CLOSURE OF COLUMNS, PARTICULARLY OF CHROMATOGRAPHIC COLUMNS.

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ABSTRACT OF THE DISCLOSURE

A closure means for a chromatographic column containing a packing material and receiving a stream to be analyzed, the closure means including a sealing member located above the packing material in the entrance portion of the column and provided with an axially extending capillary duct feeding the stream into the column, and a porous body filling the space between the exit opening of said duct and the upper level of said packing material to distribute and spread the stream into the column and to equalize and flatten the wave fronts therein.

This application is a continuation of my prior copending application Ser. No. 684,597 filed Nov. 14, 1967 which is in turn a continuation of my prior copending application Ser. No. 400,499 filed Sept. 30, 1964, and both now abandoned.

The present invention relates to a closure means for chromatographic columns.

One of the principal problems in the design of columns for column chromatographic processes, particularly those utilizing ion exchange materials, is the obtaining of an optimum compromise among a plurality of factors, the majority of which have contradictory effects. As a rule, it is primarily the question of a rational compromise between the maximum possible differentiation of components of the mixture being analyzed and the times within which a chromatographic separation is accomplished. This applies to both the semi-automatic or entirely non-automatic equipment (reception of fractions on the so-called automatic fraction receivers or by hand) and to the processes called fully automatic, this latter category also including the processes carried out using the so-called automatic analyzers of amino acids.

It is generally assumed that an optimum separation is obtained by introducing the sample manually. According to this current practice, the sample is applied to the top of a column (the liquid above this column having been previously removed by suction) by carefully discharging the sample at this level by way of the internal wall of the chromatographic column at a point situated close above the upper surface of the column filling, care being taken not to disturb the top surface of the filling of the chromatographic column. The sample is then introduced into the column by an injection and thus forced into the column in a similar way. This procedure may be repeated once or several times, if necessary. It is usually assumed that this method insures in an optimum way that the sample will enter the topmost layers of the filling of the chromatographic column. In view of the wave fronts, which are situated at right angles to the axis of the column, this procedure is expected to ensure also an optimum positioning of the sample as regards the possibility of obtaining the neatest possible division on the column. Any inclination of components of the sample surfaces, which would alter the position of the sample due to the passage through the column, including its initial stage, is to be regarded as an undesirable source of impairment of the maximum attainable resolving power of the column and of the neatness of the resulting division. The final separation is invariably impaired, if concentration waves of a given component of the sample arrive at the discharge end of the column at different times.

It is, of course, impracticable to maintain the wave fronts at right angles to the column axis during the entire time of their passage through a chromatographic column. Under standard conditions of chromatographic separation procedures whether semi-automatic or fully automated, there appears a number of additional sources that exert a joint undesirable effect even from outside the chromatographic column itself, as far as the final result is concerned.

In the case of fraction-type methods, the volumes of the individual fractions are chosen to be considerably larger (in order to obtain an acceptably low number of fractions for the whole process) than they should be, regardless of practical difficulties, a full utilization of the separation power of the chromatographic column itself were aimed at. With the continuous procedures, on the other hand, the passage of the elution fluid through pipelines and evaluating equipment is to be regarded as the principal source of error which reduces the separation achieved by the column. In continuous procedures mixing of the zones occurs in the capillary reactor, in which the colour-forming reaction with a ninhydrin reagent takes place. For the reaction there is usually specified a time of 15 minutes at a temperature of 100° C. This blurring of the separation obtained by the column usually predominates over the mixing of the zones in the photometer. Under such largely unfavourable conditions, which are generally regarded as hardly or not improvable at all, the above worsening influences usually overshadow those influences which impair the separating capacity of the column itself through deformation of wave fronts by deflection or slanting.

These influences enter into play even as a result of the methods of application of samples during chromatographic procedures carried out on standard types of apparatus. The impairing influence of not absolutely precise dosing also recedes to the background in the face of the other aforesaid unfavourable influences of the whole equipment used and of the methods adopted for the chromatographic procedure and their evaluation.

Recently, however, there is becoming evident an increasing tendency towards shortening, as much as possible, the time required for the accomplishment of an analysis. This factor is sometimes pursued even at the expense of the separating capacity of the entire equipment. One of the causes is, amongst others, the existing shortage of equipments, especially of that used for through-flow equipment, which is rarely available in the quantity required.

The shortened methods, which have come into use recently, could be improved by paying more attention to the parameters which determine the time of a chromatographic procedure on the one hand and the neatness of separation on the other hand. Certain modifications of the orthodox procedure, as they are used on an ever increasing scale in the laboratories, are for example,
to shorten the lengths of the columns only and preserving the remaining parameters, or to adopt a finer grain size filling in combination with greater length of columns which are operated at increased speeds of throughput and, naturally, at higher excess pressures which become necessary under such conditions. Such modifications can last for the steering of the time required for chromatographic procedures without impairing the separation or, on the other hand, to an improvement in the rate of separation, required for the accomplishment of the entire procedure.

