Oct. 20, 1970 HANS-GEORG ZIMMERMANN 3,535,088

HALOGEN VAPOR DETECTOR

Filed June 16, 1967

2 Sheets-Sheet 1

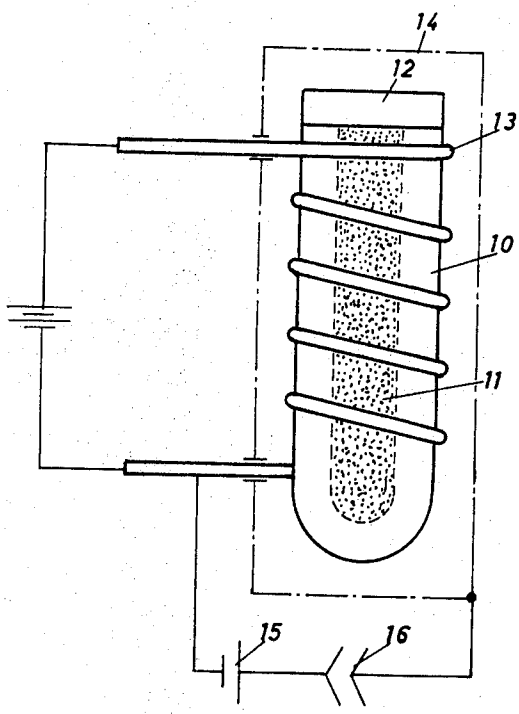


Fig. 1

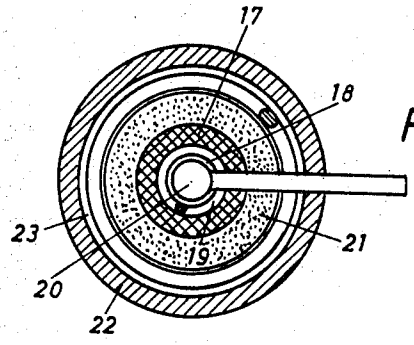


Fig. 2

Oct. 20, 1970 HANS-GEORG ZIMMERMANN 3,535,088

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Filed June 16, 1967 2 Sheets-Sheet 2

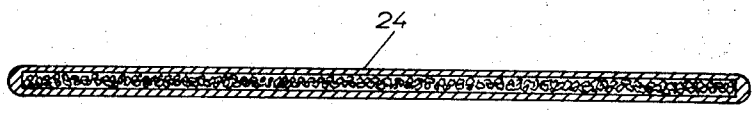


Fig. 3

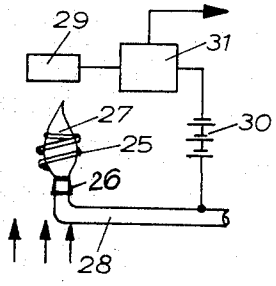


Fig. 4

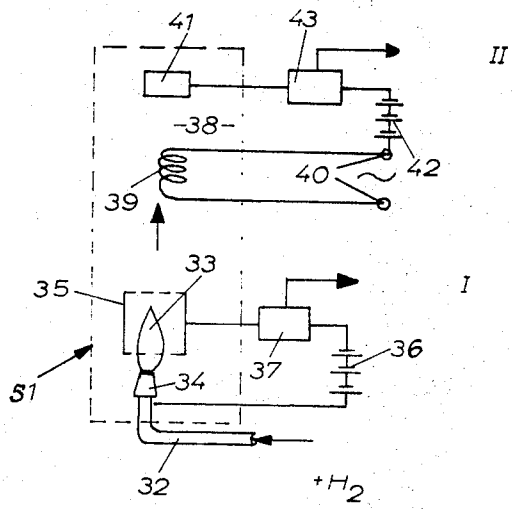


Fig. 5

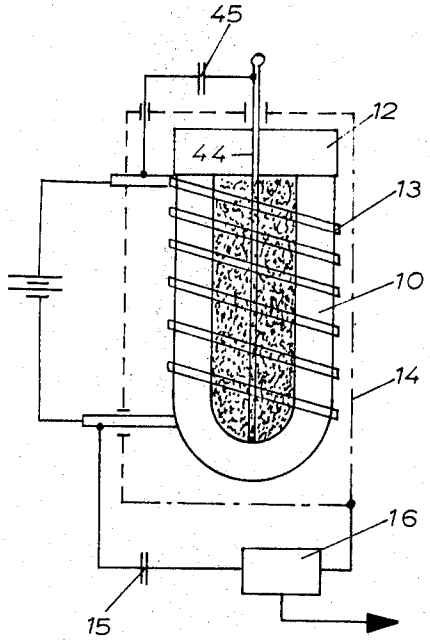


Fig. 6

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3,535,088

HALOGEN VAPOR DETECTOR

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Int. Cl. G01n 27/62
U.S. Cl. 23—254 12 Claims

