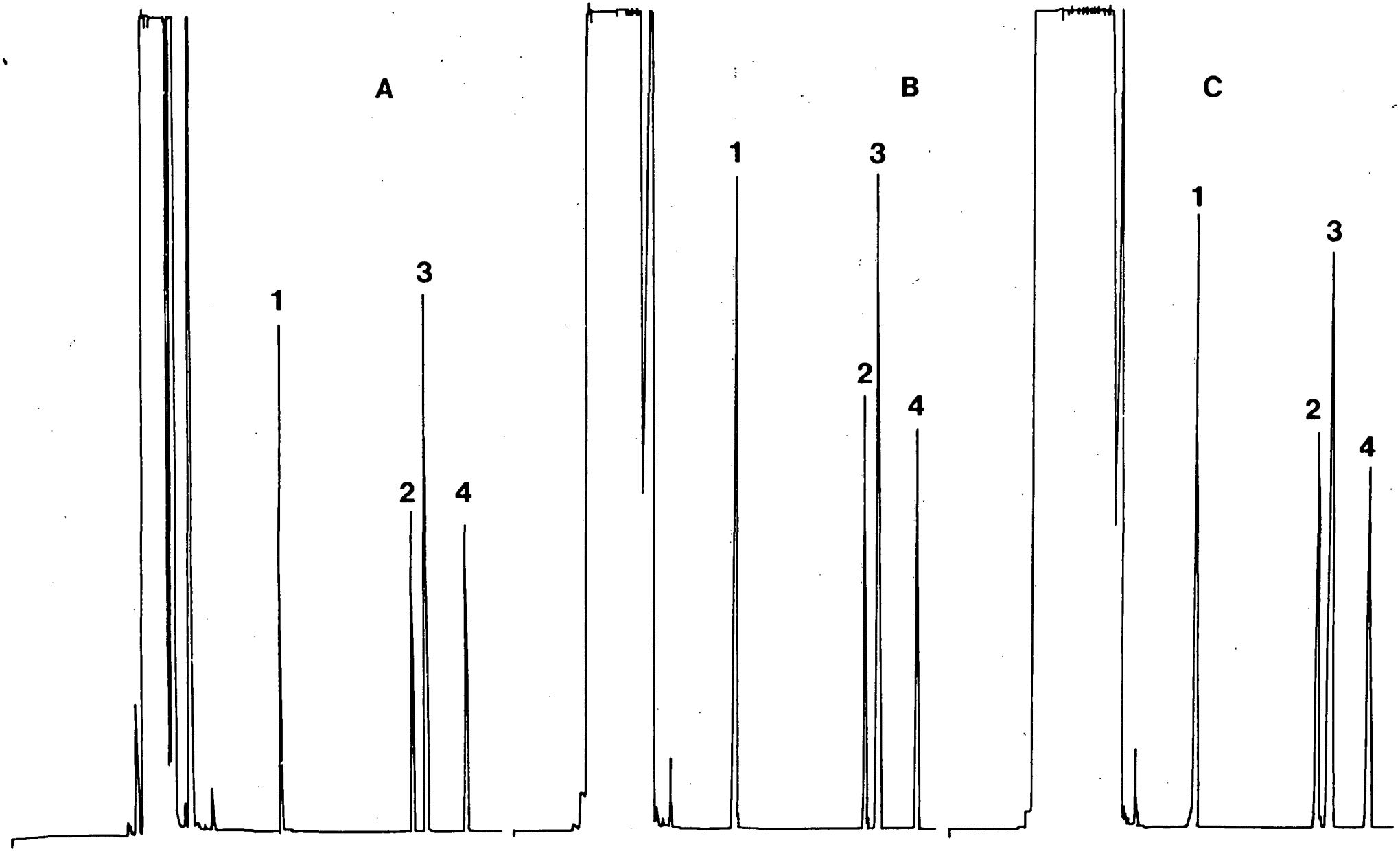

Figure 6