Supplementary devices have been made known recently which are claimed to enable one entire automatic analysis of amino acids to be carried out with one single preliminary setting. The most recent method, made known only a short time ago, carries out the analysis on specially adapted columns while in the same the respect other orthodoxy principles are adhered to.

All the types of equipment mentioned above work on the principle of manual application of samples to the individual chromatographic columns.

These disadvantages are obviated by the present invention. According to the invention there is provided a column containing the upper ends of the chromatographic columns comprising a porous body, a capillary duct for admitting a liquid to one surface of said porous body and a packing means, fitting within the column and through which said duct passes, for locating and retaining said porous body in a position which prevents the formation of a free space filled only with the liquid above the charge in the column. The porous body is clamped in a position by the rigid elements which surround it in a way which avoids free space being left on either side, while the porous body itself offers hydraulic resistance to throughput, this resistance being distributed uniformly around the axis of the column and being higher in any angular sector around the centre line than the hydraulic resistances in the regions adjacent to the said sector; these conditions exist both on the inlet side and, in particular, on the outlet side within the region of the column charge, the length of which is approximately equal to the diameter of the column or to a multiple thereof.

This new type of equipment entails the conditions necessary for building up an apparatus that enable a full automation and an appreciable shortening of the time required for carrying out chromatography or an increase of precision within given time. A possibility is afforded here of a practically instantaneous application of a sample to the column, without any interruption of the established throughtflow conditions either in the column itself or in the evaluating equipment. The entire apparatus can thus operate in a continuous manner, and the application itself of a sample to the column requires but two switching over operations, including the operation of a change-over device of a reservoir whether automatic, or manual. In this way, therefore, there is obviated the 15–40 minutes interruption which was unavoidable with the former orthodox manual application of a sample to the column, with a subsequent flushing, repeated opening and closing of the column and forcing of the liquid into the column under excess air pressure.

The present principle, in addition to the aforesaid automatic application of a sample to the chromatographic column, aims to achieve an optimum geometric shape of the concentrating wave of a sample during its passage through the column in the course of the entire chromatographic procedure, immediately from the start of the sample up to the end. The version described hereinafter enables the achievement of both the said aims.

The closure is worth while even if only one of the two said objectives is pursued.

The principal end in view is to achieve such a start of the sample as to make the wave front of the sample, or of its individual components, after they have under...
already so high due to the influence of other factors, that the impairment resulting from such a simple closure does not appreciably affect the final result.

One variant of this simplest version is the version shown in FIG. 2, where a needle extends by very slightly or not at all below the bottom surface of the closure, for example, by a rubber bung 4. Here it will be advantageous to make the chromatographic column filling the column 3, close to this plug. Since here, too, an eroded crater will be formed during the chromatographic procedure in the charge, as indicated above, it is recommended, prior to each introduction of a specimen, to rearrange and smooth down the level of the chromatographic column repeatedly even with this type of arrangement, and to tighten the closure 4 so as to exclude, if possible, any dead space above the charge 2. Even with this arrangement, the wave fronts v will be propagated in the way indicated in FIG. 2, their curvature being rendered worse whenever a smoothing of the crater eroded in the charge 2 of the column 3 by the entering elution is omitted. An important worsening effect will also be due to the gap formed between the level of charges 2 and the bottom surface of the charge 4, unless this gap has been eliminated in the said way immediately before the admission of the sample.

The possibility of the formation of an eroded crater can be appreciably reduced by the arrangement shown in FIG. 3, where between the bottom surface of the closure 4 and the bottom surface of the charge 3 is inserted a porous spacer 5 made from filter paper which completely fills the entire compartment so that no gaps whatever are left at any point. The gaps can be eliminated by a deeper introduction of the closure 4; with this arrangement even the topmost layers of the charge 2 and the column of closure 4 will show a tendency to fill the gaps which may not have been filled by the porous spacer 5. With this arrangement, conditions are afforded for a formation of concentric wave fronts v of a shape similar to those of the preceding cases, though not yet rendered worse by crater formation hazard.

