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FLAME IONIZATION DETECTION APPARATUS AND METHOD

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2 Sheets-Sheet 1

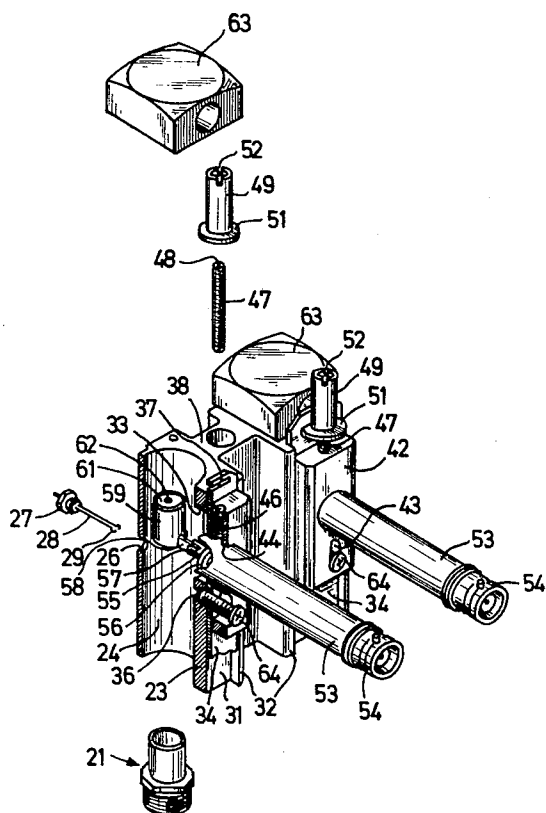


Fig. 1

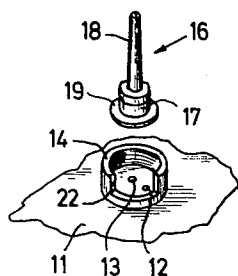


Fig. 2

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Fig. 3

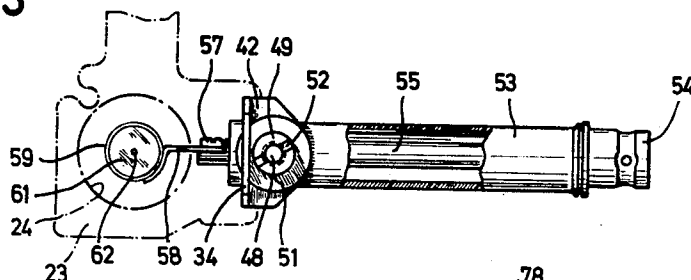


Fig. 4

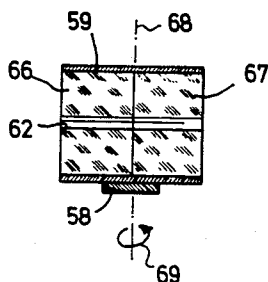


Fig. 5

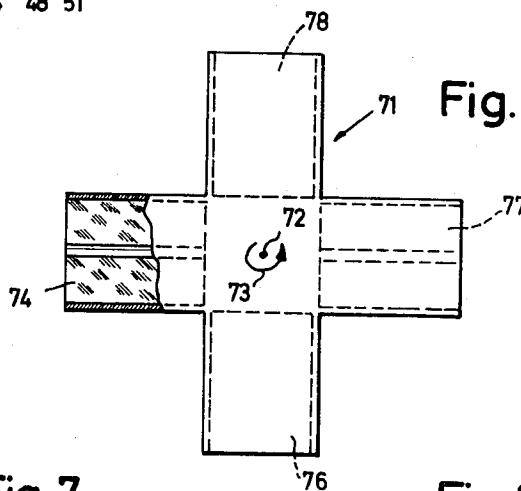


Fig. 6

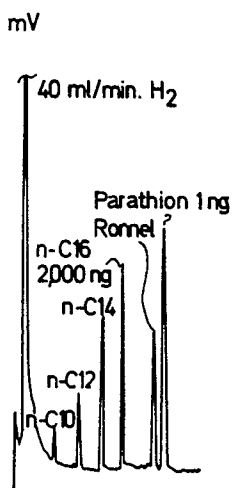


Fig. 7

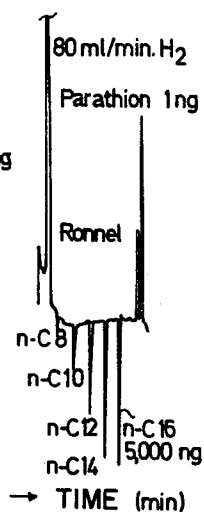
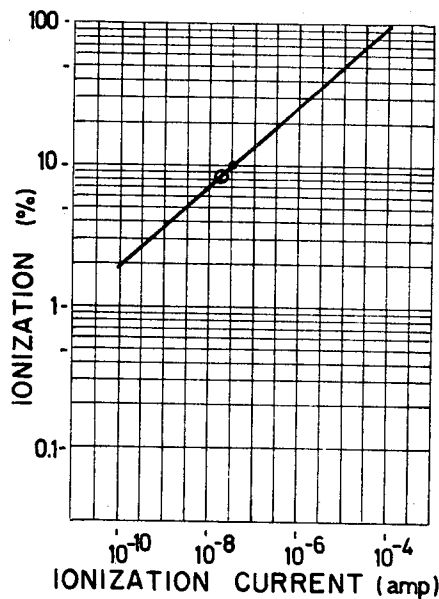


Fig. 8



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FLAME IONIZATION DETECTION APPARATUS
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10 Claims

ABSTRACT OF THE DISCLOSURE

A flame ionization detector for use in gas chromatography includes a collector ring which is positionally adjustable with respect to a flame nozzle. The collector ring supports one or more pieces of salt in an interchangeable manner, each salt being operable to amplify ionic current in a different substance. Pesticide components such as phosphorus and nitrogen are distinguished from hydrocarbons and chlorinated substances by the differences in magnitude and polarity of the corresponding peaks obtained on a chromatogram. This is achieved by optimizing the collector ionic current and gradually increasing the quantity of combustible gas supplied to the detector.

BACKGROUND OF THE INVENTION

The present invention relates in general to a flame ionization detector for a gas chromatograph.

A typical flame ionization detector includes a housing, a flame nozzle, a carrier gas and combustible gas inlet leading to the flame nozzle, a compressed air inlet leading inside the housing, a piece of salt disposed above the flame nozzle and having a longitudinal bore, a collector ring mounted above the flame nozzle, and an electrical connection to the collector ring for measuring ionic current.

