

[54] SELECTIVE IONIZATION DETECTOR

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[58] Field of Search 23/254 EF, 232 C

[56] References Cited

UNITED STATES PATENTS

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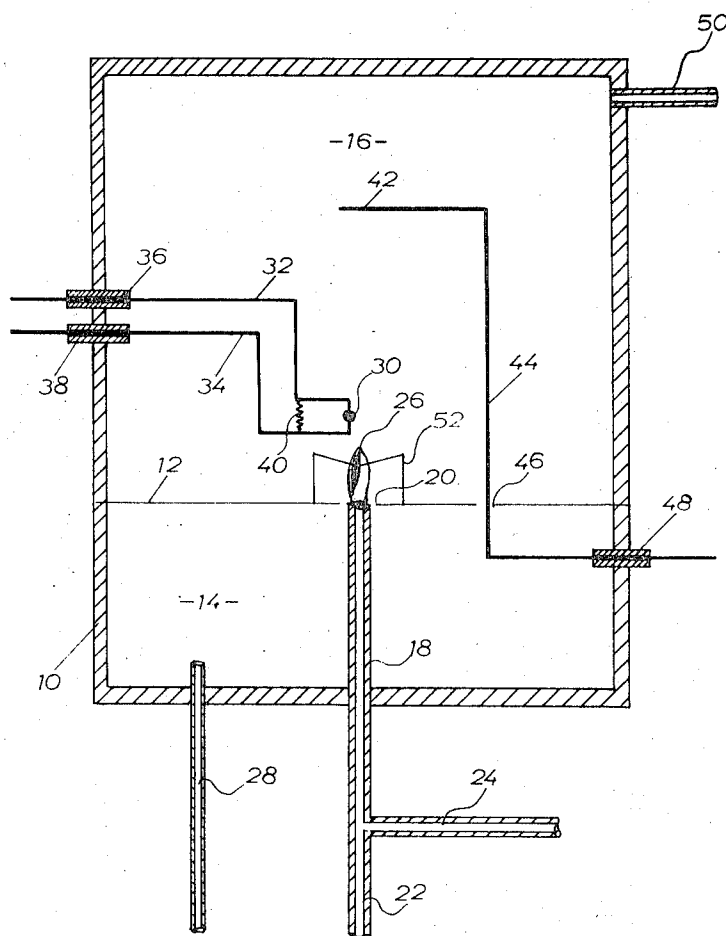
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[57] ABSTRACT

Selective ionization detector for halogen, phosphorus or nitrogen compounds of the type including a diode through which a sample gas being analyzed is fed by means of a carrier gas and an electrode including an alkali source in the form of a heated alkali-containing glass so that the electrode exhibits an increased ion emission upon the occurrence of such specific substances. The major improvement comprises maintaining the alkali glass in a heated softened state during operation of the detector. This may be accomplished by an electric resistance heater, the electric energy to which is precisely adjusted; or by the flame of a burner to which the sample gas and a combustible gas are supplied. The alkali-supplying glass is maintained negative with respect to the collecting electrode, while the (burner nozzle) emitting electrode may be maintained at the same potential as the glass body or also at a positive voltage relative thereto.

