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APPARATUS AND METHODS

FOR THE

SAMPLING AND ANALYSIS

OF FURNACE GASES

BY

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APPARATUS AND METHODS FOR THE SAMPLING AND ANALYSIS OF FURNACE GASES.

By J. C. W. Frazer and E. J. Hoffman.

INTRODUCTION.

The apparatus and methods described in the following pages were devised and used by the writers in connection with certain investigations of the technologic branch of the United States Geological Survey, especially those bearing on the improvement of furnace conditions and on efficiency in the use of fuel.

The Bureau of Mines, which has charge of such analyses and tests of fuels as were formerly made by the technologic branch of the Survey, is using the same apparatus and methods in connection with similar investigations that are being carried on at the testing plant of the bureau at Pittsburgh, Pa.

The furnace conditions prevailing both in small plants and in large industrial establishments in this country are frequently far from satisfactory. If such conditions are to be improved, they must be more thoroughly understood, and means must be found to insure complete combustion of the fuel, and yet to permit operation with such an excess of air as will result in the greatest efficiency.

In this work the services of the chemist are indispensable. A very important problem is the determination of the small percentage of unburned combustible matter that escapes from the furnace in the flue gases. Under ordinary circumstances so little as 0.1 per cent of unburned combustible matter in a furnace gas is equivalent to about 1 per cent of the fuel used; and for the determination of such small percentages of gas more accurate and refined methods are required than have ordinarily been available heretofore.

It is the purpose of this paper to describe some apparatus and methods which have proved satisfactory to those engaged in the chemical work of the investigations mentioned. While these methods and apparatus have been designed more particularly with regard to analysis of furnace gases, their use is by no means limited to that purpose. The reader will readily see their applicability to other uses in which the sampling and analysis of gases are involved.

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SAMPLING OF FURNACE GASES.

The proper sampling of gases is frequently difficult when the gas mixture under investigation is not homogeneous. The problem in sampling furnace gases is further complicated by the necessity of protecting the part of the sampling apparatus introduced into the heated gases. It is not difficult to obtain a sample of gas from a given point within a furnace; but as in most cases the composition of the gas is constantly changing, some method must be provided by which the sample will represent the average composition of the gas at the point of collection during a desired period; or the sample must be collected almost instantaneously, so that it will merely represent the composition of the gas at the point and at the instant of collection.

A sample taken in either of these ways is only representative of the gas occupying a certain space surrounding the point of collection. In order to determine the average composition of the entire volume of gas it is necessary to multiply the number of samples and to distribute the points of collection in such a manner that the average of the samples will correctly represent the entire gas body. The number of samples taken should depend on the differences in composition that are presumed to exist throughout the volume of gas to be sampled. The difference in composition between samples taken at any two adjacent points of collection should not be greater than from 0.3 to 0.5 per cent.

In the following pages methods are described for the collection of " continuous " samples, taken during any convenient period of time, and of " instantaneous " samples.

CONTINUOUS SAMPLING.

The sampling of flue gases can usually be accomplished satisfactorily by using a perforated iron pipe placed in the flue at the desired point. For a sample of flue gases to be representative it should be collected from a number of points in a given cross section. As the composition of the flue gases at any instant does not vary much at different points in a given cross section, the easiest method is to use a tube with 2-mm. perforations so shaped that it will best distribute the points from which the gas is to be drawn for analysis. In case none of the holes becomes stopped, a sample drawn through such a tube by gentle suction will be sufficiently representative for most purposes.

A common method of collecting a sample is to attach a large bottle filled with water to the outside open end of such a sampling tube and then to allow the water to escape at such a rate that the gas, which replaces the water in the bottle, is collected in the desired time.

It is not advisable to sample gases that contain a considerable proportion of carbon dioxide in this way because of the great ease with which water, or even a solution of common salt, dissolves that constituent and thus tends to equalize the content of carbon dioxide in the samples collected. To illustrate: If water is saturated with furnace gas containing 12 per cent of carbon dioxide and is then used in collecting a sample from gas having a carbon-dioxide content of 8 per cent, the water saturated with gas containing 12 per cent of carbon dioxide will give up some of the dissolved gas, and the sample will be found to contain more than 8 per cent of carbon dioxide. The magnitude of the error introduced in this way will vary with conditions, but it will depend largely on the length of the sampling period and the total time of contact of the sample with the water.

The following method of sampling was devised to obviate this difficulty, as well as certain others. As it has proved satisfactory it will be described in some detail.

COLLECTION AND STORAGE OF THE SAMPLE.

The glass vessel illustrated in figure 1 is utilized both as an important part of the sampling device and as a holder for the sample after collection. The vessel should have a capacity of 150 to 250 c. c. If, when the vessel is in the position shown and is filled with mercury, the stopcocks *a* and *b* are opened the mercury will flow from the lower tube. The gas will then be drawn through the upper tube, enter the vessel at *c*, and collect above the mercury. So long as the surface of the mercury remains above *c*, the same volume of gas will be collected in each equal interval of the sampling period, so that the sample obtained will be representative. The time required for a certain amount of mercury to run from the vessel can be varied from that taken when

FIGURE 1.—Gas-sample collector and container.

both *a* and b are completely open to a period of from 8 to 10 hours, or even longer, by attaching at *d*, by means of a rubber tube, a short piece of glass tubing drawn out to a smaller diameter. By trial these short glass tubes can be made of proper diameter to deliver the mercury at almost any desired rate.
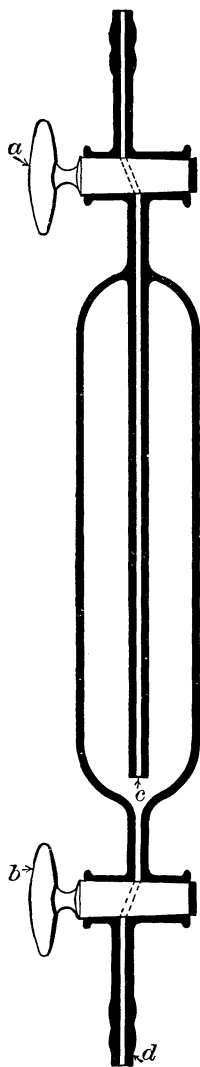
After the sample of gas has been collected the tube above a is filled with mercury from a small funnel whose stem has been drawn out to a capillary. The vessel is then inverted and, by means of a rubber tube attached to a mercury reservoir, the inclosed gas is put under a pressure of about 100 mm. of mercury. When the vessel is returned to its original position, as shown in the illustration, the stopcocks a and b are mercury sealed, and there is no danger of gas leaking into or out of the vessel.

