



(51) International Patent Classification:

G01N 30/60 (2006.01) **G01N 30/30** (2006.01)
B29C 47/02 (2006.01) **G01N 30/46** (2006.01)
B29C 47/10 (2006.01) **G01N 30/56** (2006.01)
B29D 23/00 (2006.01)

(21) International Application Number:

PCT/CA2009/000718

(22) International Filing Date:

1 June 2009 (01.06.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/138,124 12 June 2008 (12.06.2008) US
2,635,805 12 June 2008 (12.06.2008) CA

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: GAS CHROMATOGRAPHY CAPILLARY DEVICES AND METHODS

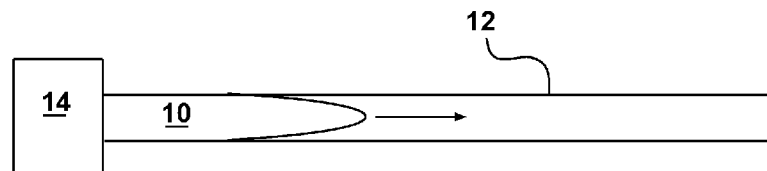


FIG. 1

(57) Abstract: A multicapillary bundle for use in a gas chromatograph. Each of the capillaries in the bundle is formed using a coating solution containing a stationary phase and a solvent. The capillaries are coated with stationary phase by reducing pressure at a vacuum end of the capillary and creating a moving interface between the coating solution and a film of stationary phase deposited on each of the capillaries. The reducing pressure at the vacuum end of the capillary and the temperature of the capillary are controlled to maintain motion of the moving interface away from the vacuum end of the capillary. Maintained movement of the interface prevents recoating of the stationary phase. A heating wire and capillaries are embedded in a thermally conductive polymer to create a highly responsive method of heating the multicapillary column. An electronic control device controls the feedback temperature of the multicapillary column using the heating wire.

GAS CHROMATOGRAPHY CAPILLARY DEVICES AND METHODS

TECHNICAL FIELD

[0001] These methods and devices relate to the field of gas chromatography.

BACKGROUND

[0002] The conventional column oven approach in gas chromatography has many undesirable characteristics such as: bulk, high power requirements, cost, high thermal mass with low response times, and longer times between runs. The application of resistive heating to the metal cladding on capillary columns provide an improvement on column heating but introduce a temperature measurement challenge and inherent temperature measurement inaccuracy. There is a need for an accurate, responsive and programmable column temperature program.

[0003] Also, it is well known that column efficiency needed to generate sharp narrow chromatographic peaks is enhanced with a reduction in the internal diameter of the capillary tubing. Generally, a reduction in the internal diameter of the capillary tubing results in a reduction in the sample capacity, and requires specialized injection ports and more expensive sensitive detectors. There is a need for reproducibility in preparing multicapillary columns. There is a need for multicapillary columns that are feasible for a wide range of applications without the individual column chromatographic variability and injector detector interface problems that have arisen when multicapillary column applications have been attempted in the past.

[0004] Low thermal mass gas chromatograph (GC) columns are available but are often complex, having a combination of separate heating and sensor wires. Additionally, current low thermal mass GC columns are generally single tube columns lacking the sample capacity associated with high efficiency small internal diameter capillary columns.

[0005] There are also drawbacks with the current coating procedures for capillaries in GC column preparation. There are conventionally two stationary phase coating procedures for GC column preparation: dynamic and static coating procedures.

[0006] The dynamic coating procedure consists of a plug of coating solution, solvent

containing the stationary phase, which is slowly moved through the tubing using gas pressure depositing stationary phase as the plug passes along the walls of the tubing. This method creates the most variable film thickness over the length of the tubing, which reduces the column efficiency.

[0007] The static coating procedure involves the loading of the tube with a coating solution consisting of the stationary phase and solvent usually chloroform or dichloromethane. Once the column is loaded the solvent is evaporated using low pressure at a constant temperature. Conventionally the pressure and temperature used to evaporate the solvent is about 100 mm Hg at approximately room temperature. However, the solvent front does not continuously move forward under these conditions. The solution moves toward the vacuum for a moment and then continues the evaporation process. This solution excursion causes a recoating of the walls of the tubing which creates variable film thickness. This variation in film thickness may not be apparent on single capillary columns but becomes very evident when comparing chromatographic data from multicapillary columns. The recoating process contributes to variable film thickness making the use of multicapillary columns impractical due to variations in retention factors and column efficiencies for each of the tubes within the multicapillary column.

[0008] If a coating solution is introduced to a capillary with helium gas pressure the dissolved gases may promote a flashing of the coating solution and leave the capillary devoid of stationary phase. A high gas pressure may promote flashing due to gas being dissolved in the capillary. A conventional rinsing and coating reservoir using gas pressure to load the capillaries can result in an unacceptably high number of tubes that flash and be devoid of stationary phase.

SUMMARY

[0009] There is provided a method of capillary preparation for use in a gas chromatograph. The method comprises the steps of A) placing a coating solution into a capillary, the coating solution containing a stationary phase and a solvent; B) drawing solvent vapor from the capillary by reducing pressure at a vacuum end of the capillary to create a moving interface between the coating solution and a film of stationary phase deposited on the

capillary; and C) controlling both the reducing pressure at the vacuum end of the capillary and the temperature of the capillary to maintain motion of the moving interface away from the vacuum end of the capillary at a rate that prevents recoating of the stationary phase on the walls of the tubing.

[0010] There is provided a system for heating a multicapillary column for use in a gas chromatograph. A multicapillary column has a bundle of at least three capillaries having an operative length L of at least one meter. Each capillary of the bundle of capillaries is in thermal communication with each of the other capillaries. A heating wire is provided along the operative length L of the bundle of capillaries.

[0011] There is provided a multicapillary column bundle for use in a gas chromatograph having a bundle of capillaries having an operative length L of at least one meter. A thermally conductive polymer binds together the bundle of capillaries continuously along the operative length L of the bundle of capillaries.

[0012] There is provided a method of capillary preparation for use in a gas chromatograph. The method comprises the steps of A) melting a thermally conductive polymer; and B) co-extruding a bundle of capillaries and the thermally conductive polymer through a die.

[0013] There is provided a polymer extrusion tool for preparing capillaries for use in a gas chromatograph. The polymer extrusion tool has a conical heating chamber. The conical heating chamber has a broad end and a narrow end. A die is in fluid connection with the narrow end of the conical heating chamber. A spool is attached to a support frame and the spool is oriented to permit a spooled capillary to be run into the broad end of the conical heating chamber during operation of the polymer extrusion tool.

[0014] There is provided a method of examining a sample using gas chromatography, the method comprising the step of supplying the sample to each capillary in a bundle of capillaries, the bundle of capillaries having an operative length L of at least one meter, in which each of the capillaries in the bundle of capillaries is in thermal communication with each of the other capillaries along the operative length L.

[0015] These and other aspects of the device and method are set out in the claims, which are incorporated here by reference.

