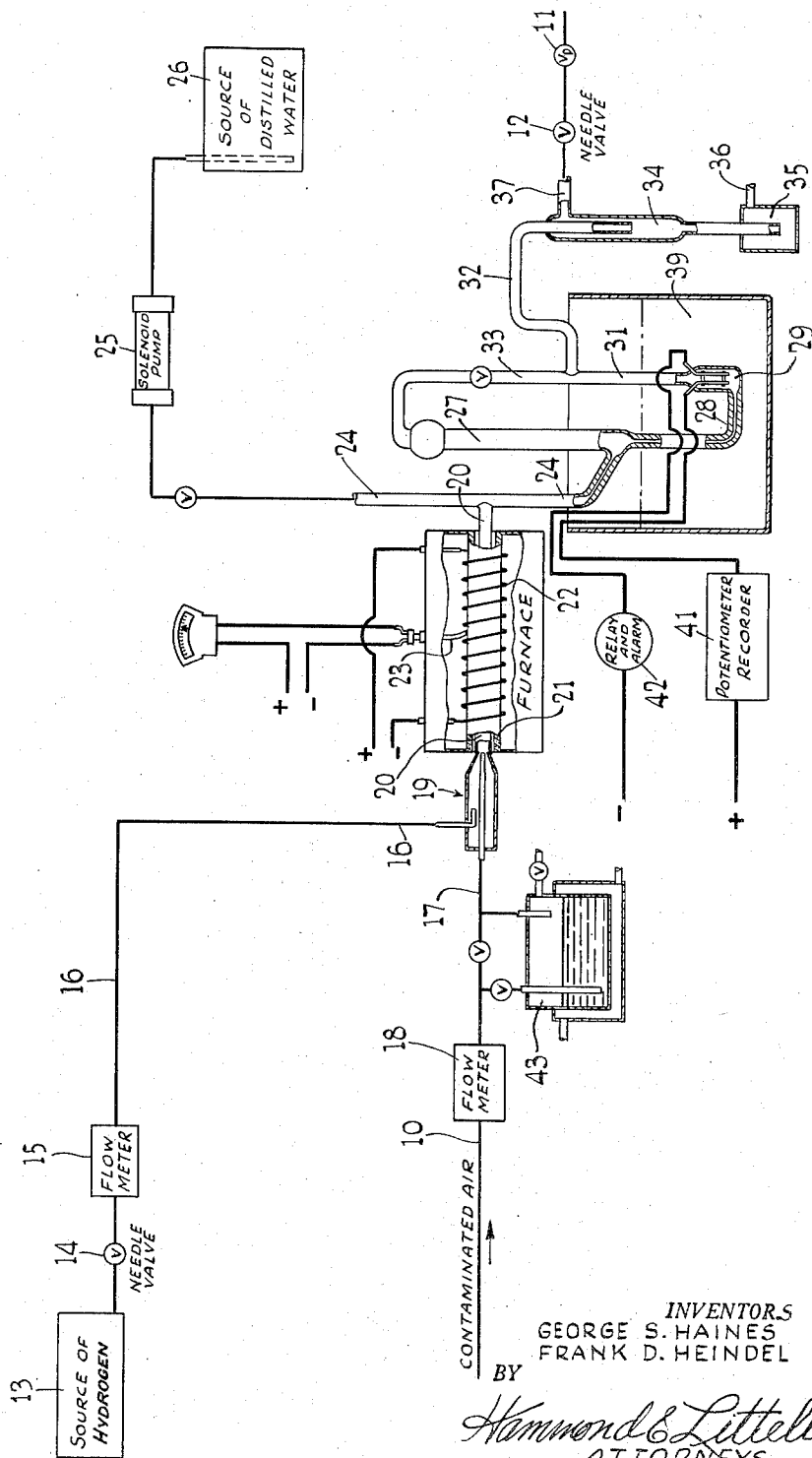


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DETECTION AND QUANTITATIVE DETERMINATION OF
HALOGENATED HYDROCARBONS IN ATMOSPHERE
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DETECTION AND QUANTITATIVE DETERMINATION OF HALOGENATED HYDROCARBONS IN ATMOSPHERE

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This invention relates to a process and apparatus primarily intended for the quantitative determination of the presence of toxic organic halides in the atmosphere in or about manufacturing or other plants where such atmospheres are or may be encountered.

In a number of industrial operation, methyl bromide unavoidably escapes into the atmosphere, and since these vapors are highly toxic, persons exposed to them in excessive concentrations, i. e., greater than 30 parts per million, may develop severe symptoms of poisoning. If the exposure is prolonged, the danger to health is especially hazardous in view of the cumulative effect.

