

entirely avoided, is materially lessened by about 20 per cent. With oleic acid, the numbers obtained by the iodide process average but 0.2 per cent. higher than the theoretical. 90 per cent., which is the closest agreement, so far as known, obtained by any process; they are 11 points lower than those obtained by the usual Hübl process. A slight substitution did occur as shown by the hydriodic acid liberated. This was increased by lengthening the time of action of the solution, as seen from the 20- and 25-hour tests; the 3-hour test was conducted to determine if the substitution could not be eliminated by a shorter time. It was found that it did take place, indicating apparently that substitution and addition occur simultaneously: a small amount of substitution was found in the case of the oils as well as with oleic acid.

Attention was called in the early part of this paper to the fact that alcoholic solutions of iodine caused a low and variable addition of halogen to oleic acid; this is more particularly the case if carbon tetrachloride be used as a solvent; chloroform seems to increase this addition very materially. With the former, 66.74, 67.32, and 65.46 per cent. of iodine were added to oleic acid, whereas with the latter. 89.02, 83.66, and 85.86 per cent. were added.

As the solution used contained no halogen but iodine, thus excluding the formation of halides of iodine, and no water, excluding the liberation of oxygen, it would seem that we had here a method which, while as ready of application as the original Hübl, possessed the additional advantage of giving the true iodine figure.

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THE IODOMETRIC DETERMINATION OF SMALL QUANTITIES OF CARBON MONOXIDE.

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IN a previous paper¹ one of us mentioned that there might be more danger to be apprehended from the continuous breathing of air containing very small amounts of water gas, such as

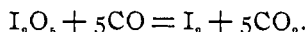
¹ *Municipal Engineer*. 17, 71.

might occur from imperfection in gas fittings than from sewer gas or arsenical wall papers. It is known that air containing 0.3 per cent. of carbon monoxide causes death, 0.2 per cent. very dangerous symptoms, and that mice quickly show the effect of the gas when the air contains only 0.05 per cent. There is reason to believe that air containing even much smaller quantities when breathed for a number of hours may have an effect on the human organism, and on this account the detection and quantitative determination of very small amounts of carbon monoxide when mixed with large volumes of air is a question of importance.

The methods of detecting and estimating very small amounts of carbon monoxide may be divided into two classes: first, those in which carbon monoxyhemoglobin is formed; second, those in which it is oxidized to carbon dioxide. Those of the first class are of little value except for the detection of the gas and they may all be considered as modifications of Hoppe-Seyler's method, first published in 1864,¹ which is based on the fact that while both carbon monoxyhemoglobin, formed by the action of carbon monoxide on arterial blood, and oxyhemoglobin, give two absorption bands in the spectrum; oxyhemoglobin is alone reduced to hemoglobin by the action of such reducing agents as ferrous sulphate or ammonium sulphide.

The method of determining carbon monoxide by oxidation to carbon dioxide has not, until the past few years, received much attention. This oxidation can be accomplished by the use of many oxidizing agents, but of all of those which have been proposed iodine pentoxide is, from our experience, the one that can best be used for the determination of small amounts of carbon monoxide.

Ditte,² in 1870, showed that at temperatures between 150°–200° iodine pentoxide was decomposed by carbon monoxide, iodine and carbon dioxide being formed.



This reaction was seemingly first used by C. de la Harpe and F. Reverdine³ for the detection of the gas, and Nicloux⁴ and

¹ *Ztschr. anal. Chem.*, 3, 439 (1864).

² *Bull. Soc. Chim.*, 13, 318 (1870).

³ *Chem. Ztg.*, 12, 1726 (1888).

⁴ *Compt. rend.*, 126, 746.

Gautier¹ have made use of the reaction for its quantitative determination.

Nicloux determined the iodine set free, by the depth of color formed in a chloroform solution, and Gautier by the amount of carbon dioxide formed. We have not, by either of these methods, been able to obtain accurate determinations of small amounts of carbon monoxide, but have obtained most satisfactory results by determining the amount of iodine set free, with an N/1000 solution of sodium thiosulphate.

The apparatus used was, with slight changes, that described by Nicloux. Twenty-five grams of iodine pentoxide were placed in a small U-tube, which was suspended in an oil-bath and connected with a Wolff blood absorption tube containing 0.5 gram potassium iodide dissolved in 5 cc. water. The tube containing the iodine pentoxide was also connected with two U-tubes, one containing sulphuric acid, the other small pieces of potassium hydroxide, so as to remove from the air to be analyzed before it came in contact with the iodine pentoxide all unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide, and similar reducing gases. In all the experiments the oil-bath in which the U-tube containing the iodine pentoxide was suspended, was heated to 150° C., as preliminary tests showed that the reaction was not a quantitative one at lower temperatures.