BRIEF DESCRIPTION OF THE FIGURES

- [0016]** Embodiments will now be described with reference to the figures, in which like reference characters denote like elements, by way of example, and in which:
- [0017]** Fig. 1 is a side view of a capillary being filled with coating solution;
- [0018]** Fig. 2 is a side view of a capillary being prepared for use in a gas chromatograph;
- [0019]** Fig. 3 is a flow diagram representing the steps in preparing a capillary for using in a gas chromatograph;
- [0020]** Fig. 4 is a graph showing the effect of pressure on solvent evaporation rate at room temperature;
- [0021]** Fig. 5 is a plan view of an electronic control device for feedback temperature control of a multicapillary system using a heating wire;
- [0022]** Fig. 6 is a cross section view of a multicapillary column with multiple capillaries and a heating wire;
- [0023]** Fig. 7 is a perspective view of a spool assembly of a polymer extrusion tool;
- [0024]** Fig. 8 is a side view of the polymer extrusion tool;
- [0025]** Fig. 9 is a combined perspective and plan view of a polymer extrusion tool having a pressure chamber; and
- [0026]** Fig. 10 shows a chromatographic separation using a multicapillary column.

DETAILED DESCRIPTION

[0027] Figs. 1 and 2 depict a capillary 12 at various stages of preparation for use in a gas chromatograph (GC). As shown in Fig. 1, a coating solution 10 is placed in a capillary 12 by a pump 14. The coating solution 10 contains a stationary phase and a solvent. Optionally, the capillary 12 may be washed, for example with chloroform, and then dried free of the solvent before pumping the coating solution. The coating solution 10 may be degassed before the coating solution 10 is pumped into the capillary 12. Helium may be used to degas the coating solution 10 to reduce the presence of dissolved gases in the solution. The pump 14 may be, for example, a high performance liquid chromatography pump (HPLC). The HPLC pump delivers the coating solution 10 under conditions that keep the pump head cool to reduce the

vapor pressure of the solvent and avoid flashing of the coating solution. The HPLC pump may use chloroform as a solvent. The coating solution 10 may also be placed in the capillary 12 by a method other than using the pump 14, for example, by using a vacuum to pull the coating solution 10 into the capillary 12. By keeping the vapor pressure of the coating solution low during the loading of the column, the risk of solution flashing may be reduced which allows for lower vacuum pressure to be used to form the stationary phase on the capillary.

[0028] As shown in Fig. 2, once the coating solution 10 is placed in the capillary 12, solvent vapor 16 is drawn from the capillary 12 by reducing pressure at a vacuum end 18 of the capillary to create a moving interface 20 between the coating solution 10 and a film of stationary phase 22 deposited on the capillary. The reducing pressure at the vacuum end 18 of the capillary 12 is controlled to maintain motion of the moving interface 20 away from the vacuum end 18 of the capillary 12.

[0029] Maintaining motion of the moving interface 20 away from the vacuum end 18 of the capillary prevents recoating of the stationary phase 22 on the capillary 12 from occurring. The evaporation rate of the solvent is maintained at a rate that does not allow the excursion of the coating solution 10 toward the vacuum end 18 of the capillary. A suitable pressure and temperature are identified to evaporate the solvent free of the stationary phase at a sufficient rate to prevent movement of the coating solution 10 toward the vacuum end 18 of the capillary. Maintaining motion of the moving interface away from the vacuum end 18 of the capillary prevents recoating of the stationary phase 22. Preventing recoating of the stationary phase helps prevent variable film thickness from occurring. A consistent film coating maintains reliable retention factors and provides a column efficiency that is the same for all tubes within a multicapillary column. The film thickness may be determined by the coating solution concentration.

[0030] A conventional graphite ferrule may be used with appropriate fittings to pump the coating solution 10 into that capillary 12. The capillary 12 may be a clean and dry fused silica tubing of uniform size. The method of capillary preparation described in Figs. 1 and 2 may also be used to load a multicapillary column, such as shown in Fig. 6, with coating solution as a single bundle rather than preparing one long tube and cutting it to generate the multicapillary column. The method provides a uniform layer of liquid stationary phase on all

capillary tubes within the multicapillary bundle. The coating solution 10 may have varying amounts of stationary phase to vary the film thickness. Varied film thickness may affect the sample capacity of the multicapillary column. The coating solution 10 may also have various types of stationary phase to vary the selectivity of the prepared column.

[0031] Fig. 3 shows the steps of preparing the capillaries of Figs. 1 and 2 for use in a gas chromatograph. First, at step 23A a coating solution is placed into a capillary. At step 23B solvent vapor is drawn from the capillary by reducing pressure at a vacuum end of the capillary to create a moving interface between the coating solution and a film of stationary phase deposited on the capillary. At step 23C the temperature of the capillary and the reducing pressure at the vacuum end of the capillary are controlled to maintain motion of the moving interface away from the vacuum end of the capillary.

[0032] The capillary internal diameter and the number of capillary tubes chosen for the multicapillary column influences the relationship between column efficiency and sample capacity. Increasing the capillary internal diameter and the number of capillaries increases sample capacity due to an increase in the amount of stationary phase loaded into the multicapillary column.

[0033] Fig. 4 shows the effect of pressure on solvent evaporation rate at room temperature. The speed at which the solvent evaporates from the coating solution is not linearly related to the pressure or the temperature of the coating solution undergoing solvent evaporation. As the pressure decreases, the evaporation rate of the solvent increases in an approximately exponential manner.

[0034] In order to form capillaries with a uniform film of stationary phase it is preferable to use tubing with a uniform internal diameter. The capillary 12 may be constructed from fused silica tubing, which provides the ability to maintain a high precision internal diameter of the capillaries in the multicapillary columns. Other material with high precision internal diameters may also be used to construct the capillaries.

[0035] The motion of the moving interface 20 may be maintained at lower pressures and higher temperatures than those used in currently known capillary preparation methods. For example, a 2-meter column may be coated reproducibly at a pressure of 40 mm Hg and at a temperature of 35 ° C. A 5-meter column may be coated reproducibly at 15 mm Hg and at 35

° C. Fused silica tubing with an internal diameter of 75 μm and outer diameter of 153 μm may be used to construct a 7-column bundle with an outer diameter of approximately 500 μm .

[0036] The column coating method enables column tubing to be reproducibly coated with stationary phase which allows all columns in the bundle to chromatograph components with similar retention factors and column efficiencies. The multicapillary column chromatographs effectively with little variation under isothermal or temperature programming conditions. Multicapillary columns are prepared with the procedure that ensures a uniform layer of a liquid stationary phase is achieved on all capillary tubes within the bundle of capillaries.

[0037] The multicapillary column may be used in fast GC, on-line GC analyzers and hand held GCs. The multicapillary column is useful for 2 – dimensional GC applications where a high capacity column with high column efficiency is advantageous. The coating method works for preparing columns of variable film thickness depending on the sample capacity and column efficiency required.

[0038] Fig. 5 shows a system 22 for heating a multicapillary column for use in a gas chromatograph. A multicapillary column 24, for example the multicapillary column of Fig. 6, has an operative length L of at least one meter. Each capillary of the bundle of capillaries in the multicapillary column is in thermal communication with each of the other capillaries. A heating wire 28 runs along the operative length L of the bundle of capillaries. The heating wire 28 may also operate as a resistive temperature sensor. The bundle of capillaries is bound together with a thermally conductive polymer 30 along the operative length L of the bundle of capillaries. The thermally conductive polymer may have thermal conductivity of greater than 2 W/(mK), for example, in some embodiments the thermal conductivity may be in the range of 2 – 4 W/(mK). A microprocessor 32 is connected to the heating wire 28. An analog-to-digital converter voltmeter 34 is embedded in the microprocessor. A heating power supply 38 is connected to a transistorized switching module 40. The transistorized switching module is connected to the heating wire 28. The heating power supply 38 and the transistorized switching module 40 receive control signals from the microprocessor 32. The microprocessor 32 is configured to output a square wave pulse width modulation signal into the heating wire 28 through the transistorized switching module 40.