An object of the present invention is to provide a continuous method and apparatus for the quantitative determination of methyl bromide or other organic halide in atmosphere likely to contain such toxic gases for the purpose of protecting personnel against the development of hazardous concentrations of these toxic materials.

Broadly considered, the process of the present invention involves the conversion of the methyl bromide or other contaminant of the atmosphere to be tested into hydrobromic or other corresponding acid by the action of hydrogen and heat in combination with the oxygen of the atmosphere, then dissolving the acid formed in distilled water or other water of known electrical conductivity and finally measuring the conductivity of the resulting electrolyte solution. In accordance with known principles, a measurement of the conductivity of the obtained solution by means of a conductivity cell and connected potentiometer or equivalent instrument indicates the amount of electrolyte taken from the combustion products and hence the concentration of methyl bromide or other such compounds in the atmosphere being tested.

More specifically, the invention contemplates a constantly operating process and apparatus wherein a continuous analysis of atmosphere containing methyl bromide or other equivalent compound is made, in which process air is withdrawn in a constant amount from the enclosure or space containing the toxic gases and after mixing with hydrogen is passed through a heating zone or furnace in which the mixture of gases is heated to a high temperature and the halide converted to the halogen acid, whereupon the resulting combustion gases are mixed with an unvarying stream of water of constant conductivity in such manner as to dissolve all of the acid therein, after which the resulting solu-

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tion is passed through a conductivity cell maintained at a constant temperature. The conductivity of the solution in the cell is preferably indicated on a connected potentiometer equipped to make a permanent record on an appropriate scale. The current in the potentiometer may be conducted through a relay to activate an alarm system whereby any increase in conductivity sufficient to indicate hazardous proportions of toxic gases in the atmosphere being tested causes an alarm to ring or show.

Among the outstanding novel features of the present invention is the procedure by which the organic halide or other contaminant in the atmosphere being tested is quantitatively converted into the acid or other electrolyte form. The proportion of the halide or other contaminant converted into the electrolyte form must not be varied during the operation of the testing process, for otherwise the conductivity readings could not be accurate. The complete conversion is obtained by mixing with the air containing the organic halide an amount of hydrogen adequate to effect or permit complete conversion of the organic halide in the air being tested to the corresponding hydrohalide and by heating the resulting mixture to a temperature at which the conversion proceeds to completion.

Under the conditions employed in the process, the oxygen of the air, organic halide, and hydrogen react and form hydrogen bromide, water, and carbon oxide. Experimentation with various proportions of hydrogen indicates that complete conversion of the bromine content to hydrogen bromide and consistently accurate determinations can be obtained only when the amount of hydrogen is theoretically sufficient to react with all of the oxygen of the air introduced. In actual operation, it appears desirable to use an amount slightly in excess of this theoretical requirement, for the possibility of error in results is thereby eliminated and experimentation has indicated that the use of an excess does not have any adverse effect on the operation or the recordings obtained.

The process and apparatus of the present invention can be readily understood from the drawing which for the most part is diagrammatic with certain detailed parts in elevation. With reference to the drawing, the air to be tested is withdrawn from the space or enclosure containing the contaminated atmosphere through a conduit 10 by means of a vacuum pump 11 at the opposite end of the apparatus. The amount of air drawn through the conversion apparatus of

the invention is controlled by the needle valve 12.

The hydrogen employed in the process is supplied from any suitable source 13 as from a pressure cylinder. After passing through needle valve 14, the hydrogen passes through a flow meter 15 into a conduit 16 which joins a conduit 17 leading from a flow meter 18 in the conduit 10, the junction being in a mechanism 19 which permits mixing of the gases only at their moment of discharge. The hydrogen and contaminated air mixture flows from this mechanism 19 inside a quartz tube 20 suitably of one third of an inch in diameter and mounted within an alundum tube 21 or other material capable of withstanding the high temperature of the furnace, the alundum tube suitably being one which is eight inches in length and five eighths of an inch in diameter. Heat is preferably supplied to the furnace by a coil 22 connected to a source of power (not shown). The furnace is provided with a pyrometer 23 for temperature determination and checking of heating conditions during continuous operation. At its discharge end, the quartz combustion tube 20 is connected to a conduit 24 conveying distilled water or water substantially free of electrolyte or of known conductivity supplied by means of a glass cylinder and piston solenoid actuated pump 25 in turn connected to a source 26 of distilled water.

The problem of delivering the small stream of water at a constant rate is most efficiently solved by the use of the solenoid pump. Not only is the delivery very constant, but the pump possesses all glass surfaces and hence does not contaminate the water. Furthermore, it is self-lubricating and requires no packing glands.

