type vacuum furnace, a 10 kw. "flux-shunt transformer, a Geryck pump, and a 15 kw. wattmeter.

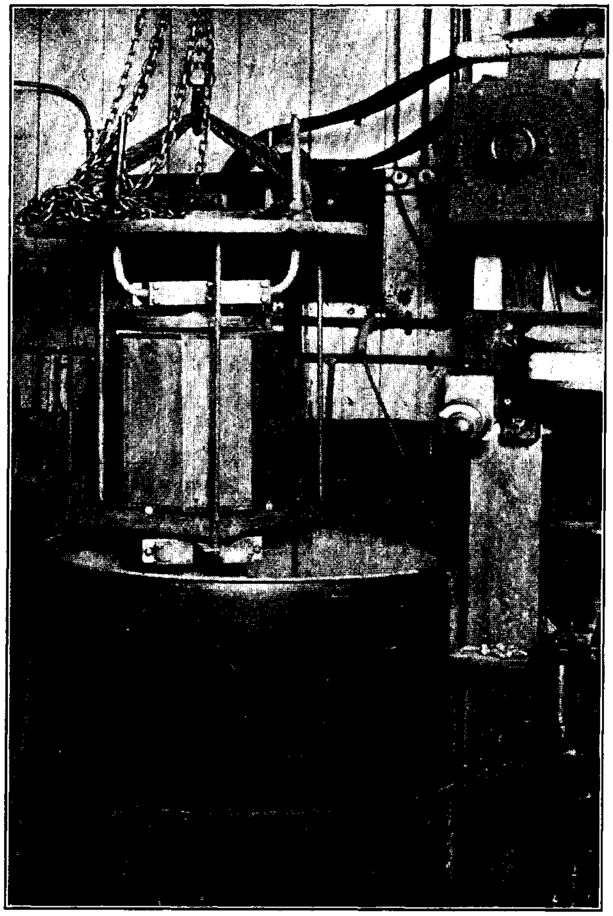

Fig. 11.—Large vertical type vacuum furnace, showing radiation screen.

THE DETERMINATION OF CARBONIC OXIDE IN ILLUMINATING GAS BY IODINE PENTOXIDE.

By Augustus H. Gill and Edward H. Bartlett.

The reaction made use of in this method for the quantitative determination of carbon monoxide is that first indicated by Ditte.[1] He showed in 1870, that if carbon monoxide was passed over iodine pentoxide at temperatures between 150° and 200° C., a reaction ensued by means of which the carbon monoxide was oxidized to carbon dioxide, this action being accompanied by a simultaneous reduction of the I_2O_5 to free iodine, expressed by the following equation:

$$I_2O_5 + 5CO = I_2 + 5CO_2$$

An analogous reaction is produced by iodic acid,

$$2HIO_3 + 5CO = I_2 + 5CO_2 + H_2O.$$

Apparently the first to actually make use of this reaction were de la Harpe and Reverdin,[2] who used it in 1888 for the detection of carbon monoxide in the atmosphere. They passed filtered air over dry iodic acid heated to 150° C. and then into a solution of starch paste. If the air contained carbon monoxide this fact was made apparent of the blue color in the starch solution.

Phillips,[1] in 1894, mentions this reaction, and says that before it can be used for analytical work it is necessary to remove the higher olefines, acetylene, and vapors of benzene and alcohol. He says further that the lower paraffins are without action on the iodine pentoxide up to temperatures at which the iodic acid dissociates.

In 1898 both Nicloux and Gautier report having used this reaction quantitatively. Gautier did not publish his method until after that of Nicloux had appeared. He claims, however, to have been using his method for several years previously. Both confined their attention to the determination of carbonic oxide in the small quantities in which it is met with in the air.

Nicloux[2] first removed carbon dioxide, sulphuretted hydrogen, sulphurous acid and water vapor from the air, and passed it over iodic anhydride at a temperature of 150°. The iodine set free was carried along by the stream of air through a tube filled with a solution of potassium hydrate—where it was absorbed. The amount of iodine was then determined by the method of Rabourdin, which consists in acidifying the potassium hydrate solution with sulphuric acid, adding a few centigrams of nitrite of soda and 5 cc. of chloroform or carbon bisulphide, and then shaking the whole vigorously. This sets free the iodine which is then taken up by the chloroform or carbon bisulphide; the color of the solution obtained is compared with the color produced from a solution of potassium iodide, the strength of which is determined by titration. Nicloux tested this method by using air, the contents of which in carbonic oxide varied from 1 part in 1000 to 1 part in 50,000. He reports his results to have shown the method to be very accurate. He also says that neither hydrogen nor methane give an analogous reaction at this temperature.

Gautier[3] devised two quantitative methods using this reaction. In his first method, he passed the air first through a tube containing I_2O_5, and then through a small tube filled with pulverulent copper. The iodine set free by the reaction was taken up from the air by copper, after which its weight was obtained by taking the difference between the weights of the tube of copper before and after the experiment. Gautier soon abandoned this method, however, for another one in which he determined

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[1] *Bull. Soc. Chim.*, **13**, 318.

