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CHEMICAL-IONIZATION DETECTION METHOD AND APPARATUS

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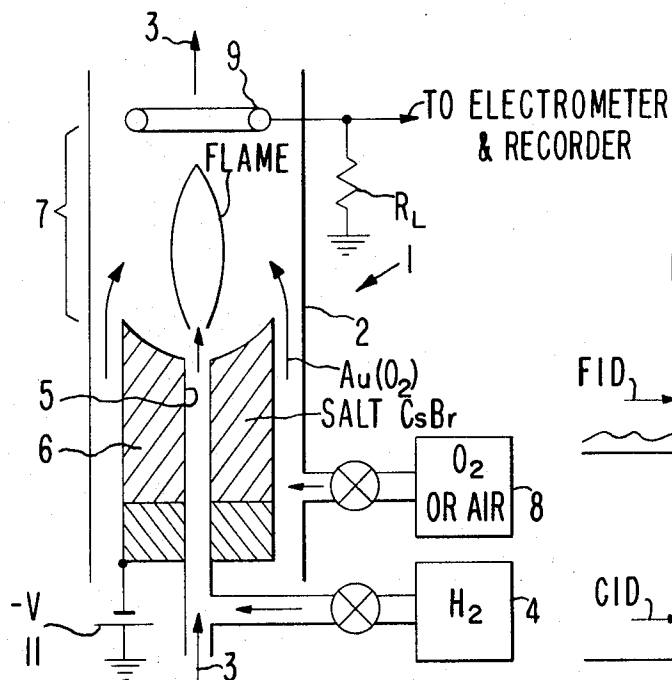


FIG. 1
PRIOR ART

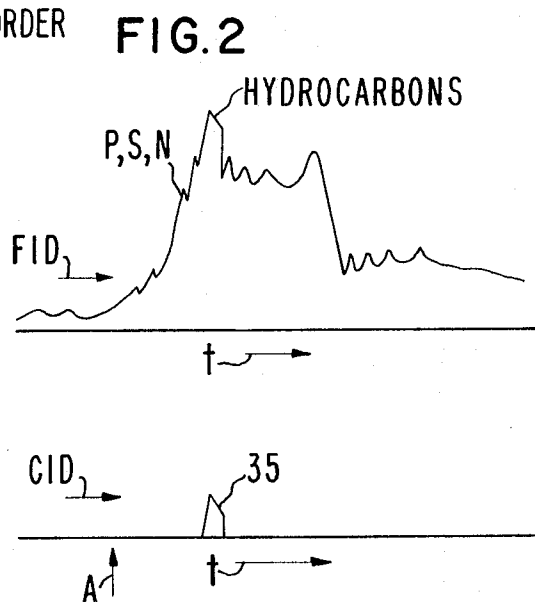
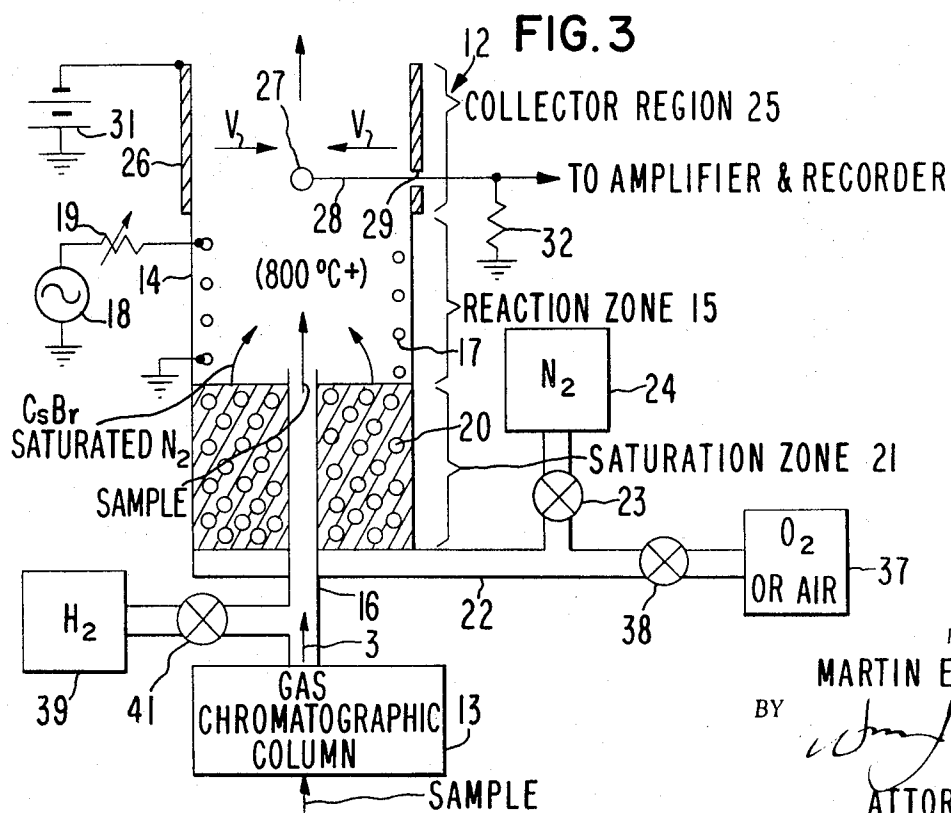


