COLORIMETRIC DETERMINATION OF CARBON MONOXIDE IN AIR BY AN IMPROVED PALLADIUM CHLORIDE METHOD*

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In the absence of other reducing substances the following reaction is an old test for the presence of carbon monoxide (1):

\[ \text{PdCl}_2 + \text{CO} + \text{H}_2\text{O} = \text{Pd} + \text{CO}_2 + 2\text{HCl} \]

The decrease in palladium chloride can be determined colorimetrically (2) and by means of iodometric titration (3). Christman, Block, and Schultz (4) determined CO in air by transferring gas mixtures to flasks at pressures of about 0.5 atmosphere, containing known quantities of PdCl₂. After 6 to 24 hours the PdCl₂ which remained was converted to PdI₂ by the addition of excess KI, the pinkish red color being compared with that of standard solutions. Instead of a calorimeter we have used a Beckman, model DU, spectrophotometer. Many accurate determinations with small quantities of reagents are easily performed in less than 3 hours. By means of special stop-cocks which fit into standard volumetric glassware of measured capacity it is possible to evacuate with a water pump and then to introduce a gas. The results on concentrated and dilute CO mixtures show that the improved method has great flexibility.

According to previous reports it is not possible to recover CO completely by the PdCl₂ method (2–4). This is probably the result of the following reaction,

\[ \text{Pd} + \frac{3}{2}\text{O}_2 + 2\text{HCl} = \text{PdCl}_2 + \text{H}_2\text{O} \]

for a 20 to 25 per cent lower recovery of CO occurs in O₂ than in N₂ mixtures (4). In recognition of the above opposing reactions, we have investigated the consistency of recovery at different times after the reaction was started and have found at the end of the 2nd hour that recovery is 99.6 per cent in the presence of air at atmospheric pressure and at room temperature.

An excellent comparison of six other methods was reported by Shepherd (5), who prepared dilute CO mixtures and then distributed these in steel cylinders to various laboratories for analysis. We were fortunate in obtaining a similarly prepared mixture which was analyzed by the improved

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PdCl₂ method with results that compare favorably with those by the best methods available in 1947.

Materials

*Palladium Chloride*—With a semimicro balance 125 to 130 mg. of 99.7 per cent pure PdCl₂ are weighed to the nearest 0.1 mg. in a 20 ml. beaker. This is then placed in a 500 ml. beaker and 100 ml. of distilled H₂O and 1 ml. of HCl solution are added. The latter is prepared by diluting concentrated HCl solution ten times with distilled H₂O. The beakers are covered with a bell jar and left at room temperature until the PdCl₂ dissolves, which takes about 12 hours. The solution is then transferred quantitatively to a 250 ml. volumetric flask and is brought to volume with distilled H₂O. The stock solution is stored at room temperature in 125 ml. reagent bottles with glass stoppers and can be used for at least 8 months.

*Aluminum Sulfate*—A 10 per cent solution of Al₂(SO₄)₃ in distilled H₂O is kept in a dropping bottle.

*Potassium Iodide*—A solution of reagent grade, granular KI is prepared daily in the proportions of 12 gm. of KI and 100 ml. of distilled H₂O, with a pan balance and a graduated cylinder.

*Glassware*—A few pieces of special glassware are necessary. Fig. 1 shows a modified Geissler type stop-cock. The lower arm has an interchangeable ground joint which is greased and inserted into the standard taper, No. 13, neck of volumetric vessels, such as 25 ml. graduated cylinders and 100 and 200 ml. volumetric flasks. The capacity of each reaction vessel is com-

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1 Palladium chloride of assayed purity can be purchased from A. D. Mackay, Inc., 198 Broadway, New York 38.

2 Made according to specifications by Metro Industries, 29-28 Forty-first Avenue, Long Island City 1, New York.
puted from the weight and the temperature of the water which fills the vessel and the capillary in the stop-cock. Among the wide choice in size of calibrated vessels, cylinders of 40 ml. capacity are used most often.

At the end of a test the solutions are removed in dropping pipettes with rubber nipples and are transferred to standard Corning, coarse fritted, Büchner type filters of diameter 10 mm. The capacity of the filters is enlarged from 2 to 8 ml. by increasing the height of the funnel. The filtrate is usually collected in 50 ml. volumetric flasks. In tests with very dilute CO, the filtrate from a 2 ml. funnel is collected in 10 ml. volumetric flasks.

