cator which had been exposed to the air in a bottle with the stopper removed. This is a portion of the same indicator solution employed several days previous in Series I and II.

Conclusions.

1. The end point is an excellent one.
2. The indicator is a reducing agent and is oxidized by the dichromate during the process of titration. A blank determination must be made to ascertain this reducing power.
3. With the above modification the method is applicable to the analysis of ores for their iron content.
4. Small amounts of iron can be determined within the accuracy of the other methods in common practice.
5. In all likelihood the principle involved can be utilized in a number of other analyses. This point is being investigated.

The oxygen ratio existing between the oxidizing agent and the indicator as obtained by different methods, the chemical reaction involved in causing the color change during titration, and the use of other compounds similar to diphenylcarbazide, especially those containing double bonds between the nitrogen atoms, are being likewise investigated.

We desire to express our appreciation to Dr. Benton Dales for his interest in the work throughout this investigation.

UNIVERSITY OF NEBRASKA, LINCOLN.

A PORTABLE PETTERSSON-PALMQVIST APPARATUS.

BY R. P. ANDERSON.

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The disagreeable and sometimes injurious effect of poor ventilation in crowded buildings is believed, at the present time, to be due to the accumulation of two products of respiration, carbon dioxide and water vapor.[1] Atmospheric air contains about 0.03% carbon dioxide and variable amounts of water vapor, while expired air normally contains about 4% of carbon dioxide and 6% of water vapor. An examination of the air in buildings to ascertain their fitness for human habitation includes determinations of carbon dioxide and moisture, but when the efficiency of a ventilating system is in question the determination of carbon dioxide is alone of value, since (1) the amount of water vapor normally present in the atmosphere is not constant, but varies within wide limits,[2] (2) water vapor is given off in varying quantities from the skin, and (3) the amount of water vapor in the air cannot increase indefinitely, but will

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[1] The presence of a poisonous organic product of respiration has been discredited by recent work in this field.

[2] The water content of the atmosphere at Ithaca varies from about 0.1 to 4.0% by volume, and even over a wider range on rare occasions.

condense when the saturation point at the prevailing temperature is reached.

The methods of determining carbon dioxide that are applicable to the cases mentioned above may roughly be divided into two groups: I, those in which the carbon dioxide is determined by absorption in a standard solution of alkali or an alkaline earth hydroxide; and II, those in which the carbon dioxide is determined by measuring the decrease in volume of a certain amount of air on absorption of the carbon dioxide. The methods under group I differ widely in the procedure to be followed in attaining the desired result. There are those (*a*) in which the carbon dioxide from a certain volume of air is absorbed by an excess of standard alkali and the excess determined by standard acid, (*b*) in which a certain volume of standard alkali is taken and sufficient air is brought into contact with the alkali to furnish enough carbon dioxide to convert it entirely to bicarbonate, and (*c*) in which a certain volume of standard alkali is brought into contact with sufficient air to furnish an excess of carbon dioxide, and the time necessary for complete conversion to bicarbonate is determined (the duration of the reaction depending on the amount of carbon dioxide that the air contains). The various modifications of the Pettenkofer method fall under subdivision (*a*) and are the most accurate of all of the methods classed under group I. In general, these modifications of the Pettenkofer method can be made sufficiently accurate for ordinary purposes by taking a large volume of air and employing proper precautions in the absorption and titration, but the determination is a lengthy one and the apparatus is not easily portable. For carrying out the methods classed under group II, either the Pettersson-Palmqvist or the Haldane apparatus may be used. The Pettersson-Palmqvist seems to be best suited for work of a high degree of accuracy, but the original apparatus is too large to be easily portable, and both types of apparatus are open to the serious objection that they do not provide adequate means of quickly bringing the sample to be analyzed to the temperature of the water in the water jacket.[1]

The following modification of the Pettersson-Palmqvist apparatus is offered as being easily portable and capable of giving quick and accurate results in the determination of carbon dioxide in amounts that do not exceed 0.5% by volume.

Description of the Apparatus.