FIG. 4



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**CHEMICAL-IONIZATION DETECTION METHOD
AND APPARATUS**

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10 Claims

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SUMMARY OF THE PRESENT INVENTION

The principal object of the present invention is the provision of an improved ionization detector.

One feature of the present invention is the provision, in an ionization detector, of a heating element for heating the gases within the reaction zone of the detector to a sufficient temperature to obtain an ionizing reaction without reliance upon an oxygen-supported flame to supply the heat for ionization.

Another feature of the present invention is the same as the preceding feature wherein an alkali metal reactant vapor is reacted with the gas to be analyzed in a substantially oxygen-free atmosphere, whereby undesired oxidation of the hydrocarbon constituents, if any, are avoided to prevent detection thereof.

Another feature of the present invention is the same as any one or more of the preceding features including the provision of a charge of alkali salt disposed upstream of the reaction zone and means for passing a carrier gas stream through the alkali salt to carry vapors of the alkali salt into the reaction zone.

Another feature of the present invention is the same as the preceding feature wherein the heating element is also disposed in heat exchanging relation with the charge material for heating the charge to a sufficient temperature to produce vaporization of a portion of the charge material.

Other features and advantages of the present invention will become apparent upon a perusal of the following specification taken in connection with the accompanying drawings wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic line diagram of a prior art flame ionization detector,

FIG. 2 is a chromatogram derived from the prior art flame ionization detector and depicting the presence of certain phosphor, sulphur, or nitrogen compounds in the presence of hydrocarbons,

FIG. 3 is a schematic line diagram depicting the chemical-ionization detector of the present invention as employed for detecting the effluent stream of a gas chromatographic column, and

FIG. 4 is a chromatogram derived from the detector of FIG. 3 and depicting the specific detection characteristics of the detector of the present invention.

**DESCRIPTION OF THE PREFERRED
EMBODIMENTS**

Referring now to FIG. 1, there is shown the prior art alkali flame detector 1. The detector 1 includes a tubular housing 2 arranged for flow of a gas stream 3 to be analyzed therethrough. Typically, the detector 1 is connected into the output stream of a gas chromatographic column, not shown, for detecting the output peaks of the gas chromatograph. Hydrogen gas from a hydrogen source 4, such as a bottle under pressure, is valved into the gas stream 3 to be analyzed. The hydrogen and gas mixture are fed through a central passageway 5 in a salt pellet 6 into a reaction zone 7. The pellet 6 forms a flame jet. Oxygen or air is fed around the salt pellet 6 from a suitable source of oxygen 8, such as an oxygen bottle or the atmosphere.

