The Detection of Carbon Monoxide^{1, 2}

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The problem of detecting quantities of carbon monoxide too small to be determined accurately by the ordinary methods of gas analysis, yet sufficiently large to produce harmful physiological effects, has been attacked by a number of investigators.

Several forms of portable apparatus for the detection of carbon monoxide in houses, mines, factories, etc., have been devised.

Racine³ attached a filament of guncotton dusted with platinum black to the terminals of an electric circuit in such way that as the guncotton was ignited by the heat of absorption of the carbon monoxide on the platinum black, the circuit was closed and a signal given. This device is capable only of detecting quantities of carbon monoxide greater than 0.75 per cent and is therefore not sufficiently sensitive for the hygienic testing of air.

Guasco⁴ constructed a toximeter for carbon monoxide consisting of two glass bulbs, one coated with platinum black, connected by a U-tube containing a colored liquid. Temperature changes produced by the absorption of carbon monoxide on platinum bulb altered the level of the liquid in the U-tube. Although Guasco claims to be able to recognize 0.01 per cent of carbon monoxide with this apparatus, it is difficult to manipulate, and useless in most industrial gas mixtures.

Lamb and Larson⁵ have recently investigated the thermometric principle and propose two accurate methods very well adapted to the continuous analysis of a gas mixture containing carbon monoxide. Their apparatus is not intended to be readily portable, but it would seem to be of special value for stationary use in laboratories and industrial plants for the analysis of combustible gases which can be freed from catalytic poison.

Nowicki⁶ patented a pocket apparatus in which strips of paper moistened with palladium chloride solution are placed in a glass tube through which the suspected gas is drawn. However, the slowness of the reaction, the need of freshly preparing the paper to be used out of contact with reducing substances, and the wide variety of reducing substances that produce similar changes to those produced by carbon monoxide, have prevented any considerable practical use of this type of detector.

Harger⁷ designed a portable apparatus for the detection of carbon monoxide in mines. The variation in the conductivity of a solution of hydrogen iodide formed from the iodine liberated by the action of carbon monoxide on heated iodine pentoxide is employed to indicate the quantity of the gas present. This method is obviously difficult of manipulation, and the apparatus is expensive and cumbersome.

Teague⁸ of the Bureau of Mines has adapted the iodine pentoxide method of analysis to the determination of carbon monoxide in automobile exhaust gases by using liquid air to remove interfering substances. A form of portable apparatus has been described, but the manipulation is rather more difficult than can be carried out by the average working man.

In practical use none of the chemical or thermometric detectors mentioned have been found to be as generally successful as small animals, especially canaries, as suggested by Burrell, Seibertl and Robertson of the Bureau of Mines.⁹ That small animals, are, however, unsatisfactory in some cases was first pointed out by the same investigators. A man moving or at work may be overcome before a small animal quietly confined, and a person may be seriously affected by long breathing of low concentration of gas which causes no appreciable symptoms of distress in small animals. Among the other objections, the following may be

mentioned: The detection by small animals is applicable only to a limited range of concentration of carbon monoxide, and there is an appreciable difference in sensitiveness of different animals of the same kind. The uncertainty and slowness of recovery of small animals unless placed in pure air or oxygen makes it impossible to make tests at frequent intervals in impure air, or after passing through impure air, without a large number of birds and special containers. When not in use, animals must be cared for at places that are readily accessible. It can therefore be concluded that there is need in many industrial operations of a more reliable, more rapid, and simpler method of detecting carbon monoxide than any yet proposed.

HOOLAMITE

Lamb, Bray and Frazer¹ have summarized the work done by the Defense Chemical Research Section of the Chemical Warfare Service upon the absorption of carbon monoxide. One of the absorbents developed, Hoolamite,² was the result of an investigation of the action of carbon monoxide on mixtures of iodine pentoxide and other substances begun in this laboratory during the summer of 1917. This work was continued after September 1917 with the personal cooperation of Lieut. Col. A. B. Lamb, director of Defense Research, as a part of the general investigation described in the article just mentioned. Subsequent to the signing of the armistice and the resulting curtailment of the activities of the Chemical Warfare Service, the problem was continued in this laboratory and the detectors described in this article developed.

