THE DETERMINATION OF VANADIUM, MOLYBDENUM, CHROMIUM AND NICKEL IN STEEL.

By Andrew A. Blair.

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The use of the comparatively rare metals, vanadium and molybdenum, in the metallurgy of steel has demanded of the chemist, accurate methods for their separation and determination. When in addition, chromium and nickel are found with them in the same steel, the question of their separation from each other and from the large excess of iron with which they are alloyed, offers a problem which has not so far been satisfactorily solved.

To prepare samples for experimental work, I took a chrome-nickel steel which had been carefully analyzed, dissolved portions of two grams each in nitric acid with the addition of hydrochloric and to the solution added definite amounts of vanadium and molybdenum, evaporated to dryness, redissolved in hydrochloric acid, evaporated until the solution was sirupy and separated the iron by the ether method. I prepared a solution containing a definite amount of vanadium by dissolving one gram of ferro-vanadium containing 26.3 per cent. vanadium in nitric acid, evaporating to dryness, redissolving in hydrochloric acid and diluting to 1 liter. Twenty cc. of this solution contained 0.00526 gram vanadium equivalent to 0.263 per cent. vanadium calculated on two grams of the sample. The molybdenum solution I prepared by dissolving 1 gram of molybdic anhydride in a sodium hydroxide solution and diluting to 250 cc. Ten cc. of the solution was equivalent to 0.0252 gram molybdenum, the molybdic anhydride containing 63.0 per cent. molybdenum.

After separating the iron by ether, the solution, which I presumed contained vanadium, molybdenum, chromium, nickel, phosphoric acid, etc., was evaporated several times with nitric acid until the hydrochloric acid was entirely displaced. This solution, slightly diluted, was dropped into a boiling solution of sodium hydroxide which precipitated the nickel and chromium while the vanadium, molybdenum and phosphoric acid dissolved as alkaline salts. After filtration, the solution was slightly acidulated by nitric acid and lead nitrate added to precipitate the corresponding lead salts, which were filtered and washed. Hillebrand[1] states on the authority of T. Fischer (*Inaugural Dissertation, Rostock*, 1904) that lead molybdate is decomposed by a strong solution of potassium carbonate, potassium molybdate being formed, while lead vanadate is not attacked. I followed this method but found that the solution filtered from the lead salt gave no reaction for molybdenum. Before pursuing the matter further, it occurred to me that a

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[1] "The Analysis of Silicate and Carbonate Rocks," W. F. Hillebrand.

part of the molybdenum might be found in the ethereal solution of ferric chloride. I found to my surprise that this solution gave a strong reaction for molybdenum and further experiments showed that not only a part but all of the molybdenum was found with the iron and that the ether method gave a perfect separation of molybdenum from vanadium, chromium, copper, manganese, nickel, and aluminum in steel or iron.

The separation of molybdenum from the large excess of iron is rather troublesome but quite accurate. It is essentially the method suggested by Treadwell.[1] It is necessary to evaporate the ethereal solution of ferric chloride containing the molybdenum with an excess of sulphuric acid to replace the hydrochloric acid, to dilute and reduce the iron to the ferrous condition with ammonium bisulphite. After the sulphurous acid is expelled, the molybdenum is precipitated by hydrogen sulphide in a pressure bottle, filtered on a Gooch crucible and weighed as molybdenum trioxide.

The method in detail is as follows:

Dissolve two grams of the sample in nitric acid with the addition of hydrochloric acid, if necessary, evaporate to dryness, redissolve in hydrochloric acid and evaporate until the solution is sirupy. Dissolve in a small amount of hydrochloric acid, 1.1 sp. gr., cool in ice water and wash into a separatory funnel of about 250 cc. capacity with as small an amount as possible of acid of the same strength. The separatory funnel should be conical in shape and should be fitted at the lower end with a Geissler stop-cock and at the upper end with a glass stopper. Both stopper and stop-cock should be most carefully ground to prevent leakage. Add to the solution in the funnel about 80 cc. of ordinary ether and shake vigorously for half a minute. An ordinary clamp with cork-lined jaws supported on a stand makes a convenient arrangement for holding the funnel. When the two strata have separated, open the stop-cock and allow the lower to run into another separatory funnel. Remove the stopper, wash the solution down with about 10 or 15 cc. of hydrochloric acid 1.1 sp. gr. shake again and allow the washings to run into the other funnel. Add 50 cc. of ether to the solution in the second funnel to remove as much of the remaining iron as possible, run the acid solution into a beaker and evaporate nearly to dryness. Add nitric acid in excess and evaporate until all the hydrochloric acid is expelled and finally when the solution is almost sirupy, add 20 cc. of hot water. Heat the solution and add a few drops of sulphurous acid to reduce any chromic acid that may have been formed. Boil and pour the solution slowly, stirring vigorously, into a boiling solution of sodium hydroxide containing 100 grams sodium hydroxide to the liter. Boil the solution

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[1] *Analytical Chemistry*, F. P. Treadwell, vol. 2, p. 222.