The gaseous reaction products from the furnace and the distilled water pass through a restricted portion (e. g. 3 mm. diameter) of the tube 24 and into a vertically disposed absorber chamber 27 having a comparatively large cross-sectional area (e. g. 2 cm. diameter). This arrangement effects rapid and complete absorption and dissolution in water of the electrolyte in the combustion products. The unabsorbed gases leave the absorber at the top and the electrolyte solution formed therein passes downwardly through a restricted conduit 28 connected to the bottom end of said chamber. This conduit 28 discharges into the bottom of a conductivity cell 29 containing therein two platinized platinum electrodes, the platinization being accomplished suitably by the method disclosed in "Physico-Chemical Methods" by Joseph Reilly et al, second edition, Van Nostrand Company, New York 1933.

After passing through the cell 29, the solution flows through the conduit 31 to the conduit 32 where it is joined by means of a valved conduit 33 connected at its other end to the top of the chamber 27. The recombined solution and unabsorbed gases in the conduit 32 pass to a separator 34 from which the solution flows to a trap 35 which discharges the water to waste through the overflow pipe 36. The gases arising in the separator 34 pass out through a conduit 37, the needle valve 12 and the vacuum pump 11 to the atmosphere.

The conductivity cell 29 is submerged in water or other liquid contained in a tank 39 adapted to maintain the temperature in the cell at any suitable constant as for example at 40° C. Its electrodes are electrically connected to a recorder timer 41 suitably of the potentiometer type and

to a relay arranged to sound an alarm, the relay and alarm being generally indicated at 42.

In the operation of the furnace, it is essential for accurate results that the temperature be maintained adequately high to effect union of all of the bromide with hydrogen. In the quartz tube furnace hereindescribed, it was found desirable at the commencement of the operation to heat to about 800° C. in order to obtain complete conversion of the methyl bromide to hydrogen bromide, but after the reaction had proceeded smoothly for a time, the furnace temperature could be decreased as low as 670° C. without causing erratic results. For safe operation, a furnace temperature of at least 700° C. is recommended. Temperatures as high as 1100° C. were tried and found not to affect the accuracy of the analyses.

The conductivity recorder 41 may satisfactorily be one adapted as manufactured to record a range of from 250 to 50,000 ohms. In view of the desirability of recording the conductivity as parts per million of methyl bromide in the air being tested, the recorder used by the present applicants was altered by replacing the ohm scale by a scale indicating parts per million following tests and normal scale transposition procedure.

The conduction characteristics of the conductivity cell were first adjusted by trimming and altering the position of the electrodes to give a desired reading on a conventional resistivity meter using a standard hydrobromic acid solution having a concentration equivalent to a selected concentration of methyl bromide. The electrodes were then sealed in a glass tube and a final calibration was made using hydrobromic acid solutions. Finally, the cell calibration was checked by means of tests using methyl bromide of known concentrations. It was calculated that if 50,000 ohms represented one part per million of methyl bromide in the atmosphere, then 250 ohms on the scale indicated a methyl bromide concentration of 175 parts per million. With the new scale in place, the test run conducted on a known methyl bromide concentration permitted adjustment of the substituted scale to obtain a correct reading. The electrodes employed were composed of platinized sheets of platinum foil 0.0025 inch in thickness and were mounted approximately 2 mm. apart by means of two glass spacers and were sealed with platinum lead wires in a glass tube of 16 mm. diameter.

Using the above-described apparatus, it was ascertained on test that all variations of the methyl bromide concentration above about 15 parts per million up to 600 were consistently within about five per cent of the actual concentrations. If for any reason greater accuracy is desired at either higher or lower concentrations, this objective could be easily obtained by altering the size of or the distance between the electrodes, by altering the rate of air flow, by altering the rate of water flow, or by making any combination of these alterations.

In a typical operation in the apparatus hereindescribed, air containing methyl bromide was passed into the apparatus at the rate of 1000 ml. per minute and the hydrogen at the rate of 420 ml. per minute. This mixture was then run through the furnace and heated to a temperature of 700° C. The reaction products were then mixed with distilled water introduced at the rate of 10 ml. per minute and the resulting solution passed through the conductivity cell of the structure hereinbefore described.

The apparatus of the present invention is par-

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ticularly designed for the determination of the presence of methyl bromide in air but may be used for the detection and quantitative measurement of any atmospheric contaminant which will react on being heated to a high temperature to give a compound which, when dissolved in water, will conduct an electric current. Among the atmospheric contaminants which may be detected in this manner are combustible compounds or organic compounds of chlorine, bromine, iodine, and sulfur, and as well, many compounds of nitrogen. The apparatus may also be effectively employed for locating leaks in containers in equipment which contains volatile or gaseous poisonous compounds.

