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APPARATUS FOR INTRODUCING LIQUID SAMPLES TO MASS SPECTROMETERS

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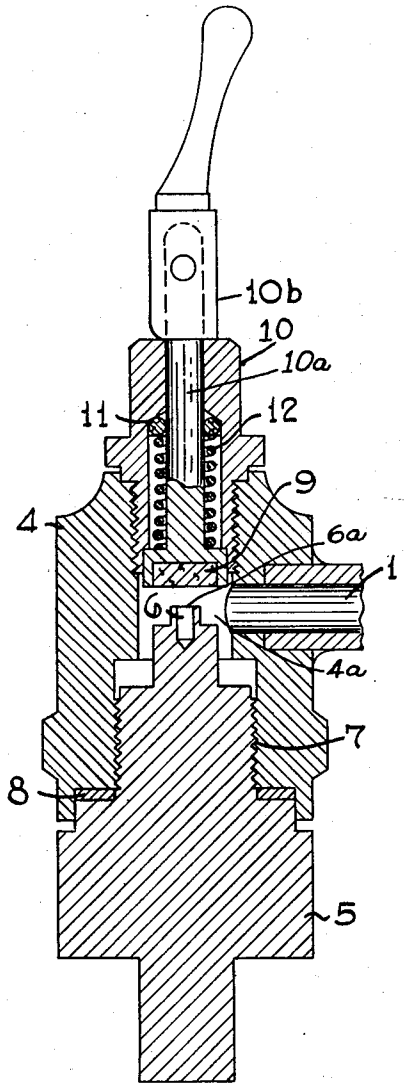


FIG.-1

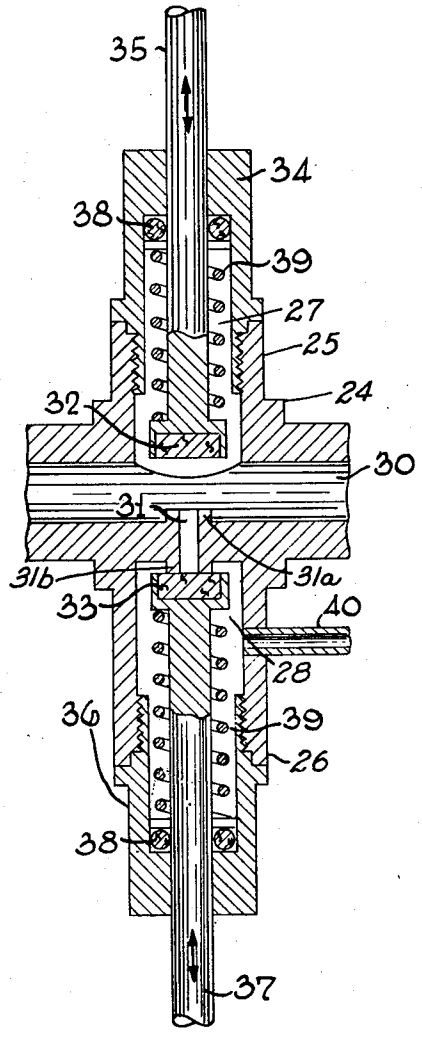


FIG.-2

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APPARATUS FOR INTRODUCING LIQUID SAMPLES TO MASS SPECTROMETERS

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This invention concerns a novel apparatus adapted for introducing liquid samples to a mass spectrometer. In accordance with this invention, apparatus is provided characterized by a sample receiver which is machined to provide a fixed volume closed off by at least one valve to permit sealing within the sample receiver a fixed quantity of liquid sample. The apparatus includes suitable connecting lines leading to the evacuation system of a mass spectrometer. This arrangement permits the liquid sample contained in the sample receiver to be completely withdrawn into the mass spectrometer when the sample receiver is uncovered.

The use of mass spectrometers for laboratory and even for plant control purposes has been greatly extended in recent times. It is now known that the mass spectrometer provides accurate, rapid, quantitative analyses of a wide variety of chemical mixtures and combinations. Particularly in the petroleum industry it has been found to be a useful analytical tool for the analyses of hydrocarbons having from 2 to 15 carbon atoms or more. However, the extension of the use of the mass spectrometer to organic compounds which are normally liquid has created a problem as regards suitable methods for introducing liquid samples to a mass spectrometer. This is particularly a problem when it is necessary to periodically sample a flow stream from a continuous process which is being monitored.

Heretofore, the methods which have been suggested for introducing liquid samples to a mass spectrometer have depended upon the vaporization of the liquid samples. For example, the sample may be vaporized by passage through a sintered glass plate or through a fine capillary sealed by mercury. However, when employing either of these procedures, it has been found that fractionation of the sample occurs so that the heavier constituents of the sample are either not vaporized into the mass spectrometer or they are not vaporized in aliquot portions. Consequently, it is the primary object of this invention to provide sample introduction apparatus adapted for use with a mass spectrometer so as to insure complete vaporization of the entire liquid sample eliminating any fractionation of the sample.

