

969

THE DETERMINATION OF PHOSPHORUS  
IN VANADIUM STEELS

A Thesis submitted to the Faculty of the  
Graduate School

of the

University of Minnesota

by

PETER MARCUS SKARTVEDT

in partial fulfillment of the requirements  
for the degree of

MASTER OF ARTS

May 21, 1913.

The Determination of Phosphorus in Vanadium Steels.

It has long been known that the methods which are ordinarily used for the determination of phosphorus in iron and steel analysis are not suitable for steels containing vanadium. The difficulty lies in the fact that vanadium interferes with the precipitation of phosphorus as ammonium phosphomolybdate. This interference may occur in various ways according to the relative proportions of phosphorus and vanadium present in the steel. Large amounts of vanadium tend to hold the phosphorus in solution when the attempt is made to precipitate the phosphorus with ammonium molybdate, while small amounts of vanadium are precipitated with the phosphorus. Again, the conditions of analysis may be such that a part of the phosphorus is held in solution by the vanadium and a part of the vanadium is precipitated with the phosphorus causing compensating errors. The presence of vanadium in the yellow precipitate is indicated by the orange yellow color which it assumes. Such small amounts of vanadium produce this characteristic color that it may be taken

-----

JUL 24 1913 B 70

as a serviceable indication of the presence of that element.

The increasing importance of vanadium steels commercially has greatly stimulated their manufacture. This has necessitated the working out of special methods of analysis for the determination of such constituents as cannot be satisfactorily determined by ordinary methods. A number of procedures have been devised to overcome the difficulties encountered in the estimation of phosphorus. Some of these are too long and complicated to be suitable for routine work, while other shorter methods are too inaccurate and unreliable.

The method adopted by the Bureau of Standards at Washington which consists in Blair's<sup>(1)</sup> basic acetate separation followed by a double precipitation as magnesium ammonium phosphate, is obviously too long for a busy works laboratory, however satisfactory and accurate it may be for standardizing purposes. C. M. Johnson<sup>(2)</sup> has devised two methods for the separation of vanadium and phosphorus. These are very long and tedious and very difficult to carry through successfully because of the multiplicity

-----

(1). Blair - Chemical Analysis of Iron, 7th Ed. p. 81.

(2). Johnson - Analysis of Special Steels, p. 21.

of operations involved. The details of Johnson's peroxidation method will be taken up later. Brearley and Ibbotson's <sup>(1)</sup> method, though short, is unreliable and cannot be recommended on that account. The mercurous nitrate method <sup>(2)</sup> is open to the same objection as Brearley and Ibbotson's, while the Graham Edgar method <sup>(3)</sup>, which involves the precipitation of phosphorus and vanadium as silver phosphate and vandate, weighing and then estimating the vanadium volumetrically and calculating the phosphorus by the difference, is an indirect method which is not desirable. Phosphorus <sup>(4)</sup> may also be quantitatively determined in the presence of vanadium by working in an atmosphere of chlorine or carbon tetrachloride, but this method is impracticable because it requires too complicated apparatus. An extended search through the literature failed to discover any other methods.

In view of the impracticability of the methods just enumerated and of the rapidly growing importance of vanadium steels commercially, we thought it worth while to attempt to work out a process for the determination of phosphorus in such steels, which

-----

- (1). Brearley and Ibbotson - Analysis of Steel Works Material, p. 165.
- (2). Treadwell-Hall Analytical Chem. Vol. II, p. 307.
- (3). Am. Chem. Journ., Vol. 44, p. 470.
- (4). Zentralblatt 1909, pt. 4, p. 1376.

should be short and accurate, and which should require no exceptional technical skill on the part of the analyst. The following pages contain an account of the work done on this problem.

For the sake of convenience and economy of time, the greater part of the work was done with standard solutions as follows: (1) ammonium phosphate, (2) tenth normal potassium permanganate, (3) ferric chloride, (4) vanadyl sulphate. The solution of di-ammonium-hydrogen phosphate was made up by dissolving 7.5 grams of the salt in distilled water and diluting to two liters. This solution was standardized by weighing out two fifty gram portions, and determining the phosphorus gravimetrically by precipitation as magnesium ammonium phosphate. Sample 1 gave .0008857 grams phosphorus per gram of solution. Sample 2 gave .0008854 grams. The solution was subsequently standardized volumetrically to insure parallel conditions to those in which it was to be chiefly used. This gave a value for phosphorus of .000883 grams per gram solution. Since the discrepancy

-----

between the two standardizations was only .000002 grams per gram of solution, the gravimetric value was used as a basis for calculations.

A solution of potassium permanganate was prepared by dissolving about 7 grams of potassium permanganate in two liters of distilled water. The solution was boiled for thirty minutes, cooled and filtered through an asbestos filter. The solution was then thoroughly mixed and allowed to stand over night. It was standardized by titration against standard iron ore containing 68.34% iron, by the Reinhardt-Zimmerman <sup>(1)</sup> method. This standardization was checked by standardization with Sorenson's <sup>(2)</sup> sodium oxalate method. The two methods checked within .000003 grams of iron per cc. of solution.

The ferric chloride solution was prepared by dissolving 375 grams of ferric chloride in two liters of distilled water to which twenty cc. concentrated hydrochloric acid had been added. Titration by the Reinhardt-Zimmerman method gave a value of .04 grams per cc. of the solution.

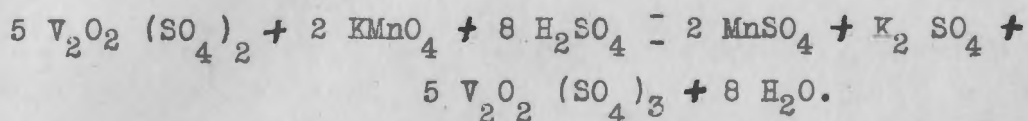
A solution of vanadyl sulphate was prepared

-----

(1). Treadwell-Hall Analytical Chemistry, Vol. II, p. 609-10.

