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Jenkins

[11] **3,883,739**

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[54] **METHOD FOR THE QUALITATIVE AND QUANTITATIVE DETECTION OF VAPOURS FROM LOW VOLATILITY COMPOUNDS**

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[30] **Foreign Application Priority Data**

Feb. 2, 1973 United Kingdom..... 5285/73

[52] **U.S. Cl.**..... **250/304;** 23/232 C; 23/254 E

[51] **Int. Cl.** **G01b 1/18**

[58] **Field of Search** ..... 250/302, 303, 304, 379, 250/380, 381; 23/232 C, 254 E; 73/23.1

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Primary Examiner—James W. Lawrence

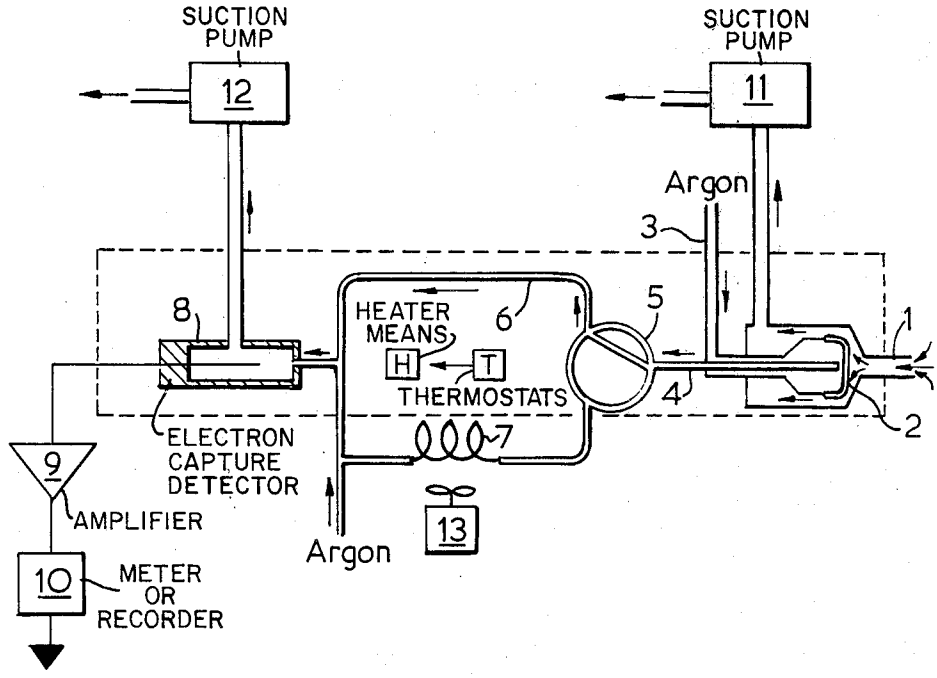
Assistant Examiner—Davis L. Willis

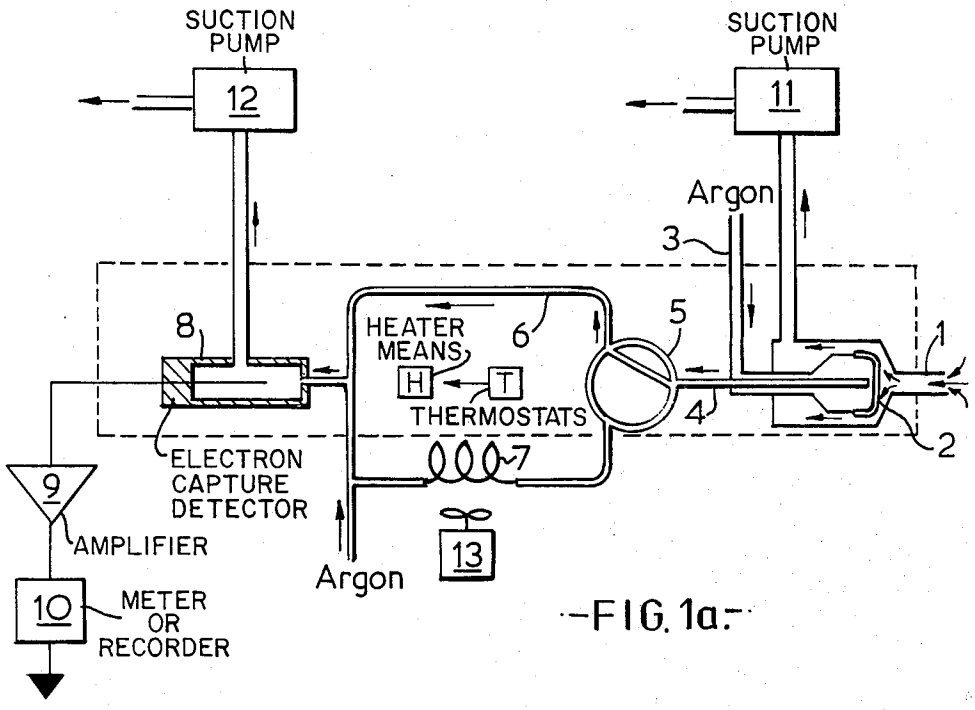
Attorney, Agent, or Firm—Woodhams, Blanchard and Flynn

