Direct Determination of Chromium and of Vanadium in Steel

o-Phenanthroline Ferrous Complex as Indicator

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After oxidizing chromium and vanadium in a steel by the perchloric acid method and adding a measured excess of ferrous sulfate to reduce the chromic and vanadic acids, the excess may be titrated at room temperature with standard permanganate, using o-phenanthroline ferrous complex as an oxidation-reduction indicator. The reaction between permanganate and vanadyl ions in this solution of high acidity is sufficiently slow so that an excellent end point is obtained. If the hydrogen-ion concentration of this solution is reduced and the temperature raised somewhat, the vanadyl ion may then be titrated with standard permanganate because the indicator has such a high oxidation potential that it is not affected by the vanadic acid formed in this reaction. This gives a rapid indicator method of determining both chromium and vanadium in a single sample.

The same double titration may be used after oxidation of the chromium and vanadium in a steel by the permanganate-azide or persulfate-hydrochloric acid method. Neither of these methods is as rapid as the perchloric acid method.

THE most exact methods at the present time for chromium involve the direct titration of the chromic acid, obtained from a persulfate or similar oxidation, with standard ferrous sulfate. The end point may be determined either potentiometrically or with an oxidation-reduction indicator. If vanadium is present in the steel, as is very often the case, vanadic acid is formed in the oxidation process, and this substance is titrated along with the chromic acid. It is necessary, then, to determine vanadium before the percentage of chromium can be estimated.

The desirability of the direct determination of chromium and of vanadium in steels has led to the suggestion of a number of methods, among which the following may be mentioned:

1. The excess of ferrous sulfate, remaining after the reduction of the chromic and vanadic acids, and the vanadyl salt may be titrated with standard permanganate (*5*). The accurate determination of this end point is difficult, especially if there is a large quantity of chromic salt in the solution, and a blank correction of rather indefinite value must always be applied. This titration has been made potentiometrically (*3*), but such a method cannot be recommended because of the very unsatisfactory character of the end point. If excess of ferrous sulfate is next added to reduce the slight excess of permanganate and the vanadic acid, and the excess removed by ammonium persulfate (*1*), a back-titration of the vanadyl salt with standard permanganate affords a method of obtaining vanadium on the same sample. The same difficulty with the end point, however, is encountered in this titration also.
2. Chromic acid may be titrated in the presence of vanadic acid with standard arsenite solution, the end point being determined potentiometrically (*13*). A very small amount of manganese must be present as catalyst, but the larger amounts usually present in steels lead to low results for chromium. All but a trace of manganese must be removed, therefore, before the titration, and it is desirable to remove most of the iron. After the chromium has been determined, the vanadic acid may be titrated potentiometrically in the same solution. Such a method for these elements is, obviously, not rapid.
3. After chromic and vanadic acids have been reduced with excess ferrous sulfate, the latter may be titrated potentiometrically at room temperature with standard ceric sulfate. The temperature of the solution is then raised to 70° to 75° C. and the vanadyl ion titrated potentiometrically with the same oxidizing agent (*11*).
4. Chromic acid may be reduced selectively in the presence of vanadic acid by a measured excess of standard arsenite (*2*). The excess of arsenite as well as any trace of vanadium which may have been reduced is titrated with standard permanganate, and a direct determination of chromium thereby obtained. The end point which is determined visually is described as satisfactory; a blank correction is required. A drop of arsenite is then added to the solution to reduce the slight excess of permanganate and the vanadic acid is titrated with standard ferrous sulfate, using diphenylbenzidine as an oxidation-reduction indicator. The results listed by the authors for chromium and vanadium in standard steels indicate that this method for chromium is fairly accurate.
5. Lang and Kurtz (*4*) have described a number of procedures for chromium and vanadium. Their results on steels, however, are not compared with those obtained by standard methods.

It is evident that direct indicator methods for chromium and for vanadium which are rapid and exact are needed, and the object of the present investigation has been to develop such methods.