(2). Bureau of Standards, Circular 40.

and standardized by Campagne's<sup>(1)</sup> method. Vanadyl chloride was evaporated several times with an excess of concentrated hydrochloric acid forming the oxychloride  $\text{VOCl}_2$ . Five cc. concentrated sulphuric acid were added and the solution evaporated to the complete expulsion of hydrochloric acid.  $2\text{VOCl}_2 + 2\text{H}_2\text{SO}_4 = \text{V}_2\text{O}_5(\text{SO}_4)_2 + 4\text{HCl}$ . The solution was cooled and diluted to one liter. Two 20 cc. portions were measured off with a pipette, diluted to 200 cc., warmed to  $60^\circ$  and titrated with the standard permanganate solution to the appearance of a faint pink color.



$10 \text{V} = 10 \text{Fe}$ ; or  $512 \text{V} = 558.4 \text{Fe}$ .  $\text{V} =$  iron value of the permanganate multiplied by .9169. This titration gave a value of .00225 grams per cc. for the vanadium solution.

To determine the degree of error caused by the presence of vanadium in the steels when determining phosphorus by ordinary methods, a series of 6 determinations was made, using the method of Dudley and Pease<sup>(2)</sup>. The

-----

(1). Blair - Chemical Analysis of Iron 7th Ed. p. 206.

(2). Journal Am. Chem. Soc. Vol. VII, p. 108,519.

sample is dissolved in dilute nitric acid in a 500 cc. Erlenmeyer flask, oxidized with a strong solution of potassium permanganate and the manganese dioxide which precipitates is dissolved by adding a bare excess of ferrous sulphate. Ammonia is then added until a slight precipitate of ferric hydroxide is formed which is dissolved with concentrated nitric acid adding enough excess to produce a bright amber color. The solution is heated to  $85^{\circ}$  and 50 cc. ammonium molybdate solution are added. The yellow precipitate of ammonium phospho-molybdate is allowed to settle and the supernatant liquid is decanted. The precipitate is washed onto the filter with a 1% nitric acid solution and finally washed with a 1% potassium nitrate solution. The phosphorus is determined by Emmerton's <sup>(1)</sup> method which is as follows:

The yellow precipitate is dissolved off the filter into the original <sup>flask</sup> with 20 cc. dilute ammonia (1:3). Fifteen grams of granulated zinc and 100 cc. of 1:5 sulphuric acid are then added and the solution is heated on the hot plate for about fifteen minutes. When the

-----  
(1). Blair Chemical Analysis of Iron, 2nd Ed. p. 95.



reduction is complete, the zinc is filtered off and the flask and filter are washed once or twice with cold water. The solution is cooled to about 40° and titrated to a faint pink with the standard solution of potassium permanganate. The steel taken for analysis was a Bureau of Standard's sample containing .035 % phosphorus and .15% vanadium. The results are given in

TABLE I.

<u>Wt. of Steel Taken.</u>	<u>Wt. of P. Recovered.</u>	<u>% P.</u>
1. 2.3642 grams	.000865 grams	.0366
2. 2.0062 "	.0008145 "	.0406
3. 2.1054 "	.0007832 "	.0372
4. 2.0466 "	.000118 "	.0577
5. 1.9984 "	.000883 "	.0442
6. 1.8896 "	.000854 "	.0452

It will be seen that the result in each case was considerably too high. The yellow precipitates were all strongly orange colored and the samples which gave the highest results had the most pronounced orange color. This series may be regarded as a confirmation of the statement that the presence of small amounts of vanadium gives

-----

high results for phosphorus when analyzed by the ordinary methods. The effect of high vanadium percentages on phosphorus determination by this method was not tried.

As a further preliminary we thought it expedient to run a few determinations to test out the most promising of the various methods that have been previously mentioned, in the hope that the work would suggest some new points of departure. In accordance with this idea two samples containing about .38% phosphorus and .225% vanadium in one gram of iron were analyzed by Johnson's peroxidation<sup>(1)</sup> method.

The steel is dissolved in dilute nitric acid and the phosphorus and vanadium are separated from the iron by precipitating out the latter element with sodium peroxide in a one liter boiling flask. About 10 grams excess are added and also 10 grams of sodium carbonate. It is then boiled for 20 minutes, cooled and filtered. The filtrate is set aside and the precipitate is dissolved off the filter and the process repeated. The two filtrates are separately treated as follows, after having added an excess of either sodium aluminate or

-----  
(1). Analysis of Special Steels, p. 25.

aluminum chloride solution to the filtrate. To the filtrate, strongly alkaline with sodium peroxide, is added dilute hydrochloric acid until the solution no longer turns turmeric paper immediately to even a faint brown. This precipitates all the phosphorus and aluminum as aluminum phosphate and aluminum hydroxide while the vanadium is held in solution by the sodium carbonate. The precipitate is filtered off and washed free from vanadium with a 1% solution of ammonium nitrate and then dissolved off the filter with dilute nitric acid, from which solution the phosphorus may be determined in the usual way by precipitation with ammonium molybdate. The results were as follows:

TABLE II.

<u>Wt. Fe taken.</u>	<u>Wt. P.</u>	<u>Wt. P. recovered.</u>	<u>Wt. V. taken.</u>
1. 1 gram	.00386 gms.	.00385 gms.	.00225 gms.
2. 1 gram	.00379 "	.00377 "	.00225 "

The results were very good, showing the method to be very accurate. However, the bulk of ferric hydroxide from even a one gram sample was so large as to be very difficult to handle and much time was consumed in washing the

-----

precipitates. It is evident that the method is not very practicable, especially for the analysis of steels so low in phosphorus content as to require a two or three gram sample. As this method has certain commendable features, it will be spoken of again.