In all the above cases there exist dead corners from the point of view of liquid throughflow, in the vicinity of which the rate of flow will drop appreciably with regard to the rate of flow in the vicinity of the center line of the column. A similar effect to that caused by dead spaces is that which is reflected in a formation of initially concentric wave fronts deformed into elongated shapes and in a deterioration of the separation which will be obtainable in the column under these conditions. By an arrangement of suitable closing according to FIG. 4 the said shortcomings can be noticeably restricted. The closure 4 formed in the simplest version by a rubber bung has a conical recess 6 in its bottom portion thereby reducing the possibility of the creation of dead spaces. After a closure of this type has been forced into a charge 2 of the column 3, the charge 2 will appear in the conical recess, and thus even in this simple case there will be obtained improved conditions for an elimination of the most important adverse deformations of the concentrating wave fronts, these deformations arising both in the case where an undesirable crater has formed and in the case where a formation of this crater has been obviated. If, however, the conical recess 6 has been filled with a porous body, then not only will the formation of an undesirable crater be prevented, but the interface between the porous body and the charge 2 of the column will have a convex shape on the side of the charge, as indicated in FIG. 4. The conditions necessary for a considerable suppression of the undesirable curvature of the wave fronts will thus be created, particularly if the porous body has a lower specific hydraulic resistance than the charge 2, with a natural assumption of a practical three dimensional homogeneity of the two mediums (i.e. the porous body and the charge) through the pores of which the liquid makes its passage. The porous filling of the conical recess 6 may comprise, for example, cotton wool which for a better effect may be separated from the charge 2 by a fine-meshed gauze 7 made, for example, of a plastics material. By an appropriate selection of the volume of this filling with regard to the pressure by which the entire closure is pressed against the charge 2, it is possible automatically to obtain a certain convexity with regard to the charge as may be seen in FIG. 4.

Both the shape and the homogeneity of the porosity will be preserved with much more perfection when fillings made of materials such as Teflon ( trademark) or sintered glass are adopted.

A much improved operation and much more comfortable handling properties will be obtained if instead of the makeshift closure by means of a rubber plug, as described in the preceding paragraph mechanical closure means are adopted as shown in the following figures.

FIG. 5 illustrates an embodiment of the principle illustrated in FIG. 4; this type of closure has a packing device 7 with a conical recess 6 filled with a porous body, the packing device being made, for example, of silicone rubber. A tubular nut 8 shaped as shown in the picture compresses the filling of the recess 6 and the packing unit 7 in the axial direction; this arrangement may have, for example, a Teflon disc 9 upon the bottom surface of the plate 10 shaped as shown, plate 10 having a thread onto which the nut 8 is screwed. By tightening the screwing of nut 8 and plate 10 it is possible to control the pressure and the deformation of the conical packing unit 7 so as to eliminate any leakage whatever. The plate 10 extends upward forming a tube 11, into which a capillary tube 1 has been inserted, this latter tube being made, for example, of a stainless steel material used for manufacture of injection needles. Capillary tube 1 extends into the porous filling of the recess 6 and forms a supply duct for the mobile phase to the chromatographic column 2; at an opportune moment the sample intended for separation on column 3 is applied through the capillary tube 1, and passes through the porous filling of the compartment 6 to this column.

In order to improve the conditions for a formation of little deformed wave fronts v, the sample advancing through the upper layers of the charge 2, the tubular nut 8 has its annular bottom surfaces 12 machined in a tapered shape. In addition, the rigid porous filling of the recess 6 can be arranged for a restricted or totally obstructed permeability in the centre of its bottom surface by, for example, applying a plastics material 13 in drop-let form which closes the pores of the filling in compartment 6 partially or totally within a limited area.

In order to make the entire closure a perfect seal on the internal surface of the chromatographic tube 3, and to enable it at the same time to be displaced along the tube so that it may be fixed in a desired position, a resilient packing sleeve 14 made, for example, of silicone rubber forms part of the closure. The packing sleeve may be compressed between the chromatographic tube 3 and the plate 10 to any given degree by means of a pressure being exerted on upper plate 15 through a tube 16. By an appropriate dimensioning of the sleeve 14 and a complete release of the pressure exerted on it by plate 15 it is possible to achieve a condition where, after the external threaded portions of the closure have been released, the latter can move freely inside the chromatographic tube 3, with a sufficient amount of play to allow the cushioning of the undesirable underpressure which will be generated during an opening operation of the closure, which might produce a partial lifting or another adverse effect upon the charge 2 of the column.

FIG. 6 and the following figures shows various convenient alternatives of the closure, in which the packing organ of the system with a sleeve 14 and the other elements shown in FIG. 5 have been preserved, there having, however, been adopted another very advantageous principle of formation of a porous body, by which a regular formation of wave fronts v of a convenient shape in the
top layers of the charge 2 is to be ensured, while the overall throughflow profiles and their uninterrupted operation from the porous body to the top layers of the charge can be easily controlled through the profiled bottom portions of the closure.