[57] **ABSTRACT**

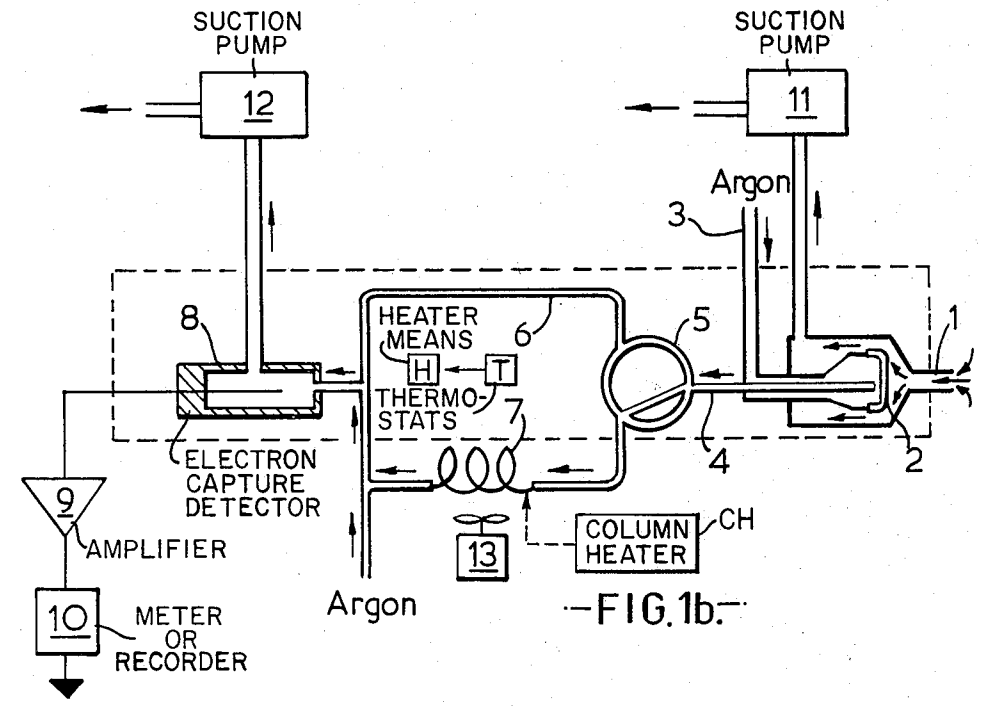
A method and apparatus for detecting and identifying low concentrations of vapours in the atmosphere and emanating from materials having low vapour pressures. The vapours are isolated from the atmosphere by being drawn through a membrane having a greater permeability to the vapours than the remainder of the atmosphere. The presence of the vapours is detected by an electron capture detector and thereafter the vapours are separated one from another for individual identification in the detector.

