Estimation of Phosphorus in Iron and Steel by S. W. Parr.

Thesis for Degree of Bachelor of Science, in the School of Chemistry.
Phosphorus in Iron and Steel.

The history of the development of the metallurgy of iron marks the stepping stones of modern civilization. Whatever discoveries have improved upon the methods of working or enhanced the value of the product, in so far have tended toward the advancement not only of the industry itself but also the condition of the race. Interesting as this development is in its general outline, it is still more interesting in its minutest details, and in its more complex conditions which are based upon the work of the chemist and analyst. These latter conditions are all of recent discovery and may yet reward the labors of the chemist.

There is perhaps no subject of more recent development than that of phosphorus in its combination with the various forms of iron. This element itself is no stranger to the early metallurgy of iron for its presence was known and recognized in the earliest ores worked, where strangely enough it was
present in very large quantities. But it is only within the last fifty years that the peculiar property of the iron due to the presence of Phosphorus has been demonstrated and accepted. Indeed, so important a work as David Mushet’s papers on Iron and Steel published in 1840, London p. 13-21 attributes this property to an entirely different cause which today is looked upon as positively erroneous. It was believed, and so explained in the work referred to, that the peculiar brittleness sometimes found in certain cast irons—a property which made the metal worthless—was due to the presence of an abundance of silicious matter; the conclusion being largely based upon the fact that certain very silicious ores produced a very brittle iron. This conclusion was largely that of the iron workers themselves and was accepted as correct until the more careful investigation of chemistry proved otherwise.
It is now proved and held without dispute that the peculiar property of iron known as "cold short," i.e., a tendency to easy fracture upon receiving a blow or severe jar is wholly due to the presence of phosphorus in some peculiar combination or manner of crystallization with the iron. This tendency to brittleness is in proportion to the amount of phosphorus contained in the iron, producing in castings containing more than 0.5% a nearly valueless product. This principle largely determines the actual value of the iron for all uses and is a very important element in determining its commercial value. Indeed, with this metal, commercial transactions are based upon the analysis furnished by the chemist, and a very important item in his analysis is the percent of phosphorus present. The fact that recent discoveries have succeeded in effecting a complete removal of this element in no wise removes the necessity for its estimation even
though the result of analysis shows the phosphorus to be entirely absent. On the contrary, it not only requires a careful estimation but a corresponding improvement in its acquirement where by the result may be obtained in a manner both quick and accurate. To find such a method has been the endeavor of a great number of chemists and the present work is rather a comparison of their methods and suggestions than an attempt at something wholly new. In the first place, it may be as well to briefly review the old method in order to better understand the desirability of some change or improvement.

First, as to obtaining the iron in solution usually only nitric acid is used; if any hydrochloric acid is used in obtaining the solution it must be entirely expelled by bringing to dryness at least once. — When simply HNO₃ is
used, the solution must be brought to dryness at 110°C and redissolved in HNO₃. After filtering from the insoluble graphite and silica an excess of ammonia is added, producing a precipitate of ferric hydrate and ferric phosphate which is washed two or three times by decantation, then dissolve in HNO₃, add NH₄NO₃ and precipitate the P₂O₅ with NH₄NO₃. This last precipitate is redissolved in NH₄OH and the P₂O₅ is reprecipitated by adding the "magnesia mixture" in the form of Ammonium magnesium phosphate: NH₄MgPO₄·6H₂O which after ignition is reduced to Mg₂P₂O₇.

It will be seen that the above process is one which requires a great amount of time. Chiefly in the following parts — bringing to dryness in the first operation — the complete formation of the precipitate after adding the Ammonium Molybdate which requires from
six to twelve or even twenty-four hours, and
finally, after procuring this precipitate and dis-
solving in Ammonia, the precipitation with the
magnesium mixture requires from four to eight
hours for its completion.

In addition to the great amount of time
consumed, there are many sources of error. In
the first place every trace of HCl must be re-
moved for the presence of any of that acid
will prevent the precipitation by the Molyb-
date solution. (Fresenius, Quant. f34.)