for a few minutes, allow the precipitate to settle, filter, wash twice by decantation and finally on the filter until the filtrate measures about 300 cc. in volume. The precipitate consists of the oxides of chromium, nickel and iron with the greater part of the manganese and any copper that may have been in the sample. The filtrate contains the vanadium, some silica and alumina from the sodium hydroxide and sometimes a little chromium. Add dilute nitric acid to the filtrate until it just turns blue litmus paper red, then add a few drops of sodium hydroxide solution to make it alkaline, boil and filter. To the filtrate add 10 cc. of a 10 per cent. solution of lead nitrate and then enough acetic acid to make it decidedly acid and boil for several minutes. Filter the precipitate which contains all the vanadium as lead vanadate and wash with hot water. Dissolve in hot dilute hydrochloric acid, evaporate nearly to dryness, add 50 cc. of hydrochloric acid and evaporate again, add 10 cc. of strong sulphuric acid and evaporate until it fumes freely. Allow it to cool and when cold, dilute to 150 cc., heat to a temperature of 60° or 70° and titrate with permanganate. The iron value of the permanganate solution multiplied by 0.9157 gives the vanadium. The method of reducing vanadium by evaporating with hydrochloric acid and then driving off the hydrochloric acid with sulphuric as proposed by Campagne[1] gives most excellent results. The presence of small amounts of iron does not affect its accuracy and the trouble of boiling off every trace of sulphurous acid when this reagent is used is avoided.

The two precipitates obtained from the sodium hydroxide solution contain chromium, nickel and copper, besides iron and manganese. Ignite the two filters and precipitates and fuse with about two grams of sodium carbonate and half a gram of potassium nitrate. Treat the fused mass with water and filter. The insoluble portion contains the nickel, copper, iron and part of the manganese, and the filtrate, the chromium and the rest of the manganese. To the filtrate add ammonium nitrate in sufficient quantity to change all the sodium salts to nitrates and evaporate to a small bulk, adding a few drops of ammonia from time to time. Dilute to about 50 cc., boil, filter, and wash with hot water. The insoluble matter consists of manganese and any silica, alumina, etc., that may have been in the reagents. Boil the filtrate to drive off the ammonia, add sulphurous acid to reduce the chromic acid, boil off the excess and precipitate by ammonia. Filter, wash, ignite and weigh the chromium sesquioxide which contains 68.46 per cent. of chromium.

Return the filter, containing the insoluble matter from the fusion, to the crucible in which the fusion was made, ignite, dissolve in hydro-

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[1] *Compt. rend.*, **137**, 570 (1903).

chloric acid, dilute, precipitate the copper by hydrogen sulphide, filter and evaporate the filtrate with excess of sulphuric acid until the hydrochloric acid is expelled. Dilute, add excess of ammonia and precipitate the nickel by electrolysis. A current of about four and a half amperes is sufficient and the iron and manganese present do not interfere with the accuracy of the results.

To the ethereal solution of the iron, which remains in the two separatory funnels, add water and shake. Draw off the ferric chloride containing the molybdenum, which separates from the ether and evaporate nearly to dryness, add 10 cc. strong sulphuric acid and evaporate carefully until the hydrochloric acid is driven off and the sulphuric acid fumes freely. Cool, dissolve in about 100 cc. of water and carefully deoxidize with ammonium bisulphite, boil off the excess of sulphurous acid and cool the solution. Transfer the cold solution to a pressure bottle of 200 cc. capacity and pass a current of hydrogen sulphide through it until it is saturated, close the bottle and heat it on a water bath for several hours. Allow it to cool slowly. Filter on a Gooch crucible, wash the precipitate first with water containing a little sulphuric acid and finally with alcohol. Place the Gooch crucible containing the precipitate on a small triangle placed inside a large porcelain crucible so that the bottom of the Gooch crucible shall not touch the porcelain crucible. Cover the latter with a watch glass and heat it carefully, raising the heat gradually until there is no smell of sulphurous acid. Replace the watch glass with a porcelain cover and heat until the precipitate of molybdenum sulphide becomes bluish white in color.

Place the Gooch crucible over a lamp and heat it to faint redness, cool and weigh. Heat it again to faint redness, weigh and repeat the operation until it ceases to lose weight. Place the crucible on the vacuum flask and dissolve the molybdic trioxide in dilute ammonia, wash, heat and weigh the crucible. The difference between the two weights is molybdenum, trioxide which contains 66.67 per cent. molybdenum. There always remains on the felt in the Gooch crucible a small amount of ferric oxide.

I found it necessary to precipitate the molybdenum sulphide from a sulphuric acid solution as it seemed almost impossible to separate all the molybdenum sulphide in one operation from a hydrochloric acid solution.

The accuracy of the method may be judged from the following analysis of the chrome-nickel steel mentioned in the beginning of this article to which 0.0252 gram of molybdenum and 0.00526 gram of vanadium were added.

	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.

Campagne[1] 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

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