When it is desired to remove the sample for analysis the vessel is again inverted and the tube above b is filled with mercury and attached to the burette. By means of the mercury reservoir previously used to put the gas under pressure, the desired volume of gas is forced out of the vessel into the burette. In case the gas is to be measured over water, the tube above the stopcock b is filled with water instead of mercury.

In order to facilitate the safe handling of these vessels it is necessary to mount them in a portable stand, and frequently it is desirable to arrange them in batteries of two to four each. Figure 2 illustrates a convenient method of mounting four of these tubes. The stand consists of the two uprights, A, supporting the two shelves, B, and having iron rods, C, extending from side to side through holes bored about 3 cm. from each end of the uprights. The iron rods not only strengthen the stand, but are convenient handles. The shelves are divided longitudinally through the center and holes for the tubes are made along these lines of division. When filled with mercury the vessels should be carefully supported at both ends. Therefore the holes for the tubes are enlarged for a distance equal to about one-half the thickness of the shelf, to receive the tapering ends of the vessels, and the open spaces around these ends are filled with plaster of paris. This is done by filling the cavity in each half of the shelf independently, so that the front half of each shelf may be taken out at any time and a vessel removed without disturbing the remaining ones.

THE WATER-COOLED SAMPLING TUBE.

The portion of the sampling apparatus which is introduced into the furnace may be either a water-cooled metal tube or, better, a water-cooled quartz tube.

A type of water-cooled metal tube that has been found satisfactory is illustrated by A, in figure 3. The inside tube, through which the gas is collected, is kept cool by cold water, which passes through the surrounding tube and returns through the outside annular compartment. When the inner tube is of quartz, the only difference in construction is the use of asbestos packing to insure a water-tight joint at each end. An apparatus provided with a quartz tube is more fragile than

one wholly of metal, but it is preferable, as it has a greater range of
utility and may even be used in the fuel bed. If the diameter of the
inner tube be small enough, the end projecting from the furnace may
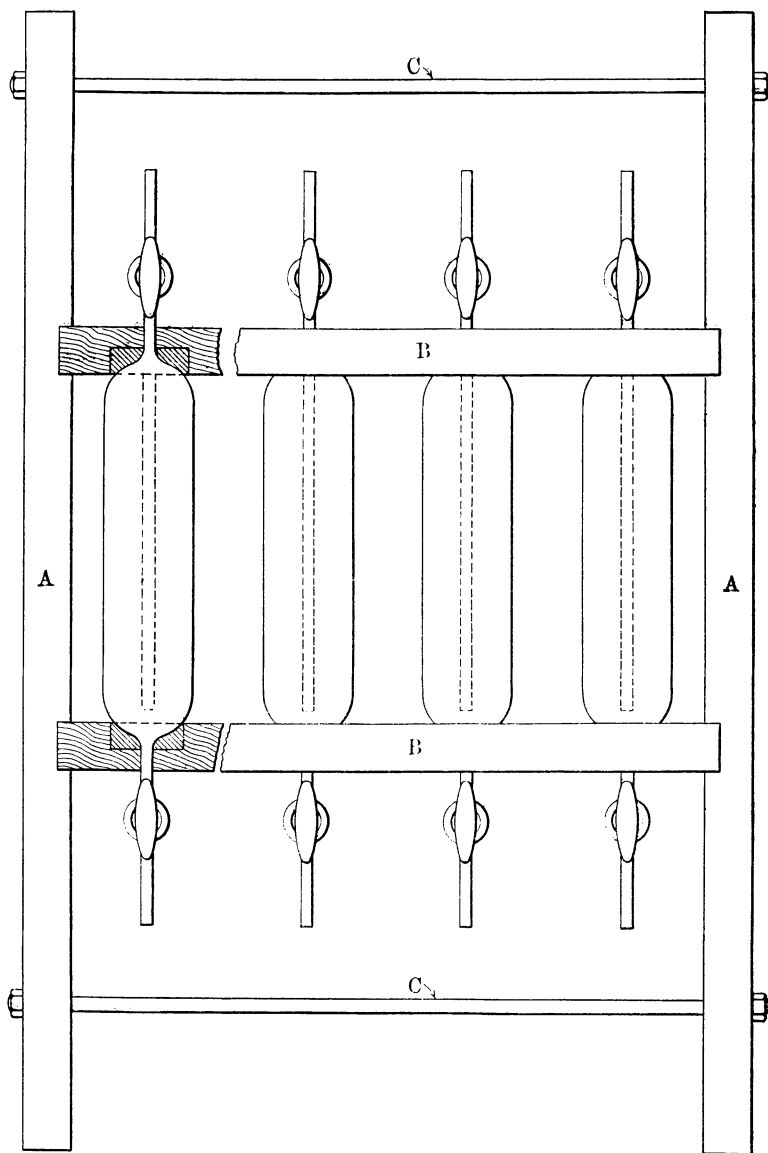be attached directly to the vessel receiving the sample of gas; but,

FIGURE 2.—Portable stand for gas-sample containers.

for the reasons given later, it is not generally practicable to have the
diameter of the tube so small. It is preferable to connect the end of
the tube with a $\frac{1}{4}$-inch lead pipe, which is brought over to a table
situated as near the furnace as possible. By connecting the other

end of the lead pipe to an aspirator, a continuous current of gas may be drawn from the furnace. If the gas is drawn through the tube rather rapidly, its composition will approximate closely that of the furnace gases at the point reached by the open end of the tube. At the table the lead pipe is perforated at a convenient point and a glass tube of small bore is inserted. This tube is connected directly with the mercury-filled sample receiver, and the sample is taken from the current of gas flowing through the lead tube.