The method used by Brearley and Ibbotson<sup>(1)</sup> was next tried. The method depends upon the fact that vanadium in the reduced form is not precipitated by ammonium molybdate. The vanadium is reduced by ferrous sulphate until a drop of the solution treated with ferricyanide gives an immediate marked blue color. The phosphorus is then precipitated by ammonium molybdate. If the amount of the phosphorus is small, it is sometimes necessary to heat to 60° for thirty minutes, but if the amount of the phosphorus is large, the <sup>precipitation</sup> is practically complete in the cold. Four determinations were made with this method on a standard vanadium steel containing .035% phosphorus and .15 % vanadium.

-----

(1). loc. cit.

TABLE III.

<u>Wt. Steel Taken.</u>	<u>Wt. P. Recovered.</u>	<u>% P.</u>
1. 2.032 gms.	.000320 gms.	.065
2. 1.9164 "	.0008237 "	.042
3. 2.2122 "	.000973 "	.044
4. 2.1368 "	.001153 "	.054

Browning<sup>(1)</sup> also states that vanadium may be separated from phosphorus by reduction of the vanadium with sulphur dioxide and precipitation of the phosphorus with ammonium molybdate. This method has been tested by A. Gressly<sup>(2)</sup> who found that the method gives correct results only when the vanadium is present as vanadyl sulphate. On standing, the vanadium is gradually oxidized by the air to vanadic acid with consequent contamination of the yellow precipitate by vanadium. Even with immediate filtration, some oxidation does occur rendering the method unsatisfactory because of the introduction of this element of uncertainty.

Before giving up the idea of precipitating the phosphorus as ammonium phospho-molybdate in the presence of reduced vanadium, it was decided to try the

-----

(1). Introduction to the Rarer Elements, p. 113.

(2). Treadwell-Hall Analytical Chem. Vol. II, p. 307.

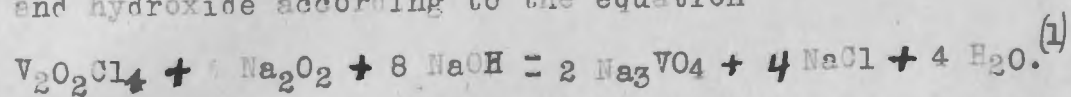
effect of a weaker reducing agent with the expectation that the excess of reducing agent need not be destroyed to effect the precipitation of the phosphorus, and thus by its presence prevent the re-oxidation of the vanadium by the air on filtering off the precipitate. The action of formaldehyde was tried on solutions containing a mixture of phosphoric and vanadic acids. It was also tried on separate solutions of these acids. The formaldehyde was added in different amounts from a bare excess to 40 cc excess. Gradations of temperature ranging from 18° to 60° were tried as was also the method of adding formaldehyde to the cold solution and heating after the addition. The net result of all these experiments proved conclusively that formaldehyde exerts no reducing action on either the vanadic or the phosphoric acid and is therefore not available for the present purpose.

A consideration of the results obtained from the samples already analyzed led us to the conclusion that the only satisfactory method of dealing with the problem would be to endeavour to effect a separation of the vanadium from the phosphorus before precipitating the latter

-----

with ammonium molybdate. It was thought that barium chloride could be used to effect this separation and a number of experiments were conducted along this line.

In order to test out barium chloride as a precipitant for vanadium it was necessary first to prepare a solution of sodium vanadate so as to avoid the interference of barium sulphate which would be precipitated in case the standard solution of vanadyl sulphate was used. The sodium vanadate solution was prepared by treating a solution of vanadyl chloride with sodium peroxide and hydroxide according to the equation



Excess of sodium hydroxide was used to prevent hydrolysis

according to the reaction  $2 \text{Na}_3\text{VO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{Na}_4\text{V}_2\text{O}_7 + 2 \text{NaOH}^{(2)}$

As this solution was used only for qualitative experiments, it was not standardized.

The attempt was made to precipitate vanadium from a mixed solution of orthophosphate and vanadate with barium chloride. The precipitation was tried first in alkaline solution, secondly in acetic acid solution, and thirdly in alcohol solutions which ranged from 40 to 80%

(1). Treadwell-Hall Analytical Chemistry, Vol. 1, p. 489.

(2). Treadwell-Hall Analytical Chemistry, Vol. I, p. 485.

alcohol. Variations of temperature ranging from room temperature to boiling were also tried. In all about twenty different conditions were tried and in every case it was found that the conditions which precipitated the vanadium as  $\text{Ba}_2(\text{VO}_4)_2$  also precipitated the phosphorus as  $\text{Ba}_3(\text{PO}_4)_2$ , and conditions which did not precipitate the phosphorus neither precipitated the vanadium.

These experiments were all qualitative. Therefore no exact data were recorded. A similar series was run using lead acetate instead of barium chloride with similar results. As these also were not a success, the idea of separation by precipitating out the vanadium was given up.

Hess and Campbell<sup>(1)</sup> have devised a very good method for the determination of aluminum in steels. It can with equal convenience be used for the determination of phosphorus. The method depends on the fact that <sup>the</sup> organic base, phenylhydrazine, quantitatively precipitates aluminum and phosphorus from a reduced neutral solution of the steel. The excellence of the method lies in the fact that phenylhydrazine is both a base and a reducing agent and acts in

-----  
(1). Journal Am. Chem. Soc. Vol. XXI, page 776.



a double capacity, both precipitating the phosphorus as aluminum phosphate and at the same time keeping the iron reduced.