The embodiment shown in FIG. 6 may be regarded as a basic one. The plate 10 is extended both up and down by threaded extensions. The upper thread 11 of the plate 10 is connected to a threaded nut 20 and the bottom thread 17 is connected to a threaded nut 21. This arrangement being made primarily with a view of facilitating the manufacture of the device. A portion of the extension in the downward direction adjacent the plate 10 is formed with a planar surface 18, the remaining portion 19 being threaded. On this thread a formed nut 20 can be screwed, as shown in the picture. Through an axial duct bored in the plate 10 and in its two extensions passes a needle-like capillary tube 1 which is tightly fixed in position, for example, by a shrinking plate 10 on to capillary tube 1, thus sealing the bottom end 21 of the capillary tube and serving to provide a tight joint between the two elements.

The thread 19 is arranged, for example, with a truncated crest (see FIG. 9) or with a longitudinal groove or with a plurality of such grooves, in order to make possible a propagation of the liquid into the hole 18 and 21 of the tube 1 to the plain surface 18 of the downward extension of the plate 10. On the plain portion 18 is fitted an annular porous body 22, which is compressed between nut 20 and plate 10 by tightening of the nut 20 on the screw 19. In order to ensure a uniformly distributed throughflow over the periphery of the porous body 22, at the point where the liquid leaves it to enter the charge 2 of the column, either the plate 10 or the nut 20, or both elements at the same time may have an annular recess machined on their faces abutting the porous body 22 (see FIG. 9) or, alternatively, the porous body may have an annular recess of this type, in order that the porous body may be clamped more securely between the said elements in the vicinity of its periphery, while the portion near the centre is clamped by a smaller applied pressure. The homogeneous outflow of the liquid from the porous body 22 along its periphery may be aided by a resilient annular cushion 23 made, for example, of silicone rubber. By using cushion 23 in combination with the porous body an even clamping pressure will be obtained in the cases where, for reasons related to manufacturing tolerances, it will not be possible to ensure an absolute parallelism of the clamped surfaces of the two elements.

It is recommended to arrange the thread 19 in such a way that it will permit slight oscillatory movements, whereby it will work as a sort of a hinge which will also aid in achieving conditions necessary for an even outflow from the periphery of the porous body 22.

Another condition for correct operation of the closure requires that the annulus between the periphery of the porous body and the inner wall of the chromatographic tube 3 should be homogeneous over its entire periphery, i.e., should be arranged equally about the axis of the column so as to enable the thickness of the charge 2 to be the same on all sides of the porous body when the charge 2 enters while the closure is introduced into the chromatographic tube. In order to reduce these compartments to a minimum, the periphery of the plate 10 is bevelled on the side adjacent the sleeve 14, this advantageous arrangement being shown in FIG. 8; thus the sleeve 14 fills the free space up to a point situated immediately above the periphery of the porous body 18 or above that of the resilient cushion 23 where provided.

After the above conditions have been met, the inside space of the chromatography tube, through which both the mobile phase and the sample flow, will be practically free from dead corners. The radial flow of the liquid at the exit from the periphery of the porous body 22 will be gradually transformed into an axial flow, so that as it flows through the column, the wave fronts v having the shape and the course indicated in FIG. 6. It is obvious that this shape and course of the wave fronts can easily be influenced by the shape imparted to the external tapered bottom surface of the nut 20, so as to adapt the resulting wave front under the closure as much as possible to the general requirements as explained in the introductory paragraph namely the requirements which call for a wave front approaching the plane edge or for a wave front deformed in such a way as to make this deformation compensate the deformation produced at the exit at the bottom end of the assembly.

The porous body as illustrated for example in FIG. 6 has an inner surface function, in addition to the aforesaid function of a favourable separation of the overflows of the mobile phase and the sample so as to produce favourable shapes of wave fronts. This additional function is that the porous body works as a sort of filter which prevents the particles of the charge 2 from penetrating into the capillary passages through which both the mobile phase and the sample are admitted.

The porous body 22 may be made of any kind of porous material which meets the mechanical, hydraulic and sometimes even the chemical specifications; porous Teflon (trademark) or a sintered glass body may be used for this purpose, for example, by being covered with a filter or chromatographic paper, there being the possibility of building up the body of a plurality of rings. This form of construction also reduces the probability of an adverse effect due to an imperfect plan parallelism of the body thus constructed.

FIG. 7 shows an outside view of the central elements of the closure illustrated in FIG. 6, the sectional view showing an alternative which makes it possible to use one and the same closure for columns of varying internal diameters, by adapting only the outside diameter of the packing sleeve 14 and that of the plate 15 to the varying diameters, the bottom plate 19 being covered on the side facing the sleeve 14 by an annular plate 24. An enlargement of the annular space between the periphery of the porous body 22 and the inside wall of the chromatographic tube 3 need not necessarily have an adverse effect on the resulting separation, particularly with larger columns and processes of medium rates. For these reasons, a closure intended and designed with optimum parameters for columns which are relatively small may serve equally as well for columns of larger diameters. The bottom plate 16, or the annular plate 24 are the elements which determine the central position of a closure in a column and, consequently these elements to be manufactured with the necessary accuracy and with a relatively small tolerance as regards the inside wall of a chromatographic tube, since it is not possible to rely too much on the resilient sleeve 14 being in a central position.

