

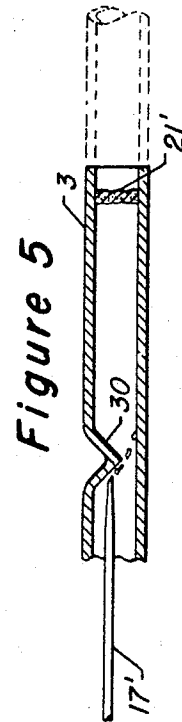
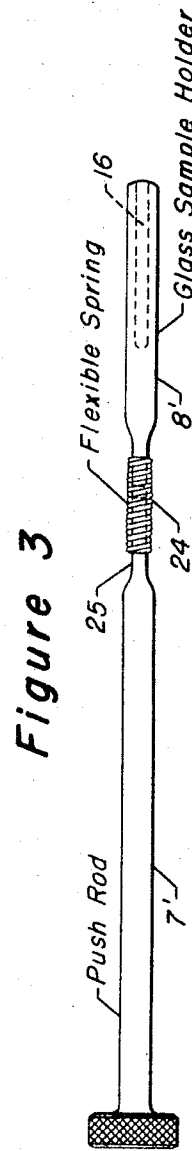
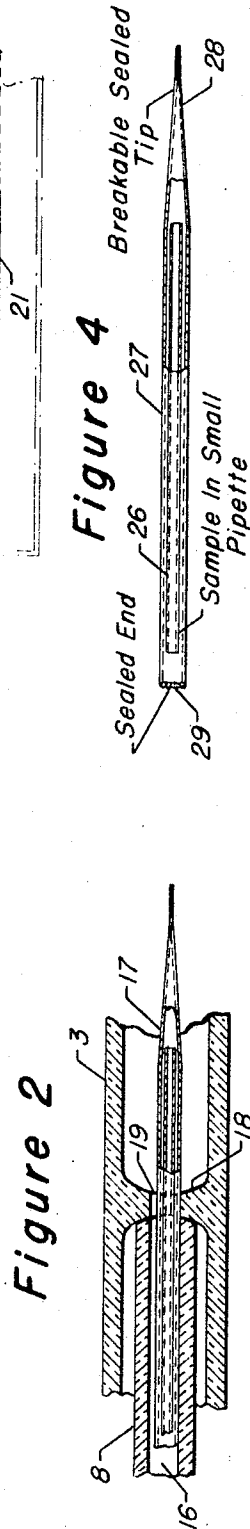
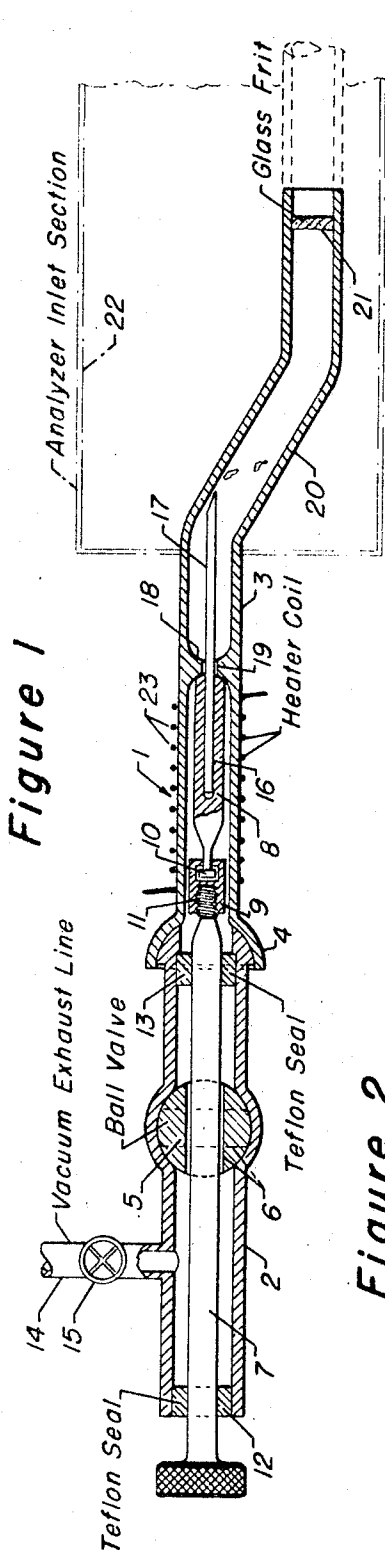
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SAMPLE INTRODUCTION APPARATUS

