Oct. 17, 1939. R. W. McALLISTER 2,176,462

AIR-TESTING METHOD

Filed April 27, 1937 2 Sheets-Sheet 1

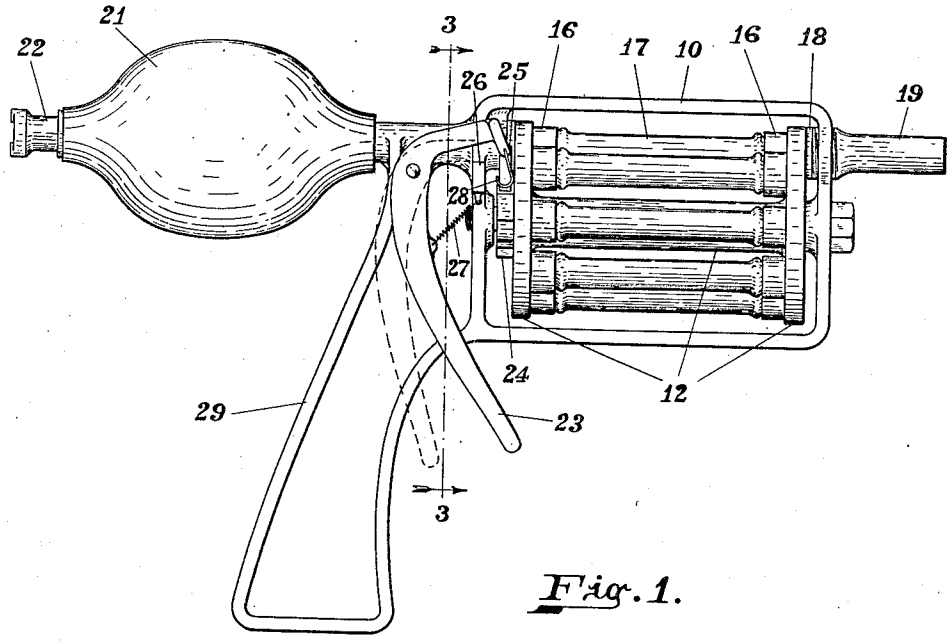


Fig. 1.

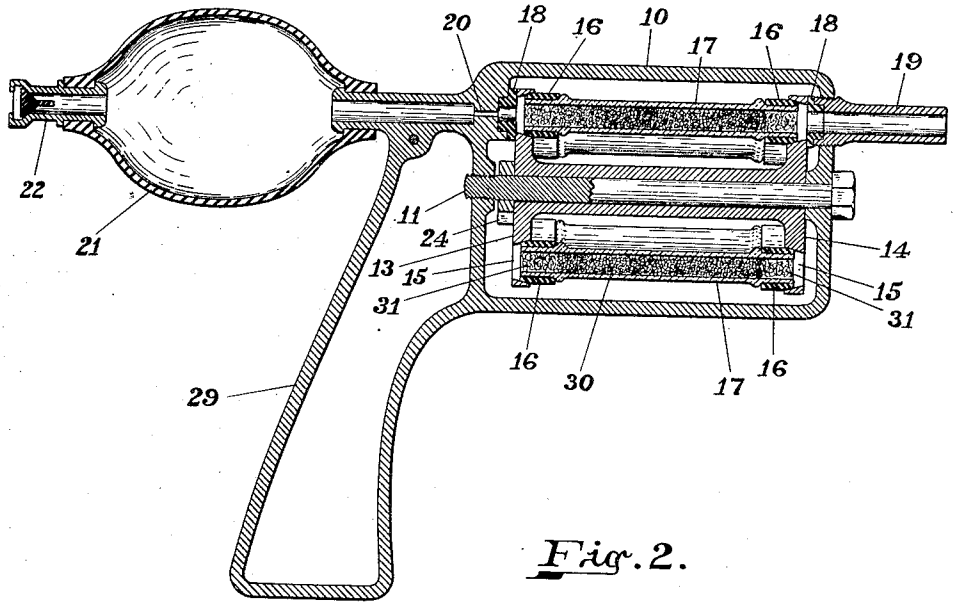


Fig. 2.