When working in the region of the flame, it frequently happens that the water-cooled tube becomes clogged by the condensed tarry matter and by the molten ash which is carried bodily through the furnace by the rapidly moving gases. The diameter of the tube should be large enough to prevent this. Water vapor derived from moisture in the fuel and from the combustion of hydrogen and its compounds also condenses in the tube, which should be so large that the tendency to form a water column by capillarity may be easily overcome by the current of gas. Otherwise such a column may form and stop the flow of gas entirely. It is advisable to use a tube with an inside diameter of about three-sixteenths of an inch. In order to be sure that the current of gas is flowing properly through the tubes it is necessary to introduce a trap at some point beyond that at which the sample is taken from the lead pipe. The trap is simply a wash bottle containing water through which the gas bubbles on its way to the aspirator, the rate of bubbling roughly indicating conditions in the tubes. Figure 3 illustrates the entire sampling system.

As previously stated, a sample taken in this way will represent only the average conditions prevailing during the period of collection in a certain space about the point reached by the end of the sampling tube. In order to ascertain conditions throughout the furnace, or throughout any given portion of it, it is necessary to multiply and properly distribute the number of points from which samples are taken. As many sampling tubes as desired may be inserted in the furnace at different points, and separate samples collected simultaneously. The same aspirator may be used to obtain all the samples, the lead pipes attached to the different sampling tubes being led to the table on which are placed the vessels to receive the samples.

INSTANTANEOUS SAMPLING.

Frequently it is desirable to ascertain the composition of gases at some point in a furnace at a certain definite instant. Such would be the case when there might be reason to suspect that the gases would decompose during a period of continuous sampling or when it might be desired to study the progress of reactions in the furnace. This method is employed by certain investigators in collecting samples

from the flame of burning gases and from the explosion flame of coal dust, etc. Further, the use of this method enables one to obtain certain information concerning furnace conditions which he might not be able to obtain by the use of the continuous-sampling method. It was for the purpose of collecting instantaneous samples that the device shown in figure 4 was constructed.
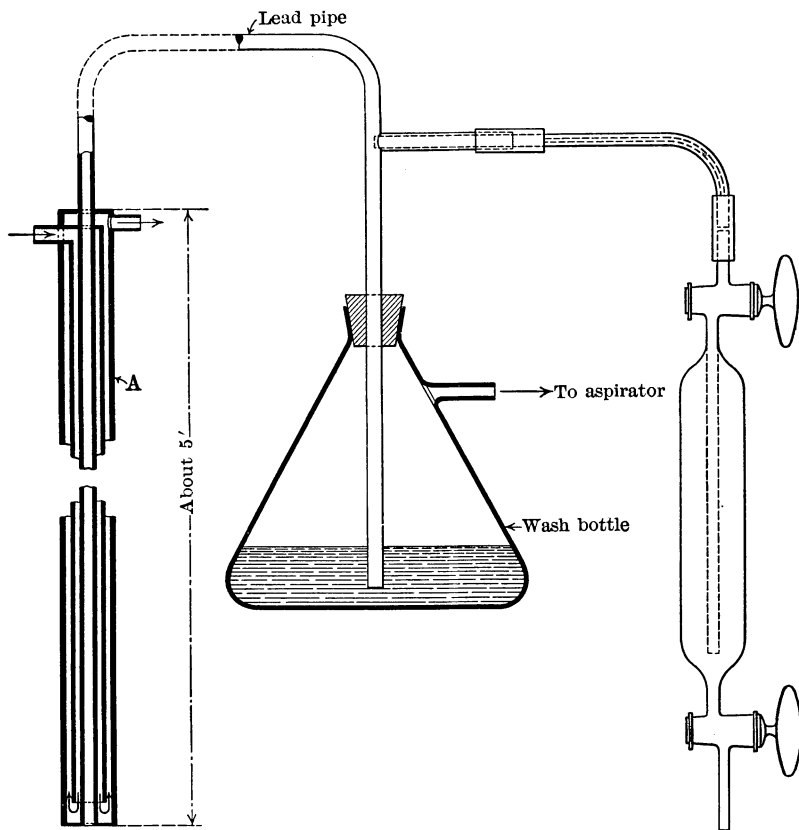

FIGURE 3.—Arrangement of apparatus for sampling furnace gases.

DESCRIPTION OF APPARATUS.

The apparatus consists of a quartz sampling tube, A, of 100-c. c. capacity, immersed in water contained in the steel tube B, which is 1.2 meters in length and 10 cm. in diameter. At each end the vessel terminates in a thick-walled quartz tube, 1-mm. bore, provided with a stopcock, as shown. One of the tubes, a, extends 150 mm. beyond the stopcock, and the open end projects beyond the end of B. An enlargement, b, 60 mm. from the stopcock, gives a firmer hold for the cement of litharge and glycerin with which the cavity in the collar c is filled; in this way c is fastened permanently to a. The device
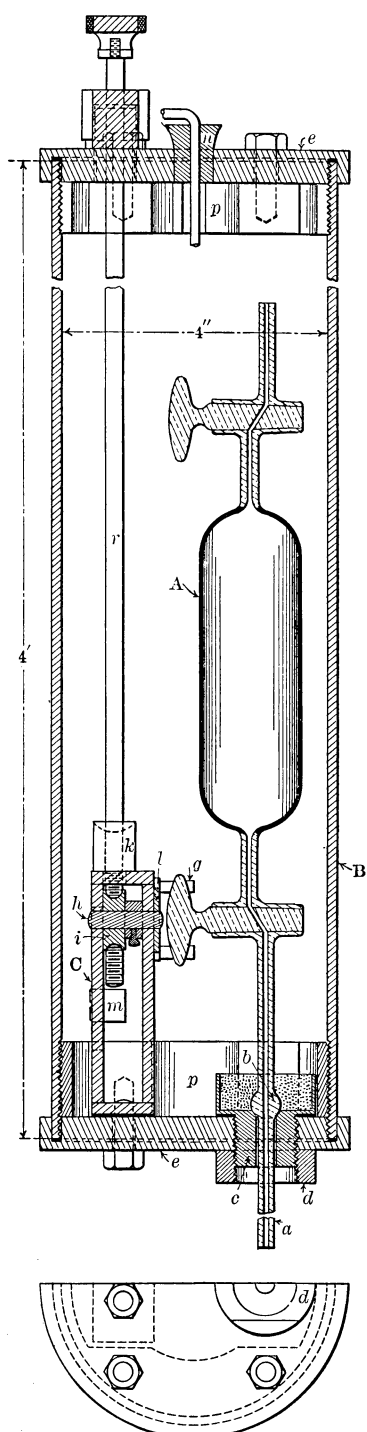
FIGURE 4.—Apparatus for taking in-
stantaneous gas samples.