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SAMPLE INTRODUCTION APPARATUS
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9 Claims

ABSTRACT OF THE DISCLOSURE

A sample introducing apparatus for use with an analyzer having a vacuum lock zone, which apparatus utilizes a breakable sealed sample holder which is broken when the sample has reached a critical stage of introduction, thereby freeing the sample for analysis.

The present invention is directed to sample introduction apparatus adapted to accommodate wide boiling range samples. More particularly, there is provided an improved sample introducing system which overcomes poor reproducibility and other operational problems, such as the loss of a portion of sample being introduced into a mass spectrometer which operates under high vacuum conditions.

Various devices and systems are in present use for effecting the introduction of samples into a mass spectrometer unit, however, all appear to have limitations with respect to certain types of samples and, in particular, low boiling point materials which may be lost in part by fractionation in the presence of a vacuum condition. As a result, there has been the need in analysis laboratories to have apparatus to provide an operating system with ease of operation and good reproducibility in effecting the introduction of samples into various types of high vacuum analyzing equipment. For example, with low boiling point samples being inserted into such types of equipment there can be a substantial loss due to fractionation in a sub-atmospheric zone, as hereinbefore noted, or an undesired intake of air with the sample. On the other hand, in connection with high boiling point materials, conventional introduction equipment for mass spectrometer analyzers has at times provided a problem from vaporization of a portion of the sample upon its insertion into the inlet or oven portion of the analyzer unit and then an almost instantaneous upstream flow and condensation of the sample on the cooler inside wall of that portion of the chamber outside the oven zone.

It is recognized that recent commercially available sample introducing devices or systems have generally provided for the elimination of the intake of air with the sample through the use of a "vacuum lock" arrangement. Such an arrangement makes use of spaced seals and an intermediate vacuum connection means such that air can be exhausted from around the sample holder means as it is being introduced into the sample introducing apparatus. In addition, recent commercially available devices have provided capillary tube holding means or "double-ended dipper means" to hold a small test sample; however, it appears that such means are generally restricted to satisfactory use with samples of C_{11} or heavier hydrocarbon materials. The C_{10} and lighter components are, as hereinbefore noted, found to be fractionated out of the dipper during the evacuation of air from the vacuum lock zone. In still other introduction systems, there has been tried the use of holding a sample in contact with a liquid metal; however, in this instance two major problems have been encountered. In certain instances the samples tend to react with the metal surfaces, while in other instances the metal surfaces tend to act as catalysts and promote the decomposition of the samples. Ideally, a sample introduc-

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tion system should provide for reproducibility and there should not be any decomposition of the sample nor of the metal holding the sample such that there will be an introduction of a different quantity of sample upon different test operations.

It may be considered a principal object of the present invention to provide a sample introducing apparatus which incorporates the use of a sealed capillary tube to hold the sample and internal means within the downstream end of the inlet chamber which will effect a breakage of the sealed capillary tube when it has reached a critical stage of introduction.

A further object of the improved invention provides, in a preferred embodiment, a special glass type of holder tube with a flexible or movable attachment to the elongated movable plunger means such that the sample holder can move slightly in a "self-aligning" manner. This arrangement precludes a preliminary breakage of the sealed capillary sample holding tube as it is being introduced through the sample introducing chamber into the analyzer means.

Broadly, the present invention provides in connection with sample introducing apparatus which is adapted to inject a small sample of material to be tested into analyzer means, and with such apparatus including means for having a vacuum lock zone in the upstream end thereof, an intermediate valve member, a removable shaft member for holding a sample and adapted to slidably fit within and pass through the elongated tubular chamber portion of the apparatus, the improved construction and arrangement which comprises providing a sealed, breakable glass tip sample holding tube means for placement in the end of the movable shaft member and, in addition, providing within the downstream end of the inlet chamber a glass breaking surface in alignment with the shaft member and the sample holding means therein whereby the breakable tip on the sample holding tube means will be shattered and provide a release of sample therefrom.