20 Claims, 3 Drawing Figures

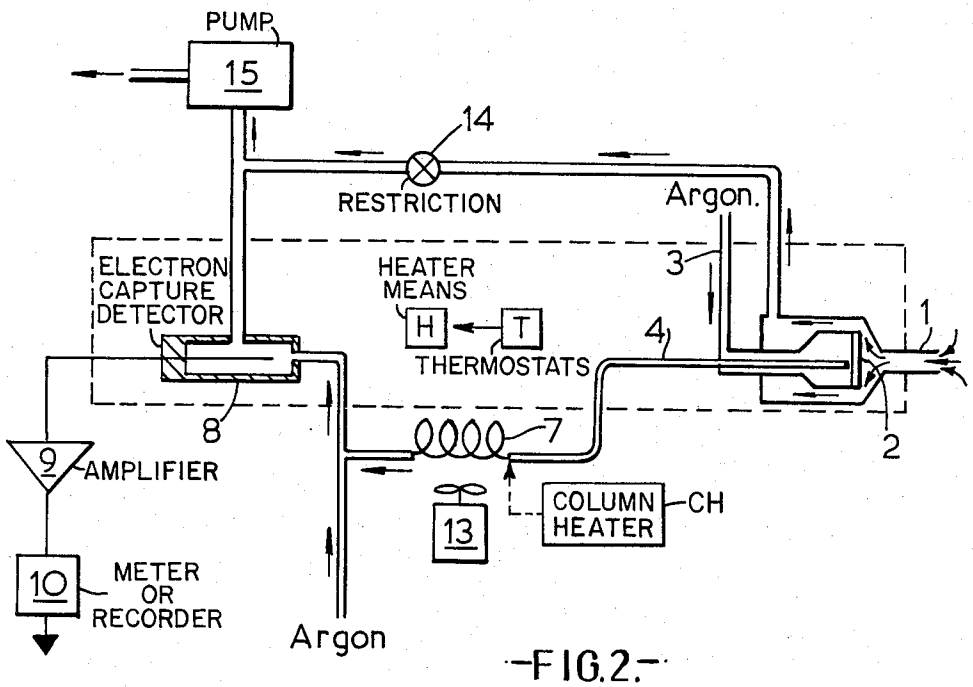



SUCTION PUMP
12
SUCTION PUMP
11
Argon
3
8
HEATER MEANS
6
5
H
T
THERMOSTATS
1
4
2
ELECTRON CAPTURE DETECTOR
7
9
AMPLIFIER
13
Argon
10
METER OR RECORDER

-FIG. 1a-


SUCTION PUMP
12
SUCTION PUMP
11
Argon
3
8
HEATER MEANS
6
5
H
T
THERMO-STATS
7
1
4
2
ELECTRON CAPTURE DETECTOR
9
AMPLIFIER
13
COLUMN HEATER
CH
Argon
10
METER OR RECORDER

-FIG. 1b-


PUMP
15
14
RESTRICTION
Argon.
3
ELECTRON CAPTURE DETECTOR
HEATER MEANS
H
T
THERMOSTATS
4
1
8
7
2
9
AMPLIFIER
13
COLUMN HEATER
CH
10
METER OR RECORDER
Argon

-FIG.2-

METHOD FOR THE QUALITATIVE AND QUANTITATIVE DETECTION OF VAPOURS FROM LOW VOLATILITY COMPOUNDS

The present invention concerns a method and apparatus for detecting and identifying extremely low concentrations of vapours emanating from certain solids, liquids and mixtures which have very low vapour pressures. The invention is particularly aimed at detecting and identifying the vapours from explosives but may also be applied to other low volatility compounds such as certain drugs and halogenated hydrocarbons.

U.S. Pat. No. 3,699,342 discloses a method and apparatus for detecting the presence of electron capture tracer gases using a membrane window to selectively isolate certain gases from an atmosphere containing the gases before being detected in an electron capture detector. This method and apparatus provides a continuous measurement of the level of electron capture material in an atmosphere but is incapable of differentiating between the responses of different electron capturing compounds. The known apparatus functions at room temperature which limits the response of the apparatus to compounds of relatively high volatility (greater than 10^{-6} Torr). The present invention seeks to improve on that described in the above patent by the addition of an identification stage and also the provision of heating facilities which allows the detection and identification of materials with vapour pressures lower than 10^{-7} Torr.