for opening and closing the sampling tube from the outside is made of brass and is supported by the two end pieces e of the steel tube B. It consists of the brass frame C, in which is supported the mechanism for turning the stopcock. This consists of the brass shaft h, on which is set the wheel i and, beneath the frame, the brass plate l, carrying four projections, g, which fit around the handle of the stopcock, as shown. In order to avoid straining the stopcock in turning, which might occur if h were not centered above the stopcock, the pieces g are small rollers. The face of the wheel i is threaded to engage with the threaded end of the brass rod r. The piece k serves as a guide for the brass rod and affords a means of adjusting the threaded end of the rod to the face of i. The adjustment is accomplished by having the hole in k through which the rod r passes eccentric to the bearing of k in C. A movable stop, m, can be set to limit the rotation of i and the extent to which the stopcock may be turned. The steel tube B is threaded internally at each end to receive the threaded steel pieces p, which are tapped to receive bolts which secure the end pieces e. The arrangement of this portion of the apparatus can be seen best by referring to the semi-circular drawing which shows the plan of the end introduced into the furnace. All joints leading to the interior of B are made tight by lead washers, on which the two surfaces are tightly drawn by means of bolts.

OPERATION OF APPARATUS.

Before collecting a sample, the end piece e, which is to carry the vessel A, is removed by unscrewing the

bolts which bind it to B. The quartz tube is placed in position and the nut tightened. During this operation c is prevented from rotating by two small dowel pins which enter holes provided for them in e. By trial m is adjusted so that when the rod r reaches it the handle of the stopcock is rotated 90°. It is customary to adjust the stopcock so that communication with A is established when r is against m as shown. The withdrawal of r then closes the stopcock. Having the stopcock properly adjusted, the end piece e is bolted to B, and the latter is suspended in a vertical position by a handle clamped on the other end, and not shown in the illustration. While in a vertical position the rod r is introduced through the brass bushing at the upper end and finds its way without difficulty into the hole in k. The steel tube B is filled with water through n, which is then closed by a perforated rubber stopper, through which passes a short glass tube bent at a right angle and having its projecting end directed upward when the apparatus is in use. This tube relieves the internal pressure when the temperature of the water rises.

The apparatus is then taken to a vacuum pump and placed in a horizontal position in two semicircular rests which prevent its moving while it is connected with the pump. When the tube A is exhausted, and while it is still connected with the pump, r is withdrawn so far that the threaded end leaves i but remains in k. This closes the stopcock. The time at which r and i become disengaged can be readily determined by the increased ease with which r moves. The pump is disconnected, and as soon as convenient the apparatus is introduced into the furnace, the open end of the tube a being placed at the point from which the sample is desired. The stopcock is opened by pushing in the rod r until it is in contact with m, and after the short time required for A to fill the rod is withdrawn and the stopcock thus closed.

As the sampler remains in the furnace only about 30 seconds, and as the quantity of water in B is considerable, it is unnecessary to provide for a circulation of this water. In collecting a sample it was found that the temperature of water in B did not rise more than 10° even when the tube was inserted in the hottest part of the furnace.

After removing the apparatus from the furnace, the water is drained from B, the rod r is withdrawn, the nut d is started to insure its subsequent easy removal, and the end piece e, carrying a, is removed. Then d is taken entirely off, and after the two glass tubes have been filled up to the stopcocks with mercury the sample in A is transferred to one of the holders illustrated in figure 1. Since it requires about 30 minutes for the complete operation of collecting a sample in this way, a series of samples is generally collected and stored in the holders before making the analyses.

The vacuum pump employed for evacuating the quartz sampling tubes is a Duplex A Geryk pump with which it is possible to secure a pressure as low as a few tenths of a millimeter of mercury in a short time. The stopcocks of the quartz tubes are always carefully polished with the finest emery and tested before using. It has been found that when one of these tubes is evacuated as completely as possible and then allowed to stand closed and detached from the pump for about 30 minutes, no leakage of air into the bulb can be detected by opening the stopcock with the end of the tube immersed in mercury.

DETERMINATION OF MOISTURE AND NITRIC OXIDE.

The results of the analyses of samples collected instantaneously show the conditions prevailing temporarily at the points of collection. If it is desired to coordinate the results of analyses with conditions of furnace manipulation, it is necessary to resort to the continuous-sampling method, which gives the average composition of the gases during the period of sampling. However, the instantaneous method provides means of obtaining data on two points, which data can be obtained with difficulty, if at all, by the continuous method.

With the apparatus illustrated in figure 4, the amount of water vapor accompanying a gas sample can be easily determined by absorbing the moisture and weighing it. Likewise, the presence of traces of nitric oxide in furnace gases has been shown by using a simple modification of the method just described. The determination of nitric oxide is accomplished as follows:

The sampling tube used is a water-cooled quartz tube similar to the one illustrated in figure 3. An evacuated 8-liter bottle is used as a receiver for the gas sample, in place of the quartz vessel A shown in figure 4. Two glass tubes, each provided with a carefully ground stopcock, pass through two holes in a rubber stopper which closes the bottle. One of these tubes extends almost to the bottom of the bottle; the other, which ends just below the stopper, is bent at a right angle and connected directly with the water-cooled quartz tube. This arrangement permits the easy removal from the bottle of the whole or part of the gas sample, or the introduction of any desired liquid into the bottle without exposing the contained gas. The stopper is completely covered with sealing wax to aid in making the bottle gas-tight. After the introduction of the sampling tube into the furnace, the evacuated bottle is filled by simply opening the proper stopcock.

After the collection of the sample, an excess of an alkaline solution of potassium permanganate is introduced into the bottle and allowed to stand for 24 hours. At the end of that time the solution is withdrawn and the free ammonia distilled off. Potassium hydroxide and

fine aluminum powder are then added and the mixture allowed to stand several hours, after which the ammonia formed is distilled into standard sulphuric acid.

