

In spite of some wide variations, for which we are unable to account, it is evident from this table that the permeability diminishes as the age increases. At the end of four weeks the membrane showed about half its original permeability.

### Summary of Results.

1. Collodion membranes in the form of sacs, or flat films, for ordinary dialyzers, even of large size, are easily made. They may be attached to supports more neatly and more perfectly than parchment paper. Dialysis occurs through them more rapidly, and therefore they are to be preferred to the more commonly used material. Membranes of gold beater's skin, however, are still better for separations by dialysis.

2. The quantity of water passing through collodion membranes is nearly a linear function of the pressure, the temperature being held constant.

3. An attempt to calculate a "pressure coefficient" of permeability for 25° gave the result:—A change of 1 mm. in pressure causes a change in the volume of water passing equal to about 0.6 per cent. of the quantity which passes when the pressure is 150. mm. mercury.

4. The quantity of water passing, pressure being constant at 150 mm. is not a linear function of the temperature. A "temperature coefficient" was not established but an increase of 20° to 30° was required to about double the quantity of water passing per unit time.

5. Different samples of collodion showed different permeabilities, but in spite of the differences in the absolute values, a change of pressure or of temperature produced the same proportional effect in all.

6. As a collodion membrane grows older, its permeability diminishes gradually, but it lasts and remains useful for one to three months.

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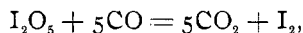
[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, NO. 146].

## THE DETERMINATION OF CARBON MONOXIDE IN ATMOSPHERIC AIR.

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All the satisfactory methods for the quantitative estimation of small amounts of carbon monoxide are based upon the reaction,



which was first observed by Ditte,<sup>1</sup> and which, according to Kinnicutt and Sanford,<sup>2</sup> is only quantitative at 150° or above, although Gautier<sup>3</sup> re-

<sup>1</sup> Bull. soc. chim., 13, 318 (1870).

<sup>2</sup> This Journal, 22, 14 (1900).

<sup>3</sup> Compt rend., 128, 487 (1899).

gards it as complete at  $60^{\circ}$ - $70^{\circ}$ . In all the methods based upon this reaction, and there are practically no others, the air to be analyzed is first passed through U-tubes containing potassium hydroxide and sulphuric acid (which remove all the other gases reacting with the iodine pentoxide as carbon monoxide does), and then through a U-tube containing iodine pentoxide, heated in an oil or glycerol bath to the proper temperature. It is only in the subsequent treatment of the products (iodine and carbon dioxide) produced by the reaction, carried out in this way, that the various methods differ from one another. Gautier<sup>1</sup> removed the iodine by passing the gas issuing from the iodine pentoxide tube over heated copper, collected the carbon dioxide by absorption in caustic soda solution, and then later liberated it with sulphuric acid and measured its volume in a graduated tube which had been exhausted by a Sprengel pump; a method which would hardly recommend itself to the practical chemist. Nicloux<sup>2</sup> determined the amount of iodine set free by the depth of color in chloroform solution. And finally Kinnicutt and Sanford<sup>3</sup> absorbed the iodine in a potassium iodide solution, titrating it subsequently with N/1000 sodium thiosulphate; but were not able to obtain accurate determinations by either of the other methods. Tóth<sup>4</sup> has also used this method for the estimation of carbon monoxide in tobacco smoke, with very good results, although the iodine pentoxide was heated to only  $60^{\circ}$ - $70^{\circ}$ .

In analyzing the compressed air in the East River Pennsylvania tunnels for the constructors, Messrs. S. Pearson & Son, Inc., we have had occasion to study the various methods for the determination of carbon monoxide, and, after considerable initial difficulty, have succeeded very well with that of Kinnicutt and Sanford. The difficulty we experienced was the continuous, apparently spontaneous, decomposition of the iodine pentoxide, even below  $100^{\circ}$ , when enclosed in a glass-stoppered U-tube, with lanoline as the lubricant. The cause of this decomposition, which was observed with all specimens used, was finally found to be the traces of lanoline which were drawn into the tube by the suction, together with the hot glycerol of the bath, with which the cool portions of the tube were bathed in order to drive out the last portions of the iodine. The remedy for this, of course, is to seal off the ends of the iodine pentoxide U-tube, in a blast lamp after filling, for experiment shows that all animal fats at  $150^{\circ}$  or less react violently, even explosively, with iodine pentoxide. It is strange that this precaution is not mentioned in any of the above papers, for it is natural for one to select a glass-stoppered tube, since rubber and cork are

<sup>1</sup> Loc. cit.

<sup>2</sup> Compt. rend., 126, 746 (1898).

<sup>3</sup> Loc. cit.

<sup>4</sup> Chem.-Ztg., 98, (1907).

out of the question, and the slightest trace of the lubricant in the tube will cause high results to be obtained.