If phosphorated compounds, such as those occurring particularly in pesticides, are passed through the column of a gas chromatograph and, afterwards, fed together with a carrier gas into the detector, its ion current is substantially increased if a certain salt is located in the flame.

In the course of time these detectors have been improved by mounting a compressed diatomite salt cylinder with a central bore on the flame nozzle. Nevertheless, a great number of problems have occurred, particularly since, in gas chromatography, it is very important to keep specific parameters constant.

Variations in sensitivity occur when the combustible gas (H_2) is discharged according to the gas regulator through leakage holes in the detector. Such a leakage outlet can be formed in the space between the pressed piece of salt and the nozzle. The sensitivity can be varied if the salt is displaced relative to the nozzle. One way to avoid these dangers is to introduce silicone between the pressed piece of salt and the nozzle. Silicone is so viscous that it holds the salt against the nozzle so that it cannot rotate. Therefore, in this case silicone constitutes an adhesive agent, and it also seals existing leaks. However, this presupposes that during chromatography the temperature of the detector cannot exceed $300^\circ C$. Otherwise, the silicone may evaporate and become uneven at some points. Therefore, the salt may become obliquely positioned on the nozzle and the flame directed more towards the collector electrode which then extracts too much heat from the flame. If the flame changes shape, the temperature and sensitivity also change. Turbulence in the flame always gives rise to flickering. Because the temperature of the detector cannot exceed $300^\circ C$, it is necessary to dispense with the so-called temperature programmed gas chroma-

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tography in this range and higher ranges of temperature.