In accordance with this invention, this objective is obtained by essentially employing a valve assembly connected to the evacuation system of the mass spectrometer, capable of sealing a particular volume of liquid sample in a valved space. By operation of the valve after the mass spectrometer has been evacuated, it is thus possible to fully vaporize all of the liquid sample so that a true and accurate vapor composition is obtained in the mass spectrometer corresponding to the composition of the liquid sample. It is a particular feature of this invention that such a sample introduction system is well adapted for application to a periodic sampling system applicable to frequent and repetitive analyses of a plant stream.

The nature of the apparatus of this invention may be appreciated by reference to the accompanying drawing in which:

Fig. 1 diagrammatically illustrates in cross-sectional elevational detail sampling apparatus adaptable to laboratory use, while

Fig. 2 illustrates in cross-sectional elevational detail an embodiment of this apparatus applicable to the periodic analysis of a continuously flowing liquid stream.

Referring first to Fig. 1, the entire apparatus illustrated is connected to and fixed to line **1** leading to an evacuation system such as may be provided by a mass spectrometer, not shown. The liquid sample introducing apparatus itself, consists of a housing assembly including two main body members or portions, an upper portion identified by the numeral **4** including a suitable type of valve, and a lower portion indicated by the numeral **5** including a sample receiver identified by numeral **6**, the housing assembly providing a hollow chamber designated by the numeral **4***a*. In the apparatus of Fig. 1, elements **4** and **5** of the apparatus are maintained in threaded relation, or other means may be employed to permit a convenient removal of the lower portion **5** from the upper portion **4**. As illustrated, this may be accomplished by providing threads **7** between elements **4** and **5** and by providing suitable bearing surfaces on elements **4** and **5** to permit compression of a sealing gasket **8** therebetween. Thus, by turning the lower portion **5**, this portion of the apparatus may be removed from the upper portion including the valve. Consequently, a liquid sample may be introduced to the sample receiver **6**, as, for example, by means of a hypodermic needle. As will be seen, the size of the liquid sample ultimately introduced into the mass spectrometer is fixed entirely by the size of the sample receiver **6** when this chamber is filled with liquid so as to be flush with the top edge of the sample receiver. However, in filling the sample receiver, no care or precision is required as it is only necessary that sufficient liquid be supplied to the receiver **6** to entirely fill this receiver, leaving a surplus of liquid in the form of a convex meniscus. On then screwing the lower portion **5** of the apparatus into the upper portion **4**, tightly sealing elements **4** and **5** by virtue of seal **8**, the liquid sample receiver **6** will be contained within the chamber **4***a* below and in the general vicinity of the valve plate **9**. The valve **10** operating valve plate **9** may be of any desired construction to permit bringing the valve plate **9** firmly against the top edge of sample receiver **6**, the top edge of the receiver forming an annular valve seat designated by the numeral **6***a*. Thus, as illustrated, valve **10** is a toggle valve assembly disposed in threaded engagement with the body member **4** and including a valve stem **10***a* secured at its inner end to a valve plate **9** and at its outer end to a toggle lever **10***b*, and equipped with the seal bearing **11** and the coil spring **12** so that on operation of the valve, valve plate **9** will be caused firmly to engage the annular seat **6***a* to seal the sample receiver **6**. This sealing operation will also be effective to squeeze out the excess liquid formerly introduced to the sample receiver so that the quantity of liquid remaining in the sample chamber will be exactly determined by the volume of the receiver **6** provided in the lower element **5**. This volume may be any volume desired, but is generally and preferably about 0.01 cc. It is apparent that a suitable material must be chosen for valve plate **9** to secure effective sealing of the sample receiver without undue deformation or wearing of the valve plate. Suitable materials, for example, are Teflon, synthetic rubber and Nylon. A preferred material for valve plate **9** is presently contemplated to be the plastic known by the trade name of Teflon consisting of fluorine and carbon having the formula: $(CF_2)_n$.

In the operation of the apparatus of Fig. 1, as indicated, element **5** is removed from element **4** to permit introducing an excess of liquid sample to the sample receiver **6**. Thereafter, element **5** is replaced in element **4** so as to tightly seal elements **4** and **5** together. Valve **10** is then operated to seal the sample receiver by the seating of valve plate **9** on the annular seat **6***a* so as to squeeze all excess liquid from the sample receiver. Thereafter, the evacuation system not shown may be operated so as to fully evacuate the interior chamber **4***a* of the housing assembly shown in the drawing except for the liquid sample sealed in sample receiver **6**. The evacuation will permit removal of excess liquid squeezed from sample receiver **6** on closure of valve **10** and evacuation of the mass spectrometer must be continued until complete evacuation of excess liquid sample has been achieved. The valve **10** may then be operated so as to expose the liquid in the sample receiver **6** causing the flash distillation of the liquid and resulting in the complete vaporization of all liquid contained in sample re-

ceiver 6. By this means it has been found that complete vaporization of a liquid sample may be achieved so that an accurate vaporized sample may be obtained in the mass spectrometer.

