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REPUBLICATION

(54) **METHOD AND DEVICE FOR VAPORIZATION INJECTION OF HIGH VOLUMES IN GAS CHROMATOGRAPHIC ANALYSIS**

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(57) **ABSTRACT**

This invention concerns a method and apparatus for vaporization injection of large volumes of liquid sample (substance to be analysed + solvent) introduced by means of the needle of a syringe onto a heated vaporization chamber which is part of an injector applied to a device for gas chromatographic analysis, the sample being sent in form of a liquid band travelling through said vaporization chamber at high speed until reaching stopping and vaporization means positioned adjacent to the inlet of a capillary to collect the vapours. In order to inject large volumes without modifying the vaporization chamber and without samples parts losses, in splitless mode, a drawing up of the sample vapours from the vaporization chamber into said capillary is made by means of a local action of volume contraction, caused by recondensation of at least the solvent vapours in this capillary, said capillary being in the form of a pre-column with no stationary phase, maintained at low temperature at least during the injection.

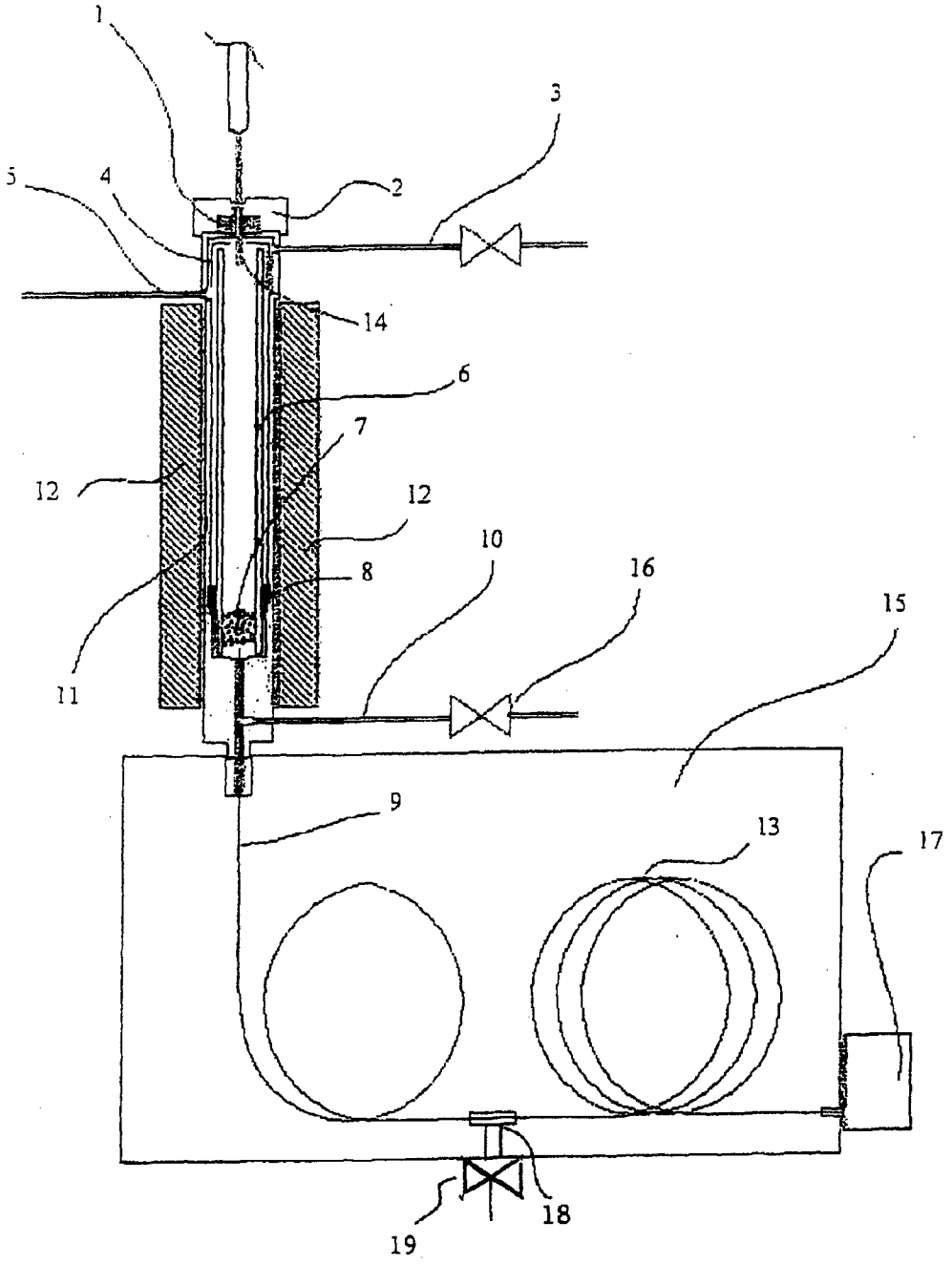

FIG. 1

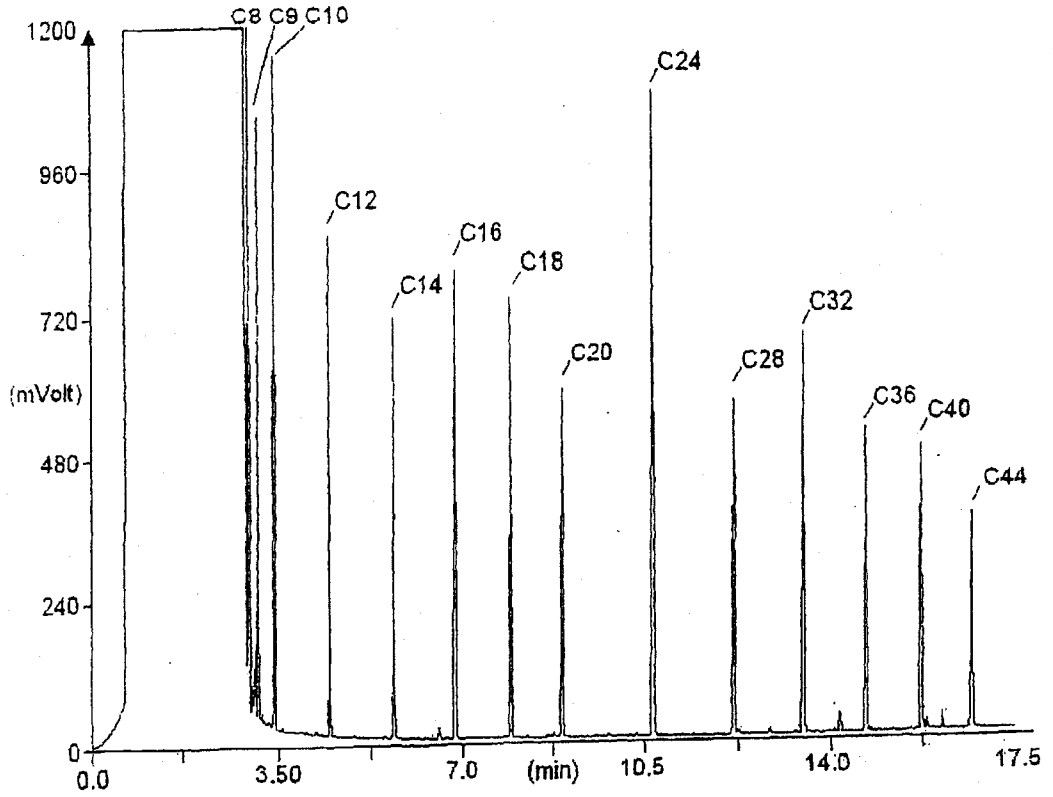
1200
960
720
(mVolt)
480
240
0
0.0
3.50
7.0
(min)
10.5
14.0
17.5
C8
C9
C10
C12
C14
C16
C18
C20
C24
C28
C32
C36
C40
C44