The presence of nitric oxide can be demonstrated qualitatively by introducing a solution of starch and potassium iodide into the bottle directly after the collection of the sample. The blue color does not appear immediately, probably owing to the presence of sulphur dioxide in the gas, but in a short time the color becomes noticeable and is soon quite pronounced.

In the gases examined the quantity of the nitric oxide found varied from 0.015 to 0.031 per cent. At the time of taking these samples the furnace conditions were not favorable to the formation of this constituent, and there is reason to believe that the percentage of nitric oxide in the furnace gases is frequently much greater. It would require further work to determine whether enough nitric oxide to be of importance is ever present in furnace gases, and also to determine whether the source of this nitric oxide is the nitrogen of the fuel or the nitrogen of the air. The presence of relatively small quantities of the constituent is of some importance, since the formation of the gas is accompanied by an absorption of heat.

ANALYSIS OF THE SAMPLE.

The sample having been collected, its analysis is performed most conveniently by the method of Hempel. The use of mercury in the burette is to be preferred to that of water; but whichever is used, the burette should always be provided with a water jacket to avoid errors due to sudden changes in temperature. While the ordinary Hempel burette is sufficiently accurate for most purposes, it does not enable the observer either to detect or to determine changes in volume amounting to 0.1 c. c. or less, since the error in reading the burette itself can not be less than this volume.

As already stated, it is a matter of some importance to be able to measure smaller percentages of combustible gases than can be determined by the ordinary Hempel method, since the flue gases are so diluted that a small percentage of combustible matter in them corresponds to a much greater percentage of the fuel. In order to determine these small percentages of combustible gases, a very accurate method is required. The apparatus described by Hempel for exact gas analysis, which provides a tube for compensating errors due to variations in the pressure and temperature of the atmosphere (the principle of Pettersson[a]), is in certain respects unsatisfactory. In this instrument a considerable portion of the air in the compensator and an approximately equal volume of the gas being meas-

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[a] Zeitschr. für anal. Chemie, vol. 25, pp. 467–484.

ured are not inclosed in the water jacket, and while there is a tendency to equalize any error due to this arrangement, the compensation is perfect only when the total volumes of the two gases are equal. Further, the burette itself can not be read with sufficient accuracy.

In 1900 A. H. White[a] published a description of an apparatus devised to obviate these difficulties. In this apparatus the principle of automatic compensation for changes in temperature and pressure as suggested by Pettersson and modified by Hempel and others is utilized in an improved form. The measuring portion of this apparatus consists of two limbs, suggested by the burette of Otto Bleier,[b] one a series of bulbs to contain the larger portion of the measured gas, the other a long straight tube of small capacity on whose scale all final readings of volume are made.

It was in order to obviate the same difficulties and to be able to measure all possible changes in volume that the apparatus described below was designed by the writers. Since this apparatus was devised entirely independently and used for some time before their attention was called to the work of Bleier and of White, and since it is believed to possess certain advantages over other similar forms of apparatus, its description is given here, but without making any claim of priority as to its essential principles.

DESCRIPTION OF APPARATUS.

The apparatus, illustrated in figure 5, consists of the burette A and the automatic compensating device B. The measuring portion of the burette A and the whole of the compensator B are inclosed in the water jacket C. The measuring portion of the burette consists of the two limbs a and b, the graduated portions of which are 66 cm. long and united at the top in an inverted Y-shaped connection to which a Greiner-Friedrich two-way stopcock is attached. Through this stopcock communication can be made with either of two short, thick-walled tubes of small bore, one of which is connected with the compensating device. Outside the water jacket C, at the lower end, is a second Y tube, each of whose limbs is provided with a stopcock and attached by rubber connections to the projecting ends of the limbs a and b as shown. To the lower end of the Y tube is attached heavy rubber tubing connected with a mercury reservoir not shown in the illustration.

The tube a consists of a series of 10 bulbs, each having a capacity of 10 c. c. between the two graduation marks immediately above and below it. The straight glass tube b has an internal diameter of about 4.5 mm., and its graduated part has a total capacity of 10.1 c. c. The

[a] Jour. Am. Chem. Soc., vol. 22, 1900, p. 343.
[b] Ber. Deutsch chem. Gesell., vol. 30, 1897, pp. 2759, 3128.

beginning of the graduated portion of each limb of the burette is at c. The compensator B, while utilizing the principle of Pettersson of counterbalancing the pressure of the gas to be measured with that of a constant mass of air occupying a constant volume, is arranged in a somewhat different form from Pettersson's device. The confined air, whose pressure at a constant volume is equalized by that of the gas to be measured, is contained in the bulb d and above the mercury surface e in the tube g, which forms the lower termination of the bulb.

The glass tube f is connected at its upper end with one of the communications through the stopcock of the burette and is sealed into the top of the bulb d. Its other end extends nearly to the bottom of g and opens beneath the surface of the mercury. It is centered in g at two points—h, which is 25 mm. above the surface of the mercury, and k, about 50 mm. from its lower end—by three small glass projections sealed on the outside of it at each of these points. The diameters of the tubes f and g are proportioned so that the distance from the inside of g and the outside of f is as nearly as possible equal to the internal diameter of f. The distance from the surface of the mercury in f to the stopcock of the burette should be as short as possible, since the gas in this portion of the tube must be drawn into the burette by decreasing the pressure. The depth of mercury in the compensator should be sufficient to require about one-third of
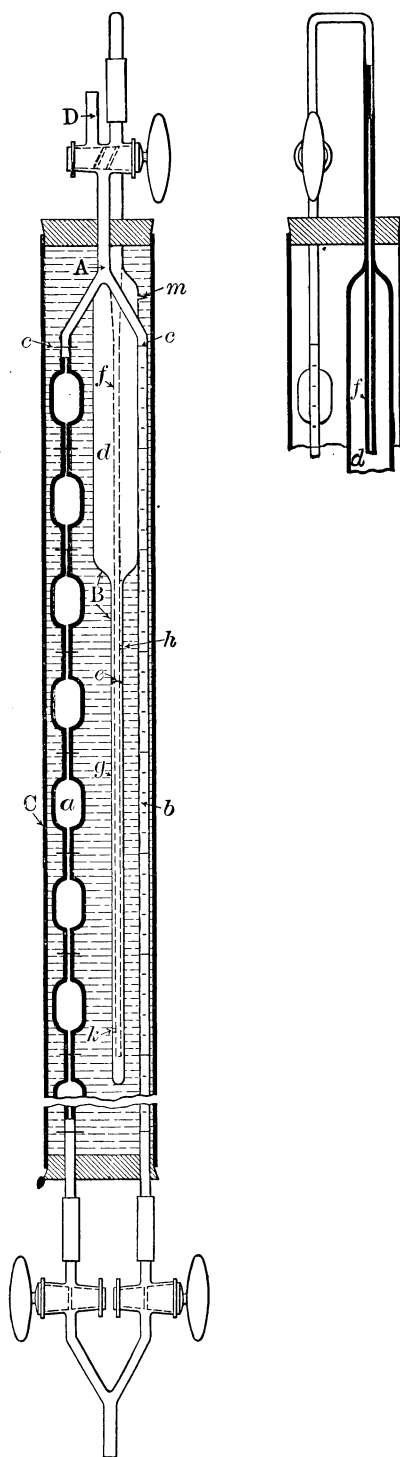