[0039] The heating power supply 38 and microprocessor 32 may operate as a stand-alone

unit or may be interfaced to a PC. The module provides all the heating and monitoring functions necessary to enable high resolution runs on an embedded resistance wire heated multicapillary GC column.

[0040] The microprocessor 32 is used to monitor the process of direct heating of a multicapillary column for gas chromatography using the heating wire 28. The microprocessor 32 accurately controls a pulse width modulation (PWM) style of heating current control, while taking direct resistance measurements of the heating wire 28 during the process results in highly accurate and flexible temperature regulation. Heat is applied to the column during the “on” time of the pulse train. Temperature is measured during the “off” time.

[0041] By providing a heating wire directly in the multicapillary column the temperature in the column may be quickly and accurately regulated. An imbedded heating wire may be used for more compact and faster GC column gas separations that are easier to implement in more portable instruments.

[0042] The heating wire 28 may have a high temperature coefficient. For example, the heating wire may be a 34 gauge Alloy 120 resistance wire constructed from nickel alloy 120 nickel iron composed of 30% Iron and 70% nickel, which has a temperature coefficient of resistance of 0.0045 ohms/ohm-°C. In some embodiments the heating power supply 38 may be capable of providing 100 Watts of power and have a voltage of 100 volts. The power supply 38 may be of the linear or switching type as long as good voltage regulation is achieved. A high temperature coefficient ensures temperature measurement accuracy and resolution is increased to a level of fractions of a degree Celsius. The resistance change versus temperature of the wire is linearly related. The resistance of the heater wire increases greatly as the temperature increases, making it easier to make resistance measurements of the heater wire and correlate them to the actual temperature of the multicapillary column.

[0043] The microprocessor 32 may output a square wave pulse width modulation signal which pulses current into the heating wire 28 through a transistorized switching module 40. The switching module 40 may incorporate a power FET transistor for switching efficiency. An opto-coupled input may also be used to isolate the microcontroller module from the 100 volt power supply.

[0044] The microprocessor 32 measures the resistance of the heating wire 28 in the

column during the off cycle of the PWM signal. This resistance is then converted into a temperature value of the column. The heating wire 28 may be the resistance element in a Kelvin 4-wire resistance measurement probe. Very accurate resistance values may be achieved by a Kelvin 4-wire resistance measurement probe and eliminate any stray resistances in the hookup to the heater wire 28. The microprocessor 32 provides a precision current source for the voltmeter to facilitate the resistance measurement during off period of the pulsed heating cycle. The current is small so that additional heating does not occur in the heating wire. The processor may also store a calibration constant in memory so that the system is accurately calibrated for ambient temperature.

[0045] The microprocessor 32 may include a MicroChip PIC18F4550 8 bit micro-controller IC. The unit may include an LCD display for displaying live data and programming set points and temperature programs. A USB and serial interface may be used to interface to the Windows based PC. The microprocessor 32 may have an internal real time clock for accurate real time logging. Serial EEPROM memory may be used to store measured data as well as for calibrating and programming set points. The internal 10-bit analog-to-digital converter converts the analog resistance measurements into accurate digital temperature values. The internal program incorporates PID feedback fundamentals to control the temperature of the column.

[0046] Fig. 6 shows a multicapillary column bundle 50 for use in a gas chromatograph. A thermally conductive polymer 44 binds together the bundle of capillaries 42 continuously along an operative length of the bundle of capillaries 42. A heating wire 46 lies in the center of the bundle of capillaries 42. The multicapillary bundle 42 is encircled by an insulative sheath 48. In some embodiments, for example where faster cooling rates are desired, an insulative sheath is not used. The thermally conductive polymer 44 is not electrically conductive. The value of electrical conductivity is sufficiently small that the conductivity of the thermally conductive polymer does not affect the functioning of the heating wire.

[0047] The low thermal mass of the multicapillary column 50 permits significantly greater temperature ramping and cooling rates compared to temperature control involving a conventional gas chromatography column oven. This enables rapid process monitoring during manufacturing processes and provide more detailed information than may be achieved

with infra red monitoring of industrial processes. The multicapillary column 50 may be prepared as a single bundle for installation into a conventional gas chromatographic oven or may be modified for on-line or hand-held GC applications using resistive heating. A single sample may be introduced into each capillary of the multicapillary column 50 simultaneously. The multicapillary column bundle 50 may be handled and inserted into the injection and detection ports of a conventional gas chromatograph. The multicapillary column 50 facilitates handling of the multicapillary column bundle rather than inserting a loose bundle of capillaries into the injector or detector ports. The multicapillary column 50, using small internal diameter tubing, allows both column efficiency and sample capacity to be increased simultaneously. The multicapillary column simplifies components of the gas chromatograph related to sample introduction and detection and also promotes fast GC since the sharp narrow peaks are forced to elute rapidly.

[0048] The low thermal mass of a column capable of resistive heating permits rapid heating which may speed analysis of components that differ widely in boiling points since the vapor pressure of the components being separated may be rapidly raised. The rapid cooling feature allows rapid turn around time, which is important in process monitoring using on-line analyzers.

[0049] In other embodiments the heating wire 46 may be replaced with an additional capillary or may be omitted entirely. The insulative sheath 48 prevents heat loss which may facilitate precise feedback control of the multicapillary bundle 50. In other embodiments, for example when the multicapillary bundle is used with a conventional gas chromatographic oven or where additional insulation is not necessary, the insulative sheath 48 is not necessary. Other numbers of capillaries may be used within the multicapillary bundle 50. In some embodiments there are at least three capillaries in the multicapillary bundle.

[0050] Figs. 7 – 9 show a polymer extrusion tool 52 (Fig. 8) for preparing capillaries for use in a gas chromatograph. As shown in Fig. 7, a spool assembly 66 has seven spools 64 attached to a support frame 56. In Fig. 8, a conical heating chamber 54 is shown lying below spool assembly 66. The conical heating chamber 54 has a broad end 58 and a narrow end 60. A die 62 is in fluid connection with the narrow end 60 of the conical heating chamber 54. The spools 64 are oriented to permit a spooled capillary, such as capillary 12 shown in Fig. 1, to

be run into the broad end 58 of the conical heating chamber 54 containing the melted polymer during operation of the polymer extrusion tool. In some embodiments the die may be a 0.5 mm die.

[0051] In Figs. 8 and 9 a pressure chamber 68 is shown with the spools 64 and the conical heating chamber 54 hidden inside this chamber. Insulating disks 70 separate the conical heating chamber 54 from the pressure chamber 68 and a column pulling device 74 to aid the cartridge heaters in maintaining the temperatures needed to melt the polymer.