COMPOSITION—Hoolamite is prepared by mixing fuming sulfuric acid with iodine pentoxide and an inert supporting material. During the early stages of the development of this absorbent it was noticed that carbon monoxide imparted to the white Hoolamite of certain range of composition colors varying from pale bluish green to brownish black, the depth of the color depending upon the amount of the gas present. The nature of the compounds of iodine and oxides of iodine with sulfur trioxide and sulfuric acid is being investigated, but has not yet been definitely determined. The green color is due to an unstable substance which can be formed from iodine and sulfur trioxide. On standing or gentle warming in the presence of sulfur trioxide, the green material changes to orange yellow and finally, upon the addition of iodine pentoxide, to a white substance. Since at ordinary temperatures Hoolamite oxidizes carbon monoxide to carbon dioxide with the liberation of iodine, if an excess of sulfur trioxide is present, the green substance will be formed and is thus indicative of the presence of carbon monoxide.

Iodine pentoxide and fuming sulfuric acid of high sulfur trioxide content form solid bodies if the weight of acid does not exceed 70 per cent of the weight of the mixture, but in order to produce the green body a greater proportion must be present and such mixtures, being pasty, must necessarily be supported on an inert porous material in order to expose them efficiently to the action of carbon monoxide. Asbestos fiber gives the most active material, but it is difficult to handle, and irregular in surface and, consequently, in action. However, a material almost as active can be prepared with granular pumice stone, and this supporting material is used for all mixtures.

Table I shows the composition of the mixtures found to be best suited to the detection of small amounts of carbon monoxide.

¹ THIS JOURNAL, 12 (1920), 213.

² Lamb and Hoover, U. S. Patents 1,321,061 and 1,321,062.

¹ Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

² Published by permission of the Director of the Chemical Warfare Service.

³ Bull. soc. chim. (3), 1 (1889), 555.

⁴ Compt. rend., 155 (1912), 282.

⁵ J. Am. Chem. Soc., 41 (1919), 1908.

⁶ Chem.-Ztg., 35 (1911), 1120.

⁷ Iron Coal Trades Rev., 88 (1914), 912.

⁸ THIS JOURNAL, 12 (1920), 964.

⁹ Bureau of Mines, Technical Paper, 62 (1914).

TABLE I—COMPOSITION OF DETECTOR MATERIAL

USE	Method of Preparation	Iodine Pentoxide Per cent	Pumice Stone Per cent	Fuming Sulfuric Acid Per cent
Approximately quantitative detection of reducing gases—Detector B	Mixed in open vessels	12.0	35.0	53.0(60%SO ₂)
Quantitative detection of carbon monoxide—Detector C	Mixed in closed vessels or in air of low humidity	10.6	33.3	56.1(60%SO ₂)
Quantitative detection of carbon monoxide—Detector C	Mixed in open vessels High humidity	11.0	34.0	55.0(80%SO ₂)

Since Hoolamite is a corrosive, deliquescent material, it must be preserved in closed vessels which are not attacked by acids or oxidizing agents. When so preserved, it gradually increases in activity for several days, finally remaining unchanged apparently indefinitely. The material is usually employed in small glass tubes which are sealed after filling and opened just before use.

SENSITIVITY—Under favorable conditions concentrations of carbon monoxide as low as 0.005 per cent can be detected by the passage of 500 cc. of a gas mixture through a glass tube containing a 50 mm. $\times$ 5 mm. column of Hoolamite. The color developed is proportional to the amount of carbon monoxide present and the cross-sectional area of the detector material, for concentrations of carbon monoxide of 3 per cent or less. The rate at which the gas is passed can vary considerably, but for quantitative results it should be kept between 30 and 60 sec. for a 500-cc. sample through a tube of 5-mm. inside diameter. The depth of the detector material should be at least 2.5 cm., 5 to 7 cm. being commonly used. Carbon monoxide reacts readily with the detector material at -10° C. Since the action is strongly exothermic the color produced is largely independent of the temperature. As a result of chemical changes such as were mentioned above, the green color indicating the presence of carbon monoxide disappears in a few minutes and the material can again be used as before. After twelve positive tests, with concentrations of carbon monoxide not greater than 0.2 per cent, the color produced becomes somewhat irregular in shade and a new sample should be employed. With higher concentration of carbon monoxide proportionately less tests can be made with one tube. Twenty to thirty negative tests in ordinary air can be made before the activity of the Hoolamite has been destroyed.