THEORETICAL CONSIDERATIONS

From the reactions:

$$Fe^{++} \rightleftarrows Fe^{+++} + e$$
$$\text{and } VO^{++} + 2H_2O \rightleftarrows VO_3^- + 4H^+ + e$$

one would conclude that the oxidation potential of the ferric-ferrous system should not be appreciably influenced by a change in hydrogen-ion concentration of the solution, whereas that of the vanadate-vanadyl system should be considerably altered under similar conditions. Figure 1 illustrates this point for the latter system.

With an indicator of such high oxidation potential that it is not oxidized by vanadic acid, it should be possible in a mixture of ferrous, vanadyl, and chromic salts to obtain under proper experimental conditions two end points when titrating with a strong oxidizing agent. If the titration is commenced at room temperature in a solution of high hydrogen-ion concentration, the reaction between ferrous ion and the oxidizing agent should be rapid, while that between vanadyl ion and the oxidizing agent should be sufficiently slow, due to the lower reducing power of the vanadyl ion in such a solution, so that a good end point could be obtained when all ferrous ion is oxidized. This has been shown to be true when ceric sulfate is the oxidizing agent used in a solution 5 *M* in sulfuric acid (*7*). In the following pages it will be shown that when permanganate is used, the same effect is obtained in a solution only 1 M in sulfuric acid. As the velocity of the reaction between vanadyl and permanganate ions is largely a function of the hydrogen-ion concentration of the solution and of its temperature, it should be possible, after reducing the acidity and raising the temperature of the solution, to titrate the vanadyl ion with permanganate, the indicator already present serving for this second end point.

o-Phenanthroline ferrous complex, an indicator of unusually high oxidation potential which has recently been described (*8*), appears to meet the necessary requirements, as it is not oxidized by vanadic acid in a moderately acid solution and is sufficiently stable for use at a temperature as high as 50° C. The indicator is red in color in reduced form and a very pale blue in oxidized form.

The experimental work which follows substantiates these theoretical considerations and shows their applicability to direct indicator methods for both chromium and vanadium in steel.

EXPERIMENTAL METHODS FOR STEELS WITHOUT TUNGSTEN

REAGENTS AND SOLUTIONS. The 0.05 N potassium permanganate was standardized by potentiometric titration against sodium oxalate from the U. S. Bureau of Standards.

The ferrous sulfate solution, prepared either from ferrous sulfate or from ferrous ammonium sulfate, contained 20 cc. of sulfuric acid (specific gravity, 1.5) per liter and was standardized each day against the 0.05 N potassium permanganate. If the perchloric acid method for chromium is used, the standardization of the ferrous sulfate should be carried out in a dilute perchloric acid solution with *o*-phenanthroline ferrous complex as indicator; with the permanganate-azide or persulfate method for chromium, the same titration should be made in a dilute sulfuric acid medium. A ferrous sulfate solution standardized by the former method was found to be 0.09949 N, and by the latter method 0.09919 N. This discrepancy, which is probably due to the fact that the indicator dissolves only slowly in the perchloric acid solution, is insignificant except with small samples of steels of high chromium content, and in any event disappears if the proper acid medium is used in standardizing the ferrous sulfate.

Since, in the reaction between *o*-phenanthroline and ferrous ion, three molecules of the former combine with one of the latter, a 0.025 M solution of the indicator may be prepared by dissolving the correct amount of *o*-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$) in a 0.025 M aqueous solution of ferrous sulfate. Ordinarily two drops of this 0.025 M indicator solution are sufficient to afford a very sharp color change in steel analyses.