In the reaction zone 7, the hydrogen is ignited with the oxygen to produce a flame which causes vaporization of a certain portion of the salt pellet 6, such salt pellet typically being cesium bromide. In the flame, the cesium vapor reacts with certain classes of compounds of nitrogen, phosphorus, etc., in the effluent gases to produce ionization of the gases to be analyzed. More particularly, hydrocarbons and other compounds of nitrogen and phos-

ABSTRACT OF THE DISCLOSURE

A chemical-ionization detector capable of being operated in a specific detection mode for the specific detection of compounds of sulphur, nitrogen, phosphorus, etc., in the presence of hydrocarbons. The detector is also capable of being operated in a non-specific mode for the detection of hydrocarbons. In the specific detection mode, a non-hydrocarbon constituent of the sample to be detected is reacted with an alkali metal vapor in a reaction zone by the application of heat supplied by a heater in heat exchanging relationship with the reaction zone. In the reaction zone, a chemi-ionization reaction occurs in the absence of oxygen with certain non-hydrocarbon constituents of the gas stream to be analyzed. The ions thus produced are collected by the action of an electric field to produce an ion current of an amplitude determinative of the amount of non-hydrocarbon constituent.

DESCRIPTION OF THE PRIOR ART

Heretofore, flame ionization detectors have employed a flame for the initiation and maintenance of the ionization reaction of oxygen and hydrocarbon constituents of a sample gas stream to be analyzed. While such an ionization detector is relatively sensitive and linear in its response to hydrocarbons, the need exists for a specific ionization detector which can detect the presence of compounds of sulphur, nitrogen, phosphorus and others to the exclusion of hydrocarbon compounds such that trace of such other compounds in the presence of hydrocarbons can be readily detected.

A flame ionization detector is made sensitive to compounds of phosphorus and nitrogen, in the presence of hydrocarbons, by introducing an alkali salt additive into the flame and operating the flame in a fuel (H_2) rich condition for cutting down on the amount of oxygen available for the chemi-ionization of hydrocarbons. The salt may comprise CsBr and is conveniently introduced by using a CsBr pellet as the flame jet. This type of detector has been characterized as an "alkali flame detector" and is found to be relatively sensitive and linear with a high degree of specificity. However, the alkali flame detector is found to be critical as regards flow rates which must be readjusted as the salt flame jet burns down. Moreover, it has been found difficult to duplicate performance under the same operating conditions with any two detectors.

Flame photometric detectors have been employed to obtain specific detection of certain compounds of sulphur, nitrogen and phosphorus by detecting the color of the flame containing such compounds. These detectors have been found to be highly specific but are non-linear in their sensitivity. Moreover, a common problem with photometric detectors is that the solvent peaks, usually present in the effluent streams of gas chromatographs, tend to extinguish the flame. Since the solvent peak typically precedes the peaks to be analyzed the flame is often extinguished before the desired peaks can be detected. Therefore, it is desired to obtain an ionization detector which may be specific to certain compounds containing sulphur, nitrogen and phosphorus and which does not rely upon a flame to produce the ionization reaction.

phorus are ionized in the reaction zone 7 and the ions are collected on an ion collector ring 9 which is operated at a positive potential relative to the support structure on which the pellet is mounted.

The ion collector potential, $-V$, is supplied from a source 11 to the salt pellet support structure. The collector electrode 9 is connected to ground via a load resistor R_L . The output signal is derived across load resistor R_L and fed to an electrometer and recorder, not shown. The collected ion current is then recorded as a function of time to produce a flame ionization detection chromatogram, as schematically indicated in FIG. 2.

The problem with the alkali flame detector 1 of FIG. 1 is that the detected output is relatively general, i.e., non-specific. Thus, compounds of phosphorus, sulphur, nitrogen and the like often appear as very small peaks superimposed upon relatively large hydrocarbon peaks in the chromatogram. When analyzing certain petroleum and pesticide products it is desired to obtain a chromatogram which is more specific to certain compounds of phosphorus, sulphur and nitrogen to the exclusion of the detection of hydrocarbon compounds.

One way to make the flame ionization detector 1 of FIG. 1 more specific to non-hydrocarbons is to reduce the flow of oxygen to the flame such that the flame is operated in a fuel rich condition. While this mode of operation reduces the sensitivity of the detector to hydrocarbons, it still produces a chromatogram wherein compounds of phosphorus, sulphur and nitrogen are often masked by much larger concentrations of hydrocarbon compounds.