[0052] During operation of the polymer extrusion tool 52 a thermally conductive polymer is melted in the conical heating chamber 54. A bundle of capillaries (not shown), which may be the capillaries that result from the preparation process shown in Fig. 2, are lowered through the conical heating chamber 54 and co-extruded with the thermally conductive polymer through the die 62. In the embodiment of Fig. 8, the capillaries on the spool assembly 56 are pulled through the melted polymer and die 62 by the column pulling device 74. The pressure chamber 68 applies additional force to extrude the thermally conductive polymer with the capillaries (not shown) supported by 56 through the die 62. In other embodiments the thermally conductive polymer and the capillaries may be extruded without a pressure chamber. A pressure chamber may be beneficial to extrude more viscous thermally conductive polymers. The capillaries may be retained on each spool 64 using a spring clip over each spool on the spool assembly or by squeezing septa between the flanges of the spool over the spooled capillaries.

[0053] The polymer chosen to imbed the tubing and wire depends on: the upper temperature chosen to operate the multicapillary column, the thermal conductivity needed to maintain a uniform tubing temperature and the melt flow index properties of the polymer acceptable for coating the tubing and the wire during extrusion.

[0054] The dimension of the die 62 influences the thickness of the polymer coating the tubing and wire as well as the overall diameter of the multicapillary column. The number of fused silica tubes within the multicapillary column is dependent upon the number of spools used to contain the fused silica tubing and wire and an acceptable outer diameter of the assembled column. The rate at which the polymer coating is applied and the column extruded is controlled by the column pulling device 74, which may be a wire feed used for meg

welders.

[0055] Fig. 10 shows a chromatographic separation using a multicapillary column consisting of six fused silica tube coated with 100% dimethylpolysiloxane. The capillaries were coated using the process shown in Fig. 3. The chromatograph is from a column bundle that had not been imbedded in a thermally conductive polymer and the column bundle was not heated using resistive heating. The column bundle was installed into the injector and detector ports of a conventional gas chromatograph and heating was generated using a conventional GC column oven. The compounds separated are octane C8, decane C10, dodecane C12, tetradecane C14 and hexadecane C16. The x-axis of the graph measures the retention time in minutes.

[0056] In some embodiments the thermally conductive polymer may be, for example, polyphenylene sulphide. Other types of thermally conductive polymers may be used in other embodiments. In some embodiments the capillaries may be, for example, made from fused silica coated with polyimide. The capillary may be made from other materials in other embodiments. In some embodiments the capillaries may be coated with, for example, dimethyl polysiloxane as the stationary phase. Other types of stationary phase may be used in other embodiments, as for example polyethylene glycol or any other suitable stationary phase now known or hereafter developed. The results, however, may be less satisfactory using a stationary phase such as polyethylene glycol that has high cohesion. In dimethyl polysiloxane, the methyl groups are on each Si atom of the polysiloxane chain but other common functional groups, such as for example, phenyl, trifluoropropyl, and cyanopropyl groups may also be used in compounds used in the stationary phase. The capillary surface may be pre-treated to assist bonding of the stationary phase to the capillary.

[0057] Immaterial modifications may be made to the embodiments described here without departing from what is covered by the claims.

[0058] In the claims, the word “comprising” is used in its inclusive sense and does not exclude other elements being present. The indefinite article “a” before a claim feature does not exclude more than one of the feature being present. Each one of the individual features described here may be used in one or more embodiments and is not, by virtue only of being described here, to be construed as essential to all embodiments as defined by the claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of capillary preparation for use in a gas chromatograph, the method comprising the steps of:
 - A) placing a coating solution into a capillary, the coating solution containing a stationary phase and a solvent;
 - B) drawing solvent vapor from the capillary by reducing pressure at a vacuum end of the capillary to create a moving interface between the coating solution and a film of stationary phase deposited on the capillary; and
 - C) controlling both the reducing pressure at the vacuum end of the capillary and the temperature of the capillary to maintain motion of the moving interface away from the vacuum end of the capillary.
2. The method of claim 1 in which placing a coating solution in the capillary comprises pumping the coating solution into the capillary.
3. The method of claim 1 or 2 further comprising degassing the coating solution before placing the coating solution into the capillary.
4. The method of claim 1 in which the capillary is one of a bundle of capillaries and the method steps A, B and C are applied to each capillary of the bundle of capillaries.
5. The method of claim 4 in which each capillary of the bundle of capillaries is supplied with a coating solution having the same concentration of stationary phase.
6. The method of claim 5 in which each capillary of the bundle of capillaries has the same nominal internal diameter.
7. The method of any one of claims 1-6 in which each capillary comprises a fused silica

capillary of uniform diameter.

8. The method of any one of claims 1-7 in which the stationary phase comprises dimethylpolysiloxane.
9. The method of claim 4 in which the bundle of capillaries has an operative length L of at least one meter; and the capillaries are bound together with a thermally conductive polymer along the operative length L of the bundle of capillaries.
10. The method of claim 9 in which a heating wire is provided along the operative length L of the bundle of capillaries.
11. The method of claim 10 further comprising using the heating wire as a temperature sensor during operation of a gas chromatograph.
12. The method of claim 9, 10 or 11 further comprising forming the bundle of capillaries by co-extruding the capillaries and the thermally conductive polymer.
13. A system for heating a multicapillary column for use in a gas chromatograph, the system comprising:
 - a multicapillary column, comprising a bundle of at least three capillaries having an operative length L of at least one meter, each of the bundle of capillaries being in thermal communication with each of the other capillaries; and
 - a heating wire provided along the operative length L of the bundle of capillaries.
14. The system of claim 13, in which the heating wire is connected to electronics to be used as a resistive temperature sensor.
15. The system of claim 13 or 14 in which the bundle of capillaries are bound together with a thermally conductive polymer along the operative length L of the bundle of capillaries.

16. The system of claim 14 further comprising:
 - a microprocessor producing control signals;
 - a current source in electrical communication with the heating wire, and the current source producing voltages in response to control signals from the microprocessor; and
 - a voltmeter connected to the heating wire, the voltmeter configured to measure voltage drops along the heating wire.
17. The system of claim 16 further comprising a heating power supply connected to the microprocessor, the heating power supply adapted to receive control signals from the microprocessor.
18. The system of claim 14 in which the heating wire has a temperature coefficient of resistance at least as high as 0.0045 ohms/ohm-°C.
19. The system of any one of claims 13 – 18 in which each capillary of the bundle of capillaries comprises a fused silica capillary.
20. The system of claim 17 further comprising a transistorized switching module, the transistorized switching module being connected between the heating power supply and the heating wire, and the microprocessor being configured to output a square wave pulse width modulation signal to the switching module to control the heating current to the heating wire.
21. The system of claim 20 in which the pulse width modulation signal has an on phase and an off phase, and in which the microprocessor is adapted to measure the temperature of the heating wire during the off phase of the pulse width modulation signal.
22. A multicapillary column bundle for use in a gas chromatograph, comprising:
 - a bundle of capillaries having an operative length L of at least one meter; and
 - a thermally conductive polymer binding together the bundle of capillaries

continuously along the operative length L of the bundle of capillaries.

23. The multicapillary column of claim 22 in which a heating wire is provided continuously along the operative length L of the bundle of capillaries.

24. The multicapillary column of claim 23 in which the heating wire has a temperature coefficient of resistance at least as high as 0.0045 ohms/ohm-°C.