PERCHLORIC ACID METHOD. This method for chromium in steels without tungsten has been developed by Willard and Gibson (*9*). Their procedure, using perchloric acid both as solvent and oxidizing agent, was followed. After the oxidation was complete, the solution was cooled quickly,[1] diluted somewhat, boiled to remove chlorine, and then diluted further and cooled in running water. Experiments showed that after a measured excess of ferrous sulfate had been added to reduce the chromic and vanadic acids, the ferrous sulfate alone could be titrated at room temperature with standard permanganate, with *o*-phenanthroline ferrous complex as indicator, and a rapid and very sharp end point obtained, because at this acidity and temperature the reaction between vanadyl and permanganate ions is quite slow. If the hydrogen-ion concentration of the solution is then reduced by adding sodium acetate, and the temperature raised to 50° C., the red color of the reduced indicator returns and the vanadyl ion is easily titrated with further permanganate solution. A temperature of 50° C. seemed most satisfactory, for at higher temperatures too much of the indicator was destroyed, while at much lower temperatures the reaction was not sufficiently rapid. The end point in this second titration was considered as reached when the solution was a clear bluish green in color and when there was no return of any pink color after an interval of a minute. From the total volume of permanganate solution used, the percentage of chromium may be calculated directly, and from the difference between the first and second volumes of the permanganate, the percentage of vanadium may be determined. Obviously this procedure, which affords a determination of both chromium and vanadium in one sample, is very rapid—not more than a half-hour is required to weigh and prepare samples for the final titration. This method has the further advantage of giving an excellent end point at room temperature in the first step in the titration, while with the permanganate-azide or persulfate method either considerable acid must be added or the solution cooled to 5° to 6° C. before the titration of the excess ferrous sulfate. If the amount of vanadium is so small that large samples must be taken, the color of the chromic salt will be so intense as to render the end point indistinct. Results obtained on a number of steels by the perchloric acid method are given in Table I.

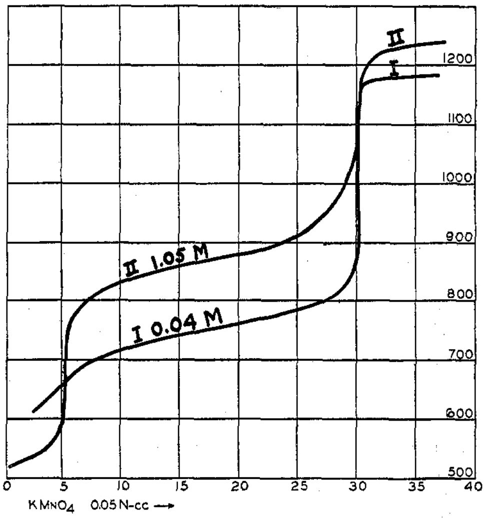

FIGURE 1. TITRATION OF MIXTURE OF FERROUS SULFATE AND VANADYL SULFATE WITH POTASSIUM PERMANGANATE

Solution I, 0.04 M in sulfuric acid; solution II, 1.05 M in sulfuric acid; temperature, 25° *C.*

TABLE I. DIRECT DETERMINATION OF CHROMIUM AND OF VANADIUM IN STEELS WITHOUT TUNGSTEN. PERCHLORIC ACID METHOD

Steel		Samples			
		I	II	III	IV
		%	%	%	%
B. S. 30 (*c*)	Cr	0.973	0.971	0.972	0.973
(0.977% Cr; 0.235% V)	V	0.234	0.239	0.237	0.237
B. S. 30 (*a*)	Cr	1.022	1.024	1.024	1.025
(1.02% Cr; 0.20% V)	V	0.208	0.201	0.201	0.203
Cr-V Steel*	Cr	0.917	0.925	0.919	0.920
(0.918% Cr; 0.134% V)	V	0.140	0.142	0.142	0.137
B. S. 72	Cr†	0.917	0.918	0.918	0.916
(0.911% Cr; 0.012% V)					
B. S. 73	Cr	13.89	13.85	13.84	13.94
(13.93% Cr; 0.034% V)					

* Chromium plus vanadium determined after persulfate oxidation by titration with ferrous sulfate, using diphenylbenzidine as indicator (*10*). Vanadium determined by permanganate-azide method (*12*).

† The vanadium is equivalent to 0.004 per cent of chromium and this value should be subtracted from each of those listed to obtain the correct percentage of chromium.

Two-gram samples of the first four and 0.25-gram samples of the last steel were used. The titration was made only to the first end point in analyzing the last two steels.