8 Claims, 6 Drawing Figures



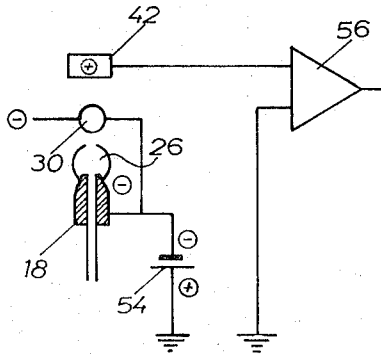


Fig. 2

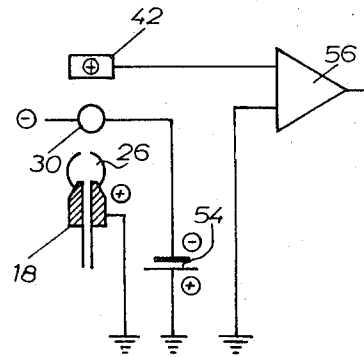


Fig. 3

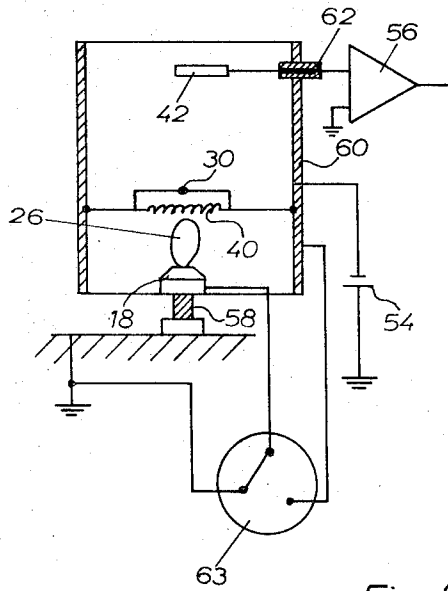


Fig. 6

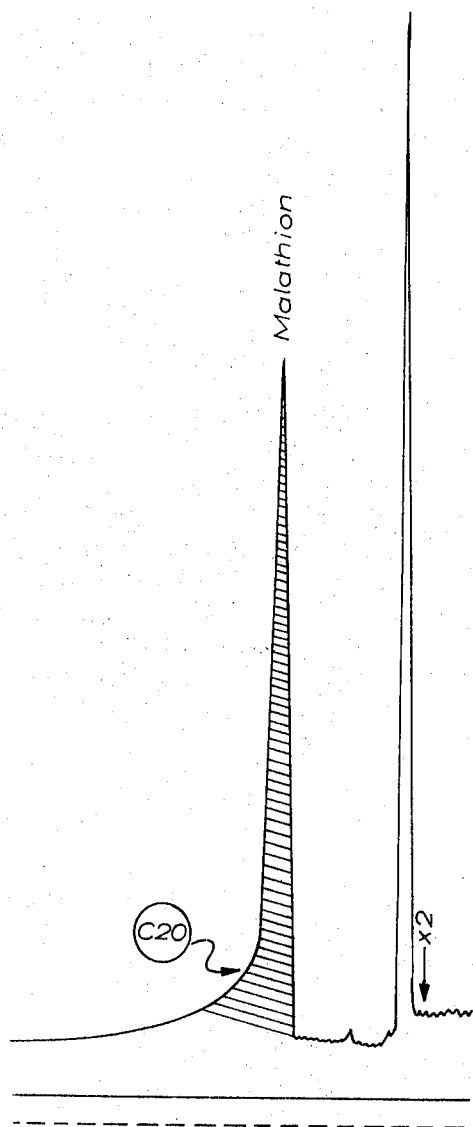


Fig. 5

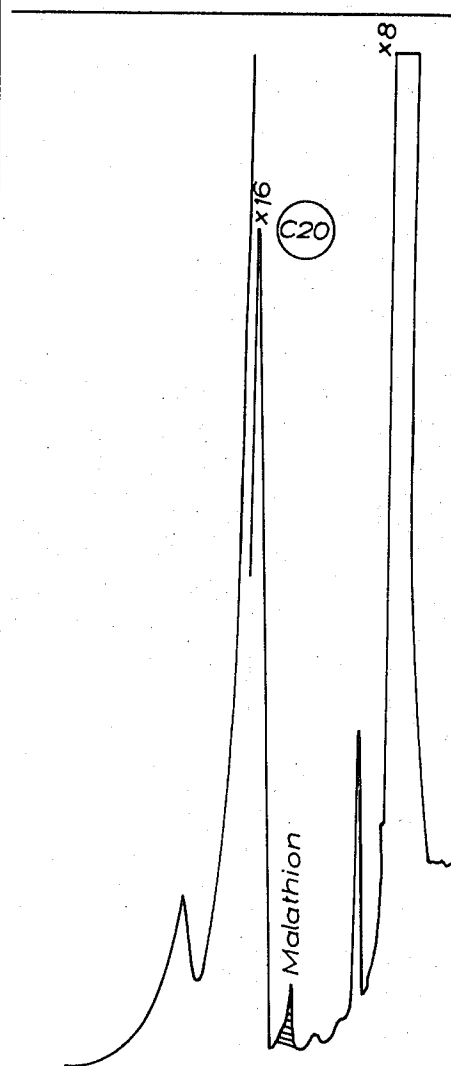


Fig. 4

SELECTIVE IONIZATION DETECTOR

This invention relates to a selective ionization detector for halogen, phosphorus or nitrogen compounds, comprising a diode through which a sample gas under analysis can be fed by means of a carrier or transfer gas, and which comprises an electrode including an alkali source in the form of a heated alkali-containing glass so that the electrode exhibits an increased ion emission upon the occurrence of such specific substances.

A prior art selective ionization detector of this type which is particularly intended for leak detecting devices or the like includes two coaxially helically wound wires each of which are heatable by means of a filament transformer winding. Between the two wires, which constitute the electrodes of a diode, a d.c. voltage source is connected in series with a measuring device. The innermost wire is wound onto a cylinder of alkali metal glass, for instance, potassium glass. By means of the alkali metal of the glass cylinder a specific sensitizing of the electrode for halogen is effected so that upon passage of halogen-containing gases or vapors between the electrodes a definite increase in the current flowing across the diodes is observed (German patent specification No. 907,223).

It is also prior art to use such detectors in gas chromatography (German patent specification No. 1,149,924). These detectors have recently obtained particular significance in the analysis of pesticide residues in vegetable or animal substances, or of medicinal or drug residues in the blood, sweat or urine.

Moreover, detectors of the above type are prior art in which an electrode and/or a separate supply of alkali metals are heated by means of a flame. These detectors are formed in the same manner as a flame ionization detector, which detector is conventional in gas chromatography. A burner nozzle is provided to which a combustible gas (for example, hydrogen) and sample gas mixture is supplied, with the sample gas in gas chromatographic detector applications again being a mixture of carrier gas plus eluted sample components. Above the flame or around the flame there is arranged a collecting electrode. Around the flame an electrode in the form of a spiral is arranged which is coated with a layer of molten alkali salt, preferably sodium sulphate (see U.S. Pat. No. 3,372,994) for sensitizing.