ABSTRACT OF THE DISCLOSURE

A halogen detector includes an enclosed body forming a reservoir for an alkali material. The body includes a portion formed of a material which is permeable to vapor of the alkali material. A heater means is adapted for causing the alkali material to vaporize and thereby diffuse through the permeable material. Means, including first and second electrodes positioned near said permeable material, establish an electric field and indicate the amplitude of current flow in the presence of a halogen vapor.

This invention relates to arrangements for detecting the presence of halogen vapors and vapors of halogen compounds.

In one form of a halogen vapor detector, the halogen vapor flows between two electrodes, one of which is heated. The heated electrode comprises a body sensitized with an alkali compound and which is pervious to the alkali. Positive ions are liberated at the heated electrode in the presence of the halogen, the number of such liberated ions increasing as the halogen vapor concentration increases. An electric potential is applied between the electrodes and a meter coupled to the electrodes provides an output indication of the halogen vapor concentration. A halogen vapor detector of this type is described in German patent specification 907,223.

A further halogen detector of this type has been proposed wherein a ceramic body is impregnated with the alkali compound and the electrodes comprise a first coil of wire positioned in an aperture of the body and a second coil of wire arranged centrally in the aperture. The operation of the detector causes a depletion of the alkali compound over a period of time and a diffusion of the alkali from the body varies accordingly. As a result, an undesired change occurs in the base line of an output signal and in the sensitivity of the detector.

Accordingly, it is an object of the present invention to provide an improved form of halogen vapor detection apparatus.

Another object of the invention is to provide a halogen vapor detector of the general type described which is adapted for operation over relatively long periods of time with substantially consistent sensitivity.

In accordance with the present invention, a halogen vapor detector comprises a hollow body defining a container for an alkali compound and wherein at least a portion of said body is formed of an alkali permeable material. An alkali compound is positioned in the container and means are provided for heating and causing the alkali compound to vaporize. Means, including first and second electrodes positioned near the permeable material, are provided for establishing an electric field and for indicating ion current flow. Thermal decomposition of the alkali compound occurs gradually by virtue of the heating and the products of decomposition diffuse through the permeable portion into the space between the electrodes. Thus, a relatively large supply of alkali compound is

provided rather than an impregnated ceramic body wherein the alkali is contained only in the pores of the ceramic body. The detector sensitivity and output signal baseline are thereby maintained substantially constant over a relatively long period of time.

These and other objects of the present invention will become apparent with reference to the following specifications and drawings wherein:

FIG. 1 illustrates an embodiment of the invention;

FIG. 2 is a sectional view of another embodiment of the invention;

FIG. 3 illustrates a body for containing an alkali compound;

FIG. 4 illustrates a detector arrangement adapted for use with the body of FIG. 3;

FIG. 5 illustrates still another detector arrangement adapted for use with the body of FIG. 3; and

FIG. 6 illustrates an alternative arrangement of the detector of FIG. 1.

Referring now to FIG. 1, there is illustrated a porous ceramic body **10** of generally cylindrical shape having a hollow space **11** or cavity containing a supply of an alkali compound. $K_2Cr_2O_4$ or $KMnO_4$ are exemplary materials suitable for use as the alkali compound. The hollow body **10** is closed by a cover **12** which can be removed in order to replenish the supply of alkali material. A coil **13** is positioned about the body **10**. This coil functions both as one electrode of the halogen detector and as a heater. A heater voltage is applied to this coil and causes a heating current to flow therein. The supply of alkali compound in hollow space **11** is thermally decomposed gradually by virtue of the heating and the alkali is caused to diffuse outwardly through the porous ceramic hollow body **10**. A chemical equilibrium is established in the hollow space at which a specific vapor pressure of the products of decomposition (alkali and residual compound) is produced as long as a supply of alkali compound is still present. The alkali diffuses through the body **10** to one electrode and substantially constant conditions are maintained over a period of time as long as there remains a supply of alkali compound in the hollow space. The ceramic hollow body **10** with coil **13** is surrounded by a wire mesh or netlike collecting electrode **14** in spaced-apart relationship. A voltage is applied between coil **13** and the collecting electrode **14** from a source **15** in series with a signal amplifier **16**. A sample under investigation flows from a source to the detector. Alternatively, the detector may be positioned in an atmosphere to determine the presence of halogen vapors. Positive ions are created in accordance with the halogen vapor concentration. A resulting output current is amplified by amplifier **16** and indicating or recording means, not illustrated, are employed for providing an output indication.