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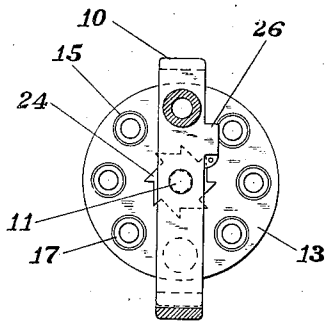


Fig. 3.

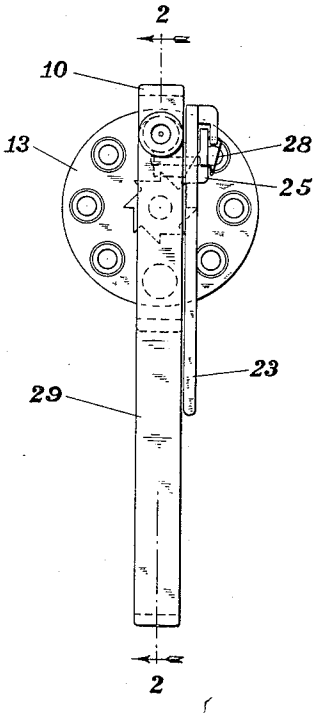


Fig. 4.

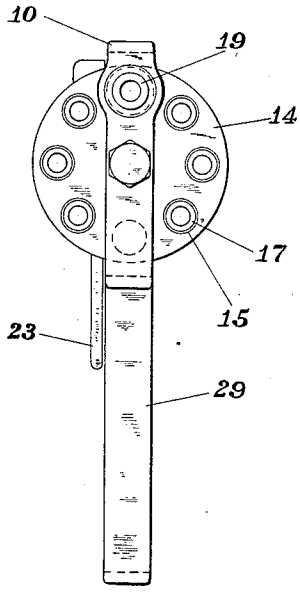


Fig. 5.

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UNITED STATES PATENT OFFICE

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AIR-TESTING METHOD

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Application April 27, 1937, Serial No. 139,332

3 Claims. (Cl. 23—232)

The present invention relates to the detection of gases in gas mixtures; more particularly, it relates to a method of detecting and determining the concentration of toxic gases, e. g., hydrocyanic acid gas, in air mixtures, and to apparatus suited for practicing such method.

Various methods of detecting the presence of gases such as hydrocyanic acid gas in air mixtures have been previously proposed. These methods, which generally require the use of liquid test solutions or test papers, are not entirely satisfactory for general application outside the laboratory. The use of test solutions is inconvenient and requires considerable experience in order to obtain reasonably accurate results, while the use of test paper is not always reliable, especially when quantitative determinations are required.

There is a very definite need of a reliable, simple method for determining whether or not toxic concentrations of hydrocyanic acid gas are present in atmospheres of spaces which have been previously fumigated. Although the general practice is to ventilate premises thoroughly after fumigation, there is always the possibility that toxic concentrations of the gas may remain in spaces which are not easily ventilated. Furthermore, even though a room which has been fumigated with hydrocyanic acid gas is subsequently ventilated, toxic concentrations of the gas frequently remain near substances which absorb the gas. Thus, in the fumigation of grains, thorough aeration of the material to remove hydrocyanic acid gas is difficult and there always remains the possibility that human beings may enter spaces enclosing the grains before the hydrocyanic acid gas has been completely removed. Hydrocyanic acid gas has been known to be present in grain storage rooms weeks after fumigation has been completed. As far as I am aware, there never has been developed a successful method for rapidly and reasonably accurately determining the concentration of hydrocyanic acid gas in air mixtures, so that the presence or absence of toxic concentrations may be ascertained in a convenient, practical manner.

It is an object of the present invention to provide a convenient and reliable method for rapidly determining concentrations of gases, e. g., hydrocyanic acid gas, in gas mixtures such as air. It is a further object to provide a compact, simple apparatus which is especially well suited for carrying out the above method. Other objects will be hereinafter apparent.