FIG 2

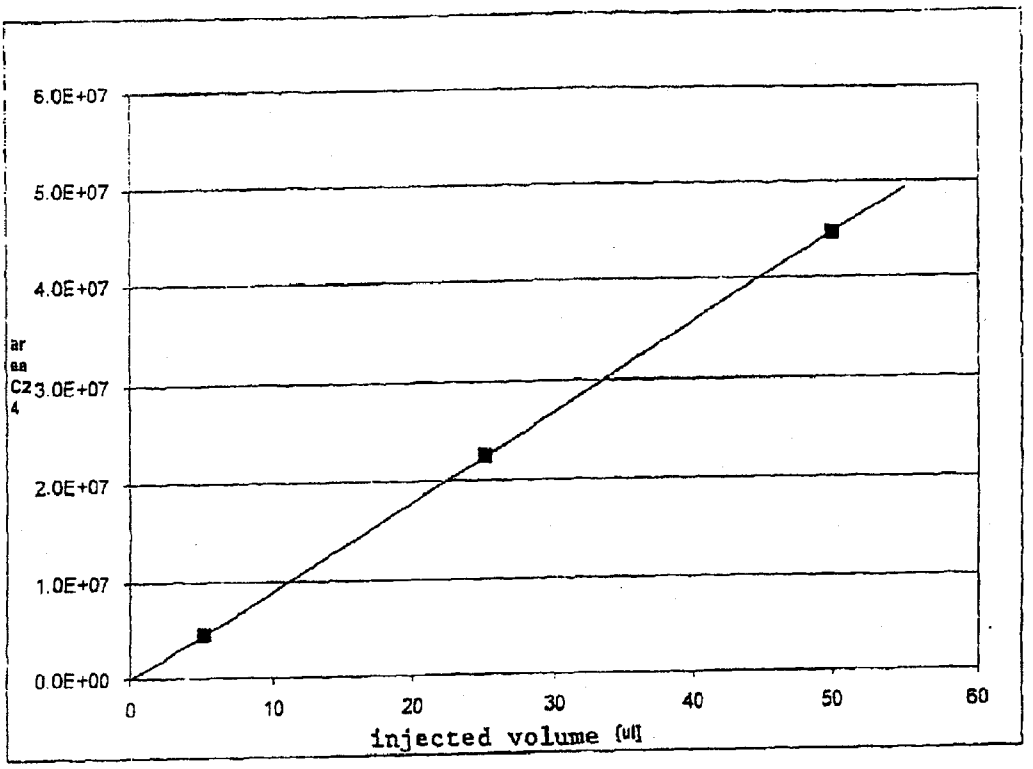
6.0E+07
5.0E+07
4.0E+07
3.0E+07
2.0E+07
1.0E+07
0.0E+00
area CZ4
0
10
20
30
40
50
60
injected volume [ul]

FIG 3

METHOD AND DEVICE FOR VAPORIZATION INJECTION OF HIGH VOLUMES IN GAS CHROMATOGRAPHIC ANALYSIS

Detailed Description of the Invention

FIELD OF THE INVENTION

[0001] The present invention relates to a method and a device for vaporization injection of liquid samples in gas chromatographic analysis equipments. More specifically, the invention relates to a method and to a device specially adapted for vaporization injection of large volumes of liquid samples in a gas chromatograph using a split/splitless injector in splitless mode.

[0002] The term "large volumes of liquids" is intended as sample volumes (composed of the substance to be analysed and the related solvent) which are large or very large in relation to the gas chromatographic column and to the injection technique conventionally used.

BACKGROUNG OF THE INVENTION

[0003] Therefore, columns with an internal diameter ranging from 0.25 mm to 0.53 mm and a vaporizaeht tion chamber (liner) of an adequate volume, which allows the introduction of samples, in splitless mode, ranging from 1 3 μl, are normally used in gas chromatography. In these cases, without modifying the column or the vaporization chamber, the present invention allows the injection in splitless mode of samples greater than 5 μl and up to 50 μl and over.