In the sketch, *B* represents the buret; *P*, the pipet; *C*, the compensation tube; *M*, the manometer; *Z*, *Z'*, *Z''*, the coil of copper tubing; and

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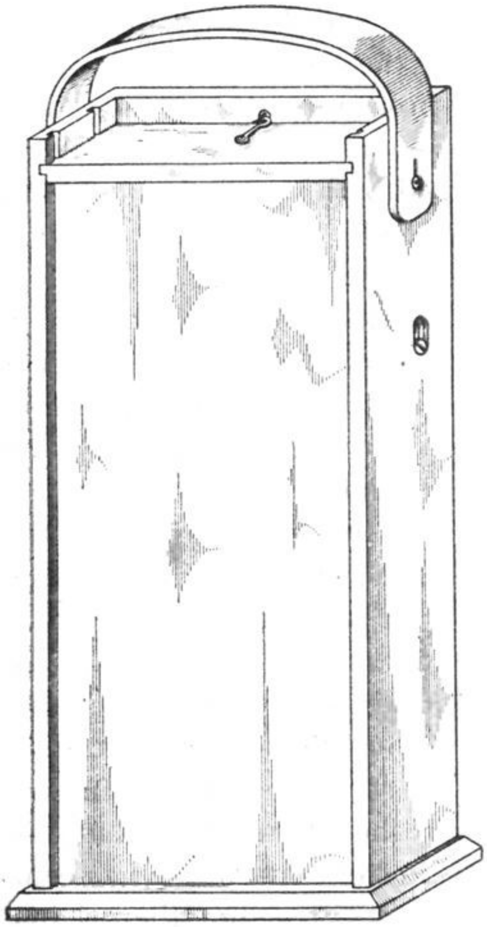
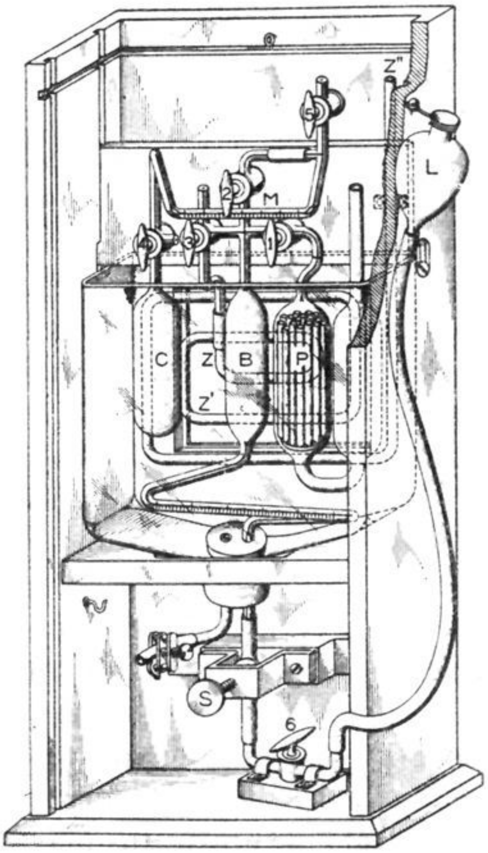
[1] At least two modifications of the Pettersson-Palmqvist apparatus have previously been constructed with the view of making the apparatus more portable, but they are both open to the same objection as the original. These modifications are by von Bleier, *Z. Hygiene*, 27, 111 (1898), and Rogers, *Catalogue of Eimer & Amend.*

L, the level bulb. The upper extremity of the buret connects with the pipet through stopcock *1*; with the manometer through stopcock *2*; and with the atmosphere, either directly or through the copper coil, through three-way stopcock *3*. The compensation tube connects with the manometer through stopcock *4*. This stopcock is made of the form shown in the sketch so that the compensation tube may be connected with the atmosphere whenever necessary. Stopcock *5* serves as an inlet for the manometer liquid. The lower extremity of the buret is connected by a piece of rubber tubing which passes under compression screw *S* to stopcock *6*, which, in turn, connects with level bulb *L* by means of a suitable length of patent rubber tubing.





The buret, pipet, compensation tube, and copper coil are immersed in water contained in a glass cell and are supported by a board that slides in grooves in the sides of the wooden box which encases the apparatus. The glass cell is of rectangular cross-section and is provided with an opening in the bottom in which is placed a two-hole rubber stopper carrying the lower end of the buret and a bent glass tube through which the water may be removed. This cell is held in place by a wooden support shaped to fit its base and provided with an opening through which the neck of the cell extends. The board carrying the buret, pipet, etc., can be lifted out of the case when the rubber tube is disconnected from the lower end of the buret and the rubber stopper is loosened from the neck of the glass cell. This allows easy access to all parts of the apparatus for cleaning and repairing. Further, the position of this board can be adjusted within certain limits by moving the bolts, upon which it rests, up or down in slots at the base of the grooves. This makes it a simple matter to adapt new glass parts to an old water jacket and case.

The buret has a capacity of about 25 cc. and is calibrated in 0.0025 cc., or in parts per 10,000. A large saving in height over the old Pettersson-Palmqvist apparatus is effected by giving the lower end of the buret the form shown in the figure. The calibrated portion is brought forward near the front face of the cell to afford greater ease and clearness in reading.