The procedure is as follows: The sample is obtained in solution, preferably as the chloride, heated nearly to boiling and the hydrochloric acid neutralized by the addition of ammonia until the iron precipitate barely re-dissolves on vigorous stirring. A concentrated solution of ammonium bisulphite is then added drop by drop until the solution becomes colorless. One or two cc. of phenylhydrazine are then added drop by drop with constant stirring. If after this has been added, no precipitate forms, it is economical to add ammonia drop by drop until a very slight permanent precipitate of aluminum hydroxide forms. Then a few drops more of phenylhydrazine are added to insure complete precipitation. The precipitated aluminum hydroxide and phosphate are filtered off and the precipitate is washed with a five or ten per cent solution of phenylhydrazine bisulphite until the washings show no test for iron with ammonium sulphide. The precipitate is then ignited to constant weight and the aluminum determined by

-----

difference after the phosphorus has been determined in a separate sample.

In order to apply this method to phosphorus it is only necessary to dissolve the mixed precipitate of aluminum phosphate and hydroxide off the filter with hot dilute nitric acid into an Erlenmeyer flask and precipitate the phosphorus in the usual way with ammonium molybdate. It is usually necessary to add a known amount of aluminum chloride to the solution in order to insure the presence of sufficient aluminum to precipitate all the phosphorus as aluminum phosphate. The solution of aluminum chloride is prepared by dissolving 44.7 grams of aluminum chloride in 500 cc. distilled water to which 10 cc. concentrated hydrochloric acid have been added. Such a solution contains approximately .01 grams of aluminum per cc. As the steel is difficultly soluble in hydrochloric acid, it is obtained in the form of the chloride <sup>(1)</sup> by dissolving in dilute nitric acid, evaporating to dryness and baking to decompose the nitrate or iron. The residue is then taken up with concentrated hydrochloric acid. By this means also, the phosphorus is oxidized to phosphoric acid. This method, without any modification,

-----  
(1). Blair - Chem. Anal. of Iron, p. 95.

gave the following results in the presence of vanadium:

TABLE IV.

<u>Wt. Fe taken.</u>	<u>Wt. P taken.</u>	<u>Wt. P recovered.</u>	<u>Wt. V taken.</u>
1. 1 gram	.00169 grams	.0024 grams	.0028 grams.
2. 1 "	.00177 "	.00162 "	.0028 "
3. 1 "	.001738 "	.00352 "	.0028 "
4. 1 "	.00172 "	.00320 "	.0028 "
5. 1 "	.001655 "	.00258 "	.0028 "
6. 1 "	.001796 "	.001122 "	.0028 "

Although this series shows very discordant results, the method gave promise of serviceability because it offered a very convenient way to get the phosphorus separated from the iron, thus rendering it possible to attempt the separation of phosphorus from vanadium by methods which could not be used in the presence of iron. That this separation is necessary is shown by the fact that the yellow precipitates were contaminated by the characteristic orange color due to the presence of vanadium. A confirmatory test with hydrogen peroxide was made on the nitric acid solution of the aluminum

-----

phosphate before the addition of ammonium molybdate and in each case the characteristic reddish color of pervanadic acid,  $\text{HVO}_4^{(1)}$ , was very distinct.

A number of modifications of Hess and Campbell's method were tried for the purpose of effecting the separation of the vanadium from the phosphorus. In the first place, we tried the precipitation of aluminum phosphate in an acetic acid instead of a neutral solution expecting that the vanadium would be held in solution by the acid. The only change this involved in the procedure given above was the addition of 10 cc. of 20% acetic acid solution just before the addition of the phenylhydrazine. One of the four samples run in this way contained no vanadium, as it was thought advisable to try the effect of the modification on a case analagous to conditions that obtain in the analysis of plain steels. The results of this set are given in Table V.

TABLE V.			
<u>Wt. Fe taken.</u>	<u>Wt. P. taken.</u>	<u>Wt. P. recovered.</u>	<u>Wt. V taken.</u>
1. 1 gram	.003063 gms.	.003139 gms.	.0028 gms.
2. 1 gram	.002412 "	.002364 "	.0000 "
3. 1 gram	.002644 "	.002855 "	.0028 "
4. 1 gram	.002238 "	.002377 "	.0028 "

(1). Browning - Introduction to the Rarer Elements, p. 115,  
also Johnson's Analysis of Special Steels, p. 5.

The yellow precipitates from samples 1, 3, and 4 were distinctly orange tinted; 3 and 4 being the more strongly colored. While the results are not extremely bad, nevertheless the presence of vanadium in the yellow precipitate shows that acetic acid is not a very efficient reagent for effecting the separation of vanadium from phosphorus under these conditions, and in all probability the presence of a very large amount of vanadium would considerably increase the percentage of error.

The next change we tried was indeed a radical departure, being nothing less than the elimination of the phenylhydrazine itself. Since a part of the function of phenylhydrazine in the Hess and Campbell<sup>(1)</sup> method is to destroy the excess of sulphur dioxide from the ammonium bisulphite, it then became necessary to remove the excess by boiling. The procedure is modified as follows: After reducing the iron with ammonium bisulphite, the excess of sulphur dioxide is removed by boiling (from 50 minutes to 2 hours). About ten grams of ammonium acetate and 5 cc. acetic acid are added and the boiling is continued a few minutes to collect the precipitate.

-----  
(1). loc. cit.

The precipitate is filtered, dissolved off the filter with hot dilute nitric acid, and re-precipitated if the first precipitate has a yellow color, which indicates the presence of vanadium. The first or second precipitate, as the case may be, is filtered off, washed with a 1% solution of acetic acid and again dissolved off the filter with dilute nitric acid, and the phosphorus precipitated with ammonium molybdate in the usual way. A series of six determinations, three of which contained no vanadium, gave the following discordant results:

TABLE VI.

