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THE SUPERIORITY OF BARIUM HYDROXIDE SOLUTION AS AN ABSORBENT IN CARBON DETERMINATIONS IN STEEL.[1]

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THE use of barium hydroxide solution as an absorbent for carbon dioxide is not new. It has long been used for that purpose in air analysis. It has also been used to a very limited extent in carbon determinations in steel.

As an absorption apparatus, Geissler potash bulbs are compact and convenient; they can be used several times without refilling, and are therefore very widely employed. Their use is, however, accompanied by at least one disadvantage; *viz.*, the error caused by differences in the temperature or degree of moisture in the laboratory air at the beginning and end of a combustion. This error sometimes amounts to more than do the small quantities of carbon dioxide whose exact weight it is desired to ascertain. This fact is well known and the error is to a considerable extent eliminated by the following precautions:

(a) Take the last weight of the bulbs from one combustion as the initial weight for the next; if the bulbs have been freshly filled with potassium hydroxide, a blank combustion is always made before taking the weight of the bulbs.

(b) During combustions, keep the bulbs in a covered box and thus shield them as completely as possible from moisture, dust, and heat.

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[1] Read at the Boston meeting, December 27, 1894.

(c) Weigh them always at the same interval after finishing the combustion.

In the Pittsburgh atmosphere, fog and smoke are often present. The changes in the degree of moisture are frequently very considerable, even in a few hours. Hence carbon determinations by potassium hydroxide bulbs are especially difficult.

When barium hydroxide solution is used as an absorbent for carbon dioxide it is possible to finish the analysis in at least three ways:

(1) The barium carbonate may be filtered off, washed, ignited, and weighed. This has been done successfully by Mr. Alex. G. McKenna, of Pittsburgh. He uses a special absorption apparatus to which the barium carbonate does not adhere.

(2) The excess of barium hydroxide solution may be titrated:

(a) By a standard oxalic acid without filtering off the barium carbonate, or (b) by standard sulphuric acid after filtering off the barium carbonate.

In either case phenolphthalein is the indicator which is used. I have found difficulty when using the oxalic acid titration in getting a satisfactory end point. With the sulphuric titration, no such trouble was experienced.

The facts that the ratios between C and $Ba(OH)_2$, $BaCO_3$, and H_2SO_4, are so much less than that of C to CO_2.

$$\begin{aligned} C : BaCO_3 &= 12 : 197.4 = 1 : 16+ \\ C : Ba(OH)_2 &= 12 : 171.4 = 1 : 14+ \\ C : H_2SO_4 &= 12 : 98.0 = 1 : 8+ \\ C : CO_2 &= 12 : 44.0 = 1 : 3+ \end{aligned}$$

show the great advantage possessed by the barium hydroxide methods over the potassium hydroxide absorption for carbon dioxide.

When we consider also that the use of standard barium hydroxide and a titration method does away with the uncertain atmospheric moisture factor, it is at once plain that the method has several distinct points of superiority over the potassium hydroxide method.

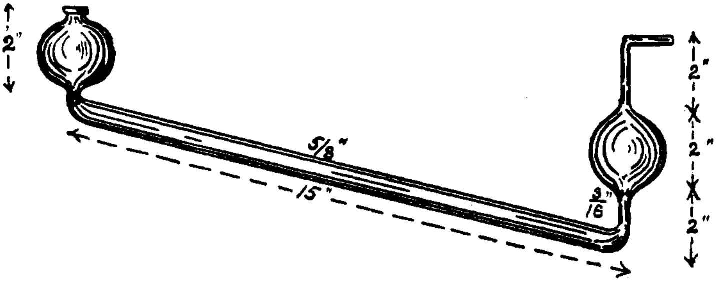
Method for Steels of 0.06 to 0.20 per cent. carbon.—Dissolve, by shaking in a glass-stoppered bottle, ten grams or more of 0.06 per cent. carbon steel or five grams of 0.20 per cent. steel in a mixture of copper and potassium chloride solution, one pound in

1,400 cc. of water, and hydrochloric acid. Use 600 cc. of the former and forty cc. of the latter for ten grams of steel and proportionately, more or less, for other amounts. Filter on asbestos which has been ignited in oxygen, wash as usual, and dry the carbon residue at 100° C. Transfer to combustion tube and make combustion as usual. Regulate the oxygen current so that one bubble starts up the absorption tube just as its predecessor reaches the top.

Between the combustion tube and the absorption apparatus I place only a U tube containing calcium chloride in the first limb and anhydrous copper sulphate in the other.