COLOR STANDARDS—Permanent color standards consisting of granules of pumice stone, normal or basic copper acetate, and chromium oxide can be prepared which match closely the colors produced in Hoolamite by a 500-cc. sample of gas containing amounts of carbon monoxide from 0.03 to 0.17, or 0.2 per cent. Above 0.2 per cent for a 500-cc. sample the colors are more irregular, and other methods than direct color comparison give better results.

ACTION WITH OTHER GASES—A substance capable of rapidly oxidizing carbon monoxide at low temperatures can also be expected to react with oxidizable gases and vapors other than carbon monoxide. Unsaturated hydrocarbons, gasoline vapor, hydrogen sulfide, arsine, hydrogen cyanide, and various complex organic compounds, especially those containing halogens or amino nitrogen, are similar in action to carbon monoxide. In the absence of carbon monoxide the material is a sensitive detector for such substances. Fortunately all interfering substances investigated are absorbed by dry active charcoal. Hydrogen, methane, sulfur dioxide, nitric acid, ammonia, and other common gases and vapors are without action.

For the determination of small amounts of carbon monoxide in the laboratory, any simple container from which definite volumes of gas can be forced under a pressure of several inches of water, appropriate color standards, and a few tubes of Hoolamite are all that are necessary.

If other reducing gases are present, it is necessary only to pass the mixture to be examined over a column of active charcoal before it comes into contact with the Hoolamite. It may be noted here that a method of determining large amounts of carbon monoxide in the usual type of absorption pipet by means of Hoolamite is also being developed.

POCKET DETECTOR FOR INDUSTRIAL USE

The most important application of Hoolamite that has yet been made is to the industrial detection of carbon monoxide. A simple and durable form of pocket detector, Type B, is shown in Fig. 1. This device is 24 cm. long

FIG. 1

over all and weighs 260 g. Its construction and operation are explained by Fig. 2. A 250-cc. sample of the gas to be examined is drawn through the guard tube, A, containing active charcoal, by means of ten compressions of the rubber bulb, B, and forced out through the detector material in the glass tube, D. The green color produced in the detector tube is compared with color standards contained in an adjoining tube as shown in Fig. 1. The range of approximately quantitative detection with this instrument is from 0.05 to 1 per cent.

In practical use this instrument (Type B) has been successful as a qualitative and approximately quantitative detector for carbon monoxide. It is sufficiently sensitive to detect in a few seconds quantities of the gas less than are harmful to men, or capable of causing symptoms of distress in small animals. The directions for use are simple and the instrument can be used by the average workman. With improved Hoolamite and revised directions to insure more definite volumes of gas and rates of passage, it should be increasingly valuable.

FIG. 2—TYPE B

FIG. 3—TYPE C

IMPROVED APPARATUS

It is evident that if the volume of gas and its rate of passage can be regulated more accurately than is possible with the device just described, analytical results of correspondingly greater accuracy will be secured. With this object in view a metal cylinder and piston were substituted for the aspirator bulb and a positively operated stopcock for the rubber valves. The exterior appearance of the im-

proved apparatus is shown in Fig. 1 (Type C). The construction and operation can be understood by referring to Fig. 3. Outward movement of the piston rod, E, draws 500 cc. of gas to be examined through the valve, G, into the cylinder, F. As the piston reaches the end of its travel a rod connected by track and gear to the valve, G, turns it 90°, thus connecting the cylinder with the guard tube, H, and the detector tube, T, through which the gas is passed by the return stroke of the piston. Completion of the stroke moves the valve to its original position.

Among the advantages of this type of instrument may be noted: Definite volume of sample, regular rate of passage governed by the size of the opening into the guard tube, the sample can be taken quickly in a dangerous atmosphere or in the dark, and the analysis made at leisure in a safe, better lighted spot.

As previously stated, concentrations of carbon monoxide greater than 0.2 per cent give somewhat irregular colors when a 500-cc. sample is forced through a 5-mm. tube of Hoolamite; hence with the type C detector the color comparison scale covers only the range from 0.03 to 0.17 per cent. Quantities of carbon monoxide greater than 0.17 per cent are determined by taking advantage of the fact that the color change produced in Hoolamite by a given quantity of carbon monoxide is independent, within the limits previously stated, of the volume of the gas sample, provided the rate of passage is properly regulated. When a sample containing more than 0.17 per cent is being expelled from the cylinder, the color corresponding to 0.17 per cent will be reached before the stroke is completed. Hence by graduating the piston rod of the apparatus (E, Fig. 3) in per cent carbon monoxide, quantities up to 3 per cent can be determined with a good degree of accuracy.