FIG. 8 illustrates an embodiment of the closure which is adapted for use in columns having small diameters, for example, in columns having internal diameters ranging from 1.5 to 3 mm. The bottom portion is identical with that shown in FIG. 6, the corresponding items having the same function. The only difference consists in the fact that the pipe 11 and its screwed joint by means of a thread 17 to the upper extension of the plate 10 are dispensed with. In order to save a radial space, the needle 1 has been used here alone as a mechanical element, which not only serves for a capillary introduction of the mobile phase and the sample, but also for generation of a compression of the sleeve 14 in the direction of the axis. Since the sleeve 14 is in direct contact with many instances the porous body 22, it is not a condition here that the mechanical joint between the plate 10 and the needle 1 should be tight, provided the transmission of an axial pressure from the needle 1 to the body of the plate 10 is ensured in an adequate manner for example, by the bottom end 21.

FIG. 9 gives a detailed view of the construction between the downward extension of the plate 10 and the unit 20, in the embodiments of FIGS. 6, 8.
The detailed Fig. 9 and the following figures show, a possibility of providing narrow slots 33 for a spanner used to tighten the nut 20 or to adjust it so as to sufficiently tighten both the porous body 28 (in Fig. 9), and the resilient cushion 23. In order to prevent any accidental alterations of this tightening, particularly when torque is applied to the closure inserted into the column during the positioning of the closure in the charge, it is possible to increase the friction of the thread 20 by making it slightly oversized, while the communication duct has remained unaltered. The thread has been described so far.

The packing and fixing of the needle 1 inside the body of plate 10 by making the major part of the length of the bore inside the plate body 10 in such a way as to slip the needle into it without any major amount of prestress. The latter is concentrated into the bottom portion where the bore is slightly offset, a deformation of the needle 1 being obtained in the aforesaid way together with a slight increase of the thread 19 provided on the body 10, this minimum increase being just sufficient to obtain a snug fit of the nut 20 with regard to this particular portion of the thread 20. A snug fit of the thread can be obtained with equal efficiency through a selection of appropriate thread 12 such as being aided by clamping the bottom end 21 of the needle 1.

Only in exceptional cases a packing formed by a sleeve 14 will be used as a locking device of the closure intended to prevent its axial displacement inside the column 3. This arrangement is possible only with slight overpressures on the column and when the wall of the chromotographic column 3 is sufficiently resistant to stand up to relatively high radial pressure which it is necessary to develop in order to achieve a sufficient friction between the sleeve 14 and the inside wall of the column 3. It will be expedient to provide sleeve 14 to function as a means to close and seal the closure in the column, without producing unnecessarily high pressures on the walls of the chromotographic column 3 which, in its standard version made of glass, has limited resistance with respect to permanently bearing of the radial pressures produced by the packing sleeve. This is particularly important especially if the walls of the column are not sufficiently thick and especially if the internal stresses due to its manufacture or to other reasons have not been eliminated.

In the left-hand part of Fig. 10 there is indicated an appropriate shaping of the sleeve 14 with central grooves, so as to ensure its resilient and relatively soft bearing and a seal inside the column 3. The circumferential grooves on the sleeve 14 can be arranged in any way desired, but it will be of advantage if they will act as a kind of flap which will tend to open under the overpressure below the closure. Besides, the lowermost flap can be conveniently arranged so as to ensure, together with the shaping of the plate 10, as shown in Fig. 10, that optimum throughflow conditions will be obtained in the immediate vicinity of the circumference of the porous body 28, dead spaces being kept to a minimum.

The right-hand half of Fig. 10 is a modified version of the sleeve 14, with only one flap provided for the aforesaid function, an expansion of its periphery during the approach of the plates 10 and 15 being obtained here rather by a slip of the flap of the sleeve 14' than through a compression of the entire sleeve, as has been the case in the left side designs described.

The right-hand half of Fig. 10, shows, at the same time, a version of the plate 24, which as above described functions as closure for application on columns of larger diameters. The inclination of the bevelling surface, whether of the additional plate 24, or of the basic plate 10, should not be too pronounced, in order to prevent a self-locking action which, during a removal of the
closure from the column would render the operation difficult or even impossible by making a flap of the sleeve 14 wedge into the space between the plate 24 and the inside wall of the chromatographic column. The dimensions of the sleeve 14 and particularly those of its flap, should be arranged with a view of making the sleeve contract to a smaller diameter by itself, when the pressure exerted by the plate 15 is being released, the afore-said difficulties being thus obviated and a certain amount of play being provided between the closure and the column to enable passage of the liquid or air from above the closure into a space that may be created between the closure and the column charge and to prevent, in this way, the generation of an undesirable underpressure which might disturb the chromatographic column itself.