The above objects are accomplished in accordance with my invention by passing a known volume of a gas mixture containing a gas whose concentration in the mixture is to be determined, through a column of a granular adsorptive material coated or impregnated with a color-forming agent which is sensitive to the gas constituent being determined. I have found that the length of travel of coloration in the column of granular adsorptive material is proportional to the concentration of the gas being determined in the gas mixture, provided the cross-section of the column is uniform throughout its length. By observing the length of travel of the coloration through the column and comparing it with the corresponding length of travel in a similar column employed using a gas mixture having a known concentration of the gas being determined, it is possible to measure quantitatively the concentration of the gas in the mixture being tested. The above method may be practiced using various types of equipment. However, I have found the apparatus which will be subsequently described and which is illustrated by the appended drawings, to be especially well suited for practicing the present method.

The term "color-forming agent" is used in the ensuing description and in the appended claims to mean a substance or composition which develops a distinct color, or undergoes a distinct color change, when contacted with the gas whose concentration in a gas mixture is being determined. The term "granular adsorptive material" is used to designate a granular material which is a good adsorbent for the gas whose concentration is being determined.

I am aware that a method has been proposed heretofore for determining the concentration of a gas constituent of a gas mixture by passing a volume of the mixture through a column of color-forming substance and noting the intensity of color developed as a measure of the concentration. My method is not to be confused with this previously proposed method since it is based upon an entirely different principle and is productive of more reliable results than those obtainable by the earlier method. In my method, it is essential that a good adsorbent for the gas being determined be employed as the support for the color-forming agent. Otherwise, the length of travel of coloration in the column may not always be proportional to the concentration of the gas in the gas mixture. On the other hand, the earlier method relies upon the intensity of the color developed throughout the entire column, or through a substantial portion thereof,

so that the use of an adsorbent for the gas is not essential and may even be omitted.

Various chemical compounds are known to become colored, or to undergo a distinct color change, when they are contacted with certain gases. Thus, o-tolidine is sensitive in this manner to chlorine, p-amino dimethyl amidine hydrochloride to hydrogen sulfide, thiocyanate to iron carbonyl, p-rosaniline hydrochloride to formaldehyde, and benzidine acetate and numerous other substances are sensitive to hydrocyanic acid. I have discovered that such color-forming substances may be employed effectively to determine quantitatively various toxic gases in gas mixtures if they are uniformly coated over, or impregnated into granular adsorptive materials instead of being used in the form of solution or on test papers as they have been employed heretofore.

The column of granular material which is coated or impregnated with the color-forming substance may be conveniently prepared by packing the material in a glass tube having a suitable diameter. In order for the results to be reasonably accurate, it is essential that the tubes employed have a substantially uniform diameter throughout their entire length. In order to prevent channelling of the gas mixture through the column of granular material, the particles of granular material should be of substantially uniform size and not too large. On the other hand, the granules should not be so small as to increase appreciably the resistance of the column to the flow of gas therethrough. Particles having a size corresponding to 20 to 40 mesh may be used in most instances with good results, although I have found that it is generally preferable to employ particles having a size within the range of 30 to 34 mesh. For ordinary use, tubing having an inside diameter of 6 to 9 millimeters is generally satisfactory, although smaller or larger size tubing may be employed depending upon the concentration of the gas being determined in the gas mixtures.

It is essential that the color-forming agent be stable in contact with the granular material upon which it is coated. It is also essential that the agent be not sensitive to more than one constituent of the gas mixture. I have found that for most determinations that are required in connection with fumigation with hydrocyanic acid gas, the use of a composition containing benzidine acetate and cupric acetate as the color-forming substance is very satisfactory. Similarly, for the determination of chlorine, o-tolidine is especially suitable while p-rosaniline hydrochloride may be used with good results for the determination of formaldehyde vapors in gas mixtures. Other color-forming agents may be employed, in accordance with my invention, for the determination of the above gases, and it is to be understood that the illustrations herein set forth are merely illustrative of my invention.