RECOMMENDED PROCEDURE, PERCHLORIC ACID METHOD. Weigh a sample of suitable size, varying from 2 grams with low chromium to 0.25 gram with stainless steels, into a 500-cc. lipped beaker of tall form or into a 500-cc. Soxhlet flask. If the latter is used, the watch glass should be placed on very thin glass hooks

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[1] G. F. Smith in a private communication to the authors has pointed out the desirability of cooling the solution quickly to prevent any reduction of chromium, which may be caused by the per-acid properties of the perchloric acid in a hot, concentrated solution.

or on a bent platinum wire about 1 mm. in diameter to prevent the formation of a liquid seal when the contents of the flask are heated. Add 20 to 25 cc. of 70 per cent perchloric acid (depending on the size of the sample) and heat very slowly to prevent the reaction from becoming violent. After the steel has dissolved (usually only 3 to 5 minutes will be required) boil the solution for 15 to 20 minutes. The longer period is better for high-chromium steels. Cool the flask and contents a moment in the air and then in a stream of running water. Add 25 cc. of water, rinse off the watch cover into the beaker, and boil the solution for 3 minutes to remove all chlorine. Dilute the liquid to 250 to 300 cc. and cool in running water. If the steel contains more than a trace of vanadium so that two end points are to be determined in the titration with standard permanganate, 15 cc. of phosphoric acid (specific gravity, 1.37) are added most conveniently at this point. Add to the solution at room temperature a measured excess of 0.1 N ferrous sulfate, and then two or three drops of 0.025 M *o*-phenanthroline ferrous complex. Much of the indicator precipitates, but sufficient of it is dissolved for the first end point and all of it dissolves on heating the solution before the second titration is commenced.

Titrate immediately after the addition of the indicator with 0.05 N potassium permanganate until the color of the solution changes from pink to a clear green. The end point is very sharp and there is almost no return of the pink color for a minute or more. Add sufficient crystallized sodium acetate to react with the free perchloric acid present. The amount of this salt required may be estimated approximately by considering that 5.4 cc. of 70 per cent perchloric acid are used to decompose and oxidize each gram of steel and that 1.6 grams of the acetate will be required for each cubic centimeter of the acid remaining. If preferred, the acetate may be added in small portions to the solution while it is being heated, until the addition of further acetate would cause the formation of a permanent precipitate of ferric phosphate. Heat the solution to 50° C., using a thermometer as stirring rod, and titrate the vanadyl ion at once with the 0.05 N permanganate. The oxidizing agent should be added slowly, as only a small volume of it will be required and also because the reaction between vanadyl and permanganate ions is not instantaneous. The color change at the end point is the same as in the first titration and the end point is considered as reached when there is no return of a pale pink shade during an interval of a minute. It is sometimes advisable to add a drop more of indicator before titrating the vanadium.

To determine the normality of the ferrous sulfate solution, add sufficient of it to require 35 to 50 cc. of the permanganate to 250 cc. of water containing 10 to 15 cc. of 70 per cent perchloric acid. Add 2 drops of 0.025 M *o*-phenanthroline ferrous complex and titrate at once with the standard permanganate solution.

PERMANGANATE-AZIDE AND PERSULFATE METHODS. In a previous paper (*12*) the authors have pointed to the possibility of using sodium azide to destroy all permanganate and thus of avoiding a filtration in the permanganate method (*6*) for chromium plus vanadium in steels without tungsten. Since the procedure for the permanganate method in this modified form is shorter than that for the persulfate method, it seemed important to ascertain the conditions under which the former might be used for the direct determination of chromium or of both chromium and vanadium on the same sample.

Samples of steel were dissolved in a mixture of sulfuric and phosphoric acids, and the ferrous salts and carbonaceous matter oxidized in the usual way with nitric acid. After dilution, the vanadyl and chromic salts were oxidized in hot solution with potassium permanganate, and the excess of the latter removed by careful addition of sodium azide to the boiling hot solution. All hydrazoic acid was removed by boiling, and the solution was then cooled in running water. A measured excess of ferrous sulfate was added at room temperature and an attempt was made to titrate the ferrous and vanadyl salts with a standard permanganate solution, using *o*-phenanthroline ferrous complex as indicator. After the ferrous sulfate was oxidized, the reaction, as was to be expected, became very slow. If the hydrogen-ion concentration of the solution was then reduced by the addition of sodium acetate and the temperature raised to 50° C., the vanadyl ion was easily titrated and a satisfactory end point obtained. The hydrogen-ion concentration of the solution may be reduced, if preferred, before any ferrous sulfate is added. The results for chromium on a number of steels which were analyzed in this way are recorded in the first column of Table II.

