

relationships. It is hoped soon to carry out a more exhaustive investigation upon the point, and also upon the similar chlorine and bromine compounds.

STANFORD UNIVERSITY,
July 20, 1897.

A COMPARISON OF VARIOUS RAPID METHODS FOR DETERMINING CARBON DIOXIDE AND CARBON MONOXIDE.

BY L. M. DENNIS AND C. G. EDGAR.

Received September 14, 1897.

THE value of gas analysis as an aid in the control and development of industrial processes is slowly being recognized by American manufacturers. Accompanying the increased use of this branch of analysis there seems to be, however, a tendency to adopt certain faulty methods of work to which it may be well to call attention. In industrial analyses chief stress will naturally be laid upon rapidity, and the accuracy demanded of the chemist will depend upon the nature of the work in hand. For example, in two processes in which carbon dioxide is regularly determined, it is sufficient in one case that the results be correct only within the range of one per cent., while in the other they should vary not more than one-tenth of one per cent. from the truth. In many cases, however, the analyst seems to be inclined to adopt some one form of apparatus and some one rapid method for the determination of each constituent and to adhere to this apparatus and method no matter what may be the conditions. Under such circumstances it is to be expected that the results obtained by different chemists on the same sample may show wide variations and even that the analyses of a single chemist, if his methods are not suited to the particular case in hand, may give rise to false deductions and cause financial loss to his employers. Difficulties similar to these were apparent, some years ago, in the analysis of iron and steel, and led to careful comparisons of the various methods by different chemists and to the development of standard methods of analysis. It was with the idea of making a beginning toward a similar comparison of some of the better known methods of gas analysis and of determining their relative accuracy and of ascertaining within what limits they might be relied upon, that Mr. Edgar undertook the

work described below. It is not claimed that the results show the absolute accuracy of the different methods, but they doubtless give quite closely their relative accuracy and the time which the average chemist would need for the various determinations.

The receiver for holding the gas mixtures to be analyzed consisted of a thick-walled, round-bottomed flask of about 700 cc. capacity. Into the neck of the flask was inserted a two-hole rubber stopper carrying two capillary glass tubes, one of these tubes ending just below the stopper and the other extending to the bottom of the flask. After firmly wiring the stopper, the flask was inverted and supported in a ring stand. The shorter capillary tube was connected by heavy rubber tubing with a level bottle containing about 800 cc. of mercury. The longer tube was bent in such a manner that it could easily be connected with the capillary of a Hempel gas burette. In collecting the samples for analysis, the air in the flask was first completely displaced by mercury from the level bottle and then measured portions of the gases to be mixed were run in through the longer capillary from a Hempel gas burette, this latter also containing mercury as the confining liquid. The flask was then shaken for five minutes and allowed to stand for some time, so that the gases might thoroughly mix. The gas mixture was at all times kept under a pressure slightly greater than that of the atmosphere, so as to prevent the possible entrance of air.

DETERMINATION OF CARBON DIOXIDE.

The gas mixture to be analyzed was prepared by mixing known volumes of air from outside the laboratory and carefully washed carbon dioxide prepared in a Kipp apparatus. The oxygen and nitrogen which might be contained in the carbon dioxide were not determined because the absolute accuracy of the different methods was in this work only of minor importance. Different mixtures of 500 cc. each were prepared, containing by measurement twenty, thirty, and forty per cent. of carbon dioxide. The solution of potassium hydroxide used for absorbing the carbon dioxide had the concentration recommended by Clemens Winkler;¹ namely, one part potassium hydroxide to four parts of water. The different forms of apparatus used were those devised by Honigmann, Bunte, Orsat, Elliot, and Hempel.

¹ Winkler: *Lehrbuch der technischen Gasanalyse*, 2te Auflage, 1892, p. 68.

Water was used in every case as the confining liquid. After each determination every measuring burette was rinsed with dilute hydrochloric acid to remove any potassium hydroxide that might accidentally have been introduced.

HONIGMANN'S BURETTE.