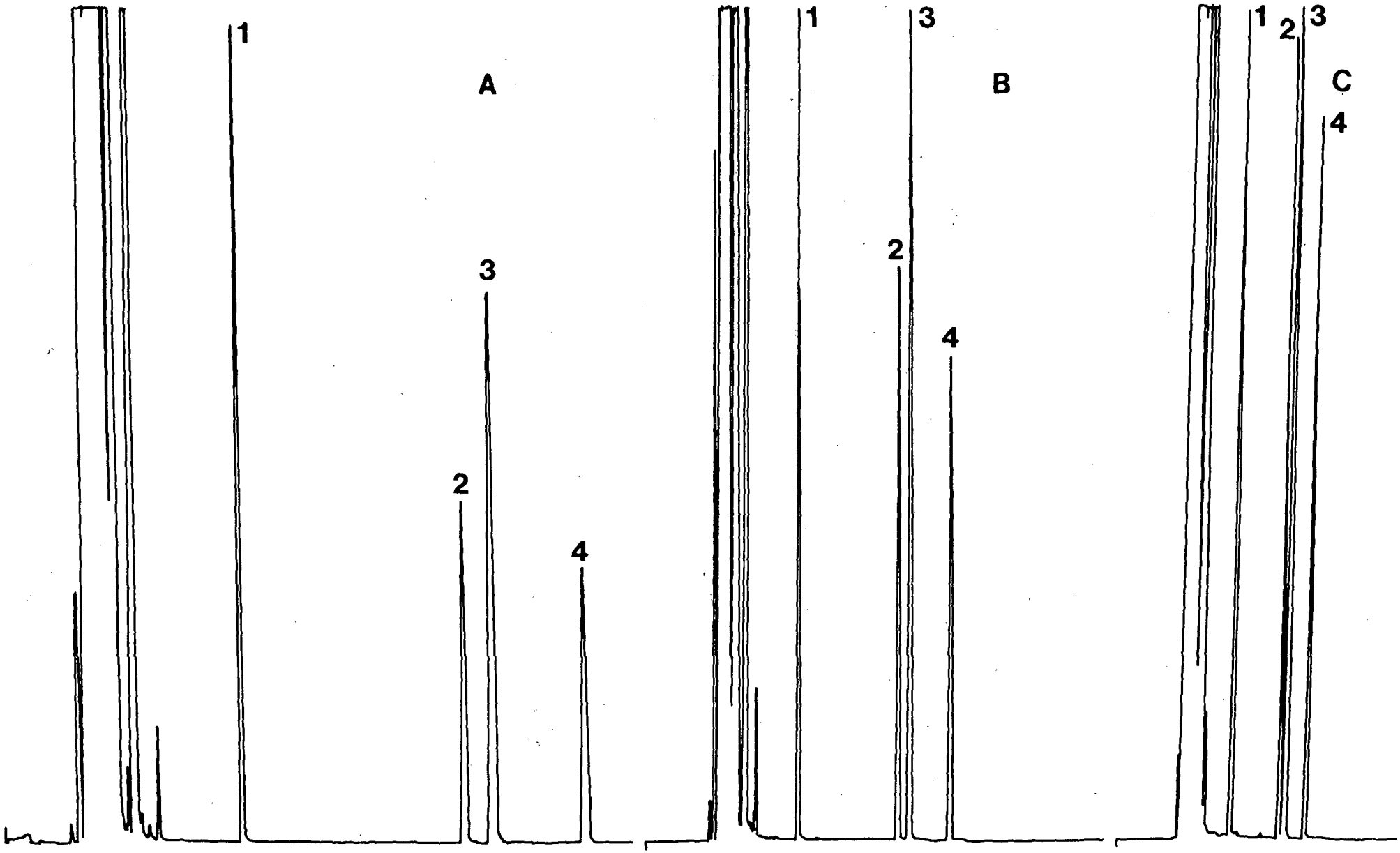

Figure 7