FIG. 10 further indicates an alternative possibility of attachment, and, if necessary, sealing of the needle 1 in the body of the plate 10 by means of a thread 34, by which the two elements are screwed together. This screwed union must be made with a certain amount of prestress of a type not intended to be taken apart, it being possible to use the union without a thread as a packing or attachment of the joint, particularly in the cases where the needle will have a slight taper in the zone of material contact, in order to provide an amount of prestress required for packing, or if the two elements will be screwed on each other with the body of the plate 10 preheated in such a way as to produce a prestress through an alteration of the dimensions as a result of an expansion under the action of heat. Since the needle 1 does not extend in this case up to the point of the thread 19 inside the nut 20, the body of the plate 10 can be severed at the level of the thread 19 by an axial cut 35 made as thin as possible, in order to ensure a capillary communication to the porous body 22, it being possible to make the thread 19 regardless of this communication and to make it somewhat possible by spreading it to either side, an arrangement made possible by a slit 25.

FIG. 11 shows a possibility of utilization of the principles just described for columns of very small diameters. The drawing tube 11 is again dispensed with here, its function being taken over by the needle 1, to the end of which, fitted with a thread or a slit 35, there is screwed a nut 20 and, in the upper part of this thread, also the body of the plate 10. The latter can have the form shown in the right-hand part of FIG. 11 as a plate 10' with an upper bevelled surface. If it is required to produce an additional pressure to force the sleeve 14 against the bore obtained by an inclined surface of contact between the sleeve 14' and the plate 15', the latter being exposed to a pressure of the tube 16, if it is necessary to seal the closure. The tube 16 and the plate 15' may be made of one piece, especially for small-diameter columns, as shown under 16 in the left-hand part of FIG. 11. If the tube 16' ends in a taper with an inclination opposite to that of the plate 15', a pressure against the wall of the column 3 is achieved even in the upper portion of the sleeve 14. A seal of plate 10 on the needle 1 has to be obtained in another way, such as, for example, through a preasure between the body 10 and the needle 1 at the point where the thread has not been sealed in the way described above. The screwed connection between the plate body 10 and the nut 20 may be adapted so as to make the body 10 function as a nut, while the extension on which the thread has been formed is not a second body 20 which, instead of serving as a nut, becomes a screw. Embodiments of this variant are shown in FIGS. 11 and 12.

In FIG. 12 the extension 36, on which a threaded connection 37 has been made, can, if necessary, be slit by a thin cut 38 extending through the axis of the extension 36, the cut having now the same function as that corresponding to the slit 35 described under FIG. 10. In this embodiment however the cut 38 extends only along part of the length of the extension 36. The plate body 10 in the version according to FIG. 12 is connected again by a thread 17 to a draw tube 11, as this was the case in FIG. 6. The needle 1 is press-fitted or fixed in some other way in the corresponding bore of the plate body 10.

The embodiment illustrated in FIG. 13 is primarily intended for very thin columns 3 and is in the same relation to FIG. 12 as the embodiment of FIG. 10 is to FIG. 11. In FIG. 13 the draw tube 11 has again been dispensed with here, its mechanical function having been taken over by the needle 1. The latter is fixed at the bottom end with a long thread 39, to which the plate body 10 has been screwed, the latter having a corresponding thread in its central bore. The threaded hole of the plate body 10 is screwed from the underside a threaded pin 35, the bottom of which is formed by body 20. The thread of pin 35 may again be slit by a thin axial cut 38 extending into part of the length of the pin, the part abutting the thread 39 of the needle 1. By this, the opening formed by the cut 38 terminates in the side of the pin and not at the bottom thereof.

The remaining items in FIGS. 12 and 13 have the same interpretation as those of the preceding figures.

If a convenient porous material is not available for porous bodies of the actual size of, for example, a Teflon of adequate porosity, the manufacture of annular porous bodies of diameters in the region of 1 mm. may entail certain technological difficulties. In that case it may be more convenient to select a porous body that has no hole at the centre. However, the manufacture of a sleeve-type nut 8 (FIG. 5) having such a small diameter and a considerable length may be an exacting technological problem. For cases of this nature, the construction according to FIG. 14 may prove advantageous. Here, a porous body 39, built up, for example, of a number of superposed discs of chromatographic filtration paper, is clamped, possibly by way of a web-stitch cushion not shown in FIG. 14, by a screw 20' against a peripheral supporting face of a hollow body 10 into which needle 1 has been press-fitted, the body 10 having in its bottom portion a thread 43 into which a threaded portion of the plug screw 20 has been introduced. This screw, the tightening of which serves to regulate the compression of the porous body 22, has along its periphery either a system of grooves which in FIG. 14 is shown only in the upper part (the serration 44), or can possibly continue even through the thread 43, or a plurality of narrow grooves 45, uniformly spaced over the periphery of the thread fitted to the screw 20'. In its lowermost portion the screw may be tapered, as shown in FIG. 14. The remaining numbered items have the same interpretation as those of the preceding instances.