[2] *Chem. Z.*, **12**, 1726.

[1] *Am. Chem. Jour.*, **16** (1894).

[2] *Compt. rend.*, **126**, 746.

[3] *Ibid.*, **126**, 793 and 931.

the amount of carbon dioxide formed instead of the iodine set free. He now passed the air after it had been in contact with the iodine pentoxide into a tube filled with glass beads, which contained a known volume of potassium hydrate solution free from carbonate. The carbon dioxide thus absorbed was again reobtained in the gaseous state by neutralizing the potassium hydrate solution with sulphuric acid. The volume of carbon dioxide thus obtained equaled the volume of carbonic oxide in the volume of air taken for analysis. Gautier investigated the accuracy of this method, using dilutions of carbonic oxide varying from 1 part in 500 to 1 part in 30,000 and keeping the tube of iodine pentoxide at temperatures ranging from 65° to 80°. He states that the method is fully accurate enough for practical purposes.

Gautier says that he has observed that the oxidation of the carbonic oxide begins at temperatures of less than 30° C., that it is active between 40° and 45°, and complete at 60°–65°. He says that this is true whatever be the dilution of the carbonic oxide in the air. With the exception of acetylene he says further that most of the hydrocarbons are not acted upon by iodine pentoxide at these temperatures. Certain gases like ethylene, however, although themselves being oxidized very difficultly at these temperatures, nevertheless have the property of hindering greatly the oxidation of carbonic oxide. He says further that contrary to the general rule this reaction goes completely, the carbonic oxide being oxidized to the very last trace. For every cubic centimeter of carbonic oxide at 0° and 760 mm. there is set free 0.00227 gram of iodine. Finally, he says that at these temperatures, 65°–80°, methane and hydrogen are not oxidized.

The problem of adopting this reaction for use in the determination of the carbonic oxide in the atmosphere was next taken up by Kinnicutt and Sanford[1] in 1899. By way of premise they say that all the methods which have been used for this purpose may be divided into two classes, to wit: those employing the reaction between carbon monoxide and the haemoglobin of blood by means of which carbon monoxid haemoglobin is formed, and those in which carbonic oxide is oxidized to carbon dioxide. The processes of the first class are of but little value from a quantitative standpoint. The most suitable oxidizing agent for use in the processes of the second class has been found to be iodine pentoxide. They report that they experimented with the methods of Nicloux and Gautier, and failed in both instances to obtain accurate results. They then proceeded to devise a method of their own. Their method is a modification of that of Nicloux. They passed the air first through a tube containing pieces of stick potash and a tube containing sulphuric acid, in order to remove from it sulphuretted hydrogen, sulphurous acid and similar reducing gases and all unsaturated hydrocarbons. They then passed the air through a tube containing iodine pentoxide heated to a temperature of 150°, after which it was passed into a solution of potassium iodide which absorbed the iodine. Finally they titrated this solution with a N/1000 sodium thiosulphite solution to determine the iodine. By measuring the carbonic oxide used in making up their samples in capillary tubes, they were enabled to read the volume to 0.001 cc. The content of carbonic oxide varied from 1 part in 2440 parts of air to 1 part in 43,479 parts of air. They report the results of fourteen analyses which show the method to have been very accurate. They found that they could determine as little as 2.5 vols. of CO in 100,000 volumes of air.

They next made experiments to determine whether or not the presence of illuminating gas in the air would vitiate the accuracy of these results. They found that the presence of the gas had no disturbing effect whatever, as is shown by the following results:

	cc.	cc.
Carbonic oxide calculated........	0.0191	0.02789
Carbonic oxide found............	0.019	0.027

This indicated that hydrogen and methane were not acted upon at this temperature. They had previously made experiments which had shown the same result. They also made experiments which showed that the reaction was not quantitative at temperatures lower than 150°. This is in direct contradiction to Gautier who says that the reaction is complete at temperatures as low as 60°–65°. These results of Kinnicutt and Sanford show that this method gives very accurate results when applied to the determination of carbonic oxide in the small quantities which are found in the atmosphere.

In 1900 Smits, Raken, and Terwogt,[1] of the University of Amsterdam, proposed utilizing this oxidation of carbon monoxide for its quantitative determination in the analysis of illuminating gas. After reviewing briefly the work of Nicloux and Gautier, they say that it is obvious that this "very sensitive" reaction, heretofore only used in the analysis of air, is also applicable to the determination of carbon monoxide in illuminating gas. They say, however, that it is out of the question to think of placing the carbonic oxide determination in line in a complete gas analysis, if the exact method of either Nicloux or Gautier is used. They

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[1] *Jour. Am. Chem. Soc.*, **22**, 14.