All glassware is cleaned by removing the metallic Pd with a few drops of chromic-sulfuric acid mixture, followed by rinsing with water.

CO Mixtures—Highly concentrated CO was obtained in steel cylinders at a pressure of 800 pounds per sq. in.

A series of dilutions was prepared by mixing CO and room air. The CO was made from formic acid and sulfuric acid, and was analyzed for purity (6). A tonometer was connected to a Douglas bag, and the contained CO flowed into the bag along with a measured volume of room air that issued from a calibrated Tissot spirometer. The gases were thoroughly mixed by beating the bag, and the analysis was performed immediately.

A 0.0382 per cent CO mixture was kindly supplied by the National Bureau of Standards through the courtesy of Dr. Shuford Shuhmann, who informs us that this mixture could be 0.0378 per cent or 0.0386 per cent as judged by independent calibration of pressure gages (5).

Procedure

Fig. 2 shows a cylinder containing a known volume, usually 1.00 ml. of PdCl$_2$ solution, and 1 drop of 10 per cent Al$_2$(SO$_4$)$_3$ connected to an Hg manometer and to a water pump. The apparatus is evacuated to a desired extent, and the Hg level is noted. Then the stop-cock (Fig. 1) is turned, closing the cylinder and connecting the manometer to room air. The Tygon tubing is removed from the vertical arm of the stop-cock, which is then connected to a rubber tube from a Douglas bag, or a rubber bladder, containing the CO mixture to be analyzed. The horizontal arm of the stop-cock is connected to a rubber tube that leads into an inverted 1 liter graduated cylinder which is filled with H$_2$O. By pressing on the Douglas bag and then opening its screw clamp, a sufficient volume of gas is expressed so that the connections are flushed with at least 10 times their volume. Manual pressure on the bag is removed, and then the stop-cock is turned so that the gas mixture enters the cylinder. After 15 seconds the cylinder

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3 Matheson Company, Inc., East Rutherford, New Jersey.
4 U. S. Stoneware, Akron 9, Ohio.
is closed, and the barometric pressure and room temperature are noted. All told, this takes about 2 minutes.

It is necessary to know roughly the CO content and to have in the reaction vessel at least 10 per cent more PdCl₂ than is required; this can be determined from the fact that 0.1261 ml. of CO reduces 1 mg. of PdCl₂. With entirely unknown mixtures, it is wise to make a series of tests on successively larger gas samples. With 0.010 per cent CO or less, the stock solution is diluted five times, or the cylinders can be replaced with larger volumetric flasks.

When the gas has been introduced, the cylinder is gently rotated by hand and is then placed horizontally without, at the same time, permitting the fluid to enter the capillary of the stop-cock. At the end of 2 hours at 20–24° the mixture of PdCl₂ and precipitated Pd is transferred to a filter. The filtrate is collected in a 50 ml. volumetric flask which contains 20 to 30 ml. of distilled H₂O. The cylinder is washed with two portions of 2 to 3 ml. of distilled H₂O, which are transferred to the filter. Then from a 10 ml. pipette, containing 12 per cent KI solution, about 3 ml. are placed.

![Fig. 2. Apparatus for introduction of gas samples into reaction vessels](http://www.jbc.org/)

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on the filter, and the rest is emptied directly into the volumetric flask.
After this the filter is washed with 2 to 3 ml. of distilled H₂O, the flask is
brought to volume with distilled H₂O, and the contents are thoroughly
mixed. When stock PdCl₂ solution diluted five times is used, the same
procedure is followed, except that 2 ml. filters drain into 10 ml. volumetric
flasks and 2 ml. of 12 per cent KI are placed directly on the filters.