Various constructions may be provided to effect the internal breakage of the internal or downstream tip end of the sample holding tube and the invention should not be limited to the designs shown in the drawing. For example, there may be the provision of an off-set wall portion within the downstream end of the sample introducing tube or chamber. However, a suitable internal baffle or shoulder like projection which extends into the path of the sample introducing shaft will serve to provide for the breakage of the tip of a sample holding capillary tube.

A preferred design and arrangement of the improved system makes use of heat resistant glass at the interior or downstream end of the sample introducing apparatus, particularly that portion of the unit which will be within a heated zone of the analyzer means where there could be an undesired reaction with the sample material. The upstream end of the device may well be formed of stainless steel or of a plated material, although a preferred design may have provision to have wall heating by an electrical coil or other means so as to preclude having a cool internal wall surface which would encourage condensation of any sample material being released within the downstream end of the unit. Generally, the upstream or inlet end of the sample introducing chamber will have spaced air-seal members, a suitable intermediate valve, and an exhaust port between the seals such that there may be a vacuum exhaustion or any air which is initially carried along with the sample introducing shaft.

The removable sample introducing shaft or push rod means may utilize stainless steel or other suitable metal for the exterior portion thereof or at least that portion which never passes beyond the inlet end of the device; however, in accordance with the present invention, a preferable design utilizes a glass section at the interior or

tube is to be held so that there is no metal present to react with the sample material upon its release into the heated inlet of the analyzer unit. In addition, such glass sample holding end portion, shall, in a preferred design, be flexibly connected to an elongated pushing section to permit downstream end of the push rod where the glass capillary the breakable sample holder to seek a non-rigid, self-aligning path through the valve and other orifices in the elongated chamber without causing a breaking of the capillary tube.

With regard to the breakable tip sample holding means itself, there is preferably utilized a small pipette or capillary tube which has a downstream end drawn out to a fine sealed tip portion which can be easily broken upon its impact with an interior projection in the downstream end of the unit. For convenience, the actual sample may be introduced into or retained within a conventional form of small pipette with unsealed ends; however, the latter should then be placed within a slightly larger capillary tube having one end sealed with the elongated breakable tip, as noted hereinbefore. Subsequently the other end should be sealed such that there is no chance of loss of sample by fractionation under vacuum conditions, or any contamination by admixture with air upon its initial placement within the sample introducing apparatus.

Reference to the accompanying drawing and the following description in connection therewith will serve to set forth the embodiment of the improved sample introducing device, as well as point out additional advantageous features resulting from the use thereof, particularly where samples are to be introduced into analysis means operating at high vacuum conditions.

FIGURE 1 of the drawing is a sectional elevational view indicating one preferred embodiment of the modified and improved sample introducing system.

FIGURE 2 indicates in an enlarged view the preferred improved construction where the glass sample holder effects a "dry seal" with an orifice section just upstream from the sample release zone.

FIGURE 3 of the drawing indicates a modification in the design and construction of the sample push rod or movable shaft means and the flexible connection of a glass sample holder means.

FIGURE 4 shows, in an enlarged view, a preferred method of sealing the sample material within a small capillary tube.

FIGURE 5 of the drawing shows, in a partial view, a modified construction and arrangement of the downstream portion of the chamber for effecting the breakage of the sample holding capillary tube.

Referring now particularly to FIGURES 1 and 2 of the drawing, there is shown an elongated tubular form of sample introducing device 1 having an upstream end portion 2, which may be formed of stainless steel or other suitable type of metal, and a downstream end portion 3 which is preferably formed of a refractory glass material. The two sections may be suitably joined together at a splice or seal section 4 such that the resulting unit is entirely air tight. The external end portion or inlet end 2 of the device is, in this embodiment, provided with a ball valve member 5 having a straight through passageway 6 of a size permitting the longitudinal passage of a push rod or shaft member 7 and a downstream glass sample holder end portion 8. In this instance, the latter is shown rigidly connected to the end of push rod 7 by means of a threaded coupling 9 which is adapted to fit over a flanged end portion 10 on the glass holder means 8 and make a tightly screwed attachment to a threaded end portion 11 on shaft 7.