Referring now to FIG. 3, there is shown an ionization detector 12 of the present invention as connected for detecting the effluent stream of a gas chromatographic column 13. The detector 12 includes a housing 14 containing a centrally disposed reaction zone 15. A stainless steel capillary tube 16 is connected into one end of the housing 14 and extends coaxially of the tubular housing 14 to the upstream end of the reaction zone 15. The effluent stream 3 of the gas chromatograph 13 is directed through the capillary 16 for passing the effluent stream 3 into and through the reaction zone 15. An electrical heating element 17 such as a Nichrome heating wire is disposed in heat exchanging relation with the reaction zone 15. The heating element may be disposed internally or externally of the housing 14. In a preferred embodiment, the tubular housing 14 includes a tubular central section of quartz or ceramic insulating material with the heating element 17 wound into a heating coil on the inside of the insulator. Heating current is supplied to the heating element 17 from a suitable source of heating current 18 via an adjustable rheostat 19.

The housing 14 contains an annular saturation zone 21 disposed upstream of the reaction zone 15. The annular saturation zone 21 surrounds the capillary 16 and is packed with a charge 20 of alkali metal reactant material such as one of the following alkali salts: cesium bromide, nitrate or chloride, potassium bromide or chloride, rubidium bromide, chloride, or sulphate, or sodium bromide or chloride. In a preferred embodiment, the alkali salt is cesium bromide and is mixed with glass beads to provide a relatively porous structure through which an inert carrier gas such as nitrogen is passed for carrying vaporized cesium bromide into the reaction zone 15. The carrier gas is introduced into the upstream end of the annular saturation zone 21 from a suitable source of nitrogen gas, such as a nitrogen bottle 24, via tubulation 22 and a valve 23. The heating element 17 is also disposed in heat exchanging relation with the charge material 20 to facilitate vaporization of the cesium bromide salt.

The current through the heating element 17 is adjusted to raise the temperature of the reaction zone to 800°C . or above. At this temperature within the reaction zone 15, alkali metal vapor, cesium bromide, reacts with non-hydrocarbon constituents of the effluent sample gas

stream 3 to produce an ionizing chemical reaction in the absence of oxygen with the non-hydrocarbon constituent for ionizing same. The ionized non-hydrocarbon constituents such as compounds of phosphorus, sulphur or nitrogen are carried through the reaction zone 15 into a collector region 25.

In the collector region, a ring-shaped cathode 26, as of stainless steel, surrounds a collector electrode 27 which is centrally disposed of the ring 26 and supported there-within via a lead 28 passing radially through the tubular housing 14 via an opening 29 in the ring 26. A potential supply 31 supplies a negative potential to the cathode ring 26 relative to the collector electrode 27 which is connected to ground via a load resistor 32. The ionized non-hydrocarbon constituents which pass into the collector region 25 are attracted to and collected on the collector electrode 27 to produce an output voltage across the load resistor 32, such as the input resistance of an electrometer, not shown. The output signal is amplified via, for example, an electrometer and the output thereof is fed to a recorder for producing a chromatogram, as shown in FIG. 4. The time scale for the chromatograms of FIGS. 2 and 4 is the same and the non-hydrocarbon peak 35 is clearly distinguished from the hydrocarbon background in the chromatogram of FIG. 4.

The chromatogram of FIG. 4 is typical of the selectivity of non-hydrocarbon peaks from a hydrocarbon background; for example, FIG. 4 is typical for the detection of tributyl phosphate in hexane. The chromatogram response to 0.5 microliter of hexane, which is a hydrocarbon solvent peak, was zero, that is, it was less than twice the noise level of the detector including the electrometer and chart recorder. Moreover, it has been found that the peak height of the non-hydrocarbon constituent is relatively linear, that is, the peak height is directly related to the amount of the constituent present in the sample gas stream 3 over relatively wide ranges of concentrations such as from 10 nanograms to 1000 nanograms. While cesium bromide salt has been found to be useful in enhancing the ionization reaction for detection of phosphates, other alkali salts may be employed which will be specific to other compounds of phosphorus, sulphur and nitrogen.