<u>Wt. Fe taken.</u>	<u>Wt. P taken.</u>	<u>Wt. P recovered.</u>	<u>Wt. V taken.</u>
1. 1 gram	.002464 gms.	.002328 gms.	.0028 gms.
2. 1 "	.002656 "	.002432 "	.0028 "
3. 1 "	.002149 "	.001794 "	.0042 "
4. 1 "	.002835 "	.002486 "	.0000 "
5. 1 "	.002996 "	.002067 "	.007 "
6. 1 "	.002242 "	.001648 "	.0000 "

On account of the exceedingly low results obtained from samples 5 and 6, a sufficient excess of ammonium

-----

molybdate was added to the filtrates from the aluminum precipitates, and the phosphorus which was thus precipitated was estimated in the usual manner. Sample 5 gave .001977 grams of phosphorus and had a distinctly orange color. The total amount of phosphorus for sample 5 which was recovered was .004044 grams or 135% of the original amount taken. Similarly sample 6 gave .00056 grams making the total for sample 6, .002208 grams or 98.54% of the original amount taken.

It appears that the low results were due to the resolution of the precipitate on cooling, that is, by a reversal of the hydrolytic action which produced the precipitate. The method was further tested by running a number (sixteen) of qualitative experiments to see if conditions could not be obtained whereby this reversal of reaction could be prevented. The experiments consisted in varying the length of time from one to ten minutes that the solution was boiled after the addition of acetic acid, and in varying the length of time for the precipitate to settle before filtering. If filtered immediately upon removal from the flame, the gelatinous

-----

precipitate clogged up the filter pores right at the start so that the latter part of the filtration proceeded so slowly as to make it impossible to prevent excessive cooling. On the other hand if allowed to stand long enough for the precipitate to settle so that the supernatant liquid could be decanted, it was found that also this plan involved excessive cooling with consequent resolution of the precipitate. Several intermediate points between these two limits were also tried. It was found that the best results were obtained by heating for thirty minutes on the water bath and then filtering immediately. However, the filtrates still gave tests for phosphorus. As there was still some doubt in our minds as to the reason for this, further modifications were tried which were calculated to throw more light on the subject.

The use of phenylhydrazine to precipitate aluminum phosphate in an acetic acid solution was not altogether satisfactory because of the formation of an oily film or scum which was very bothersome. This film manifested a great crawling tendency and also greatly interfered with rapid filtration. The precipitation of

-----



aluminum phosphate could not be made complete in an acetic acid solution without the organic base. For these two reasons we decided to use hydrazine hydrochloride, thus avoiding the oily radical of the phenylhydrazine.

Since hydrazine hydrochloride is rather expensive, it was more economical to partially reduce the iron with ammonium bisulphite and complete the reduction with the hydrazine. Sufficient ammonia was added from time to time to neutralize the hydrochloric acid liberated by the hydrazine, care being taken to add only so much as would barely precipitate a small amount of ferrous hydroxide which did not redissolve on vigorous stirring, showing that the solution was slightly alkaline. Then about ten cc. of a 20% acetic acid solution were added which unexpectedly liberated sulphur dioxide. After several hours boiling, the odor of sulphur dioxide was still in evidence. For this reason ammonium bisulphite was not used in subsequent experiments with hydrazine hydrochloride.

The complete reduction of iron by hydrazine alone was accomplished by continually neutralizing the hydrochloric acid with ammonia as fast as it was liberated.

-----

In this way it was possible to effect almost a complete reduction with the hydrazine. After the iron was reduced, five grams of sodium acetate were added to neutralize any mineral acid and then 10 cc. acetic acid were added. The precipitate was boiled a few minutes, allowed to settle, and filtered. The phosphorus was then determined as already described in the account of the Hess and Campbell<sup>(1)</sup> method. A series of eight determinations were made in this way with the following results:-

TABLE VII.

<u>Wt. Fe taken.</u>	<u>Wt. P taken.</u>	<u>Wt. P recovered.</u>	<u>Wt. V taken.</u>
1. 1 gram	.00267 gms.	.00308 gms.	.007 gms.
2. 1 "	.00276 "	.00264 "	.007 "
3. 1 "	.002402 "	.001936 "	.007 "
4. 1 "	.00224 "	.000905 "	.007 "
5. 1 "	.002162 "	.001656 "	.007 "
6. 1 "	.002546 "	.00235 "	.007 "
7. 1 "	.002666 "	.002454 "	.007 "
8. 1 "	.002544 "	.00239 "	.007 "

The filtrates from the aluminum precipitate in this series were all tested for phosphorus and in

(1). loc. cit.

each case phosphorus was obtained, although sample 1 gave 115% of the amount originally taken. This high result was due to the presence of vanadium in the yellow precipitate. Our conclusion from this series as a whole is that phosphorus cannot be completely precipitated in this way.

A further modification of the Hess and Campbell method was next tried. This consisted first in obtaining the phosphorus and vanadium free from iron as described in that method. Then the phosphate and vanadate of aluminum are dissolved off the filter with dilute nitric acid and about one-half cc. of the aluminum chloride solution is added to insure an excess of Al ions. The solution is alkalinized with ammonia and then acidified with acetic acid, boiled a few minutes to collect the precipitate, and thus promote rapidity of filtration. The precipitate is allowed to settle, filtered, and washed ten or twelve times with a hot one per cent acetic acid solution. It is re-dissolved with dilute nitric acid into the original beaker and the whole solution is transferred to a 500 cc. Erlenmeyer flask in which

---

the phosphorus is precipitated with ammonium molybdate as usual. The series of four determinations made as above described gave very discordant results although the treatment in each case was as <sup>nearly</sup> identical as it was possible to make it.

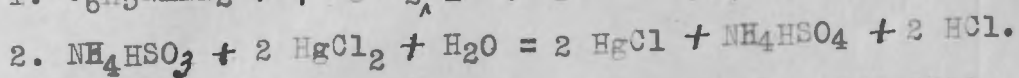
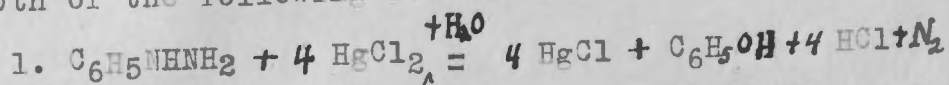
TABLE VIII.