Within the end portions of the upstream end portion 2 of the device, it will be noted that there are provided the spaced apart Teflon seal members 12 and 13. Seal ring 12 is at the very outer end of the unit and seal 13 is downstream from the ball valve member 5, such that the push rod 7 is maintained in a relatively air tight, but movable slip-fit within the unit as the sample material is being

introduced into the apparatus. Also, in accordance with a preferred design, an exhaust port 14 with valve means 15 is provided upstream from the valve 5 and between the spaced seal members 12 and 13 such that there may be a connection to a vacuum exhaust line and all air eliminated from the inlet end portion of the device as a sample is being introduced therethrough.

In accordance with a particular feature of the present invention, it will be noted that the sample holder means 8 is provided with an internal slot or elongated recess 16 sized to accommodate sealed capillary tube means 17. Also, as better shown in the enlarged FIGURE 2, there is an internal special partitioning and seating section 18 with an orifice 19 so as to permit the downstream passage of the sample holding capillary tube 17 while at the same time providing a seating surface or "dry orifice seal" with respect to the very end portion of the sample holder 8. Preferably, the upstream face of the partitioning section 18 is ground in a concave manner, or otherwise smoothed, to provide a close seal fit with a matching convex face or surface at the end tip of portion 8. Thus, there is precluded any upstream or backward flow of sample as it is released from the broken capillary tube means 17 in the release zone of the device.

It will also be noted in connection with the present embodiment of the unit, that the downstream end portion 3 of the sample introducing apparatus has an off-set wall portion 20 to provide a glass breaking wall surface in alignment with the breakable tip portion of capillary tube 17 whereby the sample material will be released as the push rod simultaneously carries the holder 8 portion forward into a dry seal contact with partition 18. In addition, it will be noted that the present improved embodiment provides for the placement of a suitable glass frit barrier 21 at the interior end of tubular section 3 so that broken glass particles from capillary tubes 17 will be prevented from passing into the analyzer equipment.

In carrying out the manual operation of the present improved sample introducing system it will of course be necessary that the shaft or push rod member 7 together with sample member 8 is initially removed from the elongated chamber portions 2 and 3, a sealed portion of sample material inserted within tube means 17 and the latter then held within the recess portion 16 of holder means 8. The holder is then inserted into the external end portion 2 of the unit and the valve 5 operated to permit the passageway 6 to be in an axial alignment with the chamber and in turn allow the entire passage of sample containing tube 17 in holding means 8 through the inner Teflon seal 13. At this stage, there is effected a vacuum exhaust operation to remove air that may be surrounding the tube holder means 8 and the presently inserted length of shaft member 7. After the removal of air and while there is a vacuum maintained on the inlet end of the system, there may be a further insertion of the rod 7 along with tube holding means 8 such that the breakable capillary sample tube 17 enters orifice 19 and proceeds toward the off-set wall portion 20 in the downstream end of the chamber section 3. Preferably, the spacing of diaphragm section 18 and the lengths of shaft 7 and holder means 8 are correlated such that as the end of the section 8 approaches contact with upstream ground seating surface of partition 18 there will be a dry seal contact between such two portions and simultaneously there shall be an impact of the breakable glass tube 17 against the face of off-set wall portion 20. The sample material will thus be released into the downstream end section 3 beyond the dry seal zone at 18 and within a vacuum zone normally provided within an analyzer inlet section, such as indicated by dash lines 22, whereby sample can be vaporized and pulled through a glass frit section 21 into the analyzer means itself. Generally, the analyzer inlet section 22, although not shown in detail, will be within a heated oven section, as well as connective with vacuum means, whereby the sample material is readily vaporized and drawn into the analyzer itself.

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After the sample has been released from the broken capillary tube means 17, then the remaining portion of such broken tube 17 can be carefully withdrawn with the rod 7 and holder means 8 from the unit, with ball valve means 5 being closed immediately as the sample holding tube portion is withdrawn therefrom, and before air can enter the inlet end of section 2.