A suitable method for preparing my preferred detector mixture, i. e. the granular material impregnated with the color-forming agent, for use in the determination of hydrocyanic acid gas is as follows:

A saturated solution of benzidine acetate in methyl alcohol is prepared, as well as a second solution containing 14 grams of cupric acetate in 200 cc. of water. Each of the above solutions are filtered to remove insoluble materials therefrom. 50 cc. portions of each solution then are added to 100 cc. of methyl alcohol and the resulting mixture diluted with 500 cc. of water. After standing for about 15 minutes, the solution is filtered to remove the dark precipitate that is formed, whereby a clear, greenish colored solution is generally obtained. If a clear solution is not obtained, filtration should be repeated. The clear solution then is poured over 30 grams of the granular adsorptive material, e. g. alumina gel, contained in a small Buchner funnel fitted with a filter paper and the liquid drawn off at once. The treated granular material is then placed upon paper to dry. Drying is continued until the material is just wet enough to be picked up upon contact with the finger tips without extra pressure from the hand. The treated granular material then is placed in stoppered, air-tight containers for storage until required for use.

Alumina gel of 30 to 34 mesh was treated in the above manner and then packed into 3-inch lengths of 6 millimeter glass tubing so as to form several compartments of uniform length in each tube, the individual compartments being separated from each other by plugs of absorbent cotton. The following table illustrates the accuracy with which hydrocyanic acid gas may be determined in air in accordance with my invention:

Volume of test sample	Known concentration of HCN	Number of compartments penetrated by the coloration
	Percent by volume	
200 cc.	0.05	2
200 cc.	.10	4
100 cc.	.10	2

Repeated laboratory tests have shown that check results may be obtained with gas mixtures containing known concentrations of hydrocyanic acid and that the length of travel of coloration in a tube of a given cross section is proportional to the concentration of hydrocyanic acid in the gas mixture when equal volumes of gas are used in the determinations. It is not essential that the material be divided into compartments; equally satisfactory results have been obtained using a continuous column of the granular material impregnated with the color-forming agent.

The above method may be employed to determine hydrocyanic acid over a wide range of concentrations. Thus, I have found that the method is applicable to determine concentrations ranging from 1 part per million to 1 part per hundred by volume with a satisfactory degree of accuracy. The method is rapid and reliable since the color formed is a bright blue and can be easily detected even by inexperienced operators. Results which are accurate within 10% and generally within 5% are readily obtainable.

For the determination of chlorine in gas mixtures, alumina gel or silica gel may be impregnated with a saturated aqueous solution of o-tolidine and the impregnated material dried as described above in the preparation of alumina gel impregnated with benzidine acetate. The procedure for determining chlorine is essentially the same as that described above for the determination of hydrocyanic acid. The color developed is an intense yellow or orange as compared with the substantially white impregnated alumina or silica gel prior to its contact with chlorine.

Alumina gel impregnated with p-rosaniline hydrochloride may be employed in the same manner to determine formaldehyde vapors in gas

mixtures such as air. The solution of p-rosaniline hydrochloride that is employed to impregnate the alumina gel may be prepared by dissolving 0.05 gram of the material in 100 cc. of water and then filtering the solution to remove insoluble substances. Before using, the solution should be substantially decolorized by the addition of a small amount of a sodium bisulfite solution. The method of impregnating and drying the impregnated granular material is essentially the same as described above in the preparation of alumina gel impregnated with benzidine acetate.

My method is also applicable in the determination of other gases, it being only necessary to employ a granular adsorptive material which is coated or impregnated with an agent that forms a distinct color or color change when contacted with the gas whose concentration is to be determined. It is generally preferable to employ a color-forming material that is colorless, or substantially colorless, prior to its contact with the gas, in order that any color that is developed may be readily detected. It is also desirable that the color developed be relatively permanent although this is not an essential characteristic.

In the determination of hydrocyanic acid gas, chlorine, or formaldehyde vapors, it is essential that the porous impregnated material be moist when used, otherwise unreliable results may be obtained. I have found that alumina gel which has been impregnated with a benzidine acetate-cupric acetate mixture is entirely satisfactory for determining hydrocyanic acid even after two months, provided it has been stored in a vapor-tight container. The material also may be used with good results even though the container in which it is stored is open to the atmosphere for several days before use. There may be some tendency for the mixture to assume a gray color; however, the intense blue color that is developed in contact with hydrocyanic acid is easily detected even though the granular material has assumed such a gray color. The effectiveness of the material is not permanently destroyed by becoming dry, since by remoistening the dry material, its effectiveness is restored.