According to one aspect of the present invention a method of detecting and identifying components in an atmosphere comprises establishing a flow of the atmosphere across means capable of isolating the components of interest from the remainder of the atmosphere, introducing the isolated flow into a detector to detect the presence in the atmosphere of the components and thereafter separating the isolated flow into its individual components and introducing the individual components in succession into the detector for identification.

According to another aspect of the present invention an apparatus for detecting and identifying components in an atmosphere comprises means for isolating components of interest from the atmosphere, a carrier gas flow for conveying the isolated components into a detector to establish the presence of the components in the atmosphere and means in the carrier gas flow for separating the components one from another for individual identification in the detector.

The invention will be described further, by way of example, with reference to the accompanying drawing; in which:

FIGS. 1*a* and 1*b* illustrate a first embodiment of the apparatus for detecting and identifying vapours,

FIG. 1*a* illustrating the detection stage and

FIG. 1*b* illustrating the identification stage; and

FIG. 2 illustrates a second embodiment of the apparatus.

With reference to FIGS. 1*a* and 1*b* an atmosphere to be sampled is drawn through a probe or nozzle 1 by means of a suction pump 11. The atmosphere impinges on a membrane window 2 which selectively allows the diffusion of the low volatility components of interest. The membrane can be a silastromer although it is not restricted to this particular material. The rear of the membrane is swept by an inert carrier gas stream supplied through a conduit 3. A suitable carrier gas is Argon. The carrier gas carries any vapour passing through the membrane 2 along a conduit 4 into a selector valve 5. In FIG. 1*a* the selector valve is positioned to direct the flow along a conduit 6 leading to an electron capture detector 8 and the presence of an electron capturing material in the carrier gas flow causes a change in the ion current through the detector. This change is amplified by an amplifier 9 and the output is presented at a meter or recorder 10. Thus the electron capture detector generally comprises an ionisation chamber containing a β particle emitter, such as tritium, as a primary source of ionising radiation. Upon entry into the chamber of the carrier gas possessing no affinity for electrons, recombination of positive ions and free electrons formed by the ionising radiation is unlikely to take place because of the high mobility of the free electrons. Thus by applying a small potential across the chamber all ions formed by the ionising radiation can be collected. When the carrier gas contains a compound having an affinity for electrons, negative ion formation occurs which is accompanied by an observed decrease in the ion current. A suction pump 12 is connected to the detector.

The portion of the apparatus enclosed within the dotted outline can be heated to a controlled temperature by heater means H controlled by thermostats T. The flow directions are indicated by the arrows in the drawings.

If the probe or nozzle 1 is placed in the vicinity of an electron capturing compound such as one of the nitrated explosives e.g. nitro-glycerine or tri-nitrotoluene, then the detector will indicate a response within a very short interval e.g. 1 or 2 seconds. When searching for explosives it is desirable to eliminate all other responses.

In operation, the selector valve 5 will initially be set as in FIG. 1*a* and the flow will be as indicated by the arrows in FIG. 1*a*. This is the detection or search stage and any response will be continuous and rapid. Upon obtaining a response the valve is switched to the position shown in FIG. 1*b* and the gas flow is directed through a chromatographic column 7 maintained at ambient temperature. A flow is obtained down the column by virtue of the suction applied to the detector by the pump 12. Low volatility components are trapped at the front of the column which can be a packed or open tubular arrangement. Volatile components which also respond in the detector pass through the column at ambient temperature and give a response within a short interval. These volatile components will not be separated and will not be identified.

