

	Amounts present.	Amounts found.
Chromium.....	1.387	1.393
Nickel.....	3.650	3.680
Vanadium.....	0.234	0.234
Molybdenum.....	1.260	1.250

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A NEW METHOD FOR THE DETERMINATION OF VANADIUM IN IRON AND STEEL.

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When vanadium is to be determined in the presence of a comparatively small amount of iron, the separation of the vanadium may be easily effected by the well known method of fusion of the oxides with sodium carbonate and extraction with water. When, however, the amount of vanadium present is under 0.5 per cent., as in the case of vanadium steel, and pig irons, the sample used must be so large that trouble is usually experienced from the amount of sodium carbonate required for the fusion.

Campagne¹ describes a method for the determination of vanadium in the absence of chromium, based upon the extraction of most of the iron by the well known "ether method" and the titration of the divanadyl sulphate obtained by repeated evaporation of the aqueous solution first with hydrochloric acid and finally with excess of sulphuric acid. When chromium is present in steel or iron, as is frequently the case in special steels, its presence renders the determination of vanadium much more difficult than would otherwise be the case. The following methods for the qualitative detection of vanadium and for its quantitative determination in steel and iron have been found to give satisfactory results in this laboratory. The detection depends upon the fact that where vanadium is present in steel or iron and the metal is dissolved in dilute sulphuric acid, a considerable proportion of the vanadium will remain in the insoluble residue, from which it may be extracted by fusion with sodium carbonate and its presence detected by the well known oxidation to the red pervanadic acid by addition of hydrogen peroxide to the cold solution after acidification with nitric acid.

The quantitative separation of the vanadium is based upon two principles, new, so far as we are aware, in their application to analytical work. First, that when vanadium and chromium are in solution, as sulphates in a concentrated solution of ferrous sulphate, this latter may be almost completely precipitated as coarse easily filtered crystals by

¹ *Compt. rend.*, 137, 570 (1903). See Blair's *Chemical Analysis of Iron*, 6th edition, p, 204.

the addition of not less than three volumes of alcohol, while the vanadium and chromium remain in solution. Second, that where a mixture of oxides containing iron, manganese, chromium and vanadium is first fused with sodium carbonate alone, and then the fusion continued after the addition of a small amount of some reducing agent, such as charcoal, the sodium chromate formed during the first portion of the fusion will be reduced to insoluble chromic oxide so that the soluble sodium vanadate may be readily extracted with water, thus effecting a sharp separation of vanadium from chromium. The details of manipulation for the qualitative detection of vanadium in steel and iron, and for its quantitative determination are as follows:

The Qualitative Detection.—Place five grams of the sample in a 250 cc. Florence or Erlenmeyer flask, add 25 to 30 cc. of water and 14 cc. of sulphuric acid, sp. gr. 1.51 (prepared by pouring concentrated sulphuric acid into an equal volume of water). Cover the flask with an inverted porcelain crucible cover and maintain at the boiling point until action ceases. Filter and wash the insoluble residue with water slightly acidified with sulphuric acid. Usually about half the vanadium will be found in this insoluble residue. Place the filter paper in a platinum crucible, char at a low heat and burn off the carbon from the filter paper. In the case of steels, the residue will be quite small, but if pig iron is being examined, the residue will contain the graphitic carbon and the greater portion of the silica derived from the oxidation of the silicon in the iron. In the latter case, after burning off the filter paper, the temperature of the crucible should be raised until the graphitic carbon is all burned off and then the silica should be volatilized by means of hydrofluoric acid before testing for vanadium.

Fuse the insoluble residue, after burning off the graphitic carbon and volatilizing the silica, with 3 grams of sodium carbonate. After fusing for 10 minutes at a moderate red heat, cool and digest with 25 to 30 cc. of hot water. Remove the crucible, filter, acidify the filtrate with nitric acid and concentrate to 10 or 12 cc. Cool to room temperature and add one or two drops of hydrogen peroxide. If vanadium is present to the extent of 0.1 mg. it will be indicated by a pink or red coloration, due to the presence of pervanadic acid. The depth of color is dependent upon the amount of vanadium present and an approximate idea of the percentage of vanadium may be obtained from this depth of color of the pervanadic acid.

Quantitative Determination.—Dissolve 5 grams of the sample in the same manner as for the qualitative detection of vanadium. When the iron is all in solution as ferrous sulphate, filter out the insoluble residue, but wash with pure hot water instead of water acidified with sulphuric acid. Treat this insoluble residue as for the qualitative detec-

tion of vanadium up to the point where the sodium carbonate for fusion is to be added. Set aside the residue for the present. Having allowed the filtrate and washings to run into a 250 cc. Erlenmeyer flask, boil down to about 50 cc., then pass in hydrogen sulphide for 5 minutes to reduce any ferric sulphate to ferrous sulphate and to precipitate copper or arsenic, if these elements are present.

