METHOD OF DETERMINING PHOSPHORUS IN STEEL.

OPERATION.

Put one gram of the steel in a ten to twelve ounce Erlenmeyer flask and add seventy-five cc. of nitric acid (1.13 sp. gr.). When solution is complete, boil one minute and then add ten cc. of oxidizing potassium permanganate solution. Boil until the pink color disappears and binoxide of manganese separates, remove from the heat and then add crystals of ferrous sulphate, free from phosphorus, with agitation until the solution clears up, adding as little excess as possible. Heat the clear solution to 185° F. and add seventy-five cc. of molybdate solution, which is at a temperature of 80° F., close the flask with a rubber stopper and shake five minutes, keeping so enclosed during the operation that it will lose heat very slowly. Allow to stand five minutes for the precipitate to settle, and then filter through a nine cm. filter and wash with acid ammonium sulphate solution, until ammonium sulphide tested with the washings, shows no change of color. Dissolve the yellow phospho-molybdate on the filter in five cc. of ammonia (0.90 sp. gr.) mixed with twenty-five cc. of water, allowing the solution to run back into the same flask and thus dissolve any yellow precipitate adhering to it. Wash until the washings and filtrate amount to 150 cc., then add ten cc. strong C. P. sulphuric acid and dilute to 200 cc. Now pass the liquid through a Jones reductor or its equivalent, wash and dilute to 400 cc. and then titrate in the reductor flask with potassium permanganate solution.

APPARATUS AND REAGENTS.

The apparatus required by this method needs no especial comment except perhaps the shaking apparatus and the modification of the Jones reductor. Accompanying cuts illustrate these two. The shaking apparatus, as will be observed, is a modification of an ordinary milk shake machine, and is arranged to shake four flasks at a time, which is about all one operator can manipulate without the solutions becoming too cold. The cut is about one-twelfth the actual size of the apparatus. The

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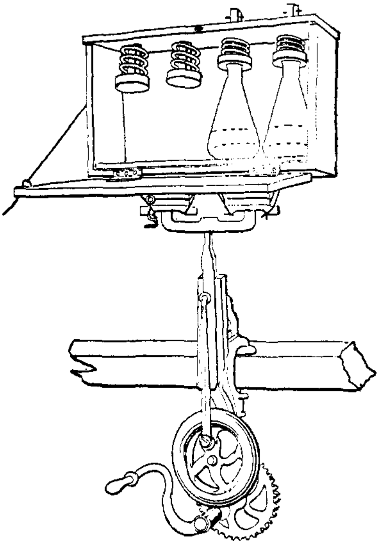
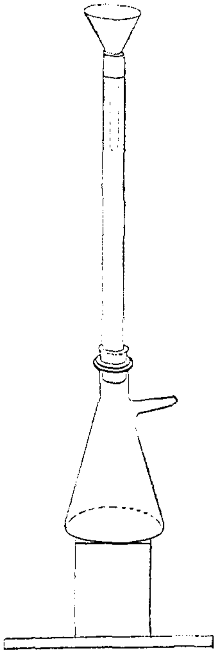
[1] [This method forms part of the specifications for steel of the Pennsylvania Railroad Company. It has been published in the *Journal of Analytical and Applied Chemistry* for February, 1895, p. 108, but on account of its importance is here reprinted in full.—ED.]

flasks containing the solutions rest on a sheet of India rubber about one-fourth inch thick and are held in position by the coiled springs as shown. There is a recess in the spring arrangement to receive the cork of the flask. In the absence of a shaking apparatus, the flasks may be wrapped in a towel and shaken by hand. Of course during use the door of the box is closed, the cut showing it open so that the interior may be seen. The modified reductor seems to work equally as well as the more elaborate apparatus. The cut is about one-eighth actual size. As will be seen the tube is fitted with two rubber corks, the top one of which holds the funnel and the bottom one a small tube which also fits into the rubber cork in the flask. Next to the bottom cork in the tube is a disc of perforated platinum; then about three-fourths of an inch of clean white sand; then another perforated platinum disc, and then the tube is nearly filled with powdered zinc. At least half the zinc may be used out before it is necessary to re-fill.





Burettes can usually be obtained in the market which are sufficiently well made and graduated with sufficient care, so that their error can be ignored. Of course this point should not be overlooked.

The specific gravities of the reagents given are essential and the temperature at which the figures are correct is 59° F. In determining these gravities it is best to use a Westphal balance, but failing this a sufficiently delicate hydrometer can be used.

The oxidizing permanganate of potash solution is made as follows: To two liters of water, add twenty-five grams of C. P. crystallized permanganate of potash, and allow to settle before using. Keep in the dark.

The molybdate solution is made as follows: Dissolve 100 grams of molybdic acid in 400 cc. of ammonia (sp. gr. 0.96) and filter. Add the filtrate to 1000 cc. of nitric acid (sp. gr. 1.20). Allow to stand at least twenty-four hours before using.