<u>Wt. Fe taken.</u>	<u>Wt. P taken.</u>	<u>Wt. P recovered.</u>	<u>Wt. V taken.</u>
1. 1 gram	.001968 gms.	.001082 gms.	.007 gms.
2. 1 "	.002164 "	.001687 "	.007 "
3. 1 "	.002014 "	.002054 "	.007 "
4. 1 "	.002355 "	.001862 "	.007 "

Since theoretically this method appeared to be a very good one, we decided to try two more modifications before giving it up. A series of six determinations were made <sup>exactly</sup> as the last four described except that the last trace of phenylhydrazine bisulphite wash water was washed out of the aluminum precipitate by hot water before dissolving it with nitric acid. Mercuric chloride was found to give an excellent test for the completeness of the washing. One drop of a five per cent solution of phenylhydrazine bisulphite is

-----

sufficient to cause a slight cloudiness in the mercuric chloride solution due to the reduction of mercuric to mercurous chloride. The reduction may be due to either or both of the following reactions:

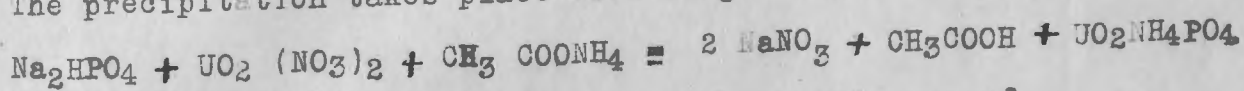


The advantage expected from this change was the assurance that failure to obtain all the phosphorus in these samples would in no way be due to the presence of phenylhydrazine or sulphurous acid in the second precipitation. Furthermore, the hydrogen peroxide test for vanadium could then be applied with greater accuracy. The presence of phenylhydrazine precludes the use of this test. This change also proved to be no improvement.

TABLE IX.

<u>Wt. Fe taken.</u>	<u>Wt. P taken.</u>	<u>Wt. P recovered.</u>	<u>Wt. V taken.</u>
1. 1 gram	.002462 gms.	.00202 gms.	.007 gms.
2. 1 "	.001916 "	.001246 "	.007 "
3. 1 "	.001424 "	.001117 "	.007 "
4. 1 "	.002423 "	.002185 "	.007 "
5. 1 "	.001788 "	.001544 "	.007 "
6. 1 "	.001653 "	.001228 "	.007 "

Engel<sup>(1)</sup> has worked out a method for the separation of uranium from vanadium using ammonium phosphate to precipitate uranium as uranyl ammonium phosphate in an acetic acid solution while vanadium goes into the filtrate. The precipitation takes place according to this reaction:<sup>(2)</sup>



It was thought that this reaction could be made use of in this case as it would involve merely an exchange of reagents. Instead of using ammonium phosphate to precipitate uranium, the idea was to use a solution of uranyl nitrate to precipitate the ammonium phosphate. In making this modification, the process as last described was adhered to as far as to the nitric acid solution of the first precipitate. At this point a moderate excess of uranyl nitrate was added instead of the aluminum chloride. It was expected that the uranium would combine with the phosphorus from any dissolved aluminum phosphate upon acidifying with acetic acid to form uranyl ammonium phosphate, and as such, be precipitated with the aluminum phosphate. In sample I, the uranyl nitrate was added before the ammonia. This one gave no test for either.

-----  
 (1). Seamon - Manual for Assayers and Chemists, p. 136-7.

(2). Treadwell-Hall - Analytical Chemistry, Vol. I, p. 127.

phosphorus or vanadium in the filtrate from either precipitate, yet the final phosphorus obtained was very low. In sample II, the uranyl nitrate was added after the acidification with acetic acid. In this case it took no part in the reaction, but passed through the filter unchanged, which showed that it could not be depended upon to precipitate any dissolved phosphorus as was expected. The figures for these two determinations disagreed by a large margin though, with the exception noted, identical conditions were preserved throughout.

TABLE X.

<u>Wt. Fe taken.</u>	<u>Wt. P taken.</u>	<u>Wt. P recovered.</u>	<u>Wt. V taken.</u>
1. 1 gram	.002246 gms.	.001352 gms.	.007 gms.
2. 1 gram	.002513 "	.002068 "	.007 "

The several series of results recorded in tables V to X, inclusive, compelled the conclusion that phosphorus cannot be quantitatively precipitated from an acetic acid solution in the presence of vanadium under the conditions outlined. Since these modifications gave little promise of success, the idea of the separation of vanadium from phosphorus by means of acetic acid was dropped. Lack of

-----

time prevented further investigation into the causes for the failure of the process.

In casting about for some efficient way to effect the separation of vanadium from phosphorus, we thought that a radical modification of Johnson's<sup>(1)</sup> method might prove serviceable. The chief objection to Johnson's method is his slow, cumbersome, and rather difficult process for removing the iron. Instead of removing the iron by peroxidizing and filtering it off in the form of ferric hydroxide, a very great saving of time could be made by removing the iron by the Hess and Campbell method and then using Johnson's method for the separation of the vanadium from the phosphorus. As this was the procedure finally adopted, a detailed description of the procedure will now be given.

A mixture of the standard solutions in proportions indicated in Table No. XI is made in a 400 cc. beaker of tall form. When a steel sample is used it is obtained in solution, evaporated, baked and converted into the chloride by the process already described.<sup>(2)</sup> The solution either of the steel sample or the laboratory

---

(1). loc. cit.