The case is provided with a removable front and top to render all parts of the apparatus easily accessible during the manipulation, and with a glass window in the back to give proper illumination when the operator desires to face the window of the room in which he is working.

Preparation of the Apparatus.

In preparing the apparatus for use, the glass parts are removed from the water jacket in the manner previously described and are thoroughly cleaned with cleaning mixture and dried. The stopcocks are well lubricated, but an excess of the lubricant is avoided, since it accumulates in the bore of the stopcocks and may cause a complete stoppage of the passage-way. Stopcock *6* and the pieces of tubing connecting it with the lower end of the buret and the level bulb are also thoroughly cleaned, since any particle of dirt or grease left inside might be carried up into the buret by the movement of the mercury used as confining liquid, thus interfering with the accurate use of the apparatus.

After replacing the glass parts in the water jacket and fastening the rubber tubing to the end of the buret, about 30 cc. of carefully purified or, preferably, distilled mercury is poured into the level bulb. A small quantity of water (equivalent to a column 3 to 5 mm. long in the bore of the capillary tubing) is introduced into the buret through the opening directly above stopcock *3* by covering the end of the capillary with a film of water and drawing the desired amount into the buret by lowering the level bulb. (Stopcocks *1* and *2* are closed, *3* and *6* open.)

The manometer liquid (azobenzene dissolved in petroleum) is introduced into the manometer in the following manner:

Buret *B* is nearly filled with mercury by opening stopcock *6*, raising level bulb *L*, and opening stopcocks *2* and *5*; then stopcock *6* is closed and compression screw *S* is tightened. A pipet containing a small amount of manometer liquid is now applied to the end of the capillary above stopcock *5* and the desired amount of liquid (enough to fill the capillary for a length of 3 to 5 mm.) is drawn in as far as the T in the capillary by loosening compression screw *S* (stopcocks *1*, *3* and *4* are closed); then stopcock *5* is closed, stopcock *4* is opened, and compression screw *S* is again tightened to force the liquid down into the manometer tube.

The pipet is filled with a solution of potassium hydroxide prepared by dissolving one part of potassium hydroxide in two parts of water. This solution is brought up to the mark on the capillary tubing below stopcock *1* by lowering the level bulb *L* with stopcocks *2* and *3* closed. Stopcock *1* is closed when this is accomplished.

Manipulation of the Apparatus.

Before beginning the examination of air in a room, the following conditions should be fulfilled: First, the temperature of the water in the water jacket should be in equilibrium with the temperature of the air in the room. This is most easily accomplished by placing the apparatus in the room and filling the water jacket a few hours before the apparatus is to be used. Second, the apparatus should not stand in the direct sunlight or in a draught. Third, the air in the manometer tube and in the compensation tube should be at atmospheric pressure. This is done by manipulation of stopcocks *4* and *5*.

(*a*) *Collection and Measurement of Sample.*—Buret *B* is filled with mercury by opening stopcock *6* and raising level bulb *L*. Stopcock *3* is turned for the escape of the air directly to the atmosphere (stopcocks *1* and *2* are closed). Then stopcock *3* is turned so that the buret communicates with the copper coil, the other end of which is connected by capillary tubing to the place from which the sample is to be taken, and air is drawn through the capillary tube and copper coil into the buret by lowering level bulb *L*. This sample is mixed with the small amount of air that was present in the connecting tubes, and for this reason is driven from the buret by turning stopcock *3* to the first position and raising level bulb *L*. Stopcock *3* is now turned to communicate with the copper coil, and level bulb *L* is again lowered until the mercury falls slightly below the zero mark on the buret. Stopcock *6* is then closed, and compression screw *S* is tightened until the mercury rises just to the zero mark. After allowing sufficient interval for the air in the buret to reach atmospheric pressure, stopcock *3* is closed. (On account of the friction met in drawing the sample through capillary tubing, the time interval until atmospheric pressure is reached inside the buret is appreciable, unless the capillary tubing is short.) Stopcock *2* is now opened and the position of the manometer liquid is read on the scale of the manometer tube. It is desirable to turn compression screw *S* back and forth slightly and to note whether the manometer liquid moves freely with each movement of the screw before the reading is taken. This is done to make sure that the gas in the compensation tube is at the same pressure as that in the buret. Stopcock *2* is then closed.