Standard solutions are prepared in triplicate with the same quantities
of reagents that are used in the tests. These are placed in 50 or in 10 ml.
volumetric flasks. At the time that the tests are filtered, the KI solution
is added to the standards and these are brought to volume with distilled
water.

\[ Q - \left( \frac{D_t}{D_s} \times Q \right) \times 0.1261 \]

where \( Q \) is the mg. of PdCl₂ originally present, \( D_t \) is the optical density of
the test solution, and \( D_s \) is the mean optical density of three standard solu-
tions. 0.1261 ml. of CO (normal temperature and pressure, dry) is
equivalent to 1.00 mg. of PdCl₂.
The volume of the gas sample (normal temperature and pressure, dry) drawn into the reaction vessel is computed as follows:

\[(C - V) \times \frac{\Delta P}{P} \times \frac{P - p}{760} \times \frac{273}{273 + T}\]

\(C\) is the ml. capacity, and \(V\) is the ml. volume of reagent solutions in the reaction vessel; \(\Delta P\) is the rise in mm. of Hg in the manometer connected to the vessel, and \(P\) is the atmospheric pressure (it is necessary to correct the manometric and barometric readings for temperature effect on the scales); \(p\) is the vapor pressure of water at room temperature; \(T\) is the temperature of the room and reaction vessel.

Concentrated CO—Industrial CO was collected over CO-saturated water. A representative gas sample was drawn into a burette of 0.128 ml. capacity, and the burette was connected through a rubber stopper to a 50 ml. Erlenmeyer flask containing 5.00 ml. of stock PdCl₂ solution. The stop-cock on the burette was opened, and the gas was introduced by means of an Hg leveling bulb. 2 hours later the test solution was filtered into a 100 ml. volumetric flask to which 20 ml. of 12 per cent KI were added.

CO in H₂O—As a control on the transfer of CO in gas mixtures, distilled H₂O was equilibrated with 96 per cent CO in tonometers from which 5.00 ml. portions were taken for gasometric determinations (7) and 2.00 ml. portions for measurement with PdCl₂. The aqueous solution was delivered directly into 5.00 ml. of dilute PdCl₂ stock solution in a 40 ml. cylinder, which was immediately closed with a greased stopper.

RESULTS AND DISCUSSION

Early in these experiments we found that PdCl₂ is rapidly reduced by CO, which is already in solution. Comparison of the results obtained by the gasometric and PdCl₂ methods shows (Table I) that the oxidation of dissolved CO was practically complete in 20 minutes. For the next 3 hours there was little difference in the results.

When CO must diffuse from a gas to a liquid phase, a longer period of time is required for the reduction of PdCl₂. To oxidize 90.8 per cent of the CO, as shown in Table II, 0.5 to 1.0 hour is required. The reaction is probably completed in 2 hours, but the corresponding reduction of PdCl₂ is complicated by a slow oxidation of Pd, as judged by progressively decreasing recoveries which fall from 98.1 per cent in 2 to 5 hours to 91.1 per cent in about 24 hours and 87.1 per cent in 48 hours. A similar effect on recovery of CO was observed by Wennesland (3).

The standard solutions served as controls for all steps except for the introduction of gas samples and the filtration of solutions. These controls (Table II) have a standard deviation of 0.90 per cent compared with 2.28
per cent for recovery, and hence the recovery of 98.1 per cent is not significantly different from 100.0 per cent. Moreover, the recovery was computed for 0.0382 per cent CO; so, if the gas were 0.0378 per cent, the recovery would be 99.1 per cent. Although the purity of the PdCl₂ was 99.7 per cent, this being less than 100.0 per cent does not improve the recovery,

TABLE I

Recovery of CO Present in 2.00 Ml. of H₂O at Intervals after Mixing with PdCl₂
Gasometric determinations carried out as described by Roughton and Root (7). Recovery is computed by taking the gasometric determinations as 100 per cent.

<table>
<thead>
<tr>
<th>Reaction period</th>
<th>PdCl₂</th>
<th>CO, gasometric</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>hrs.</td>
<td>vols.</td>
<td>per cent</td>
<td>per cent</td>
</tr>
<tr>
<td>0.3</td>
<td>1.79</td>
<td>1.82</td>
<td>98.2</td>
</tr>
<tr>
<td>1.0</td>
<td>1.98</td>
<td>1.95</td>
<td>101.5</td>
</tr>
<tr>
<td>1.5</td>
<td>1.84</td>
<td>1.82</td>
<td>101.1</td>
</tr>
<tr>
<td>1.5</td>
<td>1.95</td>
<td>1.91</td>
<td>102.1</td>
</tr>
<tr>
<td>1.7</td>
<td>1.98</td>
<td>1.95</td>
<td>101.5</td>
</tr>
<tr>
<td>2.3</td>
<td>1.83</td>
<td>1.82</td>
<td>100.5</td>
</tr>
<tr>
<td>3.0</td>
<td>1.92</td>
<td>1.95</td>
<td>98.4</td>
</tr>
</tbody>
</table>