For a perfect precipitation with the Am-
monium Molybdate, the solution must be
kept warm— but if too great a heat is
obtained the Molybdate acid will separate out in
flakes tending to retain some of the iron in
washing. — Upon treating with Ammonia, this
iron is precipitated carrying with it some
phosphate.
A modification of the above process is employed by Dr. C. Stunkel, Dr. T. Wetzke, and Prof. Paul Wagner. A synopsis of their method is given below taken from the Chemical News of Feb. 9, 1883, and appearing first in the Green's Swift Analyst's Drivm.

Phosphorus Estimation in Iron by Dr. C. Stunkel, Dr. T. Wetzke, and Prof. Paul Wagner.

Molybdate Method.

(Modification of the old method.) From 20-25 c.c. of a solution of phosphate free from silica and containing 1 to 2 grams of phosphoric acid are placed in a beaker and mixed with so much solution of Ammonium Nitrate and so much molybdate solution that the total liquid may contain 15% NH₄NO₃ and not less than 50 c.c. of molybdate solution for every 1 gram Phosphoric acid. Contents of beaker are heated 80°-90° in wa-
ter bath, set aside for an hour, filtered and the precipitate washed with dilute solution of ammonia nitrate. - Beaker is now set under the funnel. The filter pierced with a platinum wire, the precipitate rinsed into the beaker with ammonia at 2½% washing the filter paper well dissolved stirring with a glass rod, and ultimately so much of the weak ammonia added as to make up the volume of the liquid to about 750 c.c. To 1 gram of phosphoric acid - 10 c.c. of magnesia mixture are dropped in stirring continually. The beaker is covered with a glass plate and set aside for two hours. The precipitate is then filtered off, washed with 2½% ammonia and dried. The precipitate is introduced into a platinum crucible, putting in also the rolled up filter - the crucible is covered and heated till the filter is carbonized - it is then placed in a planting position in the flame of a Bunsen burner for ten
minutes, and then ignited before the blast for five minutes -- cool in desiccator and weigh.

Solutions used in the above.

I

Molybdic Solution. -- 150 grams ammonium Molybdate are dissolved in H₂O, so as to make 1 litre and poured into 1 litre nitric acid of 1.25 specific gravity.

II

Concentrated Solution N₄H₄NO₃. -- 150 grams N₄H₄NO₃ dissolved with H₂O to bulk of 1 litre.

III

Dilute Solution N₄H₄NO₃. -- 100 grams N₄H₄NO₃ dissolved to bulk of 1 litre in H₂O.

IV

Magnesia Mixture. -- 55 grams crystalline Magnesium chloride and 70 grams N₄H₄Cl dissolved in 1 litre (N₄H₄) H₂O at 21.2 °.

The above is found in Chemical News, Feb 9 - 1883.

from Zeitschrift Analytische Chemie, XXI - 353.
The above method was used as the standard for comparisons. Its own results agreed admirably in duplicate and the time occupied in making an analysis much shorter than by the old method. Allowing two hours for bringing to dryness and obtaining the iron in proper solution, a complete separation of phospho-molybdate is effected in from four to six hours—and after dissolving in Ammonia a complete precipitate of ammonium magnesium phosphate is obtained in from two to four hours.

The following results were obtained in a sample of pig iron by this method.

Weight of $Mg_2P_2O_7$ in 2 grams of iron in duplicate

I  
0.0469  

II  
0.0471  

0.643% of PbO.
It has been suggested that the method might be materially shortened by weighing and estimating the phosphorus brought down by the molybdate solution, thus avoiding the dissolving of it with ammonia and reprecipitating with the magnesia mixture. The objections urged against this plan have been that upon adding the molybdate and keeping the solution at from 80 to 90 degrees centigrade, much of the molybdic acid crystallizes out, thus giving too great a percentage of phosphorus. To obviate this difficulty, Korschell proposes a method of making the molybdate solution in such a manner that the molybdic acid will not separate upon addition of heat. Such a solution was prepared as follows—

10 grams of pure molybdic acid
10 \( \text{H}_{2} \text{O} \)
60 c.c. \( \text{H}_{2} \text{O} \)

To this solution was added when cold, 5 grams
of tartaric acid dissolved in 20 c.c. H₂O. Next add 75 c.c. of nitric acid, boil and filter while hot. The method of estimating is as follows.