It may be still further noted in connection with the embodiment of FIGURE 1, that a suitable electric heater coil 23 is indicated diagrammatically as surrounding the upstream end portion of glass tube section 3, particularly around the zone of the dry seal at orifice 19 whereby condensation of heavier sample materials will be precluded. Generally, the heater coil 23 will be of the electrical resistance type and may also be provided with suitable insulation (not shown) so as to enhance the transmission of heat through glass 3 into the interior thereof. The heater coil should, of course, provide a temperature which will be substantially equivalent to that of the analyzer section 22 in order to eliminate any tendency for released sample to have a backward flow and condense on the interior wall of a cooler inlet section. As indicated hereinbefore, particularly with respect to the heavier materials being analyzed, there can be a tendency for such fractions to immediately flow upstream and condense on a cool wall section rather than carry on downstream and into the analyzer in a vaporized form.

Reference to FIGURE 3 of the drawing shows a modification in the connection of the glass sample holder means to a steel shaft or push rod means. In other words, there is shown a glass sample holder 8' which may be of a rather similar construction to 8 within FIGURE 1 of the drawing, except for an upstream end portion is relatively smooth and is adapted to have flexible spring coupling means 24 encompass such portion. The spring 24 also wraps around and connects to a smaller diameter end portion 25 on shaft means 7' to be of the nature of a sleeve type coupler. The flexible spring 24 may be of a generally conventional spiral wound form with an internal diameter providing a tight slip-fit over the ends of the adjacent portions; however, the spring should be of a spring steel material of sufficient gage to preclude excessive bending or movement when the entire shaft assembly is removed from the elongated chamber. This modified construction has been found to provide some freedom of movement of the glass sample holder means 8' as compared with the tight sleeve arrangement of FIGURE 1, such that there may be a self-aligning aspect provided to the sample holding capillary tube means 17, as well as for the glass sample holder itself, as the push rod 7' is inserted into the elongated chamber of the unit. For example, the flexibility is of particular advantage in permitting the glass capillary tube 17 to seek out and pass through the orifice 19 in partitioning means 18 and thus eliminate any preliminary breakage of the capillary tubing until such time as it passes the off-set wall portion within the inlet section of the analyzer, as well as at such time the capillary tube holding means is ready for contact with the dry orifice seal upstream face of partition means 18.

FIGURE 4 of the drawing shows, in an enlarged view, one preferred arrangement for sealing an open-ended small capillary tube or pipette 26, after having being filled with the desired material to be tested, within a larger pipette or capillary tube 27. Generally, the capillary tubes 27 will be heated and formed so that they have elongated breakable but sealed tip ends 28 and open upstream end portions. Each of the latter can subsequently be sealed, as shown at 29, after there is insertion of a filled sample pipette 26. By following this system of introducing material into an analyzer, it will be found that substantially uniform quantities of sample may be held within the small pipettes 26 and then subsequently placed in a sealed breakable capillary tube 27

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for the entire handling and insertion periods by shaft holding means 7 and 8. The release of sample is then subsequently accomplished only after there has been careful evacuation of air and proper sealing of the entire push rod assembly within the interior of the tubular chamber portions 2 and 3 along with effecting a dry seal at the seat on section 18 almost simultaneously with the breakage of the tip portion of the sample holding capillary tube means.

FIGURE 5 of the drawing indicates diagrammatically the utilization of an indentation or small shoulder type off-set 30 within the downstream end portion 3' of the tubular chamber. This particular design and arrangement eliminates the need of a total off-set portion, such as 20 in FIGURE 1 of the drawing, for effecting the breakage of the downstream tapered end of the sample holding capillary tube means such as 17'. The depending wall portion 30 shall, of course, be sufficient to reach into the axially positioned pathway of the capillary tube means 17' and provide a breakage surface for the tip of the latter and the release of the sample into the downstream end of the unit. Again there is indicated a suitable glass frit means 21' which will permit the passage of sample material vapor therethrough into the analyzer means without, however, permitting the passage of any glass particles which will of course result from the breakage of the tapered tip portion of the capillary tube 17'.