[1] *Zeit. für angew. Chem.*, **1900**, 1002.

therefore modified Gautier's method and proceeded as follows: The gas from which the carbon dioxide, the illuminants, and oxygen had been removed in the ordinary Hempel scheme of analysis, was passed from a Hempel burette, through a U-tube containing iodine pentoxide heated to 150° by an oil bath into a Hempel pipette containing a solution of caustic potash. The caustic potash absorbed the carbon dioxide formed by the oxidation of the carbonic oxide so that the contraction in volume after the absorption was complete gave the volume of the latter present. The correction for the vapor tension of iodine was found to be negligible. It does not appear from their article that they ever actually tried their method in an actual analysis of illuminating gas. They did, however, undertake to find out whether or not hydrogen or methane would undergo oxidation on being passed through the iodine pentoxide tube. To this end they made by their method an analysis of a mixture of hydrogen and carbon monoxide, and another analysis of a mixture of methane and carbonic oxide. They report the following results:

	Found, cc.	Mixed, cc.
Hydrogen	72.7	72.6
Carbon oxide	8.7	8.8
Methane	42.7	42.8
Carbon oxide	8.1	8.0

It will be noticed that they give results for two experiments only, and that neither of these properly represents the conditions of practice, as in neither were both hydrogen and methane associated with the carbon monoxide. They do not hesitate, however, to say that their method is very exact and much superior to that in ordinary use.

The method of determination of carbonic oxide by cuprous chloride is so unsatisfactory that it was thought this promised well, and their work was repeated with the following results:

TABLE I.—SHOWING ABSORPTION OF CARBONIC OXIDE BY IODINE PENTOXIDE.

CO used.	CO found.	Loss.	Per cent. lost.	Bath temp.	Time, min.
21.8	20.8	1.0	3.6	150	90
23.2	22.2	1.0	4.3	150	150
25.9	25.5	0.4	1.0	152	32
25.6	25.6	0.0	0.0	154	29
26.4	26.0	0.4	1.0	161	32

In the last three results the carbonic oxide was mixed with air. It will be noticed that after two and a half hours' passage of the gas through the tube more than 4 per cent. of the gas remained unabsorbed. This would seem to show the impracticability of the method.

To still further test the method a mixture of carbonic oxide, methane, hydrogen and nitrogen was made of about the composition of that left after carbon dioxide, "illuminants" and oxygen had been absorbed from an illuminating gas and passed through the iodine pentoxide. The results are shown in Table II.

TABLE II.—ABSORPTION OF CARBONIC OXIDE BY IODINE PENTOXIDE FROM MIXTURE OF GASES.

Hydrogen.	Methane.	Carb. oxide added.	Carb. oxide found.	Gain.	Per cent. gain.	Bath temp.	Time, min.
24.1	44.8	25.6	28.5	2.9	11.3	157	24
24.4	42.3	26.4	31.3	4.9	18.6	152	29
23.6	46.1	25.6	27.1	1.5	5.9	152	28
26.1	46.2	24.1	27.1	3.0	12.4	152	51
24.6	53.5	25.7	28.1	2.4	9.3	152	75
20.4	43.7	27.8	31.5	3.7	13.3	148	30
24.0	46.0	26.1	26.9	0.8	3.1	150	26

It will be noticed from this table that the amount of carbonic oxide found considerably exceeds the amount originally added: The errors of the analysis are not sufficient to account for this and they show no regularity. Moreover, another observer a year previously had obtained almost identical results, the average error found by him being 7.8 per cent., whereas the average error of these results is 9.1. This error, as was shown by two different observers working independently, is not due to the action of the iodine pentoxide upon either the methane or the hydrogen nor the number of times the tube had been used nor the length of time taken by the gas in passing through the tube, but may be due to the breaking up of the iodine pentoxide.

In conclusion it may be said that the method of absorption of considerable quantities of carbonic oxide by iodine pentoxide is inaccurate, irregular in action and tedious and troublesome to use.

Finally our acknowledgments are due to Messrs. J. B. Finnegan and R. W. Lindsay by whom some of the experiments here detailed were performed.

THE COEFFICIENT OF EXPANSION OF GLYCERINE.

By ARTHUR M. COMEY AND CECIL F. BACKUS.

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Upon examination of the literature on the coefficient of expansion of glycerine, it was found there was some discrepancy between various authorities. Hehner[1] states that it amounts to 0.00058 for each degree centigrade in the neighborhood of 15.5° C. It can be calculated from the results of Gerlach's observations[2] that the value of this factor varies with the temperature according to the following table:

Temperature.	Coefficient of expansion.
5.0°	0.00057
12.5°	0.000587
20.0°	0.00060
30.0°	0.000619

The necessity of using an accurate coefficient in figuring the results obtained by determining

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[1] *J. S. C. I.*, **8**, 8 (1889).

[2] *Zeit. anal. Chem.*, **24**, 111.