Cover the flask with an inverted porcelain crucible cover and boil the solution down to remove the excess of hydrogen sulphide and to reduce the volume to about 35 cc. Remove the flask from the hot plate and cool under the tap to room temperature; if the volume is not reduced below 35 cc. no ferrous sulphate will crystallize out upon thus cooling. After cooling, rotate the flask and add gradually 100 cc. of ordinary ethyl alcohol (the amount of alcohol added should be at least three times the volume of the ferrous sulphate solution). Denatured alcohol seems to give as good results as the pure ethyl alcohol.

After adding the alcohol, stopper the flask, cool, if not perfectly cold, and shake at frequent intervals for 5 or 10 minutes to complete the precipitation of nearly all the iron as ferrous sulphate. Filter the crystallized ferrous sulphate into an Erlenmeyer flask and wash with alcohol diluted with $\frac{1}{3}$ its volume of water. If moderate suction is used in filtering out the ferrous sulphate, the crystallized salt is very thoroughly and easily washed. Rinse the filtrate and washings into a 600 cc. beaker, using 100 cc. of water for this purpose. Add 15 or 20 cc. of hydrogen peroxide in order to oxidize the small amount of ferrous sulphate still in the solution. Bring the solution to a boil and then to this nearly boiling solution add sodium carbonate until there is a slight but distinct alkaline reaction of litmus. Keep the solution at the boiling point for 10 or 15 minutes until the precipitate, which contains all the iron, chromium, manganese and vanadium, has turned darker in color and has become flocculent. Filter and wash thoroughly with a hot 0.5 per cent. solution of sodium carbonate, in order that all the soluble sulphates may be washed out. Dry the precipitate.

Then place in a platinum crucible, together with the insoluble residue which has been saved from the first step of the analysis. Cover the crucible, char the filter at a low heat, then remove the cover and complete the ignition. Allow the crucible to cool, add 5 grams of sodium carbonate, mix thoroughly with the ignited precipitate and fuse for 15 or 20 minutes in the covered crucible. The fusion should be carried on carefully to avoid spattering and the heat should not be raised above a moderate red, or just enough to keep the sodium carbonate fluid. After fusing for 15 or 20 minutes with the sodium carbonate alone, remove the cover from the crucible, add 300 or 400 mg. of powdered charcoal, replace the cover and raise the heat to a moderate red, or just sufficient

to maintain fluidity, for 10 minutes longer. Cool and extract the fused melt with 25 or 30 cc. of hot water.

By fusing with sodium carbonate alone, the vanadium will be converted into the soluble sodium vanadate, but part of the chromium, which is usually present in the special steels, will be oxidized to sodium chromate. The addition of charcoal and the continuation of the fusion for 10 minutes reduces the sodium chromate to chromic oxide but does not affect the extraction of the vanadium, so that a very sharp separation of chromium from vanadium is obtained. When the disintegration of the melt is complete, filter and wash well with hot water. The filtrate will contain all of the vanadium, but no chromium. The filtrate should be either colorless or slightly tinged with yellow, due to the presence of sodium sulphide, if the sulphates were not completely washed out of the precipitate obtained with sodium carbonate.

Add to the filtrate and washings 20 cc. of sulphuric acid (sp. gr. 1.51). Boil the solution and run in 3 or 4 cc. of a 3 per cent. solution of potassium permanganate. Boil for 5 minutes, run in sulphur dioxide until all the potassium permanganate is reduced to manganous sulphate and the solution has turned blue from the reduction of the vanadic acid to divanadyl sulphate.

Evaporate the solution until fumes of sulphuric anhydride begin to come off freely. Cool the solution and dilute with water to about 60 cc. and titrate the warm solution with $N/20$ potassium permanganate. If the excess of potassium permanganate is added and the solution boiled down before reduction with sulphur dioxide and then the excess of the sulphur dioxide destroyed by evaporating to sulphur anhydride fumes, and the warm diluted solution titrated, at about 50° , the oxidation of the divanadyl sulphate to vanadic acid is rapid and the end reaction sharp.

Since the oxidation of the vanadium is from V_2O_4 to V_2O_5 , the hydrogen equivalent of elemental vanadium must be the atomic weight of vanadium, and one cc. of $N/20$ potassium permanganate is equivalent to 0.00256 gram of elemental vanadium.

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DIRECT COMBUSTION OF STEEL FOR CARBON AND SULPHUR.

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In the preparation of Standardized Steel samples at the Bureau of Standards the criterion of homogeneity of the bar has been its carbon content, determined at varying points along the length and radius. This has necessitated many carbon determinations for each bar, and has led