(2). loc. cit.



standard, as the case may be, is then diluted to about 200 cc. volume. The solution is heated to nearly boiling and about forty five times the theoretical quantity of aluminum chloride solution is added and the solution neutralized with ammonia. The iron is then reduced by the addition of a concentrated solution of ammonium bisulphite with constant stirring until a pale blue color appears. The blue color is strong or weak at this point in proportion as a large or small amount of vanadium is present. Moreover, if chromium is present in the steel it obscures the blue color of the reduced vanadium, and complete reduction can then only be ascertained by testing a drop of the solution with potassium thiocyanate.

When the iron is entirely reduced, one or two cc. of phenylhydrazine are added slowly and with stirring to the hot solution. If no precipitate forms, ammonia is added drop by drop until a slight precipitate forms. Care should be taken at this point to distinguish between a precipitate of aluminum hydroxide and ferrous hydroxide which also forms. The ferrous hydroxide has a

-----

greenish color and can also be distinguished from aluminum hydroxide by the fact that it takes on a globular appearance, and, unless too much ammonia has been added, it will re-dissolve on vigorous stirring. If too much ammonia has been added, this may be remedied by adding a drop or two of weak hydrochloric acid. When the slight permanent precipitate of aluminum hydroxide and phosphate is obtained, a few more drops of phenylhydrazine are added to insure complete precipitation. The solution in a covered beaker is then boiled a few minutes to collect the precipitate. After settling, it is filtered and the precipitate is washed with a 5 or 10% solution of phenylhydrazine bisulphite until the washings give no test for iron with ammonium sulphide. Thereupon it is washed with hot water until the washings give no test for phenylhydrazine bisulphite with mercuric chloride. The precipitate is then dissolved off the filter into the original beaker with 20 cc. hot dilute nitric acid and all the acid is washed off the filter with hot water. The solution is diluted to 200 cc. volume and sodium peroxide is added about .5 gram at a time until any aluminum hydroxide which may have been formed is dissolved in excess alkali. Ten grams of sodium carbonate are then added and the solution

-----

is boiled for ten minutes in a covered beaker.

The aluminum phosphate is precipitated from this hot solution by the gradual addition of dilute hydrochloric acid with stirring until the liquid no longer turns turmeric paper to even a faint brown quickly. At this point the solution is still distinctly alkaline with sodium carbonate which keeps the vanadium in solution<sup>(1)</sup> and yet is sufficiently neutral to precipitate all the aluminum and phosphorus as aluminum phosphate.

The precipitate is allowed to settle and then filtered onto an eleven cm. filter, using paper pulp to mix with the precipitate so that it will be possible to wash it more thoroughly. The filtration can be most expeditiously done by putting a small amount of paper pulp in the filter and then decanting the solution onto it, allowing the precipitate to come on the filter last. In this way the paper pulp is just as efficient as if were stirred with the precipitate before filtering, and the filtration may be done much more rapidly when the bulk of the liquid can be decanted.

The precipitate is washed 15 or 20 times with

-----

(1). Mineral Resources of the U.S. - 1906 - p. 531.

a 1% solution of ammonium nitrate and then dissolved off the filter into the beaker in which the precipitation was made. This solution is washed into a 500 cc. Erlenmeyer flask taking care that all of the precipitate which was left in the beaker has been dissolved. The filter is then washed free from acid with the smallest possible amount of hot water, these washings being collected in the Erlenmeyer flask.

At this point it is most convenient to test for the presence of vanadium. If the solution is colored even a faint pink upon the addition of 1 or 2 cc. of hydrogen peroxide, not all the vanadium has been removed. The probability is that too much acid was used in precipitating the aluminum from the alkaline solution. The trouble may be easily remedied by again peroxidizing the solution and boiling with excess sodium carbonate and re-precipitating with hydrochloric acid, but unless care is taken to keep the solution distinctly alkaline the same trouble will occur again. With proper precautions in this respect, one precipitation is sufficient to remove all the vanadium in steels containing up to 1% of vanadium. If, however,

-----

at this point no pink color is produced by the addition of hydrogen peroxide, the solution is made alkaline with ammonia, the precipitate of aluminum redissolved with a slight excess of concentrated nitric acid and the phosphorus precipitated with ammonium molybdate and estimated by the Emmerton method as already described.

A comparatively long series by this method gave the following results:

TABLE XI.

<u>Wt. Fe taken.</u>	<u>Wt. P taken.</u>	<u>Wt. P recovered.</u>	<u>Wt. V. taken.</u>
1. 1 gram	.001946 gms.	.001957 gms.	.00675 gms.
2. 1 gram	.002148 "	.00222 "	.00675 "
3. 1 "	.00138 "	.00140 "	.00675 "
4. 1 "	.00236 "	.00234 "	.00675 "
5. 1 "	.00175 "	.00186 "	.00675 "
6. 1 "	.001874 "	.00183 "	.00675 "
7. 1 "	.00235 "	.00236 "	.00675 "
8. 1 "	.00190 "	.001898 "	.00675 "
9. 1 "	.00240 "	.002366 "	.00675 "
10. 1 "	.00193 "	.00200 "	.00675 "
11. 1 "	.00293 "	.00294 "	.00675 "
12. 1 "	.00222 "	.00231 "	.0270 "
13. 1 "	.00198 "	.00195 "	.0270 "
14. 1 "	.00176 "	.00175 "	.0270 "
15. 1 "	.00214 "	.00212 "	.0270 "

A slight modification of the procedure given above was made on determinations 10 to 15 inclusive. In these only half the excess of aluminum chloride prescribed by

-----

Johnson was added. This change materially shortened the process without interfering with its accuracy. It was thought that the excess of aluminum chloride could still further be diminished. Consequently in the subsequent determinations which were made on actual steels, the quantity of aluminum chloride added was again halved and the results showed that an excess of ten times the quantity theoretically required is sufficient. Six determinations were made on a Bureau of Standards sample of vanadium steel containing .15% vanadium and .035 % phosphorus with the following results:

TABLE XII.