[0004] Moreover, the use of "narrow bore"columns, with an internal diameter below 0.25 mm (typically from 0.10 to 0.18 mm), is becoming increasingly frequent. However, these columns, which have the advantage of a greater efficiency per unit of length, require the sample to be transferred from the vaporization chamber to the column in extremely brief times. This condition is exceedingly difficult to satisfy owing to the low flow rate at which these columns must work. This makes conventional splitless injection almost impossible and it is usually necessary to use a split injection, where only a small fraction of the sample is transferred to the column (usually only 1/50 1/100 of 1 μl injected). The present invention makes it possible to transfer the sample in splitless mode also in chromatography with "narrow bore"columns. This aspect extends the range of application of the present invention, summed up here: 1) splitless injections of samples greater than 5 μl and up to 50 μl and over with traditional columns and 2) splitless injection of samples up to 1-5 μl and over with "narrow bore"columns.

[0005] Attempts have been made, in traditional chromatography, to increase the injectable volume of the samples, as current trends are aimed at an increase in the volumes to be injected, in order to be able to detect even very small quantities of the compound to be analysed and in a more straightforward manner; for this purpose techniques have been developed for discharging to the outside, without introducing them onto the gas chromatographic column, the majority of the solvent vapours which are formed first and are eliminated from the vaporization injection chamber. However, this often causes loss of the most volatile compounds which escape with the discharged solvent vapours.

[0006] The Italian patent application No. MI 2000A001634 dated 19.07.2000 and the corresponding European patent application no. 01114900.2, the content of which must be considered incorporated herein for reference, describe an injection device and a method of vaporization injection, in which the sample (formed of the substance to analyse and a related solvent) is introduced into the hot vaporization chamber at a high speed, so that it travels the entire length of the chamber in the form of a liquid band. This band then hits a stopping and vaporization means, such as an obstacle, a packing or similar, at the bottom end of the chamber, where the liquid vaporizes to allow the introduction of the sample in the form of vapour onto the gas chromatographic column, the inlet to which is directly adjacent.

[0007] This technique makes it possible to avoid the problems as described in the cited application, of vaporization of the sample in the needle of the introduction syringe, and at the same time allows the length of the vaporization chamber to be extended to over 80 mm and hence samples of relatively large volume to be injected without problems of losses caused by overflow through the head of the chamber and/or the septum purging duct (see EP 699 303 for injection with overflow), and naturally without the loss of volatile substances which may occur if the solvent is eliminated before entering the column.

[0008] Nonetheless, although there is a considerable increase in the injectable volumes, from the 1-3 μl of conventional injectors to about 5-10 μl, these volumes are necessarily limited by the volume of the chamber, which cannot be increased as desired.

[0009] This being stated, the main object of the present invention is to provide a method and a device for vaporization injection in splitless mode of even larger sample volumes, without elimination of the solvent vapours towards the outside, that is by introducing the entire sample onto the gas chromatographic column and without phenomena of overflow or vaporization in the injection needle.

[0010] To attain this object it is necessary to perform a rapid injection of the sample, so as to create a liquid band of the same inside the heated vaporization chamber. This eliminates the drawbacks caused by the heating of the syringe needle. The problem of preventing the large volume of the vaporized sample, which cannot be contained in the chamber, from being dispersed, even only partly, in the head of the chamber and in septum purging duct (overflow) are still to be solved. Therefore, the vapours must be sent to the gas chromatographic column at a substantially the same speed as the speed at which they form.

[0011] A solution to this problem was proposed, among others, in the publication of Watanabe and Hashimoto (Journal of High Resolution Chromatography Vol. 13 Sept 1990, 610-613) by using an injector for packed columns, without septum purging duct and without splitting, and injecting large volumes of sample (50 μl), at a low speed (about 5 μl/s) and with an increased speed of the carrier to deliver the vapours to a capillary kept cold during injection. The publications of Suzuki et al (Journal of AOAC International Vo. 77 No. 6, 1994. 1647 1641 and Journal of Chromatography A. 662 (1994) 139-146) also propose the use a cold trap downstream of the injector, but again with a slow injection (2.5 μl/s) which produces the known problems of

vaporization with loss of heavy products which remain in the needle and cause important errors in the analysis of the sample. The cold trap recondenses only the substances to be analysed, but not the solvent, which is discharged to the outside as vapour through a specific duct controlled by a valve.