In the heretofore known apparatus, the quantity of combustible gas flow is set at an optimum for the flame. However, the optimum for the flame does not always coincide with the optimum for separation in gas chromatography. To combine both optimum conditions in the apparatus entails considerable difficulties.

The detector output may be recorded to produce a chromatogram comprising a plurality of peaks representing different substances. When pesticides are to be detected in a particular composition, it is desirable that these peaks clearly distinguish the pesticides from other substances detected, such as hydrocarbons and chlorinated compounds.

In the course of time a crater appears in the piece of salt in the known apparatus. This causes an undesirable change in the shape of the flame and thus a change in the sensitivity of the detector.

Sometimes it may be desired to use detectors which are selective for certain substances in a normal fashion, i.e. without introducing salt. If the pressed piece of salt is removed from the nozzle in the known apparatus, the residual salt may adversely affect detector accuracy. Therefore, it may be necessary to wait several days until the remaining salt on the nozzle has evaporated.

SUMMARY OF THE INVENTION

The flame ionization detector of the present invention, in one illustrated embodiment, includes a piece of salt supported in a collector ring and aligned with the longitudinal axis of a flame nozzle. The salt is movable towards and away from the nozzle to adjust the ion current. Also, the salt is frictionally supported in an interchangeable manner so that pieces of salt having various functions and sizes can be inserted into the collector ring. For example, a plurality of salt segments may be held by the collector ring, each segment having the capacity for amplifying ionic current in a different substance. The collector ring is rotatable at least 180° about an axis perpendicular to the longitudinal axis of the flame nozzle, thereby to permit exposure of either side of the salt to the flame and to permit angular adjustment of salt relative to the flame.

A feature of the present invention is that specific substances can be accurately detected. If nitrogen and phosphorus are to be detected, it has been found advantageous to use the salt rubidium sulphate (Rb_2SO_4) or rubidium bromide ($RbBr$). The detection of substances containing chlorine, bromine and iodine may be achieved by using the salt cesium sulphate (Cs_2SO_4) or cesium iodide (CsI).

According to the method of the present invention, compounds containing phosphorus, nitrogen, bromine and iodine may be distinguished from all hydrocarbons and chlorinated substances. The detector is adjusted to obtain optimum ion current when a combustible gas and oxygen are supplied thereto. The separated substances from a selective column are then applied to the detector. Thereafter, the quantity of combustible gas supplied to the detector is gradually increased until the ionic currents corresponding to the second-named group of substances above are reduced and ultimately become negative in relation to the ionic currents corresponding to the first named group of substances. These differences in magnitude and polarity between the ionic currents provide a clear indication of the substances detected.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a partial section and an exploded view of two flame ionization detectors.

FIG. 2 is a perspective view of a metal plate used in the detectors of FIG. 1.

FIG. 3 is a plan view of one of the detectors of FIG. 1.

showing a collector together with a metal plate, guide block and collector tube.

FIG. 4 shows a section through one type of collector.

FIG. 5 shows a section through a second type of collector.

FIGS. 6 and 7 show chromatograms containing phosphorus and hydrocarbon.

FIG. 8 shows a double logarithmic representation of the ion current compared with the degree of ionization of a substance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, the connections for the unshown chromatographic column or its outlet, a connection for a carrier gas pipe and a connection for compressed air are located in a base 11 which is not shown in detail. The compressed air passes out of the base 11 through an opening 12, while the carrier gas mixed with the combustible gas flows out of an opening 13. A fastening ring 14 having an internal thread is secured on the base in the manner shown in the drawing. A nozzle insert 16 having a circular insulating base 17 and a conical metal nozzle 18 mounted thereon can be inserted in said ring. The flange 19 of the insulating base 17 does not cover the opening 12 for compressed air, but the mixture of carrier gas, combustible gas and substance to be examined can flow out of the opening 13 and pass through the nozzle insert 16. The nozzle insert 16 is secured by a covered nut 21 having an external thread which fits in the internal thread of the ring 14 and holds the nozzle insert 16 tightly and rigidly. In spite of this, the compressed air can flow out of the opening 12 because the ring 14 has a cut-out section 22.