With such flame ionization detectors an increased selective sensitivity for halogen and phosphorus is obtained. However, they are also sensitive to many other substances at the normal sensitivity of a flame ionization detector. Sometimes, this is disturbing. Therefore, it is also known to burn the sample substances prior to measurement in the selective detector either at a separate flame ionization detector (German published patent application No. 1,598,118) or by flameless oxidation (German published patent application No. 1,598,132).

All these known detectors share the problem that the alkali metal necessary for proper functioning should be made available uniformly, i.e., constant in time, within the detector.

It is prior art to apply alkali salts to a metal grid in a flame ionization detector ("Journal of Gas Chromatography," volume 3 (1965), pages 336-339). This method has not been completely successful as the amount of alkali salts decrease markedly after hours of use, and the detector constantly decreases in sensitiv-

ity. A similar phenomenon is observed in the arrangement of the type mentioned hereinbefore (German patent specification No. 907,223) in which a heated coil is wound as an electrode around a cylinder of an alkali glass.

Moreover, alkali salts have been provided in supply vessels of apertured or porous materials so that by diffusion over a longer period of time alkali metal compounds are passed to the surface of these supply vessels (German published patent application No. 1,598,118). Although this method ensures an alkali supply for days or weeks, the decrease in the detector sensitivity is still disturbingly high. Moreover, these supply vessels are expensive to manufacture.

It is also prior art to attach a supply of a salt of an alkali metal to the burner nozzle of a flame ionization detector (German published patent application No. 1,900,981). In another prior art selective flame ionization detector, a solid piece of alkali salt is held in the flame by means of a mount. The mount permits change in the spatial position of the alkali salt piece relative to the flame nozzle (German published patent application No. 1,935,624). Nitrogen-containing substances can also be detected selectively by these latter detectors. However, pure salts are brittle and have only poor adhesion to other materials, so that these prior art solutions involve considerable manufacturing difficulties. In the last mentioned arrangement also the mechanical adjustment of the distance of the alkali salt piece is difficult and critical.