Sampling in the FIG. 1*b* position continues for a short interval in the vicinity in which a response was obtained when the valve 5 was in the FIG. 1*a* position. The probe or nozzle 1 is then directed to sample clean air. A few seconds are allowed for any vapour to pass through the membrane and on to the front of the column. The column is then heated to increase its temperature gradually from ambient temperature to a temperature to elute all the components of interest. As the temperature increases the trapped components are carried down the column by the carrier gas at a speed which is dependent on the partition coefficient of the particular component in the material of the column at the particular temperature. The rate of increase of temperature is such that all components of interest, if present in the sampled atmosphere, will emerge from the column

completely separated from one another. The components initiate responses in the detector and the outputs are presented, for example, as separate peaks on a chart recorder **10**. The elution time or elution temperature of each peak is used to identify the component.

As the temperature increases the flow rate through the column decreases due to an increase in viscosity of the gas. It is not desirable to introduce a constant flow regulator in the carrier gas flow upstream of the column as this would increase the pressure behind the membrane as the temperature rises and could cause the membrane to balloon. Preferably, a second carrier gas flow, as shown in the drawings and which can be Argon gas, is connected to the system downstream of the column and upstream of the detector. This second carrier gas flow is preferably many times in excess of the flow through the column. In this way, variations in the column flow cause only relatively small changes in the flow into the detector and the output from the detector, in the absence of any electron capturing material remains substantially constant.

In order to reduce sampling times it is desirable to heat and cool the column in a rapid manner. The column can be formed with a thin wall of electrically conducting material, for example stainless steel, which can be heated by the passage of an electric current along the column and such is schematically indicated in FIG. **1***b* by a column heater block CH. The column can be cooled by a stream of cold, air, generated by means of a fan **13**.

The selector valve **5** is omitted in the embodiment of FIG. **2**. In this embodiment, during a detection or search stage the column **7** is maintained at a temperature at which even the most involatile component which is being sough will pass rapidly through the column and respond in the detector within seconds of placing the probe **1** in the vicinity of the vapour. Upon obtaining such a response the column heating is terminated and the column is rapidly cooled, for example by the fan, to ambient temperature. The component can be identified in the manner as described with reference to the first embodiment.

The two separate pumps **11** and **12** of FIGS. **1***a* and **1***b* are replaced in FIG. **2** by a single pump **15**. A restriction **14** is included in the suction line between the nozzle **1** and the pump **15** in order to create a pressure drop from the detector **8** to the nozzle **1** so that a gas flow can be maintained through the column.

I claim:

1. A method of detecting and identifying components in an atmosphere, comprising the steps of:

isolating present components of interest from the atmosphere and conveying a direct continuous flow of the isolated components to a detector;

detecting the presence of the isolated components in the detector to thereby establish that the detected components are present in the atmosphere;

thereafter continuing a flow of isolated components;

separating said components of the continued isolated flow from each other;

flowing such separated individual components to the detector; and

identifying said individual components in the detector.

2. A method according to claim **1** in which said conveying of the isolated flow to the detector for detecting the presence of components is along a first path, in which the thereafter continued isolated flow to the detector is along a second path, and in which said separating of the isolated flow into its individual components is carried in said second path and prior to introduction of said individual components into said detector.

3. A method according to claim **1** including directing said isolated flow along the same path to the detector, both for initially detecting the presence of components of interest and for thereafter identifying the individual components, wherein said separating step includes releasing the separated components individually to the detector for identification therein.

4. A method according to claim **1** in which said components are low volatility components and said step of isolating includes diffusion of such low volatility components through a membrane and said step of conveying includes sweeping the rear of the membrane with an inert carrier gas stream to carry such diffused components away from said membrane and on toward said detector.

5. A method according to claim **1** in which the components of interest are low volatility components and in which said separating step includes passing the continuing isolated flow through a chromatographic column ahead of the detector while initially maintaining such column at ambient temperature to initially trap such low volatility components therein and while allowing volatile components to rapidly pass through such column and detector without separation and identification thereof, thereafter heating the column to increase its temperature gradually from abient temperature to elute said trapped components of interest trapped at corresponding differing temperatures, thereby to separate individual components flowing out of the column to the detector, said step of identifying including operating the detector to provide an output having peaks corresponding to respective individual components and using the elution time or elution temperature of each peak to identify the component.