In FIG. 1 two identical apparatus are shown, only one of which will be described in detail. A housing 23 with a large cylindrical bore 24 fitting over the ring 14 is supported on the base 11 and centrally positioned by the ring 14. On the rear side, the housing 23 has a threaded bore 26 into which can be screwed an electrically insulated bushing 27 through which two connecting springs 28 are guided, their hook-shaped ends 29 being positioned around the nozzle 18 when assembled, thereby producing an electrical connection.

An unshown means of igniting the combustible gas is located above and next to the upper end of the nozzle 18.

The wall of the housing 23 lying on the front to the right is designed on its outside in the form of a flat guideway 31 which is bounded on both sides by guide ribs 32. An opening 33 which is approximately oval and 22 mm. long is located in the upper section of the guideway. A thread 36 is cut into the guideway 31 below the opening 33. A metal plate 34 lies on the guideway 31, as shown in FIG. 2, and is as wide as the guideway 31, and extends beyond it so that the transverse slot 37 introduced therein is located above the upper face 38 of the housing 23. The metal plate 34 is provided with a bore 39 which is parallel and corresponds to the thread 36. An opening 41 which is parallel to the opening 33 is likewise provided in the metal plate 34. A prismatic retaining block 42 which is as wide as the metal plate 34 and engages externally on the guide ribs 32 is guided so as to be displaceable back and forth on the metal plate 34. The retaining block 42 has a slot 43 which extends parallel to the guide ribs 32 and is in alignment with the thread 36 as well as the bore 39. It has a circular opening 44 which is perpendicular to the guideway 31 and aligned with the opening 41 in the metal plate 34 and the opening 33 in the housing 23. A thread 46 leading into the opening 44 is cut into the upper front side of the block 42. A locking screw 47 having an upper hexagon socket 48 can be screwed into the thread 46. A nut 49 having an internal thread, a lower edge 51 and an upper transverse slot 52 can be screwed onto the locking screw 47 which has an external thread. The edge

51 engages in the transverse slot 37 of the metal plate 34.

Referring now to FIGS. 1 and 3, a collector tube 53 is supported in the opening 44 in the retaining block 42. A coaxial plug 54 is inserted in its right hand end and connected to a mechanically rigid inner conductor 55 which is mounted in a disc 56 so as to be electrically insulated at its end facing the housing 23. A sheet metal retaining panel of a cylindrical platinum collector ring 59 is secured to the projecting end of the conductor 55 by a screw 57, said collector ring being welded to the holding panel 58. In the collector ring 59, there is a cylindrical piece of salt 61 which is almost as high as the collector ring, and has a longitudinal bore 62 extending therethrough.

The bore 24 of the housing 23 is covered at the top by a cover plate 63.

It is advantageous if the flame nozzle is rigidly mounted on the housing and if the piece of salt is movably guided in the housing by the guide means. This method of movement, instead of moving the flame nozzle, is preferred because it is then unnecessary to make the pipes leading to the flame nozzle movable. Instead, only the piece of salt which is to be electrically connected needs to be moved.

It is expedient if the piece of salt is held in the collector ring by friction. Both the mechanical support and the electric contact between the piece of salt and the collector ring are very satisfactory in this case.

The piece of salt may be a single crystal. Such a piece of salt may be easily machined, for example, turned into a cylindrical shape, particularly if the salt is an isotropic crystal. If the single crystal is slightly burnt away on its front, it can be manually filed smooth again with a conventional file. Other configurations for the salt may also be used, as described hereinafter.

The particular salt used depends on the compounds to be detected. If the salt is potassium chloride, phosphorus compounds may be detected. Rubidium sulphate (Rb_2SO_4) or rubidium bromide (RbBr) may be used to detect compounds containing nitrogen. If the salt is cesium sulphate (Cs_2SO_4) or cesium iodide (CsI), substances containing chlorine, bromine or iodine may be detected.