It is an object of this invention to provide a selective ionization detector having an inexpensive and very slowly decreasing alkali source, which therefore maintains a substantially uniform detector sensitivity over long periods of time, for instance, months.

It is another object of this invention to provide a selective nitrogen detector without requiring expensive mechanical means for distance adjustment and mechanical adjustments at the detector, which is hot and not very accessible.

Starting from a selective ionization detector of the type mentioned hereinbefore the basic feature of the invention resides in the fact that the alkali glass is in a viscous or softened state during detector operation.

According to the invention the alkali source therefore consists of glass which softens during operation, whereby it is attained that the surface of the alkali source does not become impoverished as to alkali, since by molecular movement alkali is constantly supplied to the surface. In this manner, an ionization detector according to this invention differs advantageously from a detector according to the German patent specification No. 907,223 where the alkali cylinder remains in its rigid state and therefore an impoverishment of alkali at the surface soon takes place. Since only very small alkali quantities are consumed, the supply of a single glass drop is sufficient for many months. The alkali glass drop may then be readily replaced. No manufacturing costs for monocrystals, supply vessels, or the like are encountered.

The detector may be of the form that includes a burner nozzle to which a combustible gas and sample gas mixture are supplied, that above the burner nozzle an alkali glass body is mounted and is heatable by an electric resistance heater to an extent sufficient for softening of the alkali body.

The rate of alkali emission very markedly depends on the temperature of the glass. When the heating of the alkali glass body is effected electrically and not by the flame, it is not necessary to maintain constant the flame temperature, and therefore the combustible gas (H_2) flow, with the otherwise required accuracy. Upon adjustment of the gas flows, no notice need be taken of the effects of flame heating of the alkali glass body, but rather the gas flows of hydrogen and oxygen can be adapted to the respective temperature requirements, in particular, of the element desired to be detected.

Advantageously, the heating of the electric resistance heater is precisely adjustable. However, provision can be made that independently of the precise adjusting means, a fixed heating capacity sufficient for igniting the flame can be switched on by actuation of a push button or the like. Thus, the resistance heater for the alkali glass body is additionally used for igniting the flame.

A specificity for particular individual substances can be obtained by a suitable selection of the gas flows and by selection of the appropriate alkali component. By using, for instance, rubidium-containing glass it is possible to detect nitrogen compounds; while, for substances of high phosphorus content, sodium-containing glass is selective.

An advantageous selective ionization detector of the type indicated above includes a burner nozzle to which a combustible gas and sample gas mixture are supplied; above the burner nozzle an alkali glass body, heatable up to its softening temperature, is mounted; above the alkali glass body a collecting electrode is arranged; and the collecting electrode and nozzle are connected to a positive electric potential with respect to the alkali glass body. With such a potential distribution the ion currents (normal flame ionization detector signals) originating from the normal hydrocarbon (CH) components and the ion currents occurring on the surface of the alkali glass body specifically with the occurrence of halogen or phosphorus are separated from each other in a manner known per se (German published patent application No. 1,805,776). The electrons from the normal (hydrocarbon) combustion process flow to the burner nozzle, since the mount of the alkali glass body is at a potential negative relative to the nozzle and the electrons cannot overcome this potential. The electrons from the strictly thermionic process with the occurrence of, for instance, halogen, occur on the surface of the alkali glass body and are therefore picked up by the collecting electrode.

In a further modification of this invention, the nozzle and a housing which encloses the nozzle, the alkali glass body, and the collecting electrode are all provided with insulation with respect to ground; a negative voltage is connected to the housing (with respect to ground) and the alkali glass body is electrically connected to the housing, while the collecting electrode is mounted in the housing, but is electrically insulated with respect to the same and is connected to an amplifier at ground, and that the nozzle is electrically connectable alternatively to the housing (i.e., negative) or to ground by means of a switch.