FIGURE 5.—Apparatus for exact gas analysis.

an atmosphere excess pressure in the burette to force gas from the latter into the compensator, but the quantity of mercury should not be so great that its expansion or contraction will cause an appreciable change in the volume of the inclosed air. The tube f should extend nearly to the bottom of the compensator in order to displace as much mercury as possible.

The compensator may be filled so that the readings on the burette are the correct volumes of the gas at 0° C. and 760 mm. pressure, or it may be closed under known conditions of temperature and pressure and the readings corrected to standard conditions. The latter method is sufficient for most purposes, and when it is used the compensator may be closed by replacing the seal at m by a small tube and stopcock.

OPERATION OF APPARATUS.

To obtain a reading of the volume of a gas in the burette, it is first necessary to stir the water in the jacket C and allow a few minutes to elapse in order to be sure that the gas is at the temperature of the surrounding water.[a] Then by drawing nearly all the gas into the limb a and adjusting the pressure to approximately that of the atmosphere, the number of bulbs the gas will fill completely when at the pressure of the air in the compensator may be ascertained. Having determined this, the mercury in the burette is brought exactly to the level of the graduation beneath the last bulb completely filled in the trial experiment and the stopcock at the bottom of the limb is closed. The remaining fraction of a bulb full of gas is then made to enter the limb b, and the two-way cock is turned so as to place the burette in communication with the compensator. The pressure of the gas in the burette is then adjusted, by means of the mercury reservoir, until the two surfaces of mercury in the compensator are on the same level. The pressure of the gas in the burette is then equal to that of the gas in the compensator. The stopcock at the bottom of b is then closed and the reading of the burette taken. To this reading is added the predetermined capacity, K, of that part of the apparatus between the graduated portion of each limb of the burette and the mercury meniscus in the tube f. As each constituent of the gas is determined by the difference in the burette readings, before and after an absorption, this constant capacity, K, does not enter into the determination of the amount absorbed. But it is necessary to apply this correction to obtain the initial volume of the gas unless exactly sufficient nitrogen to fill this part of the apparatus is taken into the burette previous to the introduction of the sample.

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[a] The water is stirred by blowing air through a glass tube, not shown in the illustration, which extends nearly to the bottom of the water jacket.

The reading of the burette requires some practice to secure the best results, but with experience it can be accomplished quite readily and with extreme accuracy. The gases are measured in the moist condition, and the quantity of water introduced into the burette and compensator to effect this must be only sufficient to moisten the walls of the glass tubes. If there is sufficient water in the compensator to drain down upon the mercury, the accurate adjustment of the mercury surfaces is rendered difficult; while too much water in the burette is likely to stop up the narrow tubes connecting the bulbs, and in this way to interfere seriously with the distribution of pressure on the gas in the burette and consequently with the equalization of the pressures in the burette and compensator.

With this apparatus a complete analysis of gas may be made in the usual way by connecting the burette in turn with various absorption pipettes. It is, however, more convenient and accurate to connect the burette permanently with the desired pipettes. By this arrangement errors due to the repeated making and breaking of connections are avoided. The entire system may be conveniently mounted on the same wooden support, and for the analyses made thus far such an arrangement has been employed.

A series of three pipettes is connected with the tube D by means of fine capillary tubing in the manner generally employed with the Orsat apparatus. These pipettes consist of a combustion pipette provided with an electrically heated platinum coil of the type recommended by L. M. Dennis, an absorption pipette containing a solution of potassium hydroxide for the absorption of carbon dioxide, and a pipette containing phosphorus for the determination of oxygen. In order to avoid error due to the capacity of the connecting tubes, these are made as short as possible, and their internal diameter is not greater than 0.4 mm. All error from this source can be eliminated entirely either by actually determining the capacity of the connections or by filling them and that part of the apparatus between the ungraduated portions of the burette and the mercury meniscus in the tube f with pure nitrogen before introducing the sample into the burette.

DEGREE OF ACCURACY ATTAINABLE.

The limb b of the burette on which the readings are made is graduated in hundredths of 1 c. c., and tenths of these divisions can be estimated quite accurately. Experiments have shown that 50 to 100 c. c. of gas can be measured accurately to 0.01 c. c. With volumes less than 50 c. c. the readings can be more precise, as a more accurate adjustment of the mercury surfaces in the compensator is possible. The following examples show the degree of accuracy which may be safely claimed for the apparatus.

(1) A volume of nitrogen passed in succession into the pipette containing potassium hydroxide and the pipette containing phosphorus was drawn into the burette and its volume determined. The two readings were 66.516 and 66.514 c. c. The gas was then passed into the pipette containing potassium hydroxide, where it was allowed to stand two minutes, after which it was returned to the burette and measured. The duplicate readings were 66.516 and 66.506 c. c. After standing in the pipette containing phosphorus for three minutes, three readings showed 66.513, 66.526, 66.521 c. c. The gas was then passed back and forth several times from the burette to the combustion pipette, after which the reading was 66.526 c. c.

