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SUBJECT

Colorimetric Determination of Chromium in Steel

NAVAL RESEARCH LABORATORY
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NAVY DEPARTMENT

Report on

Colorimetric Determination of
~~Chromium~~ in Steel

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

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ABSTRACT

The purpose of this paper is to describe a method for the colorimetric analysis of chromium in steel which is not subject to interference by iron or alloying constituents usually present. The method is suitable for steel containing between a few thousandths and one percent chromium and is rapid, as chemical separations are not used. The basis of the method lies in the fact that ferric perchlorate, which is itself colorless, intensifies the color of the dichromate ion.

INTRODUCTION

(A) Authorization

1. Work on this problem was authorized by the Director, Naval Research Laboratory.

(B) Statement of Problem

2. In practically all of the colorimetric methods that have been employed, the determination of chromium in steel is made after it has been separated from iron. The determination is then made by measuring the intensity of the chromate or dichromate color or the color produced with dichromate and a suitable organic reagent. When large amounts of steel are taken for analysis, iron is first separated from chromium by extraction with ether. Small amounts of iron are precipitated and chromium simultaneously oxidized and dissolved by the use of an alkaline peroxide solution. In the volumetric analysis for small amounts of chromium it is also necessary to use large samples and separate the iron. Thus, in either case, the analysis is a long and tedious procedure.

(C) Discussion of Other Colorimetric Methods

3. Yoe ⁽²⁾ describes the use of disodium 1-8 dihydroxy-naphthalene 3-6 disulfonate (Koenig's reagent), diphenylcarbazide and diphenylsemicarbazide for the colorimetric analysis of chromium. These reagents are very sensitive to small amounts of chromium but are subject to interference by iron and other alloying constituents that may be present in certain steels, thus making chemical separations necessary. However, Mal'tsev and Temerinko⁽¹⁾ using diphenylcarbazide, take a small sample weight and determine up to 0.1% chromium in steel without making any previous separation. Organic reagents have been employed in those cases where the chromium content of steel is very low, as the color produced by small amounts of chromate or dichromate ion alone is too weak to allow accurate results.

(D) Description of Experimental Work

4. Solutions were prepared containing known amounts of chromium and iron, using a standard dichromate solution and Bureau of Standards sample No. 22b. These samples were dissolved and boiled with perchloric acid to oxidize chromium. After cooling and diluting to a definite volume they were transferred to an absorption tube and a colorimeter reading taken. The solutions were then reduced with a small crystal of ferrous ammonium sulfate and a second reading taken. The difference of these two readings represents the colorimeter reading due to the dichromate.

5. Results in Table I show that with increasing amounts of iron the color of the dichromate becomes more intense. It is evident that the increased color is not due to the color of ferric perchlorate since the colorimeter readings of the reduced solution (Column 2) show no appreciable change as the amount of iron is increased. It was found from subsequent experiments that a one gram sample was most suitable when the chromium content of the steel was between a few thousandths and one tenth percent. When the percentage of chromium was between one tenth and one percent, a half gram sample was taken for analysis. Accordingly solutions were prepared using a steel of known chromium content and a standard solution of potassium dichromate. Readings were taken after carrying them through the procedure described below. Graphs (Plates land 2) were drawn from the results, giving, in each case, a slightly curved line.

6. In order to determine the accuracy of the method various samples of Bureau of Standards steels were analyzed. Artificial standards were also prepared by adding nickel, copper, cobalt, molybdenum, aluminum, titanium and vanadium to weighed mixtures of Bureau of Standards steels and the resulting mixtures analyzed (Table II).

(E) The Method in Detail

(a) Preparation of Solution. Transfer 1.000 gm of sample, for steel containing up to 0.1 percent chromium, to a 125 ml Phillips beaker and dissolve in 10 ml of dilute HNO_3 (1-1) and 20 ml of HClO_4 (70-72%). For steel containing between 0.1 and 1 percent chromium take 0.500 gm sample and dissolve in 10 ml of HNO_3 (1-1) and 15 ml of HClO_4 (70-72%). Evaporate to dense fumes of perchloric acid and boil for five minutes to oxidize chromium (boiling for 8 minutes does no harm). Cool the beaker and contents rapidly in tap water. Dissolve soluble salts with 20 ml of water and transfer the solution to a 50 ml, glass stoppered, volumetric flask. Cool the solution to room temperature and dilute to 50 ml.