The acid ammonium sulphate solution is made as follows: To one-half liter of water add 27½ cc. of ammonia (0.96 sp. gr.) and then add twenty-four cc. strong C. P. sulphuric acid, and make up to one liter.

The permanganate of potash solution for titration is made as follows: To one liter of water add two grams of crystallized permanganate of potash, and allow to stand in the dark not less than a week before using. Determine the value of this solution in terms of metallic iron. For this purpose 150 to 200 mgms. of iron wire or mild steel are dissolved in dilute sulphuric acid (ten cc. of strong C. P. acid to forty cc. of water) in a long necked flask. After solution is complete, boil five to ten minutes, then dilute to 150 cc., pass the liquid through the reductor, and wash, making the volume up to 200 cc. Now titrate with the permanganate solution. It is of course essential that the amount of iron in the wire or soft steel should be known. The standard in use in the Pennsylvania Railroad laboratory is a mild steel in which the iron is known by determining carbon, phosphorus, silicon, sulphur, manganese, and copper, and deducting the sum of these from 100 per cent. Not less than two independent determinations should be made and three are better. The figures showing the value of the permanganate solution in terms of metallic iron should agree to one-hundredth of a milligram in the different determinations. A very satisfactory method of making and keeping permanganate of potash solution is as follows: Have a large glass bottle holding say eight liters and two of half the size. Paint the outside of these bottles with several coats of black paint or varnish. Fill the large bottle with the standard solution, and after it has stood a proper time, fill one of the smaller bottles from it without shaking, and standardize. At the same time fill the second small bottle, and refill the large one. When the first small bottle is exhausted standardize the second one and fill the first from the stock. When this is exhausted standardize the first again and fill the second from stock, refilling the stock bottle again and so on. By this means a constant supply of sufficiently matured permanganate is always available. Of course if the consumption is very large, larger bottles or more of them may be required. Since changes of temperature affect the volume of all solutions, it is desirable that the permanganate solution should be used at the same temperature at which it was standardized. With the strength of solutions above recommended, if the permanganate is used at a temperature of 20° F. different from that at which it was standardized, the error amounts to less than 0.001 per cent. on a steel containing 0.10 per cent. of phosphorus.

CALCULATIONS.

An example of all the calculations is given herewith. The soft steel employed in standardizing permanganate of potash solution in the Pennsylvania Railroad laboratory contains 99.27 per cent. metallic iron. 0.1498 gram of this contains therefore (0.1498 × 0.9927) 0.1487064 gram of metallic iron. This requires 42.9 cc. permanganate solution or one cc. of permanganate solution is equal to (0.1487064 ÷ 42.9) 0.003466 metallic iron. But the same amount of permanganate solution used up in producing the characteristic reaction in this amount of metallic iron, will be used up in reaction with 90.76 per cent. of the same amount of molybdic acid. Hence one cc. of permanganate solution is equivalent to (0.003466 × 0.9076) 0.003145 gram of molybdic acid. But in the yellow precipitate obtained as above described, the phosphorus is 1.90 per cent. of the molybdic acid. Hence one cc. of permanganate solution is equivalent to (0.003145 × 0.0190) 0.0000597 gram of phosphorus. If, therefore, in any sample of steel tested as above, the yellow precipitate requires 8.6 cc. of permanganate, the amount of phosphorus in that steel is (0.0000597 × 8.6) 0.051 per cent.

NOTES AND PRECAUTIONS.

It will be observed that the method given above oxidizes the phosphorus in the iron by means of nitric acid, completes and perfects this oxidation and possibly neutralizes the effect of the carbon present by means of permanganate of potash, and then separates the phosphoric acid from the iron by means of molybdic acid. The molybdic acid in the yellow phospho-molybdate is subsequently determined by means of permanganate of potash, the phosphorus being determined from its relation to the molybdic acid in this precipitate. The method given above applies to steel and wrought iron, but is not yet recommended for pig iron.

It is hardly necessary to say that all the chemicals and materials used in the analysis are assumed to be free from impurities that will injuriously affect the result.

1.13 sp. gr. nitric acid apparently oxidizes the phosphorus just as successfully as a stronger one, while by its use solution is sufficiently rapid, and there is less trouble during the subsequent filtration due to silica.

If the solution is boiled one minute after solution is complete it will use up much less permanganate than if the preliminary boiling is omitted.

Care should be taken to secure a crystallized ferrous sulphate free from phosphorus. The commercial salt is apt to be contaminated. It should be added in small crumbs so as to avoid excess. If too much has been used, a few drops of permanganate can be added to oxidize it.

The temperature at which the molybdate solution is added to the iron solution and the resulting temperature, have an influence on the result. The directions should be closely followed, a good thermometer being used to determine temperatures. Never add the molybdate solution and then heat.

In washing the yellow precipitate it shows some disposition to crawl up to the top of the filter. Care should be taken there fore to have the filter fit the funnel so closely that even if the precipitate does crawl over the top it will not be lost while washing the filter completely to the top. It is very easy to leave enough molybdic acid in the top of the filter, even though the washings are tested, to cause an error of 0.005 per cent. in the determination.