Mean ................................................... 100.5

TABLE II

Recovery of 0.0382 Per Cent CO at Different Periods after Reaction with PdCl₂

<table>
<thead>
<tr>
<th>Reaction period</th>
<th>No. of determinations</th>
<th>Degrees of freedom</th>
<th>Recovery</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>hrs.</td>
<td></td>
<td></td>
<td>per cent</td>
<td>per cent</td>
</tr>
<tr>
<td>0.5 - 1.0</td>
<td>11</td>
<td>10</td>
<td>90.8</td>
<td>4.69</td>
</tr>
<tr>
<td>2 - 5</td>
<td>16</td>
<td>15</td>
<td>93.1</td>
<td>2.28</td>
</tr>
<tr>
<td>17 - 25</td>
<td>23</td>
<td>22</td>
<td>91.1</td>
<td>2.60</td>
</tr>
<tr>
<td>48</td>
<td>2</td>
<td>1</td>
<td>87.1</td>
<td>1.49</td>
</tr>
<tr>
<td>Control</td>
<td>36</td>
<td>24</td>
<td>100.0</td>
<td>0.90</td>
</tr>
</tbody>
</table>

because the standard and test solutions were not corrected for the slight impurity.

At intervals along the ordinate in Fig. 4 are listed the various expected concentrations of CO, and opposite each interval the percentage recovery is plotted. In the right-hand border of Fig. 4 are typical sample volumes and initial quantities of PdCl₂. All tests with the PdCl₂ method ran for about 2 hours.

The first mixture (Fig. 4) is 95.1 per cent, as this is the mean of eight determinations with a microgasometric procedure (6). All of the four
determinations with PdCl₂ are in close agreement and attest to the reproducibility of the method.

The next five mixtures (Fig. 4), from 0.258 to 0.0392 per cent, were analyzed with PdCl₂ and a gasometric method (7) in which reduced hemoglobin is employed. The gasometric results generally agree with those expected from the dilution of CO with room air. The gasometric results on 0.091 per cent CO are low, and, were it not for the PdCl₂ results, would lead one to suspect that a mistake had been made in diluting the gas.

The 0.0152 and 0.0103 per cent mixtures (Fig. 4) were analyzed by a gasometric method with 300 ml. samples (7). During the analysis of the most dilute mixture an excessive quantity of O₂ may have been introduced, thus causing the gasometric results to be low and unreliable. Though slightly inconsistent, the results on the 0.0103 per cent CO with PdCl₂ are acceptable. Since the time when these measurements were performed with the two dilute mixtures, we have obtained better results by testing with one-fifth the indicated quantity (Fig. 4) of PdCl₂. For example, in experiments with 20 ml. of blood (8) in 1 liter bottles we have obtained good recovery with 10 ml. gas samples from CO mixtures as low as 0.0010 volume per cent. From these various points of view we believe that the gas samples were obtained without the introduction of a constant error and that in a 2 hour reaction period recovery is nearly perfect.

When air which is to be examined for CO also contains substances such as acetylene, ethylene, and H₂S, these can be removed by scrubbing with...
Br₂ water and KOH solutions (4). We have tested the saturated volatile substances, acetone, alcohol, and ether, which could be encountered in physiological experiments and, of course, have found that these do not reduce PdCl₂. Since Hg displaces Pd in the electromotive series, we warn that care must be taken to see that globules of Hg do not contaminate the PdCl₂ solutions.

SUMMARY

Christman’s method of analyzing CO in air by the reduction of PdCl₂ has been extensively improved so that it is suitable for use in physiological experiments. With samples of less than 100 ml. it is possible to analyze CO percentages of 94.2, 0.010, and even less. The accuracy and consistency of the method are shown by recovery of 99.6 per cent, with a standard deviation of 2.21 per cent. The lowermost limit of the method, which has not been approached, has to do with the least quantity of PdCl₂ that can be accurately measured by spectrophotometry of PdI₂ solutions.

BIBLIOGRAPHY

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