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THE DETERMINATION OF CHROMIUM, AND ITS SEPARATION FROM VANADIUM, IN STEELS

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While attempting recently to determine chromium in chrome-vanadium steels, difficulties with some of the usual methods were encountered. If a steel containing chromium as chromate and vanadium as vanadate is titrated against ferrous solutions, using ferricyanide to indicate the point at which all the vanadium and chromium are reduced and an excess of titrating solution is present, there is sometimes an indefinite end point, because as soon as some vanadium is reduced to the vanadyl condition this reacts with the ferricyanide indicator, reducing it to ferrocyanide which then gives the usual color with the ferric salts present.¹ An experienced operator can often judge the end point sufficiently closely for practical work, but the difficulty increases with increasing vanadium, and it is almost always necessary to run blanks of various kinds, increasing to that extent the uncertainties of such methods. If the excess of ferrous solution is titrated back with permanganate, some correction is also necessary for chromium oxidized by permanganate.² If in the preliminary oxidation of the vanadium and chromium, any manganese dioxide separates, as where potassium permanganate or potassium

¹ Cain: J. Ind. and Eng. Chem., 3, p. 476; 1911; other references will be found here.

² Cain, loc. cit.

chlorate are used, some chromium may be, and often is, carried down by the manganese.³ If, in order to separate vanadate from chromate, the nitric acid solution of the steel (with or without preliminary ether extraction of most of the iron) is poured into excess of sodium hydroxide solution and boiled, usually an appreciable amount of chromium goes into the filtrate with the vanadium. Many methods take no account of this chromium. The amount so lost increases with the manganese in the steel and the time of boiling, the manganese being converted in part to peroxide and this, in the strongly alkaline solution, oxidizing the chromium to chromate.⁴

Many careful tests having shown that chromium in much larger amount than the usual commercial steels carry can be precipitated completely in a few minutes by boiling the nearly neutralized (ferrous) solution of the steel with barium carbonate, cadmium carbonate, zinc oxide or magnesium oxide, it was decided to base a method for determining chromium on one of these methods of separation from iron. Probably the reason why such separations have not come into more general use is because practically all writers have directed the making of carbonate or oxide precipitation in the cold, which requires many hours' standing and is even then sometimes incomplete. The work done here has shown that but 10 or 15 minutes' boiling, with proper precautions, is all that is ever necessary, the filtrates being free from even traces of chromium (or vanadium).

Noyes and Bray⁵ have given conditions for completely precipitating chromates in the presence of vanadates which make possible a good separation of the two elements. The work here having completely confirmed their results, this separation was incorporated in the method.

DESCRIPTION OF THE METHOD

Dissolve in a covered 300-cc Erlenmeyer flask an amount of drillings, which will give not to exceed 6 or 7 centigrams of chromium, using about 10 cc of concentrated hydrochloric acid

³ Arnold and Ibbottson, *Steel Works Analysis*, 3d ed., p. 180; also Cain, loc. cit.

⁴ Cain, loc. cit.

⁵ *Technology Quarterly*, 21, p. 14. 1908.

per gram of steel. The concentrated acid (specific gravity 1.20) seems to dissolve the steel much more readily than a diluted acid. When no more hydrogen is given off, dilute to 100 or 150 cc with hot water, nearly neutralize with saturated sodium carbonate solution, add barium carbonate emulsion in slight excess, place on the hot plate and boil vigorously 10 or 15 minutes, with small additions of the barium carbonate emulsion every two or three minutes. The flask should be kept covered during all operations so as to exclude air as completely as possible. Too great an excess of barium carbonate should not be used, as this increases the difficulty of extracting the chromium in the subsequent fusion. An excess of a gram or two is the most that should be present. Remove the flask from the plate, let the precipitate settle, and filter at once on a 11-cm white label No. 589, filter, washing twice with hot water. These operations should be carried out rapidly and without delay. Place the filter and precipitate in a sufficiently large platinum crucible, burn off the filter, add 2 grams of sodium carbonate and about one-fourth of a gram potassium nitrate, and fuse for 20 minutes. Place the inverted and inclined crucible on a glass triangle, which has glass legs about three-fourths of an inch long fused to its corners, for supports; triangle and crucible are put into a 250-cc beaker, covered with boiling water, and the contents of the beaker digested a few minutes until the fusion is disintegrated. Filter into a flask, add 1 or 2 cubic centimeters of hydrogen peroxide to the filtrate and boil for 5 or 10 minutes to destroy the excess of peroxide. Cool, transfer to a 250 or 300 cc separatory funnel, add a slight excess of nitric acid (1-1), and shake vigorously a few minutes, allowing the liberated carbon dioxide to escape by inverting the separatory funnel and opening the stopcock. Transfer to a 250-cc beaker, just neutralize with sodium hydroxide solution, and then add nitric acid (1-1), 2 cubic centimeters for each 100 cc of solution. Add 20 cubic centimeters of a 20 per cent lead nitrate solution to the cold solution, stirring vigorously. The precipitate settles quickly. It is filtered on asbestos, and washed three or four times with cold water. The asbestos mat is transferred to a beaker or flask, and the lead

chromate decomposed with hot hydrochloric acid (1-4). The solution is cooled, the volume made up to 150 or 200 cc, and it is titrated against approximately N/10 ferrous sulphate solution with ferricyanide as outside indicator. Or, if desired, an excess of the ferrous sulphate solution is added and the excess titrated back against bichromate. The standard iron solution should be compared with bichromate or permanganate on the day it is used. Table I gives results obtained with synthetic solutions and with the chrome-vanadium standard steel of the Bureau of Standards.