In view of the modification shown in FIGURE 3 for the connection of sample holder tube means 8' to the external push rod means such as 7', as well as the modification of FIGURE 5 for effecting breakage of the capillary tube means, it will be obvious that still further variations in design and construction may be effected within the scope of the present invention. For example, glass breakage shoulders or projection sections within the downstream end portion of the unit may be separately inserted sections, rather than dimpled or off-set portions of the unit itself. Still further, suitable shaft or push rod means for inserting the sample may be entirely formed of glass and need not be made of the composite design providing stainless steel for the external portion and glass for the internal portion. However, in all instances, a preferred embodiment of the apparatus utilizes glass for that section or zone thereof which accommodates the release of the material so as to preclude samples from reacting with a metal wall or holder means and adversely effecting the reproducibility of analyzing operations.

A preferred embodiment of the presently improved unit also utilizes a vacuum lock arrangement between suitable air-seal means in the inlet end portion; however, again it is not intended to limit the scope of the present invention to any one type of seal means or to any one type of valving means inasmuch as various types of seals and vacuum lock arrangements may be provided to accomplish air removal and the preclusion or loss of sample exteriorly of the intake to the analyzer equipment.

I claim as my invention:

1. In a sample introducing apparatus adapted to inject a sample of material to be tested into an analyzer means, said apparatus having an elongated, open-ended tubular form of inlet chamber with an intermediate valve member, spaced air-seal means in the upstream end thereof together with an exhaust port therebetween for providing a vacuum zone therein, and a movable shaft member for holding a sample and adapted to slidably fit within and pass through said tubular chamber for the introduction of a sample into the downstream end of such apparatus, the improvement which comprises, providing a sealed breakable glass tip sample holding tube means for placement at the end of the movable shaft member and, in addition, providing a glass breaking surface within the downstream end of said inlet chamber and in alignment with said shaft member and the sample holding means, whereby the breakable tip of said sample holding tube means

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will be shattered and provide for the release of sample therefrom.

2. The apparatus of claim 1 further characterized in that a downstream wall portion of the tubular form inlet chamber has an off-set wall section providing an internal wall surface in alignment with said movable shaft member to effect the breakage of the tip of the sample holding means.

3. The apparatus of claim 1 further characterized in that transverse internal partitioning means is positioned in the downstream end portion of the inlet chamber and is provided with a central orifice permitting the passage of said sample holding tube means and such partitioning means has an upstream seating surface adapted to engage a suitably matching end portion of a sample holding section at the downstream end of the shaft member whereby there is a seal made between the two adjacent surfaces to preclude an outward flow of sample as it is released from said breakable tip sample holding tube means.

4. The apparatus of claim 1 further characterized in that the downstream end portion of said tubular inlet chamber is of glass and said movable shaft member for holding a sample has a downstream glass portion in turn provided with slotted means adapted to removably hold breakable tip glass sample holding tube means whereby entirely non-metallic materials are within the zone of the sample release.

5. The apparatus of claim 4 still further characterized in that said downstream glass portion of the movable shaft member connects with an upstream portion thereof by means of a flexible spring coupling means whereby the downstream glass sample holding portion may be free to move slightly laterally and provide self-alignment as the movable shaft member is pushed into and through the tubular chamber.

6. The apparatus of claim 1 further characterized in that a downstream end portion of elongated tubular form chamber is provided with a porous transversely positioned glass frit permitting withdrawal of vaporized sample while precluding the passage of broken glass particles.

7. The apparatus of claim 1 further characterized in

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that the tubular inlet chamber is provided with external heater means around that section which is just upstream from the zone of the sample release, whereby there is heating of the inlet chamber in a manner to preclude a cool internal wall surface which would permit condensation of released sample material.

8. The apparatus of claim 1 further characterized in that said breakable tip sample holding tube means is of a capillary size removably and frictionally held within compatibly sized recess means at the interior end of the movable shaft member to provide a sample holding end portion, and such sample holding capillary sized tube means is entirely of glass being provided with a breakable sealed tip at the downstream end thereof.

9. The apparatus of claim 8 still further characterized in that said breakable tip glass sample holding tube means comprises a capillary tube portion with a tapered sealed tip and is sized to hold a separate internally insertible open-ended sample holding pipette and subsequent to the insertion of the sample holding pipette an upstream seal is provided on said external capillary tube.

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