6. A method according to claim **5** in which said conveying step includes entraining isolated components in a first carrier gas and in which said flowing step includes introducing a second carrier gas between said column and detector substantially in excess of the flow through the column so as to minimize changes in flow into the detector due to variations in column flow due to temperature change in the column.

7. A method according to claim **5** in which said conveying and detecting steps include maintaining the path of the flow of isolated components to the detector at a temperature at which even the most involatile components of interest will pass rapidly therethrough without condensation, and in which components of interest with vapors pressures lower than 10^{-7} Torr are detectible.

8. An apparatus for detecting and identifying components of interest in an atmosphere, comprising:

a detector responsive to the presence of such components;

means for isolating said components of interest from the atmosphere;

means entraining a direct continuous flow of the isolated components from the isolating means and conveying said flow of isolated components into said detector for detection in said detector that such components are present therein, as an indica-

tion that at least some component of interest in the atmosphere; and

means in a carrier gas flow path between said isolating means and detector and actuable after said detecting for separating the isolated components one from another for individual identification in the detector.

9. An apparatus according to claim **8** in which the isolating means comprises a silastomer membrane.

10. An apparatus according to claim **8** in which the separating means comprises a chromatographic column and means for selectively raising and lowering the temperature of the column.

11. An apparatus according to claim **10** wherein a single said gas flow path is provided from said isolating means to said detector and through said chromatographic column interposed therebetween, said means for raising and lowering temperature including heating means for maintaining the column at an elevated temperature at which even the most involatile component of interest will pass rapidly through the column, so as to enable said indication by the detector that at least some component of interest is present in the atmosphere, and means for rapidly cooling said column thereafter to a reduced temperature so as to trap low volatility components of interest in the column, said separating of components one from the other being carried out by thereafter reactuating said heating means to gradually reheat said column and elute said trapped components therefrom as their elution temperatures are reached one by one.

12. An apparatus according to claim **10** in which said means for raising and lowering temperature comprises a thin wall of electrically conducting material of the column and means for passing an electrical current along said wall for heating the column and further comprises means including a fan for directing cold air at the column for cooling same.

13. An apparatus according to claim **10** in which said means for raising and lowering temperature include means for normally maintaining said column at least initially substantially at ambient temperature after there is indication of presence of a component of interest and wherein volatile components not of interest and to which the detector may respond pass rapidly through the column and detector at such ambient temperature whereas low volatility components of interest are trapped at the front of the column for later release to the detector for identification.

14. An apparatus according to claim **8** including first and second gas flow paths between the isolating means and the detector, in which said separating means comprises a chromatographic column in said second path, and further including selectively operable valve means for directing the flow along the first path to provide said indication that some components of interest are present and thereafter for directing the flow along the second path through said chromatographic column to accomplish said separating of components one from another, and means for raising and lowering the temperature of the column.

15. An apparatus according to claim **14** in which said means for raising and lowering the temperature of the column includes cooling means for normally maintaining said column at a reduced temperature so as to trap low volatility components of interest within said column and heating means for gradually increasing the temperature of the column to a temperature elevated above ambient temperature for eluting, in sequence, the trapped components of interest in separated form for sequential application to said detector, wherein said detector responds sequentially to said released components and the elution time or temperature of each detector signal identifies the particular component.

16. An apparatus according to claim **8** including a common pump means both for drawing a sample of the atmosphere into the vicinity of the isolating means and for drawing a carrier gas flow through the detector.

17. An apparatus according to claim **16** in which said common pump means directly connects to the gas output of the detector and connects through a further path to a portion of said isolating means for drawing atmosphere thereinto, the latter connection including a flow restrictor to enable a gas flow to be maintained from said isolating means through said detector.

18. An apparatus according to claim **8** in which the detector comprises an electron capture detector and said components of interest are electron capturing compounds.

19. An apparatus according to claim **18** in which the components of interest are nitrated explosives.

20. An apparatus according to claim **8** including heater means and thermostat means controlling same for heating to a controlled temperature said isolating means, said detector and the path therebetween utilized for carrying out said detecting that components are present.

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