This was described to Professor Clemens Winkler by Moritz Honigmann, in a letter dated March 15, 1881. The method of using it which we adopted was that given by Winkler,¹ except that in filling the burette with the gas, instead of aspirating the gas through the burette until the air has been completely displaced, the burette was first filled with water which had been saturated with the gas, and the water was then displaced by gas from the receiver.

| Sample No. | Carbon dioxide. Per cent. | Check result with Hempel's apparatus. Per cent. | Results with Honigmann's apparatus. Per cent. | Time in minutes. |
|------------|---------------------------|---|---|------------------|
| I. | 20 | 19.9 | 19.6 | 10 : 00 |
| | | | 18.9 | 9 : 00 |
| II. | 20 | 19.85 | 19.1 | 9 : 30 |
| | | | 19.8 | 7 : 10 |
| | | | 19.8 | 6 : 30 |
| III. | 20 | 20.1 | 19.7 | 6 : 15 |
| | | | 20.0 | 6 : 00 |
| | | | 19.8 | 5 : 30 |
| IV. | 30 | 29.9 | 19.8 | 5 : 00 |
| | | | 29.2 | 6 : 30 |
| | | | 29.1 | 7 : 10 |
| V. | 30 | 29.7 | 29.0 | 5 : 40 |
| | | | 29.4 | 5 : 00 |
| | | | 29.5 | 5 : 00 |
| VI. | 30 | 29.6 | 29.6 | 5 : 30 |
| | | | 29.3 | 5 : 30 |
| | | | 29.4 | 5 : 15 |
| VII. | 40 | 39.9 | 29.5 | 5 : 00 |
| | | | 39.2 | 6 : 10 |
| | | | 39.0 | 6 : 00 |
| VIII. | 40 | 40.1 | 38.9 | 5 : 30 |
| | | | 39.7 | 6 : 00 |
| | | | 39.8 | 6 : 15 |
| IX. | 40 | 39.9 | 39.2 | 5 : 35 |
| | | | 38.9 | 5 : 30 |
| | | | 39.5 | 6 : 00 |
| | | | 39.4 | 6 : 10 |

¹ Winkler : Lehrbuch der technischen Gasanalyse, 2te Auflage, 1892, p. 82.

AVERAGES WITH HONIGMANN'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20 | 19.6 |
| 30 | 29.2 |
| 40 | 39.31 |

BUNTE'S BURETTE.¹

Method of use was as described by Winkler, p. 84.

| Sample No. | Carbon dioxide. Per cent. | Check result with Hempel's apparatus. Per cent. | Results with Bunte's apparatus. Per cent. | Time in minutes. |
|------------|---------------------------|---|---|------------------|
| X. | 20 | 19.9 | 19.8 | 8:30 |
| | | | 19.7 | 8:15 |
| | | | 19.8 | 8:35 |
| XI. | 20 | 20.1 | 19.8 | 8:30 |
| | | | 19.7 | 8:25 |
| | | | 20.1 | 8:50 |
| XII. | 20 | 20.0 | 19.8 | 8:10 |
| | | | 19.6 | |
| | | | 19.8 | 8:00 |
| XIII. | 30 | 29.9 | 29.7 | 8:20 |
| | | | 29.8 | 8:45 |
| | | | 29.6 | 8:00 |
| XIV. | 30 | 30.1 | 29.9 | 8:20 |
| | | | 29.7 | 8:15 |
| | | | 30.0 | 8:40 |
| XV. | 30 | 29.8 | 29.8 | 8:10 |
| | | | 29.6 | 8:35 |
| | | | 29.7 | 8:15 |
| XVI. | 40 | 40.0 | 38.9 | 8:15 |
| | | | 39.3 | 8:00 |
| | | | 39.5 | 8:10 |
| XVII. | 40 | 39.8 | 39.5 | 8:25 |
| | | | 39.3 | 8:30 |
| | | | 39.5 | 8:00 |
| XVIII. | 40 | 39.9 | 39.3 | 8:00 |
| | | | 39.4 | 8:15 |
| | | | 39.5 | 8:25 |

AVERAGES WITH BUNTE'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20 | 19.8 |
| 30 | 29.7 |
| 40 | 39.33 |

¹ *Journal für Gasbeleuchtung*, 1877, p. 447.