Since the oxidation by persulfate in the presence of silver ion is a standard procedure for chromium, analyses were made using this method. After the excess of persulfate had been removed by boiling, 1 to 3 hydrochloric acid was added to destroy the permanganate formed during the oxidation process, and the solution was then boiled to remove all chlorine. From this point the procedure was the same as that just given for the permanganate-azide method. Results are shown in the second column of Table II.

Experiments in which sodium azide was substituted for the hydrochloric acid after a persulfate oxidation (*12*) always led to high results for chromium. In such a procedure the silver ion is not precipitated, and may possibly cause interference later either by acting catalytically or as an oxidizing agent in the solution of low acidity. A study of the action of silver ion in synthetic mixtures similar to steels did not confirm either of these suppositions and the cause for high results here is still unexplained.

TABLE II. DIRECT DETERMINATION OF CHROMIUM IN STEELS WITHOUT TUNGSTEN. PERMANGANATE-AZIDE AND PERSULFATE–HYDROCHLORIC ACID METHODS

STEEL	METHOD FOR CHROMIUM $KMnO_4$-NaN_3	 $(NH_4)_2S_2O_8$-HCl
B. S. 30 (*c*) (0.977% Cr; 0.235% V)	0.970, 0.992, 0.980, 0.966	0.996, 0.981 0.985, 0.981
B. S. 30 (*a*) (1.02% Cr; 0.20% V)	1.04, 1.02, 1.02, 1.02	1.03, 1.05, 1.03, 1.03
B. S. 72 (0.911% Cr; 0.012% V)	0.908, 0.915, 0.912, 0.905	0.916, 0.920, 0.921, 0.931
B. S. 73 (13.93% Cr; 0.034% V)	13.95, 13.94, 13.93, 13.89 (13.85, 13.94, 13.88, 13.78)*	13.71, 13.79, 13.84, 13.87
B. S. 101 (17.54% Cr; 0.044% V; 8.44% Ni)	17.56, 17.60, 17.54, 17.51	17.42, 17.66, 17.58, 17.52
B. S. 64 (67.9% Cr; 0.11% V)	67.83, 67.83	

* After the steel had dissolved, vanadium equivalent to 2.5 per cent was added and the usual permanganate-azide procedure followed.

Two-gram samples of the first three steels, 0.25-gram samples of the fourth and fifth, and an aliquot portion of a 0.5-gram sample of the last were used.

Because of the low percentage of vanadium in Nos. 72, 73, 101, and 64 (as compared with the chromium content), it is unnecessary to reduce the hydrogen-ion concentration of the solution or to raise the temperature before the end point is reached. In fact, the ferrous sulfate must be titrated at room temperature and the volume of permanganate for this titration may be considered the final volume.

TABLE III. EFFECT OF VARYING ACIDITY ON DETERMINATION OF CHROMIUM

H_2SO_4 Sp. Gr. 1.5	H_3PO_4 Sp. Gr. 1.37	Fe	V	NaAc-$3H_2O$	$FeSO_4$ 0.05 N	$KMnO_4$ 0.05 N	CHROMIUM PRESENT	CHROMIUM FOUND
Cc.	*Cc.*	*Gram*	*Gram*	*Gram*	*Cc.*	*Cc.*	*Gram*	*Gram*
6	0	0	0	0	20	15.54	0.02252	0.02244
6	0	0	0	15	20	15.82	0.02252	0.02221
6	10	0	0	0	50	16.09	0.07505	0.70507
6	10	0	0	15	50	16.36	0.07505	0.07482
6	10	1	0	0	20	15.56	0.02252	0.02242
6	10	1	0	15	20	15.87	0.02252	0.02215
6	10	1	0.005	15	20	15.84	0.02252	0.02218
6	10	0.25	0.005	15	20	15.82	0.02252	0.02221

In the analysis of steel 64, results which were 0.4 to 0.5 per cent low were invariably obtained if the excess of ferrous sulfate was titrated in a solution of low acidity. This error, which corresponds to 0.2 mg. of chromium for the size of sample used, would therefore be negligible for low-chromium steels.