When chlorine compounds and certain other of the mentioned compounds but not those of bromine and iodine are treated in the apparatus, the flow of hydrogen may be wholly or in part dispensed with and water vapor substituted therefor. This water may be supplied by cutting into the air conduit 17 the jacketed tank 43 into which the air is introduced below the surface of water contained therein. The amount of moisture taken up is controlled simply by regulation of the temperature of the water and saturation of the air with moisture. When chlorine compounds or other similarly reacting compounds are treated, the introduction of sufficient moisture into the air avoids the occurrence of free chlorine in the combustion products by causing quantitative formation of hydrogen chloride.

Since the present apparatus is not restricted to the detection and determination of methyl bromide concentrations, the presence of the other contaminants of the nature above described will also be detected by causing an increase in conductivity, and an additional safety factor is provided.

In the use of the process and apparatus of the present invention, it is contemplated that air be withdrawn for testing from several different sources or points where contamination is likely to occur. Since it is desirable that individual recordings be made for the tests on the atmosphere from the several sources, much of the apparatus must be duplicated for each source tested. However, any number of combustion tubes may be combined in one furnace and any number of absorber conductivity cells may be immersed in one temperature regulating bath. Furthermore, a single vacuum pump operating through a manifold can be connected to any number of conduits for the discharge of gases from the separator and one trap may likewise be used for the discharge of the tested liquid from the separator. Finally, one conductivity recorder of the six point variety can be employed for the simultaneous testing of six solutions from six sources of contaminated air.

It should be understood that the present invention is not limited to the specific details of construction or procedure herein described but that it extends to all equivalents which will occur to those skilled in the art upon consideration of the scope of the claims appended hereto.

We claim:

1. A process for quantitatively determining the presence of halogenated hydrocarbons including bromides, chlorides and iodides in an atmosphere contaminated with the same, which comprises adding to such contaminated air an amount of hydrogen gas theoretically sufficient to react with the oxygen content of the atmos-

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phere in excess of that part thereof which will react with the halogenated hydrocarbon therein, heating the resulting mixture to an elevated temperature and by the aid of such heat, (1) converting the halogenated hydrocarbons into hydrogen halides through reaction with oxygen in the air, and (2) reacting the added hydrogen present with the remaining oxygen whereby the formation of free halogen is prevented, dissolving the hydrogen halides formed in water of known electrical conductivity and measuring the electrical conductivity of the resulting solution.

2. A process for quantitatively determining the presence of brominated hydrocarbons in an atmosphere contaminated with the same, which comprises adding to such contaminated air an amount of hydrogen gas theoretically sufficient to react with the oxygen content of the atmosphere in excess of that part thereof which will react with the brominated hydrocarbons therein, heating the resulting mixture to an elevated temperature and by the aid of such heat, (1) converting the brominated hydrocarbons into hydrogen bromide through reaction with oxygen in the air, and (2) reacting the added hydrogen present with the remaining oxygen whereby the formation of free bromine is prevented, dissolving the hydrogen bromide formed in water of known electrical conductivity and measuring the electrical conductivity of the resulting solution.

3. A process for quantitatively determining the presence of methyl bromide in an atmosphere contaminated with the same, which comprises adding to such contaminated air an amount of hydrogen gas theoretically sufficient to react with the oxygen content of the atmosphere in excess of that part thereof which will react with the methyl bromide therein, heating the resulting mixture to an elevated temperature and by the aid of such heat, (1) converting the methyl bromide into hydrogen bromide through reaction with oxygen in the air, and (2) reacting the added hydrogen present with the remaining oxygen whereby the formation of free bromine is prevented, dissolving the hydrogen bromide formed in water of known electrical conductivity and measuring the electrical conductivity of the resulting solution.

4. A continuous process capable of quantitatively determining the presence of halogenated hydrocarbons including bromides, chlorides and iodides in an atmosphere which comprises, conducting a constant stream of air from the atmosphere to be tested together with a stream of hydrogen in an amount theoretically sufficient to react with the oxygen content of the air in excess of that part thereof which will react with the halogenated hydrocarbon therein, through a heating zone at a temperature which (1) converts the halogenated hydrocarbons into hydrogen halides through reaction with oxygen in the air and (2) reacts the added hydrogen present with the remaining oxygen whereby the formation of free halogen is prevented, passing the reaction products obtained containing the hydrogen halide into a constant stream of water of constant conductivity whereby said acid goes into solution, continuously passing said solution through a conductivity cell and constantly measuring the conductivity imparted by the halide, thereby determining variations in the organic halide content of the atmosphere.

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