Then, the detector can be operated by means of operation of a simple electric switch alternatively as selective ionization detector or as normal flame ionization detector.

A few illustrative embodiments of this invention will now be described more fully with reference to the accompanying drawings, in which:

FIG. 1 schematically illustrates the design of a selective ionization detector incorporating the invention;

FIG. 2 diagrammatically illustrates one possibility of electrical potential distribution in the ionization detector of FIG. 1 in which the latter operates as a flame ionization detector;

FIG. 3 diagrammatically illustrates electrical potential distribution in the ionization detector of FIG. 1 in which the latter operates as an ionization detector selectively responding to phosphorus;

FIG. 4 illustrates a chromatogram recorded with the detector in the mode of operation as shown in FIG. 2;

FIG. 5 illustrates a chromatogram of the same mixture (on a changed scale) in the mode of operation as shown in FIG. 3, the mixture having a phosphorus-containing component and a non-phosphorus-containing component; and

FIG. 6 illustrates an embodiment of the ionization detector, permitting alternatively a mode of operation according to FIG. 2 or one according to FIG. 3.

The detector according to FIG. 1 is substantially in the form of a prior art flame ionization detector (FID). A housing 10 is divided by a partition 12 into a lower and an upper chamber 14, 16, respectively. Into the lower chamber 14 a burner nozzle 18 protrudes, terminating just below an aperture 20 in the partition 12. A sample gas is supplied to the nozzle 18 via a conduit 22. When applied to gas chromatography, this conduit 22 is connected with the outlet of a separating column, and the sample gas consists of a mixture of carrier gas plus eluted sample components. A combustible gas, generally hydrogen, is added to the sample gas via a conduit 24, so that a combustible gas, sample gas mixture issues from the nozzle and during operation commonly burns with a flame 26. Combustion air is introduced into the lower chamber 14 via an air supply conduit 28.

In the upper chamber 16 above the burner nozzle 18, a bead 30 of an alkali-rich glass is mounted, specifically by means of two wires 32 and 34 which are passed through the wall of the housing 10 by means of electrical insulators 36, 38. These wires 32 and 34 simultaneously serve as current leads for an electric resistance heating element 40 arranged therebetween and in heat-conducting contact with the bead 30. The heating quantity of the electric resistance heating element 40 is precisely adjustable by conventional means not illustrated.

Above the bead 30 is positioned a collecting electrode 42. The collecting electrode 42 is secured to an electrically conducting holder 44, which is passed downwardly through an aperture 46 of the partition 12 and laterally out of the housing 10 by means of an insulator 48. The burnt gases of the flame 26 are exhausted via a connector 50. When using the detector as a leak detector a suction pump is connected here.

The electric resistance heating element 40 is so constituted that the alkali glass bead 30, when the detector is in operation, can be maintained in a viscous or softened state. In this state, a constant molecular movement and therefore a concentration compensation takes place in the alkali glass bead, so that fresh alkali metal atoms constantly migrate to the surface of the al-

kali glass bead, and therefore no impoverishment (of alkali metal) occurs.

Alternatively, it is also possible to suspend the alkali glass bead from a bracket 52 which is mounted on the partition, so that the bead is suspended in the flame 26 and is softened by the latter.

The bracket 52 and/or the wires 32, 34 preferably consist of platinum, on the one hand because platinum has substantially the same coefficient of thermal expansion as glass, and on the other hand due to its chemical inertness. The partition 12 ensures in well-known manner that the insulator 48 and the conduit lead-out are not impaired (i.e., attacked) by combustion residues.

The just described detector is particularly suited for the detection of halogen- and phosphorus-containing substances. Moreover, in addition to its selective signal it also supplies a normal FID-signal. In order to obtain a signal of high selectivity, the sample may be burnt before introduction to the alkali source, which can be effected in a known manner in the first section of a double-level flame ionization detector (FID) or by flameless oxidation.