It is not always essential that the coated or impregnated granular material be used in a moistened condition. It is known that test papers for the determination of certain gas constituents should be used in a dry rather than in a wet condition. Thus, picrate papers are best used in the dry condition for the detection of sulphur dioxide in air. It is to be understood, therefore, that my invention is not limited to the use of wet granular adsorptive material impregnated with a color-forming agent, but may be used either in the dry or wet state depending upon the color-forming agent employed and the gas being determined.

Various inert granular adsorbent materials may be used as a support for the color-forming agents. Examples of such granular materials are alumina gel, silica gel, chipped ceramic ware, shredded asbestos, and the like. It is preferable that the material be white in order not to obscure the color developed. It is essential that the granular supporting material be a good adsorbent for the gas which is to be determined. The adsorbent acts to remove quantitatively the gas constituent from the gas mixture and thus to bring it into intimate contact with the color-forming agent with which the adsorbent is impregnated. It is the effectiveness of the adsorbent material in this respect which makes possible the obtainment of quantitative determinations by my method. Alumina gel is an excellent adsorptive supporting material for color-forming substances to be used in the determination of hydrocyanic acid since it is a good adsorbent for hydrocyanic acid gas. It is also excellent for use in the determination of chlorine or formaldehyde. Silica gel is almost as good as alumina gel although I prefer to use alumina gel.

Other color-forming substances, in addition to those mentioned above, may be employed in accordance with my invention. Thus, aloin or a methyl red-mercuric chloride composition may be used in place of benzidine acetate and cupric acetate in determining hydrocyanic acid gas. While I have illustrated the general utility of my method as related to the determination of gases in general, I wish it to be understood that the method disclosed above is especially well suited for the determination of hydrocyanic acid gas, especially when a benzidine acetate-cupric acetate composition is employed as the color-forming substance.

The application of my method may be more clearly understood by the following description of an apparatus which is especially well suited for practicing my method. The apparatus is illustrated by Figures 1 to 5 of the appended drawings.

Figure 1 is a side elevational view of the apparatus and Figure 2 a longitudinal sectional view through plane 2—2 of Figure 4. Figure 3 is a sectional view through plane 3—3 of Figure 1, shown partially in elevation with trigger and ratchet pawl omitted. Figures 4 and 5 are rear and front elevational views, respectively, with the aspirator bulb not shown.

In the figures, element 10 is the body or frame structure. Bolt 11 extends longitudinally through body 10 and serves as a removable shaft around which magazine 12 may be rotated within body 10. Magazine 12 includes rear and front circular end plates 13 and 14, respectively. These end plates are provided with apertures 15 which are tapered from the inside to receive the rubber sleeve extensions 16 of the glass detector tubes or cartridges 17. The rubber sleeve extensions 16 protect the ends of the detector tubes 17, permit their removal from the magazine and insure a gas-tight fit of the tubes against the sides of the apertures 15. Apertures 15 are so made that upon rotation of the magazine 12, adjacent pairs of apertures on end plates 13 and 14 are successively aligned with the rubber washers 18 and the inlet tube 19. When any pair of said apertures is so aligned, orifice 20 permits the aspiration of gas from tube 19 through the detector tube positioned between the aligned pair of apertures, upon manipulation of the aspirator bulb 21. Bulb 21 is provided with valve 22 which functions to regulate the flow of gas through the detector tube in one direction only, from front to back, upon manipulation of the aspirator bulb 21. Inlet tube 19 also serves as an adjustment means by which the end plates 13 and 14 of magazine 12 are maintained tightly against rubber washers 18 so as to form a continuous gas-tight passage for the gas mixture from the inlet tube through the aligned detector tube into bulb 21. Tube 19 is threaded through frame 10 so that any degree of tension of end plates 13 and 14 against washers 18 may be maintained.