The iodine pentoxide was made by the action of nitric acid on resublimed iodine, and after this substance had been purified by the usual methods the last traces of free iodine were removed by passing air, freed from all reducing substances, through the iodine pentoxide contained in a U-tube heated to 150° C.

In the experiments which were made to determine the accuracy of the above process, 1 liter of air was usually taken, but as seen in the following tables amounts as small as 250 cc. were tried in several cases and the rate at which the air was passed through the tubes was about 1 liter in two hours, the rate being controlled by forcing the air out of the bottle in which it was contained by dry redistilled mercury; the flow of which was regulated by a glass stop-cock. The amount of carbon monoxide added to the air was accurately measured from a tube made of capillary glass tubing and accurately calibrated so that each

¹ *Compt. rend.*, 126, 931.

division represented 0.005 cc., and readings of 0.001 cc. could easily be made. The temperature and barometric pressure were carefully noted and all volumes were reduced to 0° C. and 760 mm. pressure, and the determination of the iodine set free was made in the Wolff blood absorption apparatus which contained the potassium iodide solution.

With this apparatus, used as described, we were able to determine as small an amount as 0.025 cc. of carbon monoxide, when contained in 1000 cc. of air, or 0.0025 per cent. by volume. The following table gives the results obtained :

ANALYTICAL RESULTS.

Volumes taken.		Iodine liberated.		Difference.
Air.	Carbon monoxide.	Theoretical.	Found.	
cc.	cc.	Mg.	Mg.	Mg.
1000	0.410	0.941	0.907	0.034
1000	0.286	0.6575	0.6375	0.020
1000	0.359	0.8178	0.7832	0.0346
1000	0.170	0.3859	0.4540	0.0081
1000	0.211	0.4809	0.4775	0.0034
1000	0.151	0.3442	0.3252	0.019
1000	0.115	0.2639	0.2758	0.012
1000	0.061	0.1391	0.1431	0.004
1000	0.023	0.0535	0.0494	0.0041
1000	0.029	0.0672	0.0689	0.0017
1000	0.023	0.0535	0.0495	0.004
500	0.131	0.2993	0.2976	0.0017
250	0.030	0.06862	0.07165	0.0029
250	0.026	0.05967	0.05855	0.0011

Volumes taken.		Carbon monoxide.		Difference.
Air.	Carbon monoxide.	Calculated.	Found.	
cc.	cc.	Per cent. By volume.	Per cent. By volume.	
1000	0.410	0.041	0.0395	0.0015—
1000	0.286	0.0286	0.0278	0.0008—
1000	0.359	0.0359	0.0341	0.0018—
1000	0.170	0.0170	0.0197	0.0027+
1000	0.211	0.0211	0.0208	0.0003—
1000	0.151	0.0151	0.0142	0.0009—
1000	0.115	0.0115	0.0119	0.0004+
1000	0.061	0.0061	0.0062	0.0001+
1000	0.023	0.0023	0.0021	0.0002—
1000	0.029	0.0029	0.0030	0.0001+
1000	0.023	0.0023	0.0022	0.0001—
500	0.131	0.0262	0.0260	0.0002—
250	0.030	0.0120	0.0124	0.0004+
250	0.026	0.0104	0.0100	0.0004—

These results showed that by the above method accurate determinations could be made of very small amounts of carbon monoxide in pure air, and it only remained to be proved that the accuracy of the process was not affected when the carbon monoxide was mixed with air containing illuminating gas, and experiments were made to determine the action of hydrogen, marsh-gas, unsaturated hydrocarbons, hydrogen sulphide, and sulphur dioxide on iodine pentoxide.

Hydrogen and marsh-gas, as was to be expected, had no effect on the iodine oxide at 150°C . and the unsaturated hydrocarbons, hydrogen sulphide and sulphur dioxide, in much larger amounts than are contained in illuminating gas, or formed by its combustion, were perfectly absorbed, when passed in the way described through U-tubes containing sulphuric acid and potassium hydroxide.

These facts having been determined, mixtures of illuminating gas and air were made, and the amount of carbon monoxide determined.

The experiments gave the following results :

The gas used contained 18.6 and 19.0 per cent. of carbon monoxide, respectively. Of the first, 0.104 cc. was added to 1 liter of air and the air was found to contain 0.019 cc. carbon monoxide, the calculated amount being 0.0191 cc. In the second case, 0.146 cc. of the gas was taken and the air gas found to contain 0.027 cc. of carbon monoxide in place of 0.02789 cc.

The results that have thus been obtained show that the presence and amount of carbon monoxide in the air of a room can be determined when the air contains above 0.0025 per cent. by volume, or 2.5 volumes in 100,000 volumes of air, and if the presence of this gas is due to leakage of illuminating gas and the per cent. of carbon monoxide in this gas is known, the amount of illuminating gas contained in the air can, of course, approximately be calculated.