<u>Wt. Steel taken.</u>	<u>Wt. P. recovered.</u>	<u>% P recovered.</u>
1. 1.2377 gms.	.000438 gms.	.0353
2. .8329 "	.000293 "	.0352
3. 2.9114 "	.00099 "	.0340
4. 2.5538 "	.000893 "	.0350
5. 3.543 "	.00123 "	.0347
6. 3.9635 "	.00142 "	.0356

In order to test this combination method on steels containing a larger percentage of vanadium, a

-----

number of determinations were made using plain steel to which a known quantity of vanadium was added. These samples were obtained in solution in the same manner as the vanadium steel and the vanadium was added to the hydrochloric acid solution. This steel contained .112% phosphorus <sup>that</sup> so, one gram samples gave suitable amounts with which to work. Four samples to which 1% vanadium was added, were analyzed with the following results:

TABLE XIII.

<u>Wt. Steel taken.</u>	<u>Wt. P recovered.</u>	<u>% P recovered</u>
1. 1.0462 gms.	.00115 gms.	.1099
2. 1.0088 "	.001142 "	.1132
3. 1.2064 "	.00134 "	.111
4. 1.1623 "	.00127 "	.109

An inspection of tables No. XI, XII, and XIII shows that the results obtained by a combination of the Hess and Campbell method with that of Johnson, using the several modifications of each as outlined, are within the limits of experimental error, and that the method can be successfully used with all the different proportions of vanadium found in steels. Furthermore, no exceptional

-----

skill is required to perform the various operations. A little extra care must be exercised to obtain just the right degree of neutrality in making the precipitations of aluminum phosphate as prescribed in the directions. The method is much shorter than the details of the procedure would lead one to to suspect, for practically all of the operations proceed with much despatch. It is very/shorter than either of the Johnson methods or the acetate method used by the Bureau of Standards, and is more satisfactory than the shorter methods is use in that the results are more reliable and the yellow precipitate is totally free from any orange tint, a circumstance which would rightly give rise to lack of confidence in the analysis.

It may properly be remarked here that since this work was undertaken, a short method for the determination of phosphorus in vanadium steels has been published by E. W. Hagmeier.<sup>(1)</sup> His method consists in reducing the hydrochloric<sub>A</sub> acid solution of the steel with sulphurous acid and precipitating the phosphorus in an acetic acid solution as cerium phosphate by the addition of 10 cc. of a saturated solution of cerium chloride. The cerium

-----  
(1). Met. and Chem. Eng. Vol. XI, No. 1, 1913, p. 28.



phosphate is washed five or six times with hot water and dissolved off the filter with dilute nitric acid and the phosphorus precipitated with ammonium molybdate in the usual manner. The phosphorus is weighed as ammonium phospho-molybdate using factor .0163 for the calculation. This method requires two precipitations for samples containing from .5 to 1% vanadium and three precipitations for samples containing from 1 to 5% vanadium. This method has been published so recently that we have not had time to test it thoroughly enough to warrant any statement about it at this time.

The method finally adopted by us seemed capable of several minor modifications calculated to shorten and simplify it. It was found, though the matter was not exhaustively investigated, that large amounts of vanadium are likely to require two precipitations of the phosphorus with hydrochloric acid from the alkaline solution to effect complete separation. It was thought that if the precipitation were made in a slightly stronger alkaline solution, the vanadium could all be kept in solution and the separation be complete with one

-----

precipitation. Four samples containing 3% vanadium were run and at the proper time dilute hydrochloric acid was added until the solution barely colored turmeric paper to a very faint brown immediately. The precipitate was filtered off and the filtrate was tested for phosphorus and an appreciable amount was found, showing that if the precipitate is made in a solution more strongly alkaline than that prescribed, some of the phosphorus is still held in solution.

Although no statement has been found in the literature regarding the solubility of quadrivalent vanadium in sodium carbonate, it was thought that the peroxidation of the nitric acid solution was not necessary. Hence four determinations were made using sodium carbonate only. The results were all high and the yellow precipitate in each case was more or less orange colored indicating the presence of vanadium. It appears that vanadium in the reduced form is less soluble in sodium carbonate than when in the oxidized form. Lack of time prevented running a sufficiently large number of determinations to warrant a definite statement regarding this point. It will be seen from Table No. XIV that the modification was not an

-----

advantageous one. A plain steel containing .112% phosphorus was used for this series. 1% vanadium was added.

TABLE XIV.

<u>Wt. Steel taken.</u>	<u>Wt. P recovered.</u>	<u>% P recovered.</u>
1. 1.3052 gms.	.00148 gms.	.1133
2. 1.4983 "	.00184 "	.122
3. 1.2347 "	.00148 "	.119
4. 1.5033 "	.00180 "	.119

An attempt was made to precipitate the aluminum phosphate from the nitric acid solution by adding a solution of sodium carbonate up to the point where the solution turns turmeric paper to a faint brown after a few seconds. The idea was to avoid the double process of going past the neutral point with alkali and then coming back with acid. A series of eight trials with this change gave such results that the modification cannot yet be recommended. We believe, however, that this idea can be used if a few cubic centimetres of hydrogen peroxide are first added to oxidize the vanadium before precipitating

-----

the phosphorus with sodium carbonate.

In conclusion we wish to state that although a method has been worked out for the determination of phosphorus in vanadium steels which gives good results and is in many respects an improvement upon methods already in use, the work is not yet to be regarded as finished. Lack of time prevented the investigation of the causes for the failure of several acetic acid separations which were tried. Moreover, it is also our intention to work out the application of the method to ferro-vanadium alloys, and to devise improvements on, and simplifications of the method which we at this time recommend for vanadium steels. We hope to be able to still further simplify the method and to apply it to the separation of large amounts of vanadium without a corresponding complication of the process. E