To investigate this error a standard dichromate solution was treated with sulfuric acid, and in some cases with sodium acetate, phosphoric acid, ferric alum, chromic sulfate, and vanadyl sulfate solutions before a measured excess of ferrous sulfate was added. The volume of the solution in every case after the addition of the ferrous sulfate was 300 cc. Two drops of 0.025 M *o*-phenanthroline ferrous complex were added and the titration with permanganate was carried out, the solution being heated to 50° C. after the ferrous sulfate had been oxidized if there was any vanadium present. The results of a number of experiments are given in Table III.

These experiments indicate that the error caused by titrating the ferrous and vanadyl salts with permanganate in a solution of low acidity is an absolute error and so small as to be negligible except in cases such as B. S. steel 64, where the chromium content is very high.

Only the permanganate-azide method was used in investigating the possibility of determining both chromium and vanadium on the same sample of steel, as this method is more rapid than the persulfate method. Steel samples were prepared as just described and the final solution containing chromic and vanadic acids was cooled in running water. If a measured excess of ferrous sulfate was added to such a solution, followed by two drops of the indicator, and the ferrous sulfate alone was titrated with permanganate, it was impossible to obtain an end point because the hydrogen-ion concentration of the solution was not high enough to make the rate of oxidation of the vanadyl ion by the oxidized indicator sufficiently low. Numerous experiments, however, indicated that a sharp end point could be obtained in the titration of the ferrous sulfate in either of two ways: by cooling the solution so that its temperature at the end of the titration was not above 6° to 8° C., or by titrating at room temperature after the addition of considerable sulfuric acid. The first method is preferable, as the hydrogen-ion concentration of the solution must in any case be reduced before the titration of the vanadyl salt. The necessary concentration of acid for a titration at room temperature is indicated in the procedure given later. In the analyses listed in Table IV, the temperature of the solution at the first end point was 6° to 8° C. The hydrogen-ion concentration was then reduced by adding sodium acetate and the temperature of the solution raised to 50° C. before the titration of the vanadyl salt was made.

Table IV. Direct Determination of Chromium and of Vanadium in Steels without Tungsten. Permanganate-Azide Method

Steel		Samples			
		I	II	III	IV
		%	%	%	%
B. S. 30 (*c*) (0.977% Cr; 0.235% V)	Cr	0.972	0.977	0.977	0.973
	V	0.232	0.226	0.230	0.236
B. S. 30 (*a*) (1.02% Cr; 0.20% V)	Cr	1.019	1.028	1.030	1.015
	V	0.203	0.206	0.194	0.206

Recommended Procedure, Permanganate-Azide Method. Place a 2-gram sample in a 600-cc. beaker, add 15 cc. of water and 15 cc. of phosphoric acid (specific gravity, 1.37), and run in a measured volume of sulfuric acid (specific gravity, 1.83) from a buret. Allow 1.5 cc. of the latter for each gram of steel and 3 cc. excess. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 cc. of water and heat until the salts have dissolved. Add nitric acid (specific gravity, 1.42) in small portions to the hot liquid until the violent oxidation of ferrous sulfate is over (2 to 3 cc. of acid are sufficient). Avoid any appreciable excess. Boil the solution to destroy oxides of nitrogen and dilute to 300 cc. A few small pieces of broken porcelain in the solution will prevent bumping later. Heat to boiling, add a 2 per cent permanganate solution until a deep purple color remains, and boil the solution for 2 minutes. Add 0.1 M sodium azide (do this in a hood) to the boiling hot solution until a few drops excess are present. It is very important that the solution be boiling hot during the addition of the azide, especially if manganese dioxide is present. The azide will destroy the permanganate color first. Then add further azide, drop by drop, while stirring constantly until the solution clears. Boil for 5 minutes to remove all hydrazoic acid and cool the solution in running water. From this point either of two procedures may be used if both chromium and vanadium are to be determined on the same sample:

A. After adding 10 cc. of sulfuric acid (specific gravity, 1.5), cool the solution in ice to 5° C. or lower. Add a measured excess of 0.1 N ferrous sulfate and two drops of 0.025 M *o*-phenanthroline ferrous complex. Titrate the ferrous sulfate at once with 0.05 N permanganate solution. The change in color from pink to a clear green at the end point is very sharp. In a short time, however, the pink shade begins to return. To reduce the hydrogen-ion concentration of the solution, add slowly while stirring 10 cc. of concentrated ammonium hydroxide and then crystallized sodium acetate until more would cause a permanent precipitate of ferric phosphate. Twenty grams will be found the correct amount if the quantity of sulfuric acid specified above has been used. Heat the solution to 50° C., using a thermometer as stirring rod, and titrate the vanadyl salt at this temperature with the standard permanganate. (See procedure under the perchloric acid method for the precautions to be observed and the character of the end point.)

B. To the solution at room temperature to which 35 cc. of sulfuric acid (specific gravity, 1.5) have been added, add a measured excess of 0.1 N ferrous sulfate, and proceed as directed under *A*. The first end point is sharp here but less permanent as the pink color of the indicator appears again much more quickly, owing to its reduction by the vanadyl salt. Add slowly, while stirring, 25 cc. of concentrated ammonium hydroxide and then crystallized sodium acetate as in *A*. Approximately 30 grams will be required. Proceed from this point as directed under *A*.

To determine the normality of the ferrous sulfate solution, add sufficient of it to require 35 to 50 cc. of the permanganate to 250 cc. of water containing 10 cc. of sulfuric acid (specific gravity, 1.5). Add 2 drops of 0.025 M *o*-phenanthroline ferrous complex and titrate at once with the standard permanganate solution.

If only chromium is to be determined, cool the solution containing chromic and vanadic acids in running water and reduce the hydrogen-ion concentration by adding crystallized sodium acetate as in *A* above. Add a measured excess of 0.1 N ferrous sulfate, 2 drops of 0.025 M *o*-phenanthroline ferrous complex, and titrate at room temperature with 0.05 N permanganate. If it is impossible to obtain an accurate end point, the presence of vanadium is indicated. In such a case heat the solution, after the ferrous iron has been titrated, to 50° C. and complete the titration as directed in *A*. If a sharp and permanent end point is obtained at room temperature, heat the solution as usual to 50° C. to determine whether there is any return of the pink color. If there is, complete the titration of the vanadyl salt at 50° C. with the permanganate. If no pink color appears in the solution on heating, the end point obtained at room temperature is considered the final end point. In such a case, the acidity of duplicate samples of the same steel should not be decreased before the titration with the standard permanganate.

Application of Methods to Steels Containing Tungsten

Attempts to develop an indicator method for the direct determination of chromium and of vanadium in chrome-vanadium-tungsten steels were not successful. If the tungsten was kept in solution as a complex fluoride and the persulfate–hydrochloric acid method was used to obtain chromic and vanadic acids (*12*), it was found that, after the addition of a measured excess of ferrous sulfate, the determination of the excess of this reducing agent by titration with standard permanganate was not satisfactory, as the color change at the end point was not sharp. Quantitative results can be obtained in this titration if the solution is cooled to 5° to 8° C., or if the acidity is high, but the direct titration of the chromic and vanadic acids in such a solution with standard ferrous sulfate, using oxidized diphenylamine sulfonic acid as indicator, is much to be preferred, as in this case a very sharp end point is obtained. As was to be expected, it was impossible in continuing the titration with permanganate to obtain an end point in the titration of the vanadyl salt, because of the formation of a complex manganic fluoride.

When phosphoric acid was used instead of hydrofluoric acid to keep the tungsten in solution, a dark brown color developed upon the addition of excess ferrous sulfate. This color, which was caused possibly by a complex phospho-vanado-tungstic acid, disappeared only slowly when permanganate was added to the solution. An end point when all ferrous and vanadyl ions were oxidized could not be detected.