The longitudinal bore in the piece of salt serves as a channel for discharging the burnt gases; however, it can also be used in the present case for adjusting the flame nozzle and the crystal relative to one another. The adjustment is complete when it is possible, in looking through the longitudinal bore, to see directly into the opening of the flame nozzle.

The collector ring can be rotated through at least 180° about an axis which is perpendicular to the longitudinal axis of the flame nozzle. If the piece of salt is burnt away too much on one side so that the metal of the collector ring becomes visible, which would extract heat from the flame, the collector ring only needs to be rotated and then it is possible to use the other side of the salt. Moreover, the adjustment of the salt relative to the flame nozzle can hereby be improved if the flame nozzle does not burn coaxially to the housing, but burns a slightly inclined flame for example, because the flame nozzle is bent.

The described detector is operated as follows:

First, a clamping screw 64 which passes through the slot 43 of the retaining block 42 and the bore 39 of the metal plate 34 and is screwed into the thread 36 is released. Then the locking screw 47 in the block 42 is also loosened. The collector tube 53 together with the collector ring 59 and the piece of salt 61 is then slid in or out until the longitudinal bore 62 of the piece of salt 61 lies coaxially in the bore 24 of the housing 23.

In addition, it is necessary to rotate the collector tube 53 about its longitudinal axis. Then the locking screw 47 is tightened again. With the flame burning, the nut 49 is then turned until the lower side of the piece of salt 61 is touched by the flame in an advantageous manner or until it has a certain spacing if required. The clamping screw 64 is then tightened and the desired setting obtained.

Substances are introduced into the column used for gas

chromatography; a voltage supply of a first potential is connected to the inner conductor 55 and therefore also to the collector ring 59; a voltage supply of a second potential is connected to the bushing 27, i.e. to the connecting springs 28; and a measuring device is inserted in the circuit. It is then possible to observe changing ion currents after a certain time.

The detector may be used to distinguish compounds containing phosphorus, nitrogen, bromine and iodine from all hydrocarbons and chlorinated substances. The detector is set for optimum ionization in the presence of combustible gas and oxygen. Thereafter, the substances to be separated from one another are introduced into a separating or selective column, and the quantity of combustible gas supplied to the detector is increased until the second ionic currents corresponding to the second-named substances above are reduced in relation to the first ionic currents corresponding to the first-named substances. Thus, distinction between classes of substances is made possible simply by gradually increasing the quantity of combustible gas supplied to the detector. Preferably, the quantity of combustible gas is increased until the second ionic currents become negative in relation to the base range of the first ionic currents.

FIGS. 6 and 7 illustrate the chromatograms obtained from a graphic recording instrument which monitors the detector output. As shown in FIG. 6, the substance n-C 10, n-C 12, n-C 14, n-C 16 contains ronnel and parathion, the quantities of the substances being partially indicated. In FIG. 6, all the substances produce an amplitude of positive direction and can be clearly separated from one another. In this case, the piece of salt 61 has been set for a maximum yield of ionic current in the presence of 40 ml./min. of H_2 .

As shown in FIG. 7, if the flow of combustible gas is increased to 80 ml./min., a maximum reverse can be established. In this case, it is evident that the distinction between phosphorated and non-phosphorated compounds becomes clear because the latter are distinguished by a negative amplitude.

FIG. 8 shows another feature of the detector according to the invention. Unlike before only the flow of combustible gas is altered in this case, and the piece of salt 61 kept in its original position which is the most favorable for the yield of ion current, but the piece of salt 61 is set at an optimum distance from the flame when the combustible gas flow is increased since the nut 49 is turned whenever the combustible gas flow is increased. It can be seen, on the one hand, that a completely linear association occurs within the range of 10^{-10} to 10^{-4} amperes and that, on the other hand, it is possible to ionize the substance to be examined up to 100 percent ionization. The ordinate does not represent the ionization of air which is quantitative, but the ionization of a phosphorated substance. Therefore, a range of amplification of more than 10^{-6} is obtained and is completely linear, the amplification factor being equal to 10,000. Thus, the apparatus can also be used in some cases as a transformer or amplifier, and it is highly linear if it is necessary to transform or amplify operations in which the rate of change is very small.