The synthetic solutions were made by adding the chromium from a carefully standardized bichromate solution and the vanadium from a sodium-vanadate solution to the hydrochloric-acid solution of a vanadium and chromium free steel.

Table I

Experiment	Iron present	Vanadium present	Chromium present	Chromium found	Difference
	Gram				
1	1	0.0012	0.0140	0.0137	-0.0003
2	1	.0024	.0280	.0277	-.0003
3	1	.0024	.0420	.0420	.0000
4	1	.0036	.0560	.0558	-.0002
5	1	.0048	.0700	.0700	.0000
6	1	.0060	.1120	.1122	+.0002
7	1	.0120	.1680	.1685	+.0005
8	1	.0180	.2800	.2805	+.0005
⁶ 9	4			.0536	

⁶ Chrome-vanadium standard; 4 determinations; each gave 1.34 per cent. Average of results of cooperating analysts: Chromium, 1.36 per cent; vanadium, 0.204 per cent.

NOTES AND PRECAUTIONS

Numbers 6, 7, and 8 of Table I show that very large amounts of chromium can be completely precipitated by the barium-carbonate method carried out as above described. However, if the amount of chromium exceeds that recommended in the method described herein it can not be readily extracted by 2 grams of sodium carbonate, particularly if too great an excess of barium is present. The amount of sodium carbonate used was governed by

the directions of Noyes and Bray,⁷ who state that for a successful separation of chromium not too much sodium nitrate should be present. The separations described herein were made in a volume of 250 cc, and inasmuch as 2 grams of sodium carbonate were used for fusions the resulting sodium nitrate concentration was about 1.3 grams per 100 cc. The filtrates were tested for chromium by removing the excess of lead with sulphuric acid, filtering, concentrating to about 10 or 15 cc, and making alkaline with sodium hydroxide. No color indicative of chromate was ever obtained, even after adding a little hydrogen peroxide and boiling to oxidize any chromium that may have been reduced. Possibly the larger amounts of chromium could have been completely extracted by one fusion had more sodium carbonate been used, but the manipulation is then less convenient. Moreover, with the usual range of chromium content in commercial steels one need never work with more than 7 or 8 centigrams to secure an accurate determination.

The boiling with hydrogen peroxide in alkaline solutions before precipitation with lead nitrate is done in order to destroy any nitrite formed during the fusion. If this were present when the solution is acidified, the resulting nitrous acid would possibly reduce some chromium or vanadium. Five minutes' boiling will insure destruction of the excess of peroxide if only 2 or 3 cc of the usual 3 per cent solution are used. The hydrogen peroxide should be completely removed before acidifying, inasmuch as it reduces chromic acid.⁸

The freeing of the solution from carbon dioxide is an important step, for if this is not done the precipitate does not settle out rapidly and is not so easy to filter; shaking in a separatory funnel, as described, is a convenient way of accomplishing this.

The solutions containing the chromium after titration were treated with enough sulphuric acid to precipitate the lead, which was filtered off and washed with dilute sulphuric acid. The filtrates were evaporated on the hot plate until free from hydrochloric acid and then electrolyzed with a mercury cathode⁹ until

⁷ Cain, loc. cit., p. 48, note 4.

⁸ Perchromic acid is first formed, but is rapidly decomposed.

⁹ Cain, loc. cit.

free from iron and chromium. The solution in the electrolyzing apparatus was then tested for vanadium by hydrogen peroxide, none being found in most cases and in others only traces, showing that the separation under the conditions given is practically perfect.

It is well to examine the insoluble from the fusion for chromium by again fusing it with sodium carbonate and potassium nitrate. The solution from the second fusion is almost invariably colorless when working under the conditions herein recommended. Should there be a slight yellow color, however, the chromium causing it can be estimated colorimetrically. A determination of chromium can easily be made in one and one-half hours.

CONCLUSIONS

1. Sources of error in some of the usual methods for determining chromium in chrome or chrome-vanadium steels, which limit the accuracy of the results, are described.

2. The precipitation of chromium from solutions of steels and its separation from practically all the iron can be effected quickly and easily by boiling with a number of precipitants, herein described.

3. The chromium may be readily extracted from the precipitates by fusion and separated from vanadium by precipitating as lead chromate under the conditions prescribed.

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