In the embodiment of FIG. 2 a ceramic body **17** is provided with a central aperture **18**. One electrode is formed by a coil of wire **19** abutting the inner wall of aperture **18**. The other electrode **20** is arranged centrally in aperture **18**. The gas to be analyzed is passed through the aperture **18**. The ceramic body **17** is surrounded by a hollow space **21** which is defined between the ceramic body **17** and an outer jacket **22**. In the hollow space **21** there is also arranged a supply of alkali compound. On the inner wall of jacket **22** there is provided a heating coil **23**, whereby a thermal decomposition of the alkali compound and a diffusion of the alkali is effected inwardly into the aperture **18**.

In FIG. 3 the hollow body is shown to comprise an elongated platinum tube **24** of relatively small diameter which is filled with alkali and closed at the ends thereof. The tube can be of capillary dimensions. It has demonstrated the characteristic that the alkali atoms diffuse

through the body along the grain boundaries of the platinum tube. In a particularly advantageous arrangement, the platinum body of FIG. 3 contains carbon in addition to the alkali material. Because of the presence of the carbon, the grain-boundaries of the platinum are expanded and the diffusion of the alkali therethrough is facilitated. An exemplary material contained by the tube is a mixture of graphite and an alkali compound. A decomposable carbonaceous alkali compound provides an advantageous filling material. Alkali alcoholate has proven to be a suitable material. The carbon is then produced as a product of decomposition of the alkali compound.

In the embodiment according to FIG. 4 the filled platinum tube **24** of FIG. 3 is bent to form a coil **25** which is mounted on a burner nozzle **26** on which a hydrogen flame **27** is burning. The hydrogen is supplied via a line **28**. The coil **25** is mounted in the oxidizing portion of the flame and is heated thereby. Coil **25**, nozzle **26** and line **27** constitute one electrode of the detector. Above the flame—or thereabout—there is arranged a counter-electrode **29**. A voltage is applied between electrode **29** and line **28** from a source **30** through a signal amplifier **31**. The sample gas is introduced in the direction of the arrows from below.

FIG. 5 illustrates a flame ionization detector **51** comprising an additional arrangement for measuring or determining halogen vapors. A mixture of sample gas, carrier gas (in gas chromatography) and hydrogen is introduced through a line **32**. This mixture is burned in a flame **33** adjacent a nozzle **34**. The flame **33** is surrounded by a counterelectrode **35** in jacket-like manner. A voltage source **36** and a signal amplifier **37** is coupled between nozzle **34** which constitutes one electrode, and the counter-electrode **35**. The signal amplifier supplies a signal I, which is the normal flame ionization detector signal. For detecting and measuring halogen vapors there is provided a second device generally referenced as **38** above the flame ionization detector. This second device contains a coil **39** of a platinum tube filled with alkali. However, this one is not heated by a flame in the manner of FIG. 4, but is heated by applying an A.C. voltage to the ends **40** thereof. A voltage source **42** and signal amplifier **43** are coupled between coil **39** and a counterelectrode **41**. The amplifier **43** supplies a signal II which is specific for halogen vapors which rise together with the combustion gases of the flame ionization detector upwardly through coil **39**.

FIG. 6 illustrates an alternative arrangement of the detector of FIG. 1. Equivalent parts in FIG. 1 and FIG. 6 are provided with the same reference characters. One electrode **44** protrudes into the hollow space filled with alkali, which electrode is connected with the heating coil **13** acting as electrode via a voltage source **45**. In this manner, the diffusion of alkali outwardly can be adjusted electrolytically in accordance with the potential applied to electrode **44**.