25. The multicapillary column of any one of claims 22 – 24 in which the thermally conductive polymer is not electrically conductive.

26. The multicapillary column of any one of claims 22 - 25 further comprising an insulative sheath encircling the thermally conductive polymer and the bundle of capillaries.

27. The multicapillary column of any one of claims 22 – 26 in which each capillary of the bundle of capillaries comprises a fused silica capillary.

28. The multicapillary column of any one of claims 22 – 27 in which each capillary of the bundle of capillaries is coated continuously by the thermally conductive polymer along the operative length L of the bundle of capillaries.

29. A method of capillary preparation for use in a gas chromatograph, the method comprising the steps of:

melting a thermally conductive polymer; and
co-extruding a bundle of capillaries and the thermally conductive polymer through a die.

30. The method of claim 29 in which the step of co-extruding a bundle of capillaries and the thermally conductive polymer through a die further comprises co-extruding a heating wire through the die.

31. The method of claim 29 in which the step of co-extruding the bundle of capillaries and the thermally conductive polymer through a die further comprises the step of using pneumatic pressure to extrude the thermally conductive polymer through the die.
32. The method of claim 29 in which the step of co-extruding the bundle of capillaries and the thermally conductive polymer through the die further comprises unwinding the bundle of capillaries from a spool and lowering the bundle of capillaries through the die.
33. The method of any one of claims 29 – 32 in which each capillary of the bundle of capillaries comprises a fused silica capillary.
34. A polymer extrusion tool for preparing capillaries for use in a gas chromatograph, the polymer extrusion tool comprising:
a conical heating chamber, the conical heating chamber having a broad end and a narrow end;
a die in fluid connection with the narrow end of the conical heating chamber; and
a spool attached to a support frame, the spool oriented to permit a spooled capillary to be run into the broad end of the conical heating chamber during operation of the polymer extrusion tool.
35. The polymer extrusion tool of claim 34 in the spool is one of a plurality of spools, and each of the plurality of spools is attached to the support frame and is oriented to permit a spooled capillary to be run into the broad end of the conical heating chamber during operation of the polymer extrusion tool.
36. The polymer extrusion tool of claim 34 further comprising a pressure chamber in fluid connection with the broad end of the conical heating chamber, in which the pressure chamber has a capillary inlet.

37. A method of examining a sample using gas chromatography, the method comprising the step of supplying the sample to each capillary in a bundle of capillaries, the bundle of capillaries having an operative length L of at least one meter, in which each of the capillaries in the bundle of capillaries is in thermal communication with each of the other capillaries along the operative length L .