Instead of the ion current, the quantity of combustible gas, in this case H_2 , could be shown on the abscissa. Only a different scale would be required.

It is advantageous if the piece of salt is interchangeably disposed in the collector ring. Pieces of salt having various functions and sizes can then be inserted in the collector ring. If the piece of salt is removed, the detector can then be used as a normal non-selective detector.

The piece of salt may comprise a plurality of segments, each segment having the capacity for amplifying ionic current in different substances. It is then possible to detect as many substances as there are segments, which substances directly follow after one another in time. According to FIG. 4, two different pieces of salt 66 and 67 dis-

posed adjacently to one another can be inserted in the collector ring 59, one piece of salt amplifying the ionization of one substance and the other piece amplifying the ionization of the other substance. If the collector ring 59 is rotated about its axis 68 which is parallel to that of the collector tube 53, and through 180° according to the arrow 69, two different substances can be indicated in succession.

A plurality of cylindrical collector rings may be arranged to form a star. In each collector ring, there is located a piece of salt having the capacity for amplifying ionic current in different substances. The star arrangement can be rotated about the axis which is perpendicular to the longitudinal axis of the flame nozzle. FIG. 5 shows a cross-shaped arrangement 71 which can be rotated about an axis 72 according to the arrow 73 and which accommodates four different pieces of salt 74, 76, 77 and 78. In this case, four different substances can be indicated in succession.

Since the ion current according to FIG. 8 is in linear proportion to the quantity of combustible gas, the apparatus can also be used as a flow-meter which is once calibrated for an absolute quantity of combustible gas. Instead of using soap bubble measuring devices, it is now possible to measure the ion current and, as a result, to make an accurate reading of the rate of combustible gas flow. Even if it is impossible to calibrate the apparatus for an absolute rate of flow, relative measurements can be made in any case. For example, it is possible to set precisely that quantity of combustible gas flow which was set on the previous day, e.g. during an experiment, because the ion current is of like magnitude in both cases.

What we claim is:

1. A flame ionization detector for a gas chromatograph comprising:
 - a flame nozzle;
 - inlet means for directing a mixture of a carrier gas, a combustible gas and a sample substance to said flame nozzle;
 - means providing a collector ring disposed above the flame nozzle;
 - a piece of salt disposed in said collector ring;
 - electrical connection means for receiving ionic current from the collector ring; and
 - means for adjustably mounting said flame nozzle and said collector ring so as to be movable towards and away from one another along the longitudinal axis of said nozzle to optimize ionic current.
2. The flame ionization detector as claimed in claim 1 wherein said piece of salt is frictionally supported in an interchangeable manner in said collector ring.
3. The flame ionization detector of claim 1 said piece of salt being selected from the group consisting of cesium sulphate and cesium iodide to detect compounds containing chlorine, bromine and iodine.
4. The flame ionization detector of claim 1 said piece of salt being rubidium sulphate to detect compounds containing nitrogen.
5. The flame ionization detector as claimed in claim 1 wherein said piece of salt has a longitudinal bore.
6. The flame ionization detector of claim 1 including:
 - a plurality of cylindrical collector rings disposed in fixed relation to one another and rotatable about a common axis which is perpendicular to the longitudinal axis of said flame nozzle; and
 - a plurality of pieces of salt respectively mounted in said cylindrical collector rings, said pieces of salt having the capacity for amplifying ionic current in different substances.
7. The flame ionization detector of claim 6 wherein said plurality of cylindrical collector rings are disposed in a cross-shaped arrangement.
8. The flame ionization detector as claimed in claim 1 wherein said collector ring is rotatable through an angle

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of at least 180° about an axis which is perpendicular to the longitudinal axis of the flame nozzle.

9. The flame ionization detector of claim 8 wherein said salt includes a plurality of segments, each of said segments having the capacity for amplifying ionic current in different substances. 5

10. The flame ionization detector of claim 9 wherein said salt includes two halves disposed adjacent to one another in the direction of the longitudinal axis of said collector ring.

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U.S. Cl. X.R.

23—232 C, 255 E