ORSAT'S APPARATUS.

The form of this apparatus which we employed was that now made by Robert Muencke, Berlin, and it was used in the manner described by Winkler, p. 89.

| Sample No. | Carbon dioxide. Per cent. | Check result with Hempel's apparatus. Per cent. | Results with Orsat's apparatus. Per cent. | Time in minutes. |
|------------|---------------------------|---|---|------------------|
| XIX. | 20 | 19.8 | 19.7 | 7:00 |
| | | | 19.6 | 8:00 |
| | | | 19.8 | 7:45 |
| XX. | 20 | 19.9 | 19.6 | 8:15 |
| | | | 19.7 | 8:00 |
| | | | 19.6 | 7:15 |
| XXI. | 20 | 19.8 | 19.5 | 8:10 |
| | | | 19.6 | 8:00 |
| | | | 19.5 | 7:50 |
| XXII. | 30 | 29.8 | 29.2 | 6:50 |
| | | | 29.3 | 7:00 |
| | | | 29.0 | 6:40 |
| XXIII. | 30 | 29.7 | 29.2 | 7:00 |
| | | | 29.3 | 7:15 |
| | | | 29.3 | 8:00 |
| XXIV. | 30 | 29.9 | 29.3 | 7:00 |
| | | | 29.4 | 7:35 |
| | | | 29.3 | 7:40 |
| XXV. | 40 | 40.0 | 39.2 | 7:00 |
| | | | 39.1 | 6:10 |
| | | | 39.2 | 6:00 |
| XXVI. | 40 | 39.9 | 39.3 | 5:45 |
| | | | 39.2 | 6:00 |
| | | | 39.3 | 6:10 |
| XXVII. | 40 | 39.8 | 39.4 | 6:50 |
| | | | 39.3 | 7:10 |
| | | | 39.4 | 7:00 |

AVERAGES WITH ORSAT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20 | 19.62 |
| 30 | 29.45 |
| 40 | 39.46 |

ELLIOT'S APPARATUS.

This apparatus is described in the *Chem. News*, 1881, 44, 289.

| Sample No. | Carbon dioxide. Per cent. | Check result with Hempel's apparatus. Per cent. | Results with Elliot's apparatus. Per cent. | Time in minutes. |
|------------|---------------------------|---|--|------------------|
| XXVIII. | 20 | 19.8 | 19.7 | 6:50 |
| | | | 19.6 | 7:10 |
| | | | 19.7 | 7:00 |
| XXIX. | 20 | 19.9 | 19.7 | |
| | | | 19.6 | |
| | | | 19.5 | |
| XXX. | 20 | 20.0 | 19.8 | |
| | | | 19.5 | |
| | | | 19.8 | |
| XXXI. | 30 | 30.0 | 29.6 | 8:15 |
| | | | 29.5 | 8:10 |
| | | | 29.6 | 8:40 |
| XXXII. | 30 | 28.9 | 29.5 | |
| | | | 29.7 | |
| | | | 29.6 | |
| XXXIII. | 30 | 29.9 | 29.4 | 7:10 |
| | | | 29.6 | 7:00 |
| | | | 29.5 | 6:50 |
| XXXIV. | 40 | 39.9 | 39.2 | 6:20 |
| | | | 39.3 | 6:15 |
| | | | 39.0 | 6:10 |
| XXXV. | 40 | 39.9 | 39.5 | 6:50 |
| | | | 39.4 | 7:00 |
| | | | 39.8 | 6:35 |
| XXXVI. | 40 | 39.8 | 39.3 | 7:00 |
| | | | 39.6 | 6:50 |
| | | | 39.5 | 6:10 |

AVERAGES WITH ELLIOT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 20 | 19.66 |
| 30 | 29.55 |
| 40 | 39.41 |

HEMPEL'S APPARATUS.