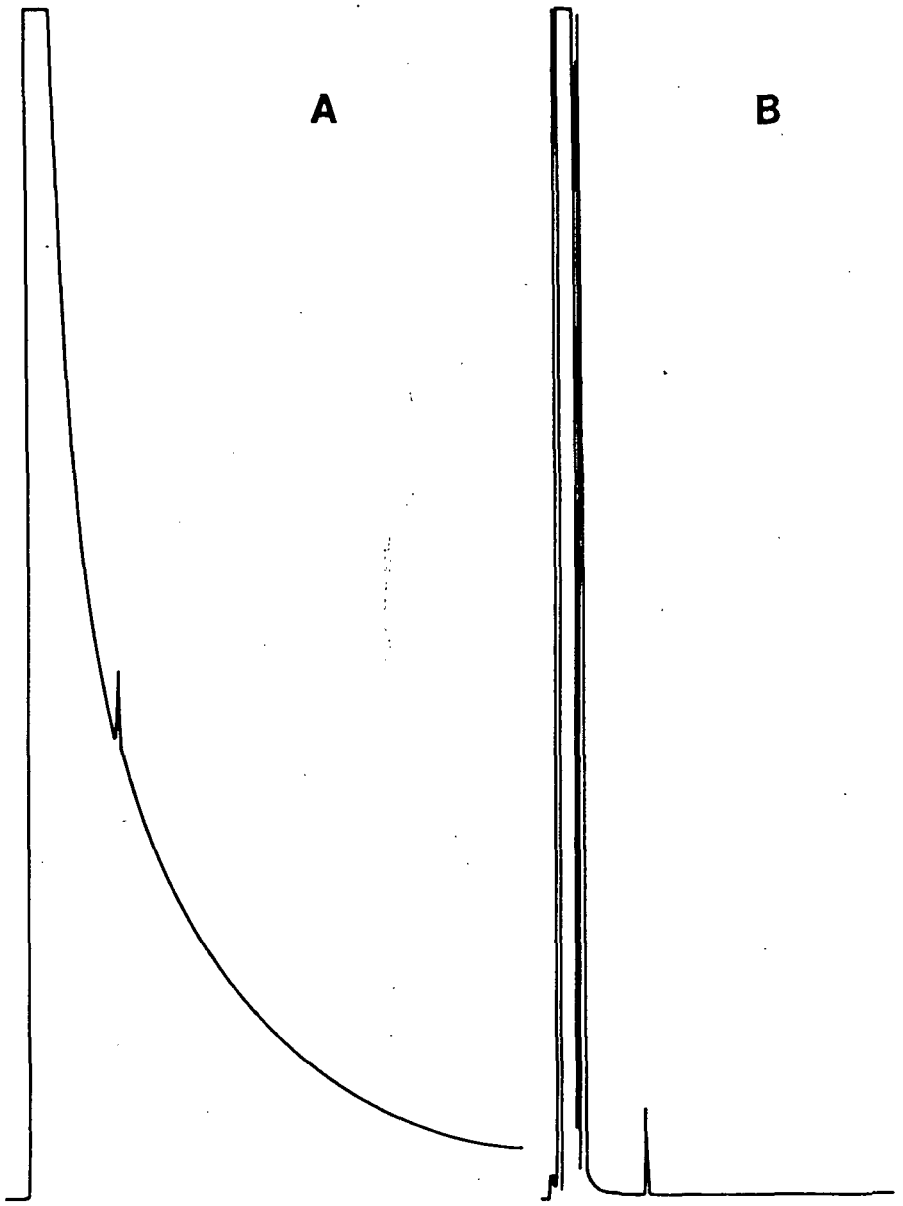

Figure 8