Although by this method our results (all at  $150^{\circ}$ , for the sake of rapidity) were very satisfactory, we finally resorted to a modification of it which has many advantages, for it is somewhat simpler, and, with very little trouble, enables one to get checks by two methods on the same sample of gas, thus eliminating the possibility of error. The modification is exceedingly simple. It consists in passing the iodine free gas issuing from the potassium iodide tube, used by Kinnicutt and Sanford, through a long test tube ( $24. \times 2.5$  cm.) containing 50 cc. of the solution of barium hydroxide used for the determination of carbon dioxide in air by Hesse's method, and finding the volume of carbon dioxide absorbed by titration with the standard solution of oxalic acid usually used for this purpose, *i. e.*, one containing 1.12650 g. of crystallized oxalic acid in one liter of water, using phenolphthalein as indicator. Tests on measured and unmeasured amounts of pure carbon monoxide mixed with air (See table below) show that by titrating both the iodine absorbed in the potassium iodide, and the carbon dioxide in the barium hydroxide solution, very satisfactorily checking results are obtained, showing that it was only the difficulty in measuring the volume of carbon dioxide by Gautier's method, and not the principle upon which the method is based, that prevented Kinnicutt and Sanford from obtaining accurate results for carbon monoxide by the determination of the carbon dioxide set free.

Every cubic centimeter of carbon monoxide, measured at  $0^{\circ}$  and atmospheric pressure, liberates 0.00227 g. of iodine, and 1 cc. of carbon dioxide, *i. e.*, enough to transform into carbonate, the amount of the barium hydroxide solution which is equivalent to 5 cc. of the above oxalic acid solution.

One advantage of this modified method is observed when it is necessary to determine the amount of carbon dioxide, as well as of carbon monoxide, in the air. Then it is simply necessary to place another narrow test tube, containing 50 cc. of the barium hydroxide solution, in front of the caustic potash and sulphuric acid tubes. In this way, by the same reagents, the amount of free carbon dioxide is found by titration of the contents of the first barium hydroxide tube, and the amount of free carbon monoxide, transformed into dioxide by titration of the contents of the second; and all in one operation.

## COMPARISON OF METHODS FOR CO.

Per cent. CO Found.

Per cent. CO taken.	Per cent. CO Found.	
	Iodine titration.	CO <sub>2</sub> titration.
0.0803	0.081	0.0850
0.0838	0.0859	0.0820
Unknown	0.0454	0.0480
"	0.0465	0.0460
"	0.0618	0.0613

The results of this paper may be summarized as follows :

I. In the determination of carbon monoxide by passing it over heated iodine pentoxide, the ends of the U-tube should be sealed off after filling, since the presence of organic matter, such as might come from the lubricant used with glass stoppers, also causes the decomposition of the iodine pentoxide, and would give too high results.

II. A modified method for carbon monoxide is presented, in which, after the iodine formed by the reaction is removed by a potassium iodide solution, the carbon dioxide is absorbed in barium hydroxide solution and determined by titration with oxalic acid. A check on the same sample can then be obtained, if desired, by titrating the iodine absorbed in the potassium iodide solution with  $N/1000$  sodium thiosulphate.

III. By placing another barium hydroxide tube before the one containing the iodine pentoxide, both the free carbon dioxide and the carbon dioxide produced by the free carbon monoxide, can be determined in one operation by two titrations with the same reagent.

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## RAPID ANALYSIS BY ELECTROLYSIS WITHOUT ROTATING ELECTRODES.

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In a preliminary paper<sup>1</sup> I have described two forms of apparatus for the rapid determination of metals in the electrolytic way, without the use of a motor or rotating electrodes. The purpose of this paper<sup>2</sup> is the description of the improved forms of this apparatus<sup>3</sup> as they have been worked out since the earlier publication.

In the first apparatus (fig. 1.) the solenoid consists of about 500 turns of 1.5 mm. insulated copper wire (about No. 14 B and S gauge) and is wound on a copper cylinder 6 cm. in diameter and 11 cm. high. The flanges on the end of the cylinder are of sheet-iron. A hollow iron cylinder (height 4 cm., thickness of iron 1 cm.) stands in the lower part of the copper cylinder. The solenoid is surrounded by an iron mantle, 2 mm. thick, which serves the double purpose of protecting the insulation of the solenoid and of presenting a short path for the magnetic circuit on the outside of the coil. In this way the entire magnetic force of the solenoid is concentrated in that portion of its core lying above the inner iron cylinder.

<sup>1</sup> Z. Elektrochem., 13, 308.

<sup>2</sup> Also published in the Z. angew. Chem.

<sup>3</sup> D. R. G. M. applied for by the Vereinigten Fabriken für Laboratoriumsbedarf, Berlin (American agents—The Kny-Scheerer Co., New York) who are sole owners of the right to manufacture the apparatus for sale, and to whom I am indebted for the two drawings here published.