Another possibility of alternatively obtaining a high selectivity is shown by a comparison of FIGS. 2 and 3.

FIG. 2 illustrates a circuit in which the "normal" FID-signals resulting from the (hydro-carbon) combustion are also obtained. The burner nozzle 18 and the alkali source (softened alkali glass bead 30) are connected to a negative potential with respect to ground by a voltage source 54. The collecting electrode 42 connects to a grounded amplifier 56, thus practically at ground potential. With this mode of circuit arrangement, both selective signals, for instance, for halogen and phosphorus from the thermionic ion currents which originate from the bead 30, and also "normal" FID-signals, for instance, from the hydrocarbon components are obtained. Though, in this mode of operation the relative sensitivity with respect to halogen and phosphorus is in general increased, however, the detector is not sensitive specifically only to these substances. Such a performance of the detector may be desirable. An increase in the sensitivity is obtained for nitrogen-containing compounds if the flame is operated under reducing conditions.

In the electrical potential distribution according to FIG. 3, the collecting electrode 42 again connects to the amplifier 56 with respect to ground. However, now the burner nozzle 18 is grounded, and only the alkali glass bead 30 and its mount are maintained at a negative potential (with respect to ground) by the voltage source 54.

Normal (hydrocarbon) combustion takes place in the flame below the alkali source, i.e., the bead 30. If the burner nozzle 18 is at a positive potential relative to the bead 30 the electrons from the combustion process will flow to the nozzle because they cannot overcome the negative potential of the bead 30 (and of its mount). The electrons from the strictly thermionic process, however, are produced on the surface of the bead 30 above the flame 26 and are therefore picked up by the collecting electrode 42. This thermionic process therefore substantially solely supplies the signal across the amplifier 56.

The correctness of this assumption is substantiated by the actual chromatograms of FIGS. 4 and 5. Both chromatograms were recorded with the same substance

mixture, first (FIG. 4) with the electrical potential distribution of the detector as shown in FIG. 2, and secondly (FIG. 5) with the electrical potential distribution shown in FIG. 3. Of interest are the peaks of malathion, a phosphorus-containing substance, and of eicosan, a 30-carbon hydrocarbon. While during normal FID-operation according to FIG. 4 (with the malathion peak at a gain factor of 8) a strong eicosan-peak is recognizable, this latter peak has disappeared completely in FIG. 5 made with a grounded burner nozzle 18. From this, the gain in specificity can be seen very instructively, and no decrease in the sensitivity of the malathion peak is recognizable. With this construction a "double-level" arrangement of the FID is not required.

FIG. 6 illustrates an embodiment which permits the alternative operation according to FIG. 2 or according to FIG. 3 in a simple manner. Corresponding parts are referenced by the same reference numerals as in the FIGS. 1 to 3.

The burner nozzle 18 is insulated with respect to ground by an insulating piece 58. Burner nozzle 18, alkali glass body 30 and collecting electrode 42 are enclosed by a cylindrical housing 60 which is mounted for insulation with respect to ground. The collecting electrode 42 is mounted in this housing 60 by means of an insulator 62. By means of the voltage source 54 the housing 60 is connected to a negative potential, for instance -130 volts with respect to ground. By means of switch means 63 the burner nozzle 18 can be alternatively connected electrically to the housing 60 and therewith to the negative potential or to ground. The alkali glass body 30 and its conduits are electrically connected to the housing 60.

The detector of the invention described can be used in various manners in order to obtain selectivity for various substances.

The glass bead 30 can be formed of sodium-containing glass and be excited to alkali emission by electric heating, while the flame 26 burns reducingly (O_2 supplied at 40 ml/min; H_2 at 15 ml/min). Then, a selective phosphorus signal is obtained. When using rubidium-containing glass a selective nitrogen (N_2) signal can be obtained by corresponding adjustment of the gas flows (O_2 at 0 ml/min, H_2 at 5 ml/min) when the glass bead 30 is heated electrically. The hydrogen does not operate a flame.