In the design according to FIG. 14 there has been somewhat violated the aforesaid principle, according to which the charge of the column should have no access into the capillary holes or grooves. With the short lengths of the porous body, such as that in FIG. 14, this hazard is negligible for a small-sized column, and need not involve any obstacles to the application of this type of closure, with regard to those quoted above.

With the expansion-type closures of columns (according to FIG. 6) it may happen after a prolonged operation that the porosity and permeability of the porous body is gradually impaired, particularly if the body has been built up of rings made of filtration or chromatographic paper. An increase of hydraulic resistance due to a deterioration of the capillary structure causes the inside of the body results in an increase of pressure on the column. By a removal of the closure from the column it may be ascertained that the pressure surge is due to the closure. For elimination of this defect it is, as a rule, sufficient to release the pressure by which the porous body 22 is clamped, a new moderate compression of the impending carried out, if necessary. With a standard construction of the closure according to FIG. 6 and the following illus-
trations, this operation naturally requires a withdrawal of the closure from the column. With the embodiment illustrated in FIG. 5 it is possible to release or regulate the clamping body without a removal of the closure from the column, even under full operation of the latter, this advantage being of much importance particularly for procedures of a continuous character, where one analysis is followed immediately by the next one. An arrangement of the lower end of the closure is shown in FIG. 15 and differs from the basic arrangement according to FIG. 6 and the following figures in principle only by the fact that the formed nut 50 screwed on the thread 51 can be axially displaced within small limits with regard to the plate 10, while both its exact position with regard to the plate 10 and the pressure which is exerted against the plate 10 through the porous body and the resilient cushion are variable from the outside by the arrangement of the thread 19 on the needle 1. The latter is not rigidly attached here to the plate body 10 or to the other elements connected to it, but merely clamped in position by a packing sleeve 47 with an amount of prostress necessary for the introduction of the latter between the needle 1 and the hollow interior of the plate body 10. This sleeve 77 through providing a seal against the overpressure inside the column allows a slight axial displacement of the needle 1 and thereby of the nut 20 with regard to the plate body 10.

The left and right-hand half of FIG. 15 show somewhat different details as identified by reference symbols with interpretations in FIG. 6 and the subsequent figures. The nut 20 sits tightly on the thread 19 in order to prevent its spontaneous release during pressure regulation from outside, this adjustment being performed by tightening of the nut 48 on the thread fitted to the needle 1, as shown in FIG. 16. The nut 48 bears against the upper end of the draw pipe 11, fitted with a long thread on which the nut 28 is screwed, by a tightening of which the thrust tube 16 is forced downward against the draw tube 11, a clamping effect being thereby produced through a compression of the sleeve 14. Besides, on the same thread of the draw tube 11 there is fitted a tumbler (a wrench) or a disc 49 against which bear one or two lock nuts 50, 51 sufficiently tightened in such a way that, while the wrench 49 is held firmly, it is possible to lock in position the draw tube 11 when either the nut 28 or the nut 48 is tightened.

The version according to FIG. 17 differs from that of FIG. 16 only in that the thread for the nut 48 is not fitted to the needle 1, which might present sometimes technological difficulties in view of its thinness, but, instead, the needle 1 is drawn upward towards the draw pipe 11 by a clamp 52 attached to it, the jaws of this clamp being pressed together by a screw 53, while the nut 54 of the shape shown in the picture, screwed on the thread fitted to the draw tube 11, exerts a pressure on the clamp 52 from the underside.

What is claimed is:

1. Closure means for a chromatographic column, said column having a longitudinal axis and containing a packing material for receiving a sample stream to be analyzed, comprising

(a) sealing means in the entrance portion of said column;

(b) duct means for feeding a stream to be analyzed through said sealing means and into said column,

(c) means including a portion having a substantially conical shape coaxial with said axis of said column, said means extending below the surface of said packing material and cooperating with said duct means to equalize and flatten the waveform of said stream passing through said packing material.

2. Closure means for a chromatographic column according to claim 1 wherein said duct means is operative to direct samples to be analyzed successively toward and into said column.

3. Closure means for a chromatographic column according to claim 1 comprising a porous body consisting of at least one substantially disc-like component.

4. Closure means for a chromatographic column according to claim 1 comprising a substantially conical downwardly widening chamber in the lower portion of the sealing member, said chamber receiving at its apex the end of the capillary duct and housing the porous body above the packing material.