(2) A sample of air was collected and the carbon dioxide and oxygen were determined. In this case the capillary connections and that part of the apparatus between the graduated portion of each limb of the burette and the mercury meniscus in the tube f were filled with nitrogen before introducing the sample. In analysis (a) the volume of air used was 60.506 c. c. and in analysis (b) it was 60.906 c. c. The analyses gave: (a), $CO_2=0.057$ per cent, $O_2=20.866$ per cent; (b), $CO_2=0.046$ per cent, $O_2=20.834$ per cent.

The data obtained in this way from the analysis of air may be used for determining K^a and the capacity of the capillary connections. To do this the whole system is filled with air whose analysis is accurately known, and the volume included in the graduated portions of the burette is read. The carbon dioxide and oxygen are then absorbed, and the contractions observed complete the data required for determining the total volume of air introduced into the apparatus, and consequently the volume contained in the capillary connections and that part of the apparatus between the graduated portions of the burette and the mercury meniscus in the tube f.

The above description of the manipulation of the apparatus involves the use of a leveling bottle attached to the lower **Y** tube. With care the pressures in the burette and compensator can be equalized accurately by the use of the leveling bottle alone, but the equalizing can be accomplished more rapidly and with greater precision by making the final adjustments by means of a screw plunger fitting tightly in its bearings in a closed steel reservoir filled with mercury. The steel reservoir has two openings, one connected with the **Y** tube by means of a short piece of rubber tubing, and the other connected with the leveling bottle through a longer rubber tube. A glass stopcock is placed between the reservoir and the leveling bottle, by means of which communication between the two is cut off previous to the final adjustment of pressure by means of the screw plunger. The steel reservoir also serves as a trap for much of the dirt which becomes loosened from the inner walls of the connecting rubber tubes, and would otherwise find its way into the burette.

CALIBRATION APPARATUS.

The principle of the screw-plunger reservoir has been utilized in constructing a device for calibrating burettes and pipettes, or other similar apparatus used in volumetric work. This device is illustrated in figure 6. It consists of the steel plunger A, to which is attached the steel cylinder B, whose circumference at a is divided into 100 divisions, the steel piece D, in which is cemented the glass tube E, and the steel piece C, which is threaded to receive the lower end of A.

The plunger A is the part that has to be made with the greatest care. Its diameter is so related to the pitch of the thread cut on its lower end that one complete revolution changes the capacity of E by 1 c. c. The plunger is finished by careful grinding.

The joint around A is packed with a hard-rubber washer, F, turned to fit between the two pieces C and D and the face of A. The shape of the shoulders of C and D at this point is such as will tend to produce a tight joint with A when C and D are screwed together.

The glass tube E is cemented in D with a mixture of litharge and glycerin. The exposed surfaces of the cement between E and D are subsequently coated several times with a solution of rubber in carbon bisulphide. After each application the rubber coating is hardened until a tight joint is obtained which will withstand the pressure of the liquid within.

The motion of A changes the capacity of E by the volume of that portion of the plunger entering or leaving the hard-rubber ring F. The scale on which this motion is read is a series of horizontal lines drawn on the face of C and indicating the number of whole revolutions of the plunger. The divisions of the circumference of B at a show the fractions of a revolution in hundredths. A second scale is superimposed on the first scale on C and consists of a series of 11 vertical lines spanning the same distance as 10
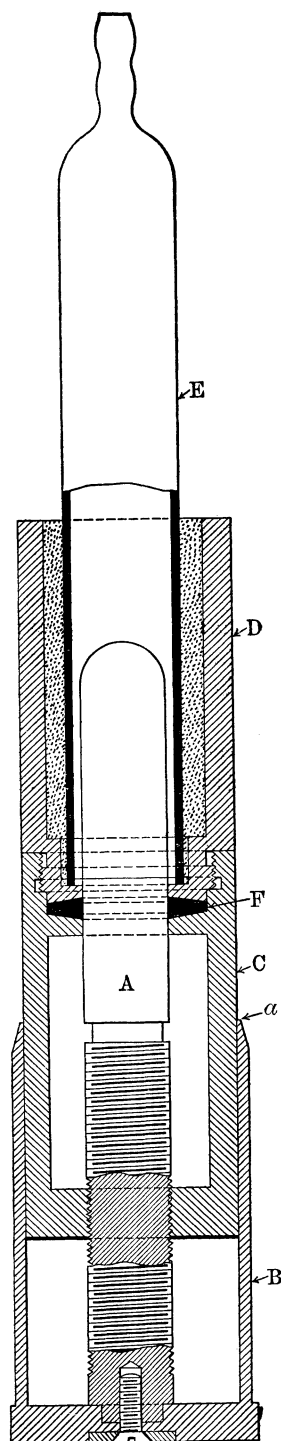

FIGURE 6.—Calibration apparatus.

lines on B. This vernier subdivides the divisions on B and permits the reading of the rotation of A to one one-thousandth of a revolution. When A is ground so that it displaces 1 c. c. when advanced one turn, the readings on the vernier are thousands of a cubic centimeter. However, the grinding can rarely be done with sufficient accuracy for each revolution of the plunger to represent exactly 1 c. c., but to calibrate the apparatus it is only necessary to fill E with mercury and weigh the quantity displaced at each complete revolution. The instrument should be calibrated at various temperatures, and to insure accurate readings it is necessary either that the lower portion of B have a grip of nonconducting material or that the operator wear a woolen glove on the hand used for manipulating the instrument.

By means of this apparatus instruments may be calibrated with either mercury or water. If water is used the water is introduced on top of enough mercury to prevent the water from coming in contact with the plunger at any time.

The following table gives the data obtained by calibrating an ordinary 50 c. c. burette with water by means of the above described instrument. A previous determination of the volume of mercury displaced by each revolution of the plunger showed that it was so nearly 1 c. c. that it could be assumed as such in a calibration of this kind. Starting with zero on the burette scale, each successive reading of the burette was made after the plunger had been withdrawn exactly two revolutions. As shown in the table the two series of readings made on the same burette agree closely. The time required to obtain both series of results was less than one hour.

Calibration data.