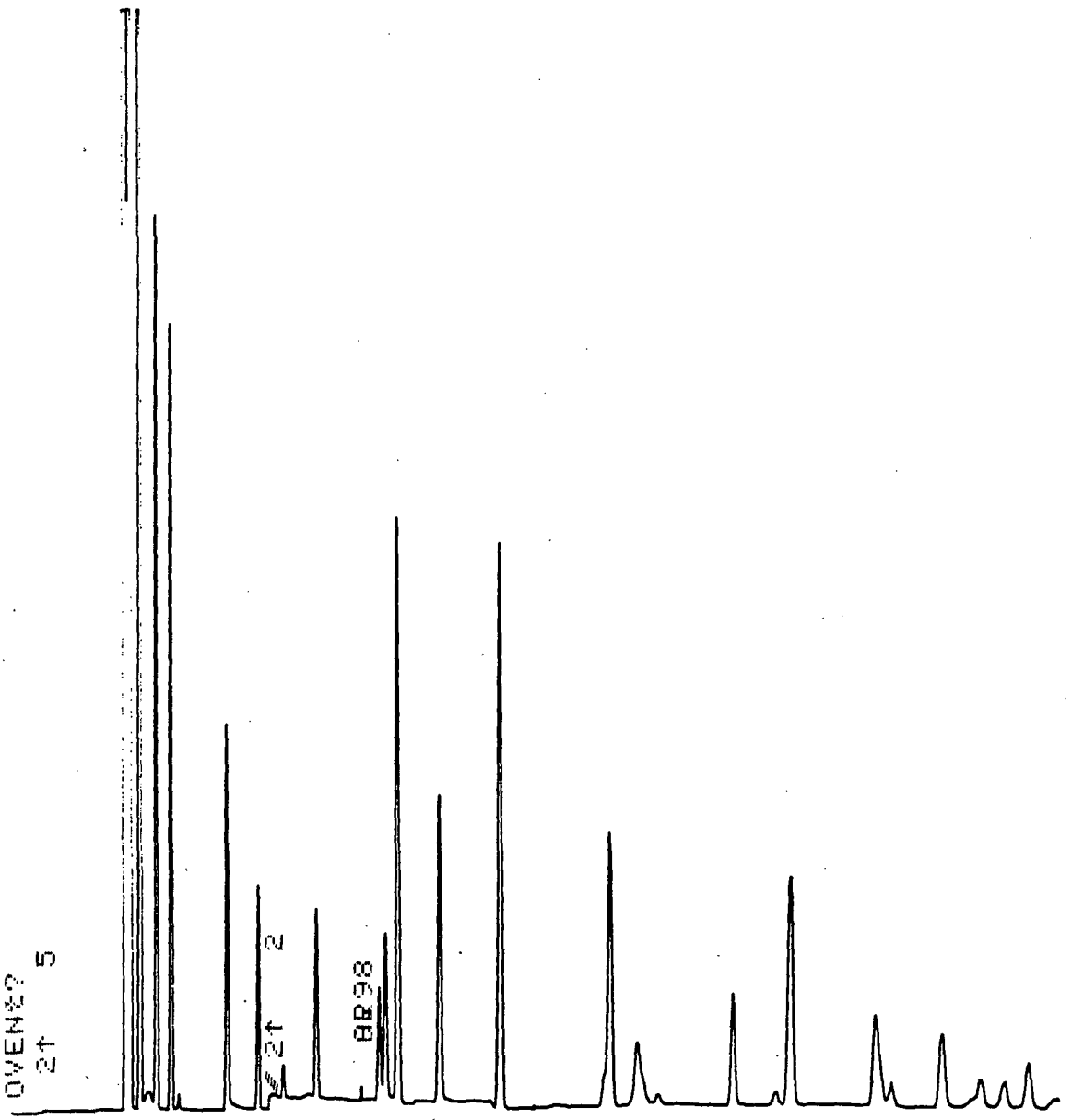

Figure 9