One gram of the iron was dissolved in the smallest possible amount of HNO₃, brought to dryness, redissolved in HNO₃, and filtered. The filtered liquid was allowed to drop into about 30 c.c. of the above described molybdate solution — kept warm on a water bath, and after the filtering was complete and the residue washed, the solution was allowed to stand until the separation was complete when the phospho-molybdate precipitate was collected on an equilibrated filter, dried at 120°, and weighed. Of this weight the ratio of Phosphorus is 1:73.

The following estimation was made:

I. 0.600 per cent.
II. 0.650 %

By the old method the same iron was found to con-
tain 643 %.

The objections to this method are still numerous—
the composition of the precipitate is not constant
and it is always objectionable to use tared or
equipoise filters both on account of time required
in drying and also liabilities to error. On the
whole, this method can not be recommended as
an improvement on the ordinary one.

Another series of methods have been recommended,
based upon the fact that when the metal is treat-
ed with HCl, the phosphorus passes off in union
with the hydrogen as PH₃. Various methods for
securing the phosphorus thus liberated have been
tried. Such as (a) passing through a solution
of silver nitrate. The phosphorus uniteing to
form phosphate of silver. By precipitating the
silver with HCl, the filtrate may be at once
treated with the magnesia mixture for the
separation of the phosphorus.
Another method (3) was tried – that of passing the gas through an ammoniacal solution of Peroxide of hydrogen, which from its property of easily parting with oxygen, readily decomposes the PH₃ into phosphoric acid – P₂O₅.

The method of liberating as a gas is strongly recommended in "Crooke Select Methods" p. 100 – and the process suggested is that of passing the gas through a nearly neutral or slightly acid solution of silver nitrate, and thus securing the phosphorus as a precipitate of silver phosphide by filtering and dissolving this in Nitro-hydrochloric acid. The Phosphorus could be at once precipitated with the magnesia mixture.

It was further positively affirmed by the same authority that no trace of phosphorus whatever could be found remaining in the same after digesting with HCl. Upon this assurance the process was tested – The gas was passed first
Through a strong solution of KH\textsubscript{2}PO\textsubscript{4} to absorb the H\textsubscript{2}S gas, then into a silver solution. It was found that the precipitate of silver phosphide very readily decomposed into silver phosphate which made it necessary to treat the filtrate from the phosphide for the phosphorus there contained. Hence some other medium was employed, such as H\textsubscript{2}O\textsubscript{2} or a solution of AgNO\textsubscript{3} strongly acidified with HNO\textsubscript{3}. By using the acidified AgNO\textsubscript{3}, all the phosphorus, especially if a slight heat were applied, was converted into silver phosphate easily soluble in the liquid; from this the Ag was precipitated leaving the phosphorus as P\textsubscript{2}O\textsubscript{5} to be precipitated as ammonium magnesium phosphate.

Numerous operations were tried with the almost uniform result of from 2.15 to 2.23% in an iron known to contain 1.43%. It was now tried by passing the gas through an ammowi-
ocal solution of \( \text{H}_2\text{O}_2 \) with the result in phos-
phorus of 21.5%. The residue was now tested
for phosphorus and found to contain from
.389% to .4% of Phosphorus, which added to the
estimations obtained from the gas would make
from .6% to .639% in an iron known to con-
tain .643% of Phosphorus.
The method by liberating as a gas seemed thus
to be impracticable, and indeed Weismann is
authority for the statement that, "The method of
precipitation with Molybdate is the only exact one."
As a conclusion from a comparison of the fore-
going analyses, it may be said that the method
employed by Drs. Stunkel and Wetzke is the best.
In addition to the description of the same as
already given, it may be said that the smaller
the amount of metal taken with a corresponding-
ly small amount of \( \text{H}_2\text{O}_2 \) consistent with accu-
arcy in results, is altogether desirable. The
longest part of the operation consists in bringing
the solution in HNO₃ to dryness. Small amounts
facilitate this part of the process.
The final evaporation should take place at 100°
or 110° C., for while 130° does no injury, it forms
a crust not easily redissolved. A further precaution
should be observed in collecting the molybdate pre-
cipitate. It should be thoroughly washed with a
weak solution of NH₄NO₃ to insure removal of all
iron. If, however, upon redissolving this precipitate
there should be found a turbidity from slight
presence of iron, a small amount of citric acid
will clear up the liquid before final precipita-
tion with the magnesia mixture.
The results of this method are always reliab-
le. Other methods as at present known, if
more rapid are so at the expense of accuracy.