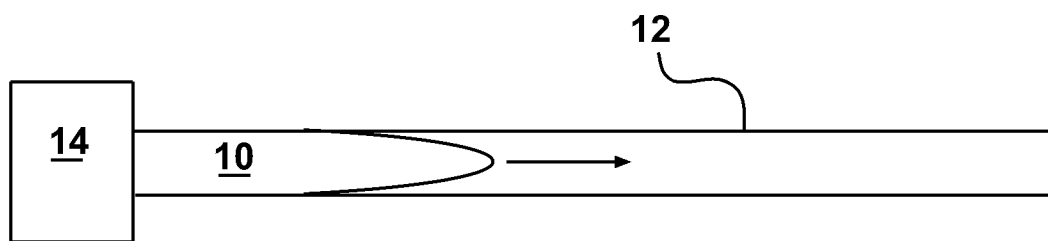


FIG. 1

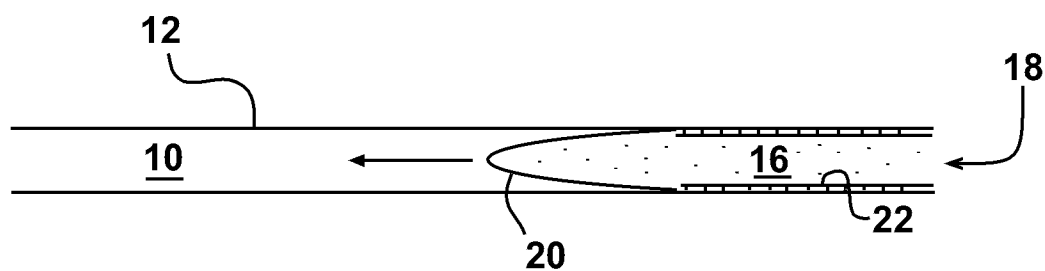


FIG. 2

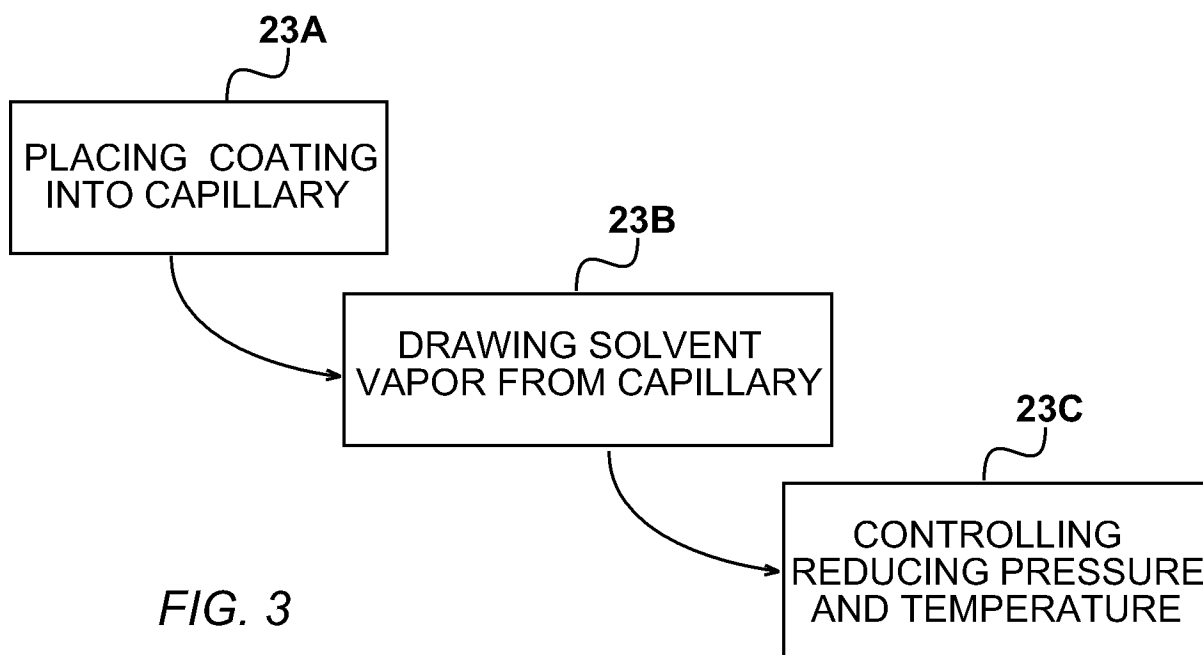
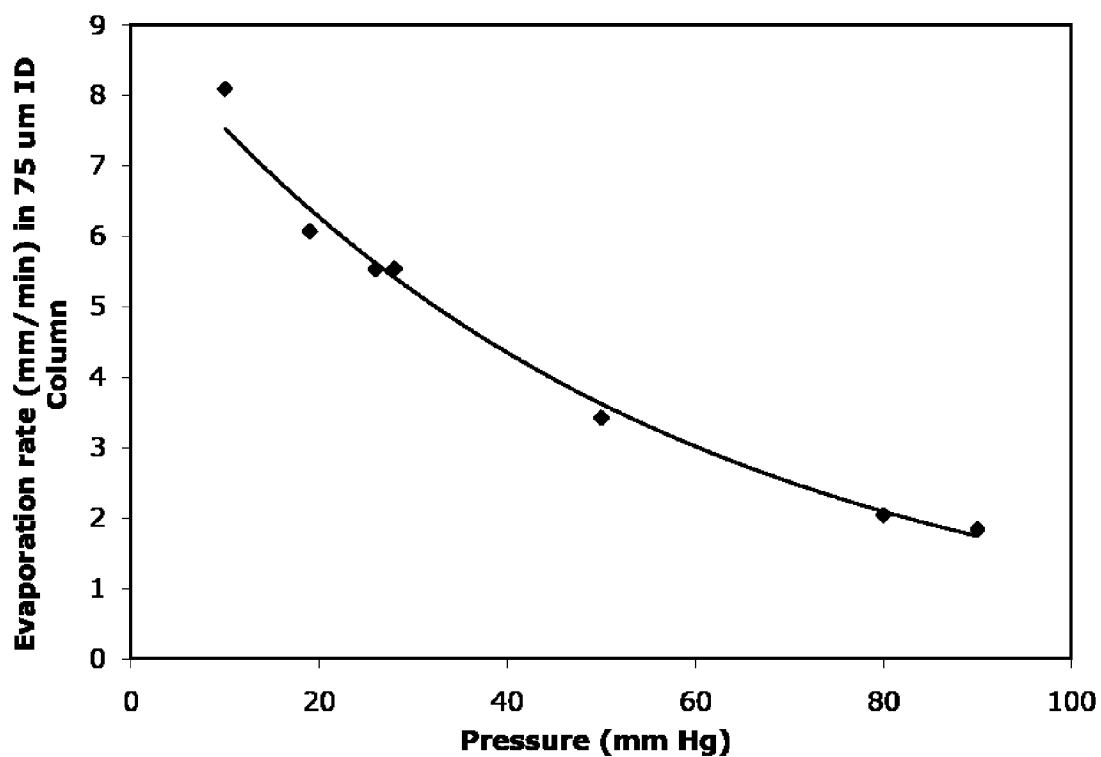
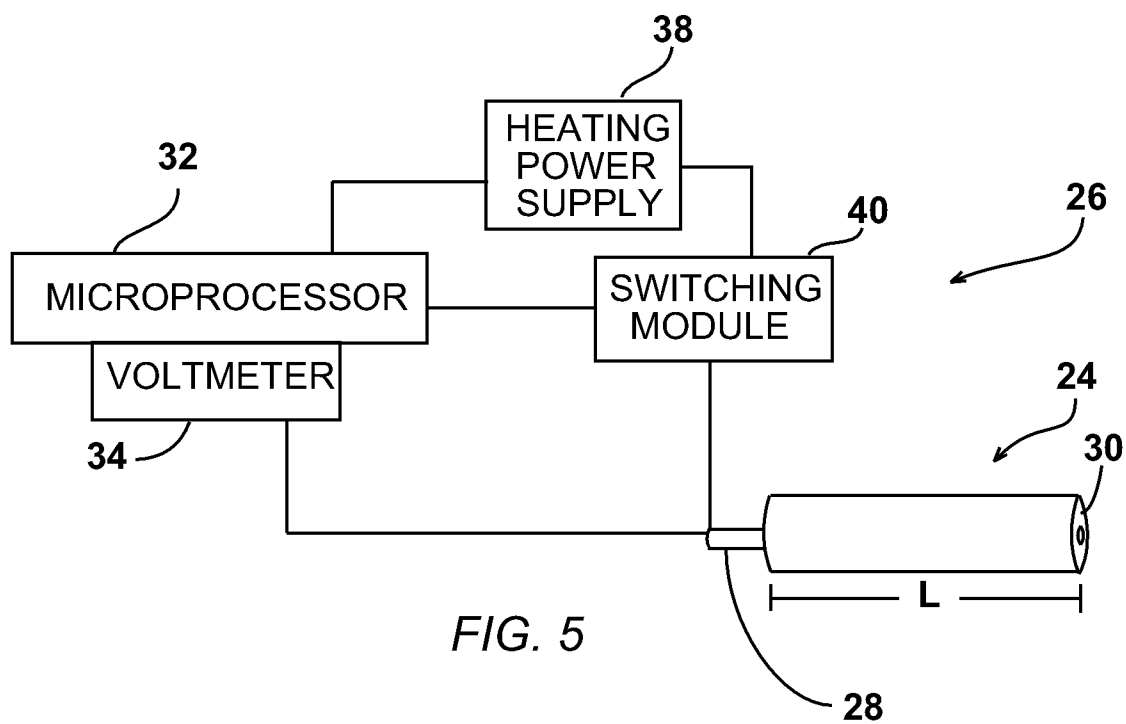