Generally, the detector can be operated in the following ways:

1. As a normal flame ionization detector (FID), air and hydrogen are supplied, the flame 26 burns, and the electric resistance heating element 40 is inoperative. The operating conditions are for instance: N_2 (carrier gas) at 25 ml/min; O_2 at 300 ml/min; H_2 at 30 ml/min.

2. As FID with selective sensitivity for halogen and phosphorus compounds when a reducing (burning) flame is utilized, and additionally a heating current flows through the electric resistance heating element 40 so that the glass bead 30 softens. The operating conditions are for instance: N_2 at 25 ml/min; O_2 at 40 ml/min; H_2 at 15 ml/min; heating current (I) = 2.5 amps.

3. As selective detector for halogen and phosphorus compounds while suppressing the "normal" FID-signals, if in the just described mode of operation (2)

an electrical potential distribution according to FIG. 3 (with grounded nozzle 18) is utilized.

4. As FID with conventional sensitivity and additional sensitivity for halogen and phosphorus, if the glass bead 30 is arranged on the bracket 52 in the flame 26 and is heated by the flame. The operating conditions are for instance: N₂ at 25 ml/min; O₂ at 380 ml/min; H₂ at 40 ml/min.

5. As selective detector for nitrogen compounds, if no oxygen is supplied to the detector, and the flame does not burn, but through the electric resistance heating 40 a heavy heating current flows. The operating conditions are for instance: N₂ at 25 ml/min; H₂ at 5 ml/min; heating current (I) = 2.5 amps.

Advantageously, the resistance heating 40 is also used for igniting the flame 26 when operation of the detector is started. For this purpose, a push button switch (not shown) may be provided by which, independently of the precisely effected adjustment of heating quantity (to element 40), a fixed amount of heating can be applied to the resistance heating element 40 which is fully sufficient to ignite the flame 26.

We claim:

1. A selective ionization detector of the type for detecting halogen, phosphorus and nitrogen compounds, comprising a diode through which a sample gas under analysis is fed by means of a transfer gas, and an electrode including an alkali source in the form of a heated alkali-containing glass, so that the electrode exhibits an increased ion emission upon occurrence of such specific substances, the improvement in which:

said alkali source comprises alkali glass maintained in a heated softened state during operation of the detector.

2. A selective ionization detector as claimed in claim 1, in which:

said alkali glass is a sodium-enriched glass.

3. A selective ionization detector as claimed in claim 1, in which:

said alkali glass is a rubidium-enriched glass.

4. A selective ionization detector as claimed in claim 1, further comprising:

a burner nozzle (18) to which a combustible gas and sample gas mixture is supplied:

an alkali glass body (30) heatable up to softening mounted above said burner nozzle (18);

a collecting electrode (42) arranged above said alkali glass body (30);

said collecting electrode (42) and burner nozzle (18) being connected to an electrical potential positive with respect to the alkali glass body (30).

5. A selective ionization detector as claimed in claim 4, in which:

a housing (60) encloses said burner nozzle (18);

said alkali glass body (30) and said collecting electrode (42) are mounted by means of insulation (58) with respect to ground;

said housing (60) is connected to a negative voltage source with respect to ground;

said alkali glass body (30) is electrically connected to said housing (60);

said collecting electrode (42) is mounted in the housing (60) but is electrically insulated therefrom and is connected to an amplifier (56) which is grounded; and

said burner nozzle (18) is electrically connectable alternatively to the housing (60) or to ground by means of a switch means.

6. A selective ionization detector as claimed in claim 1, further comprising:

a burner nozzle (18) to which a combustible gas and sample gas mixture is supplied;

said alkali source is in the form of an alkali glass body (30), mounted above said burner nozzle (18) and heatable by an electric resistance heating means (40) to an extent sufficient for softening of said alkali glass body (30).

7. A selective ionization detector as claimed in claim 6, in which:

the heating energy supplied to the electric resistance heating means (40) is precisely adjustable.

8. A selective ionization detector as claimed in claim 7, in which:

independently of said precisely adjustable energy, a separate heating quantity sufficient for igniting the flame can be supplied to said heating means by actuation of a manually operated means.

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