[0012] Elimination of the solvent with the method described in the cited works also produces a loss of light components and, moreover, a deformation of the chromatography peaks, making a correct quantitative evaluation of the compounds with medium or high volatility impossible.

[0013] It must also be mentioned that Watanabe and Suzuki inject at controlled speed, which may be attained manually with extreme difficulty, and normally requires a special automatic sampler. Moreover, the appropriate speed must be optimized through experimentation.

SUMMARY OF INVENTION

[0014] The object of the invention is now perfectly attained by means of a method and device as defined in the attached claims. In practice, a pre-column which is not coated with stationary phase and maintained at least during the injection at a temperature that causes recondensation of the solvent vapours, is provided between the injector and the gas-chromatographic column. This vapour recondensation produces a drop in pressure upstream which determines a collection (drawing up) of the vapours from the vaporization chamber. This allows large quantities of injected sample to be treated rapidly, as the vapours are collected from the chamber at substantially the same speed as they form, and therefore without these vapours expanding under pressure towards the top of the chamber and out of it, independently from the dimensions of the chamber.

[0015] In other words, while according to prior art in splitless mode vaporization injections and with the rapid introduction of the sample the volume of this was necessarily limited by the volume of the vaporization chamber, according to the invention this limitation is now overcome thanks to the collection of the solvent vapours substantially at the same speed as they form.

BRIEF DESCRIPTION OF DRAWINGS

[0016] The invention will be now described in greater depth with reference to the schematic representation in **figure 1** attached which shows a device for gas chromatographic analysis according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0017] With reference to **figure 1**, the body of an injector 11 houses a vaporization chamber 6 over which a septum 1 is positioned fixed to the injector by a sealing element 2.

[0018] The vaporization chamber 6 is heated preferably only in the lower portion thereof by well known heating elements 12, while the upper portion, closed by a cap 4, is preferably not heated.

[0019] The injector has a duct 5 for feeding the carrier gas and a duct 3 used to clean the septum by means of the carrier. The vaporization chamber is fixed to the injector body by means of a seal 8. The duct 10 schematically indicates a splitting line, with a related valve 16. The sample, taken using known techniques, is introduced into the chamber by means of a syringe, the needle 14 of which, in case smaller than conventional needles, perforates the septum 1 to reach a predetermined point in the chamber and inject the sample in liquid state as a "band" jet which travels the rest of the highly heated vaporization chamber at a speed that makes the transfer of heat and subsequent vaporization negligible. In any case, the liquid band is repelled by a sort of "buffer" effect determined by the vaporization of minimum quantities of solvent on the walls of the chamber, so that the band remains unaltered while travelling longitudinally through the chamber, and following the configuration of the same.

[0020] In particular, the sample is injected at or in the vicinity of the preferably unheated upper portion of the vaporization chamber, by a short needle 14 of a length which, for example, penetrates the chamber for a distance of no more than 30 mm. Alternatively, a longer needle may be introduced only partially.

[0021] For vaporization, the liquid sample is transferred to a stopping and vaporization means such as packing made of glass wool, deactivated fused silica or a material for packed columns, indicated in the figure with reference number 7. Alternatively, the sample is stopped on an obstacle or trapped between obstacles, as occurs in the case of the "laminar liner" supplied by the company Restek. The position of said packings or obstacles inside the chamber determines the central vaporization point of the sample and therefore they make it possible to prevent drops of liquid from entering the column 9 or passing directly into the splitting duct.

[0022] The operations to collect and introduce the sample onto the vaporization chamber 6 may be performed manually or using an automatic sampler.

[0023] It was found that an output speed of the sample from the needle, as normally obtained by manual injection, equivalent to about 10 m/second, is sufficient to transfer the liquid to the packing 7 without producing appreciable vaporization.

[0024] According to the invention of application MI 2000A001634, to allow high quantities of sample to be injected the capacity of the chamber is increased, also tending to eliminate the external "dead volumes", which allows enhancement of the "pressure pulse" effect obtained in a substantially automatic manner during the vaporization injection (auto pressure pulse).