The gas burette was that shown in Fig. 17 of the English edition of Hempel's Methods of Gas Analysis. The absorption pipette shown in Fig. 21, *b*, was employed, this being filled with iron wire gauze and potassium hydroxide, as described on page 157.

In some of the determinations given below the water was allowed to run down the walls of the burette for the usual time, three minutes. In others this time was shortened to one-half a minute to see whether the work could be hastened without too great a sacrifice of accuracy.

| Sample No. | Carbon dioxide. Per cent. | Results with Hempel's apparatus. Per cent. | Time allowed for running down of water. | Time in minutes. |
|------------|---------------------------|--|---|------------------|
| I. | 20 | 19.9 | 3 min. | 10:00 |
| II. | 20 | 19.85 | 3 " | 9:00 |
| III. | 20 | 20.1 | 3 " | 10:00 |
| X. | 20 | 19.9 | 3 " | 8:50 |
| XI. | 20 | 20.1 | 3 " | 9:00 |
| XII. | 20 | 20.0 | 3 " | 8:40 |
| XIX. | 20 | 19.8 | 30 sec. | 4:00 |
| XX. | 20 | 19.9 | 30 " | 4:15 |
| XXI. | 20 | 19.8 | 30 " | 4:09 |
| XXVIII. | 20 | 19.8 | 30 " | 4:00 |
| XXIX. | 20 | 19.9 | 30 " | 4:10 |
| XXX. | 20 | 20.0 | 30 " | |
| IV. | 30 | 29.9 | 3 min. | 9:00 |
| V. | 30 | 29.7 | 3 " | 9:00 |
| VI. | 30 | 29.6 | 3 " | 9:00 |
| XIII. | 30 | 29.9 | 3 " | 9:00 |
| XIV. | 30 | 29.9 | 3 " | 9:50 |
| XV. | 30 | 30.1 | 3 " | 9:00 |
| XXII. | 30 | 29.8 | 30 sec. | 3:30 |
| XXIII. | 30 | 29.7 | 30 " | 4:00 |
| XXIV. | 30 | 29.9 | 30 " | 3:50 |
| XXXI. | 30 | 30.0 | 30 " | 4:00 |
| XXXII. | 30 | 29.9 | 30 " | 4:10 |
| XXXIII. | 30 | 29.9 | 30 " | 4:05 |
| VII. | 40 | 39.9 | 3 min. | 9:00 |
| VIII. | 40 | 40.1 | 3 " | 8:45 |
| IX. | 40 | 39.9 | 3 " | 9:00 |
| XVI. | 40 | 40.0 | 3 " | 8:50 |
| XVII. | 40 | 39.8 | 3 " | 9:00 |
| XVIII. | 40 | 39.9 | 3 " | 9:00 |
| XXV. | 40 | 40.0 | 30 sec. | 4:00 |
| XXVI. | 40 | 39.9 | 30 " | 3:30 |
| XXVII. | 40 | 39.8 | 30 " | 4:10 |
| XXXIV. | 40 | 39.9 | 30 " | 4:15 |
| XXXV. | 40 | 39.9 | 30 " | 4:25 |
| XXXVI. | 40 | 39.8 | 30 " | 6:15 |

AVERAGES WITH HEMPEL'S APPARATUS.

| Per cent. | | Per cent. | |
|-----------|---------------------|-----------|--|
| 20 | 3 min. running down | 19.97 | |
| 20 | 30 sec. " " | 19.87 | |
| 30 | 3 min. " " | 29.85 | |
| 30 | 30 sec. " " | 29.87 | |
| 40 | 3 min. " " | 39.93 | |
| 40 | 30 sec. " " | 39.89 | |

DETERMINATION OF CARBON MONOXIDE.

The gas mixture to be analyzed consisted of a mixture of nitrogen and carbon monoxide, the latter being prepared from oxalic acid. Mixtures containing by measurement three, nine, and fifteen per cent. of carbon monoxide were used. The gas was absorbed by means of a hydrochloric acid solution of cuprous chloride. For preparing this solution of cuprous chloride, we have used for some years in this laboratory the method which was suggested by Sandmeyer,¹ and which has been found superior to any other that we have tried.