FIG. 3

Effect of Pressure on Solvent Evaporation Rate*FIG. 4**FIG. 5*

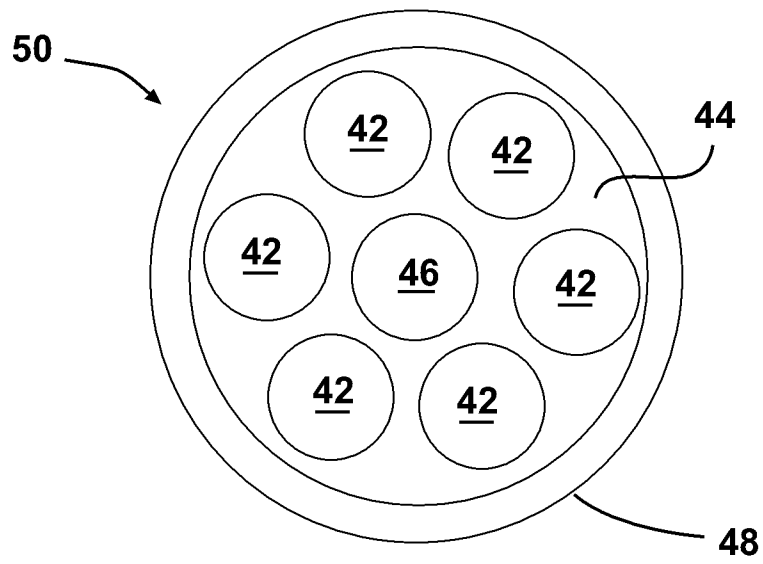


FIG. 6

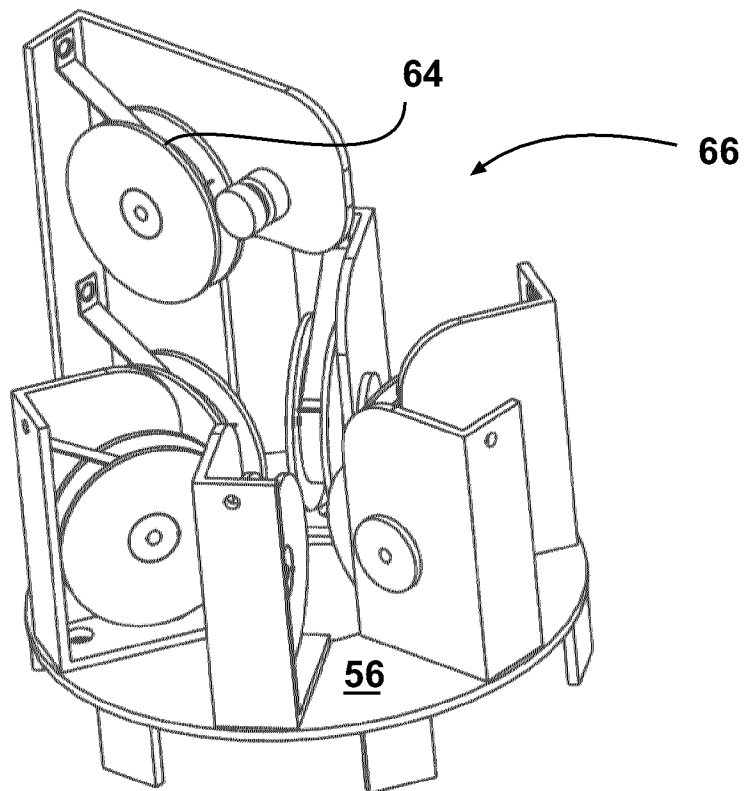
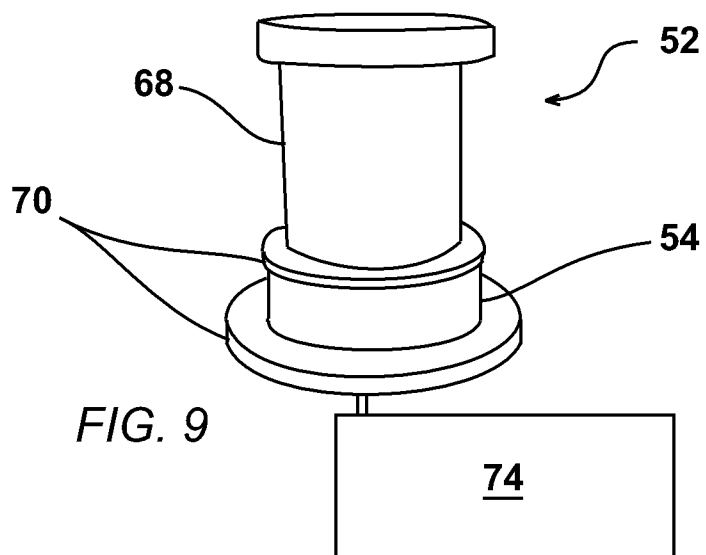
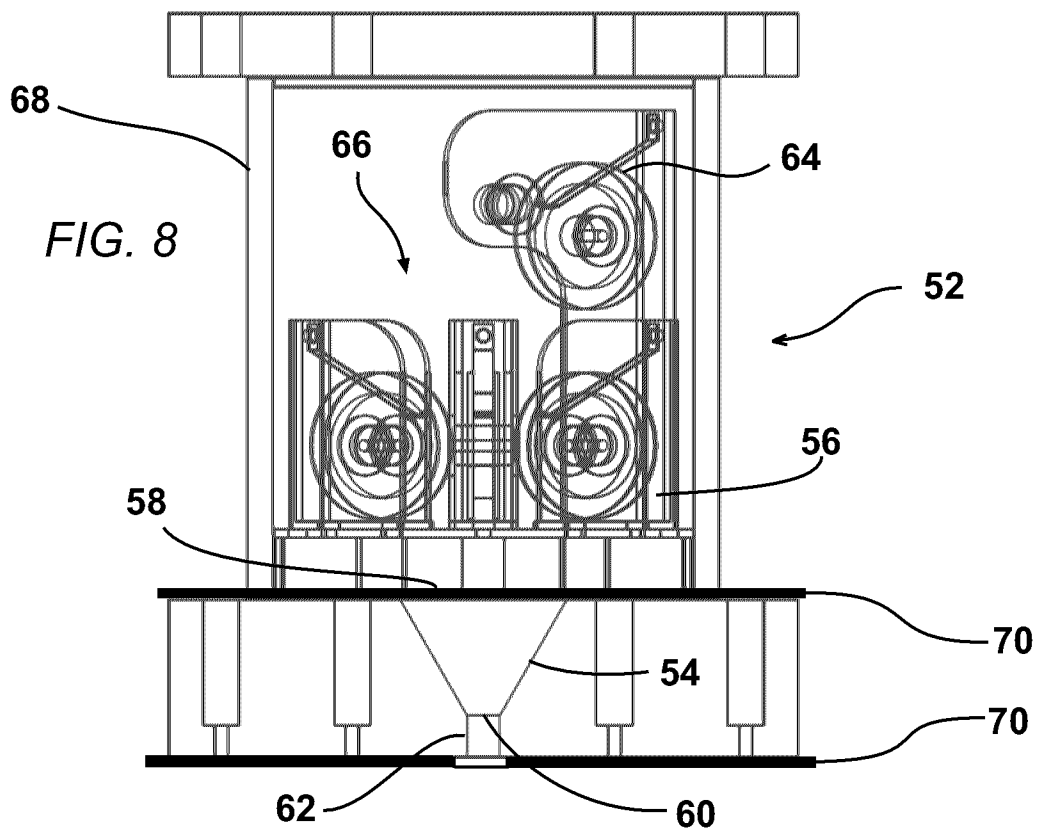
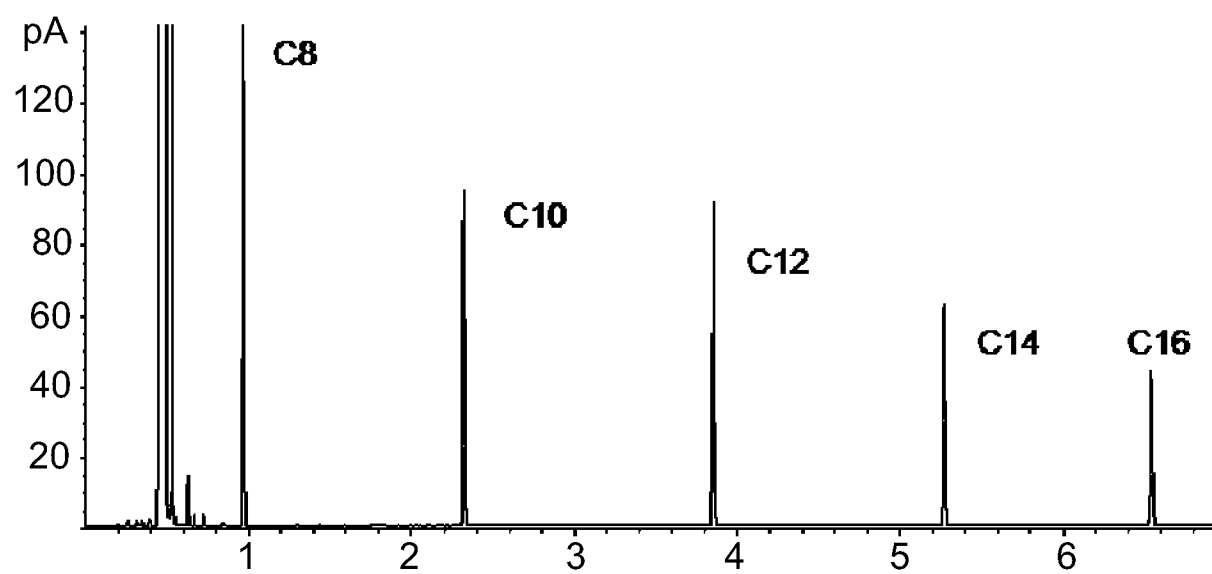