5. A sealing member for a chromatographic column, said column having a longitudinal axis and containing a packing material for receiving a stream to be analyzed, comprising

(a) sealing means in the entrance portion of said column;

(b) a porous body located between said sealing means and the upper level of said packing material excluding empty space therebetween; and

(c) means passing through said sealing means for directing said stream into said column, said means being operative to direct said stream through said porous body in a direction substantially transverse to said axis of said column;

(d) said duct means including a first member disposed below said porous body and positioned immediately over the surface of said packing material, said first member having a geometry to expose an annular exterior surface portion of said packing material directly to said stream passing through said porous body;

(e) said first member having a substantially conical shape coaxial with said axis of said column and extending below the surface of said packing material to equalize and flatten the waveform of said stream passing through said packing material.

6. Closure means as defined in claim 5 comprising a compressible porous body.

7. Closure means for a chromatographic column according to claim 5 wherein said duct means includes a second member cooperating with said first member to compress said porous body.

8. Closure means for a chromatographic column according to claim 7 wherein said first member includes a cavity and said duct means pass through said porous material into said cavity, said stream being initially introduced into said cavity and directed to flow axially through said porous body onto said annular surface portion of said packing material.

9. Closure means for a chromatographic column containing a packing material and receiving a stream to be analyzed, such closure means comprising in combination

(a) an elastic sealing member positioned in the entrance portion of the column;

(b) gripping means including an upper and a lower gripping member embracing and adjustably compressing said sealing member in axial direction thereof to seal said column and a porous body adjustably connected to the lower gripping member;

(c) a capillary duct substantially centrally arranged in said sealing member and said gripping means, said capillary duct feeding the stream to be analyzed through said porous body towards and into the column, said packing material filling the column substantially up to the sealing member without leaving empty spaces therebetween.

10. Closure means according to claim 9 comprising a chamber for housing said porous body and communicating with the column.

11. Closure means according to claim 10 comprising a nut member screwed with its upper end to the lower gripping member said nut member having an orifice in
its bottom end and forming said chamber for the porous body.

12. Closure means according to claim 11 wherein said orifice is tapered towards the column.

13. Closure means according to claim 11 comprising in said chamber a second sealing member having an axial conical cavity tapering towards the orifice in the bottom of the nut and housing said porous body.

14. Closure means for a chromatographic column containing a packing material and receiving a stream to be analyzed, such closure means comprising in combination
(a) an elastic sealing member positioned in the entrance portion of the column;
(b) gripping means including an upper and a lower gripping member embracing and adjustably compressing said sealing member in axial direction thereof to seal said column;
(c) a capillary duct substantially centrally arranged in said sealing member and said gripping means;
(d) a nut member adjustably attached to the lower gripping member to form a chamber for receiving from said capillary duct the stream to be analyzed; and
(e) a substantially disc-like porous member between said nut member and said lower gripping member, said porous member having an outer diameter smaller than the inner diameter of the column.

15. In closure means of the type described for a chromatographic column containing a packing material and receiving a stream to be analyzed, such closure means comprising in combination
(a) an elastic sealing member in the entrance portion of the column;
(b) gripping means including an upper and a lower gripping member embracing and adjustably compressing said sealing member in axial direction thereof to seal the column;
(c) a capillary duct substantially centrally passing through the upper gripping member and the elastic member into the lower gripping member, and having its exit end secured therein;
(d) a screw member screwed into the lower gripping member having a head portion of smaller diameter than the column; and
(e) a porous body between said head portion and the lower gripping member.

16. In closure means of the type described for a chromatographic column containing a packing material and receiving a stream to be analyzed, such closure means comprising in combination
(a) an elastic sealing member adjustably positioned in the entrance portion of the column;
(b) gripping means including an upper and a lower gripping member embracing and adjustably compressing said sealing member in axial direction thereof to seal the column;
(c) a capillary pipe substantially centrally passing through the upper gripping member and the elastic member into the lower gripping member, and having its exit end secured therein;
(d) a screw member engaging the lower gripping member opposite the exit end of the capillary pipe and leaving a chamber therebetween; and
(e) a porous body in said chamber.

17. In closure means of the type described for a chromatographic column containing a packing material and receiving a stream to be analyzed, such closure means comprising in combination
(a) an elastic sealing member adjustably positioned in the entrance portion of the column;
(b) gripping means including an upper and lower gripping member embracing and compressing said sealing member in axial direction thereof to seal said column;
(c) a capillary duct substantially centrally passing through said sealing member and said gripping means;
(d) a nut member screwed to the exit end of the capillary duct and having an outer diameter smaller than the inner diameter of the column; and
(e) a porous body between said nut member and said lower gripping member.

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