The methods for determining carbon monoxide which were compared were those of Orsat, Elliot, and Hempel. After absorption by the cuprous chloride, the gas residue was always treated with potassium hydroxide, to free it from any acid vapors, before the final reading was made.

ORSAT'S APPARATUS.

The gas sample was passed into the cuprous chloride tube and allowed to remain there for three minutes. It was then run back and forth from the burette for two minutes longer. Then it was passed into the potassium hydroxide tube and finally brought into the burette and measured.

¹ Sandmeyer: *Ber. d. chem. Ges.*, 17, 1633. Twenty-five parts of crystallized copper sulphate and twelve parts of dry sodium chloride are placed in fifty parts of water and heated until the copper sulphate dissolves. (Some sodium sulphate may separate out.) 100 parts of concentrated hydrochloric acid and thirteen parts of copper turnings are then added and the whole is boiled in a flask until decolorized. Platinum foil will hasten the process. The solution is kept in glass-stoppered bottles until wanted.

| Sample No. | Carbon monoxide. Per cent. | Results with Orsat's apparatus. Per cent. | Time in minutes. |
|------------|----------------------------|---|------------------|
| I. | 3 | 2.3 | 13:00 |
| | | 2.5 | 12:10 |
| | | 2.2 | 11:00 |
| | | 2.1 | 13:00 |
| II. | 3 | 2.0 | 12:10 |
| | | 2.3 | 11:50 |
| | | 2.7 | 12:30 |
| | | 2.4 | 11:15 |
| III. | 9 | 8.4 | 14:00 |
| | | 8.5 | 10:10 |
| | | 8.4 | 10:30 |
| | | 8.6 | 10:00 |
| IV. | 9 | 8.5 | 15:40 |
| | | 8.4 | 11:00 |
| | | 8.5 | 10:30 |
| | | 8.7 | 10:45 |
| V. | 15 | 14.5 | 14:00 |
| | | 14.2 | 15:00 |
| | | 14.4 | 13:50 |
| | | 14.6 | 14:10 |
| VI. | 15 | 14.7 | 16:10 |
| | | 14.3 | 15:40 |
| | | 14.6 | 14:00 |
| | | 14.4 | 15:15 |

AVERAGES WITH ORSAT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 3 | 2.31 |
| 9 | 8.5 |
| 15 | 14.4 |

ELLIOT'S APPARATUS.

The gas was here also treated with potassium hydroxide after the absorption of the carbon monoxide.

| Sample No. | Carbon monoxide. Per cent. | Results with Elliot's apparatus. Per cent. | Time in minutes. |
|------------|----------------------------|--|------------------|
| VII. | 3 | 2.4 | 10:00 |
| | | 2.3 | 10:30 |
| | | 2.4 | 9:50 |
| | | 2.1 | 10:10 |
| VIII. | 3 | 2.5 | 10:10 |
| | | 2.3 | 11:00 |
| | | 2.4 | 10:50 |
| | | 2.0 | 10:30 |
| IX. | 9 | 8.4 | 11:00 |
| | | 8.5 | 10:50 |
| | | 8.3 | 11:40 |
| | | 8.0 | 10:20 |
| X. | 9 | 8.4 | 13:00 |
| | | 8.0 | 12:10 |
| | | 7.9 | 11:50 |
| | | 8.3 | 10:00 |
| XI. | 15 | 14.1 | 14:10 |
| | | 13.9 | 15:00 |
| | | 14.0 | 13:50 |
| | | 14.4 | 14:30 |
| XII. | 15 | 14.0 | 14:00 |
| | | 14.4 | 13:10 |
| | | 13.8 | 13:40 |
| | | 14.2 | 14:10 |

AVERAGES WITH ELLIOTT'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 3 | 2.3 |
| 9 | 8.2 |
| 15 | 14.1 |

HEMPEL'S APPARATUS.