Trigger 23, together with ratchet wheel 24 and ratchet pawl 25, provides a means for rotating magazine 12. Trigger stop 26 functions to arrest the rotation caused by each pull of the

trigger when each successive detector tube is brought into proper alignment with inlet tube 19 and orifice 20. Trigger spring 27 functions to return the trigger to its normal resting position after each pull thereof and pawl spring 28 serves to maintain the ratchet pawl in operative contact with the teeth of ratchet wheel 24. Element 29 is a handle which may or may not be a part of the apparatus, since its use is more a matter of convenience rather than a necessity.

The apparatus illustrated by the drawings is simple to operate. The detector tubes are filled with the appropriate detector composition 30, e. g., alumina gel impregnated with a benzidine acetate-cupric acetate solution when hydrocyanic acid gas is to be determined. Composition 30 is held in position in the tubes by cotton plugs 31. The filled tubes then are inserted into the magazine and the rubber sleeves adjusted so that the tubes are held snugly in position. Inlet tube 19 then is placed in the gas mixture to be tested and the aspirator bulb is squeezed the required number of times in order to draw through the detector tube the desired amount of the gas mixture. Thus, if a volume of 600 cc. is desired and the aspirator bulb has a capacity of 60 cc., 10 squeezes will be necessary. The distance from the front of the detector composition in the detector tube which is colored is an indication of the concentration of hydrocyanic acid in the gas mixture. By comparing the length of travel of coloration in the tube with a similar length of travel obtained using corresponding detector tubes and gas mixtures containing known concentrations of hydrocyanic acid, a quantitative measure of the concentration of hydrocyanic acid in the gas mixture is obtained.

After one determination as described above, the trigger is pulled to bring into proper alignment a second detector tube. The apparatus then is ready for use to make a second determination. The apparatus may be employed repeatedly until all of the detector tubes in the magazine have been used. The magazine then may be refilled with new detector tubes or the old tubes may be removed and refilled for further use. Although not illustrated in the drawings, the detector tubes may be calibrated so that concentrations may be read directly in per cent or parts per million. If desired, the apparatus may be provided with a calibrated scale positioned in close proximity to the detector tube in use, from which the concentration may be read directly in any desired unit.

The purpose of orifice 20 is to prevent any substantial back flow of spent gas through the detector tube upon squeezing bulb 21, and also to prevent gas from being drawn too rapidly through the detector tube when the bulb is permitted to assume its original shape after being squeezed. In order for accurate results to be obtained, the gas should be passed through the detector tubes at a rate no faster than the maximum rate at which the hydrocyanic acid is completely adsorbed by the composition in the tubes. The size of orifice that should be employed can be readily determined by a few tests.

I have illustrated an apparatus which contains 8 detector tubes or cartridges in the magazine. It is to be understood that the magazine and apparatus may be so constructed as to contain a greater or lesser number of cartridges without departing from the spirit of my invention. Other modifications may likewise be made. Thus, instead of using a bulb and handle as illustrated in the drawings, the handle may be omitted entirely, or a rubber handle which serves both as an aspirator and as a handle may be used with good results. My invention is not to be restricted by the drawings, examples, or procedural details herein set forth, which are intended to be illustrative and not restrictive in nature.

I claim:

1. A method for determining hydrocyanic acid gas in a gas mixture comprising passing a volume of said gas mixture through a uniform column of a granular adsorptive material impregnated with a color-forming substance which is sensitive to hydrocyanic acid and noting the length of travel of coloration in said column, said length of travel being proportional to the content of hydrocyanic acid in said gas mixture.

2. A method for determining hydrocyanic acid in a gas mixture comprising passing a volume of said gas mixture through a column of granular alumina gel impregnated with a composition comprising benzidine acetate and cupric acetate and noting the length of travel of coloration in said column, said length of travel being proportional to the content of hydrocyanic acid in said gas mixture.

3. A method comprising impregnating granular alumina gel with a benzidine acetate-cupric acetate solution, arranging said impregnated gel in the form of a column having a substantially uniform cross section throughout its length, passing a gas mixture containing from one part per million to one part per hundred by volume of hydrocyanic acid through said column and determining the content of hydrocyanic acid in said gas mixture by measuring the length of travel of coloration in said column.

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