(*b*) *Absorption of the Carbon Dioxide and Measurement of the Residue.*—Stopcock *1* is opened and the gas sample is forced over into the pipet by opening stopcock *6* and raising level bulb *L*. When the mercury reaches the side arm on the capillary tube, stopcock *1* is closed and the gas is left in contact with the potassium hydroxide for one minute. Then stopcock *1* is opened, level bulb *L* is lowered, and the sample is drawn back into the buret, closing stopcock *1* as soon as the solution of potassium hydroxide reaches the mark on the capillary. None of the solution should be allowed to enter the buret. The mercury in the buret is next brought approximately to the zero mark and stopcock *6* is closed. Stopcock *2* is then opened and the liquid in the manometer is brought back to its original position by turning compression screw *S*. The reading of the mercury in the buret gives directly the amount of carbon dioxide absorbed, expressed in parts per 10,000.

Advantages.

The advantages of this modification of the Pettersson-Palmqvist apparatus over the original are:

First, it possesses greater ease of manipulation. The compactness of the entire apparatus brings all the stopcocks within easy reach of the operator and enables the readings of buret and manometer to be made without radical change of position of the head or body. The shortness of the buret lessens the distance through which the level bulb must be moved in filling and emptying the buret. The importance of these features becomes emphasized when consecutive determinations are to be made over a period of several hours, in studying ventilation problems.

Second, it is more easily portable. The outside dimensions of the apparatus shown in the figure are 11 × 18 × 42 cm., while those of the Pettersson-Palmqvist apparatus furnished by Greiner and Friedrichs, Stützerbach, Germany, are 24 × 24 × 92 cm. This decrease in size is brought about by giving the buret the form shown in the figure, rearranging the position of the glass parts, and making the apparatus more compact throughout. No decrease in accuracy is caused by these changes, but the sharp bends in the lower part of the buret retard the flow of mercury in filling and emptying the buret and, as a result, increase slightly the time required for a complete determination.

Third, it is provided with a coil of copper tubing submerged in the water in the glass cell as a convenient means of quickly bringing the sample to the temperature of the apparatus. The need of this device is due not only to the fact that it may be desirable to take a sample from some spot at a different temperature from that of the air where the apparatus is located, but also that the temperature of the water in the glass cell is usually lower than that of the surrounding atmosphere on account of evaporation from its surface. This is especially true in winter weather, when low humidity usually prevails indoors, and at such times the difference in temperature between the water and the surrounding atmosphere may amount to 4° or more. It takes some time for the sample to attain the temperature of the water, if it is drawn directly into the buret, and if accurate results are to be obtained with the original Pettersson-Palmqvist apparatus or with any of the forms mentioned under group II, the manipulation cannot be continued until this condition has been satisfied. In many cases the movement of the manometer liquid resulting from the change of volume due to this cause alone is greater than would result from the removal of the carbon dioxide that the sample contains. The necessity for delay is completely obviated when the sample is drawn through the copper coil.

The apparatus is manufactured by Greiner and Friedrichs, Stützerbach in Thüringen, Germany.

CORNELL UNIVERSITY, ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE DETECTION OF TRACES OF COPPER.[1]

BY WESLEY B. PRITZ, A. GUILLAUDEU AND JAMES R. WITHROW.

Received December 4, 1912.

A frequent feeling of uncertainty regarding the significance of qualitative tests for the completeness of the electrolytic precipitation of copper, made it desirable to know the limits of the sensitiveness of the recommended reagents, as commonly employed. It was also desired to modify, if necessary,, the sensitiveness of one of the reagents to meet the requirements of the work on electrolytic precipitation of copper in progress in this laboratory. As it is often essential in electro-analysis to remove only such volume of solution for the qualitative test as will contain an insignificant weight of copper, the method selected must be made applicable to samples not greater than about one cc. Of the reagents recommended, the ones which in our experience are in most general use are ammonium hydroxide, ammonium sulfide and potassium ferrocyanide. Since a study of the sensitiveness of these three, under the conditions in the copper work on hand, showed that ferrocyanide could be made to answer our purpose, other methods were not examined.

Heine[2] appears to have utilized color for the detection of copper as early as 1830. Müller, in 1855,[3] with his complement colorimeter using 5 cc. of solution was able to detect 50 parts of copper in one million, using ammonium hydroxide as reagent. Wagner, in 1881,[4] stated that the

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[1] Read before the Indianapolis meeting of the American Chemical Society.

[2] Heine, *Bergwerksfreund*, **1**, 33; **17**, 405; *Z. anal. Chem.*, **46**, 644.

[3] *J. prakt. Chem.*, **66**, 203.

[4] *Z. anal. Chem.*, **20**, 351.