While I illustrated and described particular embodiments of my invention, it will be understood that various modifications may be made therein without departing from the spirit of the invention.

I claim:

1. In a flame ionization detector having a burner nozzle, an electrode member, means for establishing an electric potential between said nozzle and said electrode and for indicating current flow therebetween, means for conducting a combustible gas and a sample to flow to said nozzle for burning said sample and forming a flame thereby, the improvement comprising an elongated alkali vapor permeable platinum capillary tubulation of relatively narrow cross section sealed at opposite ends thereof, and containing an alkali compound, said tubulation formed in a coil configuration and disposed with respect to said nozzle in a manner for causing said flame to heat said tubulation.

2. In a flame ionization detector having a burner nozzle, an electrode member, means for establishing an electric potential between said nozzle and said electrode and for indicating current flow therebetween, means for conducting a combustible gas and a sample to said nozzle for burning said sample to thereby provide combustion products, the improvement comprising an elongated alkali vapor permeable platinum capillary tubulation of relatively narrow cross section sealed at opposite ends thereof and containing an alkali compound and a second electrode disposed in a flow path of said combustion products, electrical circuit means for causing an electric current to flow in said tubulation heating said tubulation, means for establishing an electric field and for indicating current flow between said tubulation and said second electrode.

3. A halogen vapor detector comprising:

an enclosed body defining a container for an alkali compound;

said body including a portion thereof formed of a material which is permeable to vapors of an alkali compound;

said body including an inner tubular member formed of said permeable material;

an alkali compound positioned about said inner tubular member;

heater means comprising a heater coil formed about said alkali compound for causing said compound to vaporize and to thereby diffuse through said alkali permeable material; and,

means, including first and second spaced-apart electrodes positioned within said tubular member for establishing in a space between said electrodes an electrical field and for indicating current flow between said electrodes, said body positioned with respect to said electrodes for providing introduction of diffusion of alkali vapors into the space between said electrodes, thereby enhancing current flow between electrodes in the presence of a halogen vapor.

4. A halogen vapor detector comprising:

an enclosed body defining a cavity for containing an alkali compound;

an alkali compound positioned in said cavity of said body;

said body including a portion thereof formed of a material which is permeable to vapors of the alkali compound;

heater means adapted for causing said alkali compound to vaporize and to thereby diffuse through said alkali permeable material;

said enclosed body including demountable means providing access to said cavity for replenishing said compound when said compound is depleted by vaporization;

means, including first and second spaced-apart electrodes for establishing an electric field in a space between said electrodes and for indicating current flow between said electrodes, said body positioned with respect to said electrodes for providing introduction of diffusing alkali vapor into the space between said electrodes thereby enhancing current flow between the electrodes in the presence of a halogen vapor.

5. A detector in accordance with claim **4** including means defining a flow path for conducting a sample under investigation between said electrodes.

6. The detector of claim **4** including means for establishing an electric field for controlling the diffusion of said alkali compound through said permeable material.

7. A detector in accordance with claim **4** wherein said body comprises an elongated generally cylindrical hollow member and a closure member, and said heater means includes a heater coil formed about said body.

8. A halogen vapor detector comprising:

an enclosed elongated tubular body of relatively narrow cross section which is sealed at opposite ends thereof and which defines a cavity for containing an alkali compound;

an alkali compound positioned in said cavity of said container;

said body including a portion thereof formed of a material which is permeable to vapors of the alkali compound;

heater means adapted for causing said alkali compound to vaporize and to thereby diffuse through said alkali permeable material; and,

means including first and second spaced-apart electrodes for establishing in a space between said electrodes an electrical field and for indicating current flow between said electrodes, said tubular body positioned with respect to said electrodes for providing introduction of diffusing alkali vapors into the space between said electrodes thereby enhancing current flow between the electrodes in the presence of a halogen vapor.

9. A detector in accordance with claim **8** wherein said tubulation is of capillary dimension and is formed of platinum.

10. A detector in accordance with claim **8** wherein said tubulation is formed as a coil of platinum and includes a carbon material positioned within said body.

11. A detector in accordance with claim **9** wherein said tubulation contains a decomposable carbonaceous alkali compound.

12. A detector in accordance with claim **11** wherein said alkali compound comprises alkali alcoholate.

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U.S. Cl. X.R.

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