The amount of molybdate solution given above is enough to convert all the iron into molybdate, and still leave enough to carry down the phosphorus.

It is best to make up molybdate solution frequently as it slowly changes on standing. We think it unadvisable to use a molybdate solution over ten days old. It is best to keep the molybdate solution in the dark at a temperature not above 80° to 85° F. The solution should always be filtered before using. Much of the so-called molybdic acid of the market is molybdate of ammonium or molybdate of some other alkali. This fact cannot be ignored in making up the molybdate solution. A series of experiments with various molybdic acids and alkaline molybdates obtained in the market indicates that if the amount of molybdic acid in the solution is that called for by the formula, irrespective of whether this amount is furnished by pure molybdic acid or any of the commercial molybdates referred to, the result will be much nearer the truth, than if this is not done. Good molybdic acid is best, but the alkaline molybdates can be used. The amount of molybdic acid in these molybdates can readily be determined by dissolving 0.1000 gram in 100 cc. of water to which a little ammonia has been added, and filtering. Now add ten cc. stong C. P. sulphuric acid, dilute to 200 cc. and pass through the reductor. Wash and dilute to 400 cc. and titrate with permanganate. The method given in the calculation above enables the amount of molybdic acid to be determined.

It is not advisable to make up the acid sulphate of ammonium solution for washing the yellow precipitate by using sulphate of ammonium and sulphuric acid, as the commercial sulphate of ammonium frequently contains phosphorus in some form.

The description and measurements given along with the cut of the modified reductor above will perhaps enable any one to make a suitable apparatus for themselves if they desire. The powdered zinc used is that which will pass through a twenty mesh sieve, and not pass through a thirty mesh sieve. It may be obtained from Baker & Adamson, Easton, Pa. It is essential before using the reductor to pass two or three blanks through, containing all the materials except the substance being analyzed, and then titrate these blanks. The last two blanks should agree exactly, and the amount of permanganate used up by the last blank should be deducted from the final figure obtained on titration of the substance being analyzed. This preliminary preparation of the reductor is essential after a new charging with powdered zinc, and also equally essential after the reductor has stood idle even over night. The rate at which the material passes through the reductor can be controlled somewhat by the suction. The apparatus is very efficient, and there seems little danger of too rapid a rate, but it is of course essential that the reduction should be complete. The properly reduced yellow precipitate solution should be green or slightly so, depending on the amount of molybdic acid present. A trace of "port wine" color in the reduced solution before titration with the permanganate indicates lack of complete reduction and renders the result of the analysis doubtful. In case of incomplete reduction pass the liquid through the reductor again. If the rate is somewhat slow and the solution being reduced somewhat warm, hydrogen gas enough may be generated to throw some of the liquid up against the sides of the tube above the zinc, and also bubble up through the liquid in the funnel. Care should be taken that this latter does not result in loss, and that the liquid adhering to the sides of the tube is removed by the subsequent washing.

There is some analytical evidence when using the method described above, that a portion at least of the arsenic which may be present in a sample of steel under examination, is precipitated along with the phosphorus, and counts as such in the final result. Until some simpler method of overcoming this difficulty than any at present known has been devised, and until the injurious effect of arsenic on steel has been demonstrated to be so small that arsenic can safely be ignored, the results obtained by the above method, will be regarded as the phosphorus content of the various steels purchased in accordance with Pennsylvania Railroad specifications.

Samples of steel in which the phosphorus has been determined will be sent to parties asking for the same in order to enable them to make such comparisons as they may desire.

In formulating the method given above, the published work of Emerton, Wood, Drown, Hundeshagen, Colby, Shimer, Handy, and Jones, has been freely consulted and used. It would be difficult to state in detail what is due to each.

METHOD OF DETERMINING CARBON IN IRON AND STEEL.

OPERATION.

Put three grams of fine borings of the iron or steel in a sixteen ounce beaker or pint dissolving jar, and add 200 cc. of an acid solution of the double chloride of copper and potassium which is at a temperature not above 100° F. Allow to dissolve, taking pains to agitate the liquid during solution. As soon as the separated copper has all disappeared, allow to stand a little while to settle if necessary, and then pour the supernatant liquid, on an asbestos filter in a platinum boat, taking pains at the last to pour out all the liquid, and at the same time leave as much of the separated carbon in the beaker or dissolving jar as possible. Now add about ten cc. of dilute hydrochloric acid (sp. gr. 1.1) to the beaker or jar and so manipulate that this acid shall touch all parts of the beaker or jar which has been in contact with the solvent liquid. Pour this acid on the filter, and wash the carbon out of the beaker or jar by means of a wash bottle containing acid of the same strength. Continue the washing with the acid until all color has disappeared from the washings, and then wash with water until the washings no longer react for hydrochloric acid. After the washing is complete the filtrate should be poured into a large beaker and diluted with clean water, and acid added if necessary to hold the sub-chloride of copper in solution, until it is possible to see whether any carbon has escaped the filter. If any is found, of course the liquid must be passed through the filter again, or