Series 1.		Series 2.	
Readings on the burette.	Differences.	Readings on the burette.	Differences.
0.00	....	0.00	....
2.01	2.01	2.01	2.01
4.01	2.00	4.01	2.00
5.99	1.99	5.99	1.98
7.97	1.98	7.98	1.99
9.94	1.97	9.94	1.96
11.93	1.99	11.94	2.00
13.92	1.99	13.93	1.99
15.91	1.99	15.92	1.99
17.90	1.99	17.91	1.99
19.89	1.99	19.90	1.99
21.88	1.99	21.88	1.98
23.85	1.97	23.85	1.97
25.82	1.97	25.83	1.98
27.81	1.99	27.82	1.99
29.81	2.00	29.82	2.00
31.80	1.99	31.80	1.98
33.78	1.98	33.79	1.99
35.74	1.96	35.77	1.98
37.73	1.99	37.74	1.97
39.72	1.99	39.72	1.98
41.69	1.97	41.69	1.97
43.68	1.99	43.68	1.99
45.65	1.97	45.65	1.97
47.63	1.98	47.65	2.00
49.65	2.02	49.66	2.01

PUBLICATIONS ON FUEL TESTING.

The following publications, except those to which a price is affixed, can be obtained free by applying to the Director of the Bureau of Mines, Washington, D. C.   The priced publications can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C.

PUBLICATIONS OF THE BUREAU OF MINES.

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl.

BULLETIN 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls.

BULLETIN 5. Coking and washing tests of coal at Denver, Colo., July 1, 1908, to June 30, 1909, by A. W. Belden, J. W. Groves, K. M. Way, and G. R. Delamater. 1910. 62 pp.

BULLETIN 6. Coals available for illuminating-gas manufacture, by A. H. White and Perry Barker. 1911. 77 pp., 4 pls.

BULLETIN 7. Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams, and C. N. Haskins. 1911. 58 pp., 1 pl.

BULLETIN 8. The flow of heat through furnace walls, by W. T. Ray and Henry Kreisinger. 1911. 32 pp.

BULLETIN 9. Recent development of the producer-gas power plant in the United States, by R. H. Fernald. 82 pp., 2 pls. Reprint of United States Geological Survey Bulletin 416.

BULLETIN 11. The purchase of coal by the Government under specifications, by G. S. Pope. 1910. 80 pp. Reprint of United States Geological Survey Bulletin 428.

PUBLICATIONS OF THE UNITED STATES GEOLOGICAL SURVEY.

PROFESSIONAL PAPER 48. Report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1906. In three parts. 1492 pp., 13 pls. $1.50.

BULLETIN 261. Preliminary report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, in St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1905. 172 pp. 10 cents.

BULLETIN 290. Preliminary report on the operations of the fuel-testing plant of the United States Geological Survey at St. Louis, Mo., 1905, by J. A. Holmes. 1906. 240 pp. 20 cents.

BULLETIN 323. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 1907. 49 pp. 10 cents.

BULLETIN 325. A study of four hundred steaming tests made at the fuel-testing plant, St. Louis, Mo., 1904, 1905, and 1906, by L. P. Breckenridge. 1907. 196 pp. 20 cents.

BULLETIN 332. Report of the United States fuel-testing plant at St. Louis, Mo., January 1, 1906, to June 30, 1907; J. A. Holmes, in charge. 1908. 299 pp. 25 cents.

BULLETIN 334. The burning of coal without smoke in boiler plants; a preliminary report, by D. T. Randall. 1908. 26 pp. 5 cents. (See Bull. 373.)

BULLETIN 336. Washing and coking tests of coal and cupola tests of coke, by Richard Moldenke, A. W. Belden, and G. R. Delamater. 1908. 76 pp. 10 cents.

BULLETIN 339. The purchase of coal under Government and commercial specifications on the basis of its heating value. with analyses of coal delivered under Government contracts. by D. T. Randall. 1908. 27 pp. 5 cents. (See Bull. 428.)

BULLETIN 343. Binders for coal briquets, by J. E. Mills. 1908. 56 pp.

BULLETIN 362. Mine sampling and chemical analyses of coals tested at the United States fuel-testing plant, Norfolk, Va.. in 1907. by J. S. Burrows. 1908. 23 pp. 5 cents.

BULLETIN 363. Comparative tests of run-of-mine and briquetted coal on locomotives, including torpedo-boat tests and some foreign specifications for briquetted fuel, by W. F. M. Goss. 1908. 57 pp.. 4 pls.

BULLETIN 366. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 1908. 44 pp., 3 pls.

BULLETIN 367. Significance of drafts in steam-boiler practice, by W. T. Ray and Henry Kreisinger. 1909. 61 pp.

BULLETIN 368. Washing and coking tests of coal at Denver, Colo., by A. W. Belden. G. R. Delamater. and J. W. Groves. 1909. 54 pp., 2 pls. 10 cents.

BULLETIN 373. The smokeless combustion of coal in boiler plants, by D. T. Randall and H. W. Weeks. 1909. 188 pp. 20 cents.

BULLETIN 378. The purchase of coal under Government specifications, by J. S. Burrows. 1909. 44 pp. 10 cents. (See Bull. 428.)

BULLETIN 382. The effect of oxygen in coal, by David White. 1909. 78 pp., 3 pls. 25 cents.

BULLETIN 385. Briquetting tests at the United States fuel-testing plant, Norfolk, Va., 1907-8, by C. L. Wright. 1909. 41 pp., 9 pls.

BULLETIN 392. Commercial deductions from comparisons of gasoline and alcohol tests on internal-combustion engines, by R. M. Strong. 1909. 38 pp.

BULLETIN 393. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 1909. 29 pp. 5 cents.

BULLETIN 402. The utilization of fuel in locomotive practice, by W. F. M. Goss. 1909. 28 pp.

BULLETIN 403. Comparative tests of run-of-mine and briquetted coal on the torpedo boat *Biddle*, by Walter T. Ray and Henry Kreisinger. 1909. 49 pp. 10 cents.

BULLETIN 412. Tests of run-of-mine and briquetted coal in a locomotive boiler, by Walter T. Ray and Henry Kreisinger. 1909. 32 pp.

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