Another feature of the ionization detector 12 is that it is readily converted into a conventional flame ionization detector by valving off the nitrogen source 24 via valve 23 and valving oxygen or air via valve 38 through the salt charge 20. In this mode of operation, hydrogen from a suitable hydrogen source 39 is valved into the gas stream 3 via valve 41. Also in this mode it is not necessary to employ the heating element 17 such that this element is de-energized. A flame is ignited in the reaction zone and the ionization detector 12 functions as the typical prior art flame ionization detector.

Alternatively, the ionization detector 12 may be employed in a flameless mode of operation by passing oxygen or air from the source 37 via valve 38 and tubulation 22 through the salt charge 20. Alternatively, the salt charge may be removed. The hydrogen source 39 is valved off via valve 41 and the hydrocarbons in the gas stream 3 interact in the reaction zone 15, which is now heated by the heating element 17, to produce a flameless ionizing reaction between the hydrocarbons and the oxygen in the presence of the heat produced by the heating element 17. This represents an improvement over the conventional flame ionization detector since the separate source of hydrogen, such as a hydrogen bottle, and a separate source of oxygen, such as an oxygen bottle, are not required. A conventional blower, not shown, may be employed for supplying air to the reaction zone 15.

Since many changes could be made in the above construction and many apparently widely different embodiments of this invention could be made without departing from the scope thereof, it is intended that all

matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a method of ionization detection the steps of, heating a stream of gas containing a non-hydrocarbon constituent to be detected and an alkali metal reactant vapor in an oxygen-free zone to produce a chemi-ionization in the absence of oxygen with the non-hydrocarbon constituent to ionize same, and collecting the ionized sample constituent to produce an ion current of an amplitude determinative of the amount of the non-hydrocarbon constituent.

2. The method of claim 1 wherein the alkali metal reactant vapor comprises vapor of an alkali salt.

3. The method of claim 1 wherein the gas stream includes hydrocarbon constituents whereby undesired oxidation of the hydrocarbon constituents are avoided to prevent ionization and detection thereof.

4. In an ionization detector, means forming a housing having a reaction zone therein, means for flowing a sample gas stream containing a certain constituent to be detected through said reaction zone, the improvement comprising, a heating structure disposed in heat exchanging relation with said reaction zone for heating the sample gas in said reaction zone to ionize the constituent to be detected, and means for collecting the ionized constituent to produce a detector output signal of an amplitude representative of the amount of the constituent to be detected in the sample gas stream.

5. The apparatus of claim 4 wherein the sample constituent to be detected is a non-hydrocarbon constituent, and including means for flowing an alkali metal reactant vapor mixed with the sample gas stream through said reaction zone, said reaction zone being relatively free of oxygen, to produce a flameless chemi-ionization reaction in the absence of oxygen within said reaction zone to ionize the certain non-hydrocarbon constituent of the sample gas stream.

6. The apparatus of claim 5 wherein said housing includes a zone containing a porous charge of alkali salt, means for heating said alkali salt charge to vaporize a portion thereof, and means for passing a carrier gas stream through said alkali salt into said reaction zone to carry vaporized alkali salt into said reaction zone for reaction with the non-hydrocarbon constituent of the sample gas stream.

7. In an ionization detector for detecting constituents of a gas stream, means forming a detector housing surrounding the gas stream and through which the gas stream to be detected is caused to flow, said housing containing a reaction zone within which a chemical ionization reaction is caused to occur for ionizing certain constituents, if any, of the gas stream, means forming an ion collector electrode structure disposed downstream of said reaction zone for collecting the ionized constituent of the gas stream, means forming a charge of alkali metal reactant material disposed upstream of said reaction zone, means for passing a gas stream by said charge material to carry vapors of said alkali metal reactant material into said reaction zone, the improvement comprising, means forming a heating structure disposed in heat exchanging relation with said reaction zone for heating said reaction zone to a temperature sufficient to cause the ionizing reaction to occur.

8. The apparatus of claim 7 wherein said heating structure is an electrical heating element.

9. The apparatus of claim 7 wherein said heating structure is also disposed in heat exchanging relation with said charge material for heating said charge to a sufficient temperature to produce vaporization of a portion of said charge.

10. The apparatus of claim 7 including a gas chromatographic column producing an effluent gas stream to be analyzed, and wherein the ionization detector is connected downstream of said gas chromatographic column for detecting the constituents thereof.

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