The improved detector has not yet been put upon the market, but practical tests indicate that it is superior in accuracy and range to the smaller, type B, instrument, although somewhat more cumbersome. Table II gives the results of comparative tests of the two detectors which support the statements just made.

Source of Carbon Monoxide	Detector B Per cent	Detector C Per cent	Iodine Pentoxide Laboratory Analysis Per cent
Pure gas	0.5	0.6	0.583
Flue gas	0.5	0.4	0.431
Illuminating gas	0.3	0.2	0.181
Pure gas	0.2	0.12	0.127
Illuminating gas	0.1	0.07	0.069
Illuminating gas ¹	0.0	0.04	0.034

¹ Charging floor, water gas plant.

The two devices are designed to supplement each other, the simpler being suited to occasional use in the hands of persons engaged in work exposing them to the danger of breathing carbon monoxide such as is met in mines; producer, water, and blast furnace gas plants; garages; boiler rooms; tunnels and excavations near gas mains; army and navy work, etc. The more accurate device is intended to meet the needs of chemists, engineers, inspectors, and other persons responsible for the welfare of workmen, the regulation of plant operations, laboratory tests, and the conduct of industrial research.

SUMMARY

1—A mixture of pumice stone, iodine pentoxide, and fuming sulfuric acid reacts with carbon monoxide to give a green color varying in depth with the concentration of the gas.

2—Two portable devices by means of which this reaction can be applied to the approximately quantitative determination of carbon monoxide are described.

The Determination of Tannin^{1,2}

By John Arthur Wilson and Erwin J. Kern

LABORATORIES OF A. F. GALLUN & SONS CO., MILWAUKEE, WISCONSIN

A rather widespread controversy has arisen over a new method of tannin analysis described by the authors in two previous papers,³ in which it was shown that the methods adopted as official both here and abroad are greatly in error, exceeding 200 per cent in some cases. Changing a method of analysis upon which millions of dollars of tanning materials are bought and sold annually is admittedly a serious matter. Were the new method to supplant the old in the sale of extracts, drastic price changes would have to be made and many extracts would no longer hold their present relative standings or reputation as to tanning value. Since the official methods have been clearly proved unreliable, it would seem that the new method must now be tested generally to determine whether or not it will meet all the conditions that ought to be required of a method so important. Until now its use has been restricted because the procedure as originally described was both cumbersome and time consuming, all of the first efforts having been directed exclusively to devising an accurate method. But the procedure has since been developed until it is now quite as simple as that of any method in general use. In this paper we describe the simplified procedure, and also refute the objections which have been raised against the new method.

DEFINITION OF TANNIN

A thorough review of the literature shows that it has

¹ Received July 28, 1921.

² To be presented before the Leather Chemistry Section at the 62nd Meeting of the American Chemical Society, New York City, September 6 to 10, 1921.

³ THIS JOURNAL, 12 (1920), 465, 1149.

been generally agreed to class as tannin that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. Much confusion would have been avoided in discussion by making it clear whether the criticism was directed against the definition or the method.

CHANGES IN PROCEDURE

In the method as originally described, the tanned hide powder had to be washed by shaking with water for 30 min., squeezing through linen, and repeating with fresh water until free from soluble matter, which usually required about twelve washings. This is now accomplished with very little effort in a washing apparatus to be described later. The washed powder, after drying, was analyzed for water, ash, fat, and hide substance ($N \times 5.62$), and the percentages of these subtracted from 100 gave the per cent of tannin in the powder. It was suggested earlier that this figure might be obtained simply by noting the increase in weight of the dry powder after tanning and washing, provided the washing operation were so conducted that no powder was lost, making the determination direct instead of by difference and increasing the accuracy for unskilled analysts. The new washing apparatus not only makes this possible, but reduces the amount of hide powder required for a determination to one-sixth.

PRESENT PROCEDURE

A solution of the tanning material is prepared of such