[0025] With these methods, it is possible, for example, to introduce up to 10 μl of a samples dissolved in hexane.

[0026] In order to operate with larger quantities of sample with a vaporization chamber having the same or even smaller dimensions, the present invention provides a pre-column 9, composed of a capillary with no internal coating and of an adequate length (for example, 0.32 mm i.d. x 5 m or 0.53 mm i.d. x 3 m) positioned between the injector and the gas chromatographic column 13, inside an oven 15. Downstream of the column 13 a detector 17 is provided. The temperature of the oven and therefore of the pre-column 9 is maintained, at least for the entire duration of injection, at a value that determines recondensation of the solvent vapours entering the pre-column from the injection chamber. More

specifically, this temperature must be below the dew point of the solvent vapour/carrier mix at the carrier pressure.

[0027] Recondensation of the solvent vapours in the pre-column 9 determines a great reduction in the volume and consequently a decrease in pressure in the upper zone of this pre-column, which "draws up" the solvent vapours in the pre-column at a speed substantially the same as the speed at which the vapours form in the chamber.

[0028] The dimensions of the pre-column 9 must allow for sufficient liquid retention capacity to contain almost all the sample.

[0029] The stopping and vaporization means 7 is preferably composed of deactivated glass wool positioned immediately over the inlet of the pre-column 9 to minimize the volume of carrier, present between the means 7 (glass wool) and the pre-column inlet, which must be introduced into the pre-column before the solvent vapours. The packing volume must be sufficient to retain the sample, while allowing the carrier to flow through. A volume of about 2-3 times the injected liquid volume is recommended.

[0030] As illustrated in the previously cited patent application by the same applicant, during rapid vaporization of the solvent a pressure pulse is created which helps to push the vapours into the column. In the present case, it is advisable for this pressure pulse to be as high as possible and therefore the injector is advantageously designed to minimize the "dead volumes", that is the volumes accessible around the vaporization chamber; moreover, it is also advisable to totally, or at least partially, close the purging outlet 3 of the septum during the entire injection. For the same reason, all filters (typically activated charcoal) between the vaporization chamber and the valve 16 for closure of splitting must be eliminated. If this filter (not shown) is required, it must be positioned downstream of the valve 16.

[0031] It must be noted that due to the pressure pulse and the violent vaporization of the solvent in the chamber, transfer of the vapours in the pre-column is hardly influenced at all by the carrier, the feed conditions of which (pressure and flow rate) may remain the same as those present during analysis.

[0032] It must also be noted that to obtain optimum transfer of the sample from the pre-column 9 to the gas chromatographic column 13 it is advisable to increase the temperature of the oven 15 only after evaporation of the solvent in the pre-column is terminated and the solvent has been removed from the pre-column by the carrier.

[0033] According to a possible alternative embodiment of the invention, a valve 19 can be placed at the junction 18 of the pre-column 9 to the column 13 to controllably discharge the solvent vapours or part of the solvent vapours before the introduction of the sample into the column 13.

[0034] Following the precepts of the invention, several 40 μl samples of n-alkanes in n-hexane in the quantity of 1 ng/ml each were analysed. The column was of the type SE52, 15 m in length, internal diameter 0.32 mm with a phase thickness of 0.15 μm, while the pre-column was formed of an empty (uncoated) capillary 2 m in length with an internal diameter of 0.53 mm. The oven temperature was maintained at 70°C for the time of the injection and then increased for analysis at the speed of 20°C/min. up to 345°C, while the injector was maintained at 300°C. The splitless period was 0,80 min and during that time the purge duct of the septum was closed. Finally, helium was used as carrier at a flow rate of 2 ml/min.

[0035] The chromatogram of fig 2 was obtained and, on the basis of 10 analyses, the repeatability indicated in the table below was obtained.

[0036]

[0037] Finally, on the basis of several analyses on different quantities of sample (from 5 to 50 μl) completely linear results were obtained, as shown in figure 3.