Referring now to Fig. 2, a second embodiment of this invention is shown operating on the principles described in connection with Fig. 1, but being adapted to the sampling of a flowing liquid stream. Thus, as illustrated, the housing assembly includes a body member 24 which defines a conduit 30 through which a liquid stream to be sampled is passed continuously. Conduit 30, for example, may either be a conduit through which a total process stream is conducted or through which a side stream is passed for recirculation to a main stream or reactor. The body member 24 also includes diametrically opposed housing portions 25 and 26, each defining an outwardly opening interior chamber designated by the numerals 27 and 28, respectively. As shown, the chamber 27 opens inwardly into the conduit passageway 30, and the outer end is closed by means of a valve bonnet 34 threaded into the outer end of the housing portion. The outer end of chamber 28 is closed by means of a similar valve bonnet 36. Each of valve bonnets 34 and 36 supports a valve stem 35 and 37, respectively. Each valve stem extends through a bonnet longitudinally thereof into the interior of one of said of the related chambers 27 and 28, respectively. The valve stems 35 and 37 terminate at their inner ends in valve plates 32 and 33, respectively. As indicated by directional arrows in Fig. 2, the valve stems 35 and 37 are movable reciprocally and longitudinally in the bonnets 34 and 36. A drilled elongated port 31 is provided in the wall of conduit 30 having bosses at either end thereof, which, as will be seen, provide annular valve seats 31*a* and 31*b* for valve plates 32 and 33, respectively, at either end of the drilled port. The drilled port 31 in combination with either or both valve plates 32 and 33, when applied to the seats 31*a* and 31*b*, respectively, constitutes the liquid sample receiver in the apparatus of Fig. 2 and so is to be drilled to provide a cylindrical volume of the desired size, as, for example, a volume of about 0.01 to 0.3 cc. As illustrated, the valve construction includes seal rings 38 and coil springs 39 operative to force valve plates 32 and 33 firmly against the upper and lower valve seats 31*a* and 31*b*, respectively, of the sample receiver 31. While any desired valve may be used for this purpose, to permit manual operation of the sampling device, it is preferred that the valves be of the motor driven cam or solenoid type to permit automatic electrical operation, as will be described. A conduit 40 leads from the interior of valve bonnet 36 connecting to the expansion chamber of a mass spectrometer. Consequently, assuming that a liquid sample of the material flowing in conduit 30 is trapped in sample chamber 31 by closure of both valve plates 32 and 33 against the seats 31*a* and 31*b*, respectively, operation of the evacuation system of the mass spectrometer will be effective to completely evacuate the interior chamber 28 in housing portion 26. On then lowering valve plate 33 by operation of valve stem 37 while maintaining upper valve plate 32 against the upper portion of sample receiver 31, the liquid sample contained in the sample receiver will be flashed into the mass spectrometer through conduit 40. At the same time, this operation will evacuate the sample receiver 31 so that on raising valve stem 37, the sealed sample receiver will be highly evacuated. On then raising valve stem 35, a liquid sample from conduit 30 will be pulled into the sample receiver to fill the vacuum. The sample sequence can then be repeated by again lowering valve stem 35 against the upper boss of sample receiver 31 to seal the liquid sample in the sample receiver and to permit removal of the sample into the mass spectrometer on the subsequent lowering of valve stem 37.

As described, therefore, operation of the apparatus of Fig. 2 simply depends upon the sequential operation of valve stems 35 and 37. As indicated, while this sequential operation may be manually conducted, it is particularly contemplated that motor-driven cams or solenoids be employed to operate valve stems 35 and 37 in the desired manner. The solenoids may be automatically operated to provide any desired cycle of sampling.

What is claimed is:

1. A liquid sample transfer apparatus, comprising a housing assembly, including a hollow chamber therein, a liquid sample receiver wholly contained in said housing assembly and having an open end portion communicating with said chamber, an annular valve seat encircling said open end portion, a valve means supported within said chamber for reciprocal motion toward and away from said valve seat and engageable in fluid tight relation therewith to seal said receiver from the chamber, and a separate conduit communicating directly with said chamber for evacuating said chamber and therethrough said sample receiver when in communication with said chamber.

2. An apparatus according to claim 1, in which said housing assembly comprises a pair of mated structural body members engageable in fluid tight relation to define said hollow chamber between them, said liquid sample receiver is a recessed portion in one of said body members and said valve means includes a valve stem and a valve plate carried by the other body member of said mated pair so as to be extensible into said chamber to engage said annular valve seat.

3. A liquid sample transfer apparatus, comprising a housing assembly including a body member defining a fluid conduit passageway therethrough, a first hollow housing portion carried by said body member, a second hollow housing portion carried by said body member in opposed relation to said first portion diametrically of said body member, each of said portions defining an interior chamber, there being an elongated port provided between said conduit passageway and said interior chamber defined by said second housing portion, said port opening at one end into said conduit passageway, and at the other end into said chamber, an annular valve seat at each end of said port, valve means disposed in the interior chamber of each housing portion, each valve means including a valve stem and a head portion thereon disposed for reciprocal motion toward and away from one of said annular valve seats, alternately to place said port in communication with one of said conduit passageway and said interior chamber defined by said second housing portion, said port in conjunction with said valve head portions forming a sample receiver, and a separate conduit communicating with the interior chamber in said second housing portion for evacuating said chamber and thereafter said sample receiver when in communication with said chamber.

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