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Iodine Value of Rubber and Gutta-Percha Hydrocarbons

As Determined by Iodine Chloride

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The reactivity of various halogens towards rubber and gutta-percha hydrocarbons has been studied quantitatively. The behavior of both hydrocarbons toward halogens is very similar. The order of reactivity of the halogens is chlorine, bromine, iodine chloride, iodine bromide, and iodine. The results show that gutta-percha possesses a greater initial reactivity towards iodine than does rubber.

Data and detailed procedure are presented which offer further refinements to the iodine chloride method for the determination of the unsaturation of rubber and gutta-percha hydrocarbons.

Methods for the preparation of pure rubber and gutta-percha hydrocarbons are included and the corresponding iodine values found by the use of modified iodine chloride procedure are shown to be in close agreement with the theoretical.

It is recommended, in the case of gutta-percha hydrocarbon, that a greater excess of iodine chloride be used and that the reaction be carried on at room temperature for a longer period of time than that required for rubber.

HALOGEN absorption methods employing solutions of bromine, iodine bromide, or iodine chloride are widely used for determining the unsaturation of organic compounds. In the use of these methods the choice of halogen reagent, the amount employed, and the time and temperature for the reaction are all important factors which must be given careful consideration in order that the best results may be obtained. Certain structural differences in unsaturated organic compounds may have a decided influence on the reactivity of these substances toward halogens. For example, the presence of negative groups on one or both of the unsaturated carbon atoms protects against halogen addition; thus maleic or fumaric acids do not add iodine chloride (*7*). Styrene adds iodine chloride quantitatively, but in the case of cinnamic acid only a slight reaction takes place (*4*). No addition of iodine chloride occurs with dichloroethylene and very little with vinyl bromide (*3*). The authors have found that polyvinyl chloride (Du-Prene) adds iodine chloride to only 30 per cent of theory. A triple-bonded compound, such as diphenylacetylene (*4*), shows only partial addition of iodine chloride, as would be expected from the negative effect of the first additive halogen. The unsaturated terpenes vary widely in their reactivity with halogens, extensive substitution occurring along with addition (*5*), particularly in the case of pinene. Aside from these complications, however, numerous investigators have shown that one or more of the halogens add quantitatively to a wide range of unsaturated hydrocarbons, acids, glycerides, alcohols, esters, etc. Of the many methods proposed the well-known Wijs procedure involving the use of 0.2 *N* iodine chloride in glacial acetic acid has been widely used and accepted.

In a previous investigation (*5*), various halogen absorption methods for determining the unsaturation of rubber and gutta-percha were studied and it was found that the Wijs reagent (iodine chloride in glacial acetic acid) was the most satisfactory for this purpose. It was shown that under suitable conditions iodine chloride adds quantitatively to the double bonds in rubber hydrocarbon in close agreement with theory—i. e., one molecule of iodine chloride adds to each C_5H_8 grouping. This is equivalent to a theoretical iodine value of 372.8 and values found by the iodine chloride method for pure rubber hydrocarbon agree to within less than 0.5 per cent of this figure.

The method previously described (*5*) involves swelling 0.10-gram samples of rubber, etc., in 75 cc. of carbon bisulfide, adding 25 cc. of 0.2 *N* iodine chloride in glacial acetic acid, allowing the solution to stand 2 hours at 0° C., and titrating the excess iodine chloride with 0.1 *N* sodium thiosulfate immediately after addition of potassium iodide solution, using starch as the indicator. Excellent results were also obtained by allowing the reaction to proceed at room temperature for one hour, although substitution occurred slowly at this temperature. Since conducting the reaction under ice-cooling is a troublesome feature, one of the purposes of the present investigation was to determine the best conditions for operating at room temperature without sacrifice in the accuracy of the method. Another related objective was to determine if any differences exist between rubber and gutta-percha hydrocarbons with respect to their reactivity towards iodine chloride and other halogens. This phase of the study is of