Two double gas pipettes were employed, the one which was used second containing a fresh solution of cuprous chloride.¹ The gas was passed into the first pipette, which was then shaken for two minutes; then into the second pipette and shaken for three minutes; then into a potassium hydroxide pipette, and finally into the burette, where it was measured.

¹ Hempel: Methods of Gas Analysis, p. 161.

| Sample No. | Carbon monoxide. Per cent. | Results with Hempel's apparatus. Per cent. | Time in minutes. |
|------------|----------------------------|--|------------------|
| | | 3.2 | 10:10 |
| | | 3.0 | 9:50 |
| XIII. | 3 | 2.9 | 10:00 |
| | | 2.8 | 9:40 |
| | | 2.8 | 10:00 |
| XIV. | 3 | 3.0 | 9:50 |
| | | 2.9 | 9:30 |
| | | 2.8 | 9:20 |
| | | 8.7 | 9:30 |
| XV. | 9 | 8.8 | 9:10 |
| | | 8.9 | 9:15 |
| | | 8.8 | 9:30 |
| | | 8.8 | 9:10 |
| XVI. | 9 | 9.0 | 8:50 |
| | | 8.9 | 9:00 |
| | | 8.7 | 8:45 |
| | | 14.7 | 9:00 |
| XVII. | 15 | 14.6 | 8:40 |
| | | 14.8 | 8:50 |
| | | 14.5 | 9:00 |
| XVIII. | 15 | 14.7 | 8:30 |
| | | 14.8 | 9:00 |

AVERAGES WITH HEMPEL'S APPARATUS.

| Per cent. | Per cent. |
|-----------|-----------|
| 3 | 2.9 |
| 9 | 8.85 |
| 15 | 14.77 |

The above results show that in the determination of carbon dioxide all of the five methods tested are accurate to within less than one per cent., and all except Honigsmann's, to within one-half of one per cent., provided the amount of carbon dioxide present does not exceed thirty per cent. The most exact results in every case, however, are those obtained with Hempel's apparatus, and when the carbon dioxide is as high as forty per cent., this is the only method in which the error does not exceed five-tenths per cent. As regards speed, the Hempel method, with only thirty seconds allowed for the running down of the water, seems to have been the shortest, but was closely followed by the

Hönigsmann method. Attention may also be called to the fact that while in the methods of Hönigsmann, Orsat, and Hempel, the same potassium hydroxide is used repeatedly, in the Bunte and Elliot methods the reagent cannot be used twice, these methods being thus extremely wasteful.

In the determination of carbon monoxide the superiority of the Hempel method, both in accuracy and speed, is even more marked. Better results than those cited can be obtained with both the Orsat and Elliot apparatus but only by greatly prolonging the time.

CORNELL UNIVERSITY,
JULY, 1897.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY
No. 23.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM.

BY DANIEL L. WALLACE AND EDGAR F. SMITH.

Received September 9, 1897.

ABOUT a year ago Max Heidenreich¹ published an article in which he reviewed methods proposed by one of us (S) for the electrolytic determination of certain metals. In some instances he confirmed the observations of Smith, but in most cases differed with him. Recently S. Avery and Benton Dales² announced that so far as the determination of cadmium was concerned their "result was in complete harmony with the experiments of Heidenreich." In consequence of these experiences with the electrolytic methods suggested by Smith for the determination of cadmium, we have repeated them and offer new results obtained by us.

It was in 1878³ that Smith stated that "0.1450 gram of cadmium oxide was dissolved in acetic acid, the excess of the latter expelled upon a water-bath and the platinum crucible then about half filled with water, and * * * connected with the negative pole of a two-cell Bunsen battery * * *. The deposition of the cadmium was regular * * * a perfectly crystalline, grayish white layer." The precipitation was complete in about three hours. The experiment was repeated, but a bichromate battery was substituted for the Bunsen cells. At the time when these

¹ *Ber. d. chem. Ges.*, 29, 1585.

² *This Journal*, 19, 380.

³ *Proc. Am. Phil. Soc.*, November, 1878.