The absorption apparatus consists of two glass tubes like the one shown in the sketch.

Each tube contains fifty cc. of barium hydroxide solution. Tubes of this shape seem to give the bubbles of gas a rapid rotating motion as they rise through the barium hydroxide solution. As a result, the absorption is very perfect. This is an important point. Many forms of apparatus fail utterly in this particular.



When the combustion is complete and pure air or oxygen has been passed long enough to expel all carbon dioxide, the absorption apparatus is disconnected and the contents filtered.

During the filtration, air purified by bubbling through potassium hydroxide solution is kept playing on the surface of the barium hydroxide solution. This prevents the formation of barium carbonate by the action of atmospheric carbon dioxide on the excess of barium hydroxide. Since laboratory air is often very impure, this precaution is imperative.

The barium carbonate precipitate is washed with distilled water which is free from carbon dioxide. That which has been freshly distilled is best. The water from wash-bottles or flasks is unavailable. When kept in a stock carboy, connected with the laboratory still, I have always found my distilled water free from carbon dioxide. The excess of barium hydroxide solution is quickly titrated after filtering off the barium carbonate and washing it with water free from carbon dioxide.

Standard sulphuric acid is used, with phenolphthalein as indicator. Certain precautions are necessary when filling the absorption tubes with barium hydroxide solution.

By connecting a potassium hydroxide wash-bottle and calcium chloride tube with the blast-pipe, pure air can be easily obtained.

Force pure air through the absorption tubes for ten minutes; then close them by rubber connections. While drawing up the fifty cc. of barium hydroxide solution have the pure air current passing into the barium hydroxide bottle. When ready, allow the barium hydroxide solution to run into the absorption tube closing the same again and keeping so until ready to connect with the combustion train.

EXPERIMENTS.

	KOH Method Chemist "L" "C"	$Ba(OH)_2$ method Chemist "H"	Color test KOH standard.
Steel "A" Carbon	0.14	0.134	0.14
" 11834.7 "	....	0.109	0.11
" 11857.0 "	0.17	0.178	0.17
" "M" "	0.08%	0.090 0.093 0.091 and 0.092	0.08

STANDARD SOLUTIONS.

Standard Barium Hydroxide Solution.—Twenty grams of barium hydroxide are dissolved in water in a stoppered graduate and then made up to one liter. Filter into a bottle containing pure air, (air which has passed through the potassium hydroxide wash-bottle). Keep a current of pure air playing on the surface of the solution during filtration. It will then remain clear and bright even if the laboratory air is quite impure. Of this solution fifty cc. are more than sufficient for the carbon from five grams of two-tenths per cent. carbon steel. A second absorption tube is usually kept in the train but is rarely necessary.

Standard Sulphuric Acid.—A decinormal solution is used. Of this one cc. = 0.0006 gram carbon.

This method is best adapted for low carbon steels, because only small quantities of barium carbonate have to be filtered and washed.

When analyzing high carbon steels I have used smaller weights of steel (one or two grams) and have rinsed the barium carbonate and excess of barium hydroxide solution into a liter flask; after making up to one liter with pure water, I filter off 200 cc. and titrate by standard sulphuric acid. Steel 11920 gave 1.35 per cent. and 1.35. per cent. carbon by this method.

The work which I have been able to do seems to me to suffice to call attention to the merits of the barium hydroxide methods.

THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.

BY THOMAS H. NORTON.

[*Continued from page 147.*]

The interaction involved the formation of gypsum and aluminum chloride, which, in turn, precipitated the gelatin and converted it into a leatherlike insoluble substance. The object was to fill the pores of the fabric with gypsum and cover the surface with a hard binding material. Sir Frederick Abel, in reporting on the feasibility of this process found that it rendered the canvas very difficult of ignition, but that it also gave to it a degree of rigidity and harshness which forbade its use. In 1856 Maugham[1] patented the use of ammonium phosphate and starch; and in 1857 Thouret[1] patented the use of a mixture of three parts of ammonium chloride and two parts of ammonium phosphate, adopting these proportions on account of cheapness, although the ammonium phosphate alone gave most excellent results.

During this period the importance of better protection for the scenery of theaters was recognized. After a serious fire in the Berlin opera house, the custom was inaugurated of soaking all scenery in a strong alum solution.[2] In 1857 a commission in

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[1] Amer. Arch., 13 and 14.

[2] Frémy, *Dict. de Chimie*, 10.