FIG. 7



*FIG. 10*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2009/000718

A. CLASSIFICATION OF SUBJECT MATTER IPC: G01N 30/60 (2006.01) , B29C 47/02 (2006.01) , B29C 47/10 (2006.01) , B29D 23/00 (2006.01) , G01N 30/30 (2006.01) , G01N 30/46 (2006.01) , G01N 30/56 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC																				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC: G01N (2006.01) , B29C (2006.01) , B29D (2006.01) (using keywords) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Canadian Patent Database, Delphion, Esp@cenet, QPAT, United States Patent Database (USPTO). Keywords: capillary, coating, gas chromatography, pressure, solvent, stationary phase, temperature, vacuum, vapor.																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>US 5856616 (Maswadeh et al.) 5 January 1999 (05-01-1999) - see entire document</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>US 5141532 (Sacks et al.) 25 August 1992 (25-08-1992) - see entire document</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>JP 03261061 (Kozo) 20 November 1991 (20-11-1991) - see entire document</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>CA 2533533 (Biermans et al.) 25 July 2006 (25-07-2006) - see entire document</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>CA 2341238 (Malik et al.) 2 March 2000 (02-03-2000) - see entire document</td> <td>1-12</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	US 5856616 (Maswadeh et al.) 5 January 1999 (05-01-1999) - see entire document	1-12	A	US 5141532 (Sacks et al.) 25 August 1992 (25-08-1992) - see entire document	1-12	A	JP 03261061 (Kozo) 20 November 1991 (20-11-1991) - see entire document	1-12	A	CA 2533533 (Biermans et al.) 25 July 2006 (25-07-2006) - see entire document	1-12	A	CA 2341238 (Malik et al.) 2 March 2000 (02-03-2000) - see entire document	1-12
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A	CA 2341238 (Malik et al.) 2 March 2000 (02-03-2000) - see entire document	1-12																		
[] Further documents are listed in the continuation of Box C. [X] See patent family annex. <table border="1"> <tbody> <tr> <td>* Special categories of cited documents :</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </tbody> </table>			* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family	"O" document referring to an oral disclosure, use, exhibition or other means		"P" document published prior to the international filing date but later than the priority date claimed							
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Date of the actual completion of the international search 26 August 2009 (26-08-2009)		Date of mailing of the international search report 1 September 2009 (01-09-2009)																		
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Tung Nguyen 819-956-3859																		

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/CA2009/000718**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons :

1. ☐ Claim Nos. :
 because they relate to subject matter not required to be searched by this Authority, namely :

2. ☐ Claim Nos. :
 because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :

3. ☐ Claim Nos. :
 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows :

see page 6.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. : 1-12

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
 ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
 ☐ No protest accompanied the payment of additional search fees.

Continuation... Box No. III

There are 4 inventions claimed in the international application covered by the claims indicated below:

Group A: Claims 1-12 are directed to a method of capillary preparation for use in a gas chromatograph, the method comprising the steps of placing a coating solution into a capillary, drawing solvent vapor from the capillary to create a moving interface between the coating solution and a film of stationary phase, and controlling the pressure and temperature of the capillary to maintain motion of the moving interface.

Group B: Claims 13-28 and 37 are directed to a system for heating a multicapillary column having a bundle of at least three capillaries having an operative length L of at least one meter, and a heating wire provided along the operative length L of the bundle of capillaries.

Group C: Claims 29-33 are directed to a method of capillary preparation comprising the steps of melting a thermally conductive polymer, and co-extruding a bundle of capillaries and the thermally conductive polymer through a die.

Group D: Claims 34-36 are directed to a polymer extrusion tool comprising a conical heating chamber having a broad end and a narrow end, a die in fluid connection with the heating chamber, and a spool attached to a support frame, wherein the spool is oriented as to permit a spooled capillary to be run into the broad end of the heating chamber during operation of the extrusion tool.

It is considered that **the international application does not comply with the requirements of unity of invention** (Rules 13.1, 13.2 and 13.3) since the inventions listed as Group A, B, C and D do not relate to a single inventive concept under PCT Rule 13.1 and they lack the same or corresponding technical features under PCT Rule 13.2.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2009/000718

Patent Document Cited in Search Report		Publication Date	Patent Family Member(s)	Publication Date
US	5856616A	05-01-1999	None	
US	5141532A	25-08-1992	CA 2069734A1	29-03-1992
			CA 2069734C	23-12-1997
			CA 2070448A1	06-12-1992
			CA 2070448C	23-12-1997
			CA 2070619A1	19-12-1992
			CA 2070619C	18-03-1997
			CA 2082013A1	07-07-1993
			CA 2082013C	21-01-1997
			DE 69114121D1	30-11-1995
			DE 69114121T2	09-05-1996
			DE 69205910D1	14-12-1995
			DE 69205910T2	11-04-1996
			DE 69210687D1	20-06-1996
			DE 69210687T2	26-09-1996
			EP 0503053A1	16-09-1992
			EP 0503053A4	17-02-1993
			EP 0503053B1	25-10-1995
			EP 0519614A2	23-12-1992
			EP 0519614A3	13-01-1993
			EP 0519614B1	15-05-1996
			EP 0525950A1	03-02-1993
			EP 0525950B1	08-11-1995
			EP 0550957A1	14-07-1993
			EP 0597602A1	18-05-1994
			JP 2539314B2	02-10-1996
			JP 2632668B2	23-07-1997
			JP 2684540B2	03-12-1997
			JP 2759238B2	28-05-1998
			JP 5180815A	23-07-1993
			JP 5188047A	27-07-1993
			JP 5502734T	13-05-1993
			JP 6201670A	22-07-1994
			JP 6258304A	16-09-1994
			KR 100212177B1	02-08-1999
			KR 100221931B1	15-09-1999
			KR 100243995B1	01-02-2000
			US 5096471A	17-03-1992
			US 5141534A	25-08-1992
			US 5205845A	27-04-1993
			US 5281256A	25-01-1994
			WO 9205850A1	16-04-1992
JP	03261061	20-11-1991	None	
CA	2533533A1	25-07-2006	AU 2006200280A1	10-08-2006
			EP 1683573A1	26-07-2006
			EP 1683573B1	05-08-2009

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2009/000718

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
		JP 2006250920A	21-09-2006
		US 2006163161A1	27-07-2006
CA 2341238A1	02-03-2000	AU 765881B2	02-10-2003
		AU 5578799A	14-03-2000
		EP 1105723A1	13-06-2001
		EP 1105723A4	17-10-2007
		JP 2002523742T	30-07-2002
		US 2007172960A1	26-07-2007
		WO 0011463A1	02-03-2000