What is Claimed is:

1. A method for vaporization injection of large volumes of liquid sample (substance to be analysed + solvent) introduced by means of the needle of a syringe onto a heated vaporization chamber which is part of an injector applied to a device for gas chromatographic analysis, the sample being sent in form of a liquid band travelling through said vaporization chamber at high speed until reaching stopping and vaporization means positioned adjacent to the inlet of a capillary to collect the vapours, characterized by a drawing up of the sample vapours from the vaporization chamber into said capillary by means of a local action of volume contraction, caused by recondensation of at least the solvent vapours in this capillary.

2. A method as claimed in claim 1, characterized by the choice of said capillary in the form of a pre-column with no stationary phase, maintained at low temperature at least during the injection.

3. A method as claimed in claim 2, in which the injector has an inlet for the carrier gas, characterized in that said pre-column is maintained at a temperature below the dew point of the sample vapours/carrier mixture, at the carrier pressure.

4. A method as claimed in claim 2 or 3, characterized in that said pre-column has an internal surface sufficient to retain the recondensed sample.

5. A method as claimed in claim 2, 3 or 4, characterized in that the increase of temperature program of the pre-column starts after evaporation of the solvent in said pre-column has terminated.

6. A method as claimed in one of the previous claims, characterized by feeding the carrier during injection in flow and pressure conditions substantially equal to those foreseen during the gas chromatographic analysis.

7. A method as claimed in one of the previous claims, characterized in that the sample is sent through the injector as a liquid band, employing conditions that substantially avoid its vaporization in the needle.

8. A method as claimed in claim 7, characterized in that vaporization of the liquid band occurs at the end of the vaporization chamber opposite to the one at which the sample is introduced, immediately above the inlet of the pre-column.

9. A method as claimed in at least one of the previous claims, characterized in that the injection is performed in splitless mode and the injection sample has a volume greater than 5 μl.

10. A method as claimed in at least one of the claims from 1 to 8, applied to gas chromatography with narrow bore columns, characterized in that the injection is performed in splitless mode.

11.A method as claimed in claim 10, characterized in that the injected sample has a volume greater than 0.5 μl.

12.A device for gas chromatographic analysis of samples (substance to be analysed + solvent), composed of an injector (11) of the vaporization type, a gas chromatographic column (13) housed in an oven (15) and a detector (17), in which the injector (11) comprises a heated chamber (6) with a septum (1), which can be penetrated by a needle (14) for fast injection of the sample in the form of a liquid band, the chamber also having a stopping and vaporization means (7) for the band adjacent to the inlet of a capillary for collecting the vapours and sending them to the separation column (13) and a duct (5) for feeding the carrier gas, characterized in that said capillary is in the form of a pre-column (9) not coated with stationary phase, positioned between the injector (11) and the separation column (13).

13.A device as claimed in claim 12, characterized in that the vaporization chamber (6) has means (12) to heat the same, positioned and operating so that the temperature profile on the longitudinal axis of the injector (11) is such that the part in which the needle (14) of the syringe penetrates is heated only slightly and the subsequent part is sufficiently hot to repel the liquid from the walls due to the formation of a vapour buffer.

14.A device as claimed in claim 12 or 13, characterized in that the stopping and vaporization means (7) is composed of a packing with a volume at least double of the injected volume.

15.A device as claimed in claim 14, characterized in that the packing (7) is made of glass wool, fused silica or similar deactivated materials.

16. A device as claimed in claim 12 or 13, characterized in that the stopping and vaporization means (7) is composed of obstacles.

17.A device as claimed in claim 12 or 13, with a duct (3) to purge the septum by means of the carrier, characterized in that in comprises means to close or choke said septum purging duct.

18.A device as claimed in claim 12, characterized in that no filter is provided between the vaporization chamber (6) and the splitting control valve (16).

19. A device as claimed in claim 12 or 13, characterized in that a filter is interposed between the valve for splitting closure and the valve for splitting control.

20. A device as claimed in one or more of claims 12 to 19, characterized in that a controllable solvent vapour exit valve (19) is placed upstream the gas-chromatographic column (13).

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