(b) Taking the Colorimeter Reading. Transfer a portion of the solution to the absorption tube and reduce with a small crystal of ferrous ammonium sulfate. Adjust the colorimeter so that the readings on this solution is zero. Discard the solution in the absorption tube, refill with the oxidized solution and take a second reading. This reading is a measure of the color due to the dichromate. In the absence of elements which form highly colored ions such as copper, nickel, cobalt, etc., it is not necessary to reset the colorimeter at zero. All subsequent colorimeter measurements are made by taking a reading on an oxidized solution, reducing the solution in the absorption tube with a small crystal of ferrous ammonium sulfate and taking a second reading. The difference between the first and second readings then represents the color due to the dichromate present. If appreciable amounts of highly colored ions are present the colorimeter is adjusted to read zero on the reduced solution before a reading is taken on the oxidized sample.

(F) Description of Colorimeter

7. A Klett-Summerson photoelectric colorimeter was used. This colorimeter has a logarithmic scale and when Beer's Law applies, the scale readings are proportional to the color intensity. Measurements were made in an absorption tube of 12.5 mm inside diameter and with a color filter transmitting between 410-480 millimicrons.

SUMMARY

8. Reference to Table II shows that duplicate determinations agree well and the results obtained compare favorably with the Bureau of Standards certificate values. Moderate amounts of the ordinary alloying constituents do not affect the accuracy of the method. The presence of iron is essential since it increases the intensity of the dichromate color. As iron is not separated from chromium, the analysis is more rapid than most methods for the colorimetric determination of chromium in steel. A single chromium determination may be made in 15 minutes.

BIBLIOGRAPHY

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TABLE I
Effect of Iron on Intensity of Dichromate Color

Milligrams of chromium	1.000 Gram Iron			0.500 Gram Iron			No Iron		
	1 Oxidized Solution	2 Reduced Solution	3 Differ- ence	1 Oxidized Solution	2 Reduced Solution	3 Differ- ence	1 Oxidized Solution	2 Reduced Solution	3 Differ- ence
0.070	13	0	13
0.240	42	2	40
0.570	91 ⁰⁰	3	88
0.870	132	4	128
0.950	150	5	145	78	1	77	37	0	37
1.15	170	6	164						
1.85	272	7	265	152	4	148	72	0	72
2.30	332	10	322	188	5	183	90	1	89
2.75	382	11	371	222	7	215	109	2	107
3.65	464	13	451	289	8	281	145	3	142
4.55	354	8	346	182	5	177
5.55	427	11	416	222	7	215

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TABLE II

Determination of Chromium in Bureau of
Standards Samples

<u>Composition</u>	<u>"Alloying" Element Added</u>	<u>Percent Chromium Present</u>	<u>Percent Chromium Colorimetrically</u>
1.000 gm 8d	None	0.007	0.007
1.000 gm 11d	"	0.008	0.008
1.000 gm 13d	"	0.023	0.009
1.000 gm 15c	"	0.055	0.023
0.500 gm 30c	"	0.977	0.055
0.500 gm 72	"	0.911	0.056
0.500 gm 72a	"	0.655	0.98
0.500 gm 100	"	0.180	0.98
0.300 gm 20d + 0.700 gm 22b	"	0.087	0.91
0.400 gm 20d + 0.600 gm 22b	"	0.115	0.91
0.970 gm 13d	3% Cu	0.022	0.66
0.500 gm 100 + .470 gm 11d	"	0.095	0.66
0.485 gm 100	"	0.175	0.19
0.485 gm 72	"	0.883	0.087
0.970 gm 13d	3% Ni	0.022	0.087
0.500 gm 100 + 0.470 gm 11d	"	0.095	0.19
0.485 gm 100	"	0.175	0.087
0.485 gm 72	"	0.883	0.087
0.500 gm 11d + 0.500 gm A*	1.38% Mo	0.108	0.092
0.400 gm 72 + .100 gm A*	0.67% Mo	0.764	0.092
0.100 gm 106 + 0.900 gm 11d	0.1% Al	0.137	0.75
0.250 gm 106 + 0.250 gm 11d	0.5% Al	0.65	0.137
0.990 gm 13d	1% Co	0.023	0.64
0.500 gm 100 + 0.490 gm 22b	"	0.092	0.021
0.495 gm 100	"	0.178	0.092
0.495 gm 72	"	0.902	0.186
0.495 gm 72	1% V	0.902	0.90
1.000 gm HJN**	1.5% Ti	0.115	0.88
0.250 gm HJN** + 0.25 gm 72	0.75% Ti	0.51	0.102
0.167 gm HJN** + 0.333 gm 72	0.50% Ti	0.646	0.49
			0.65

* N.R.L. Alloy No. A, contains 2.76% molybdenum and 0.208% Chromium

** N.R.L. Alloy No. HJN, contains 1.50% titanium and 0.115% Chromium

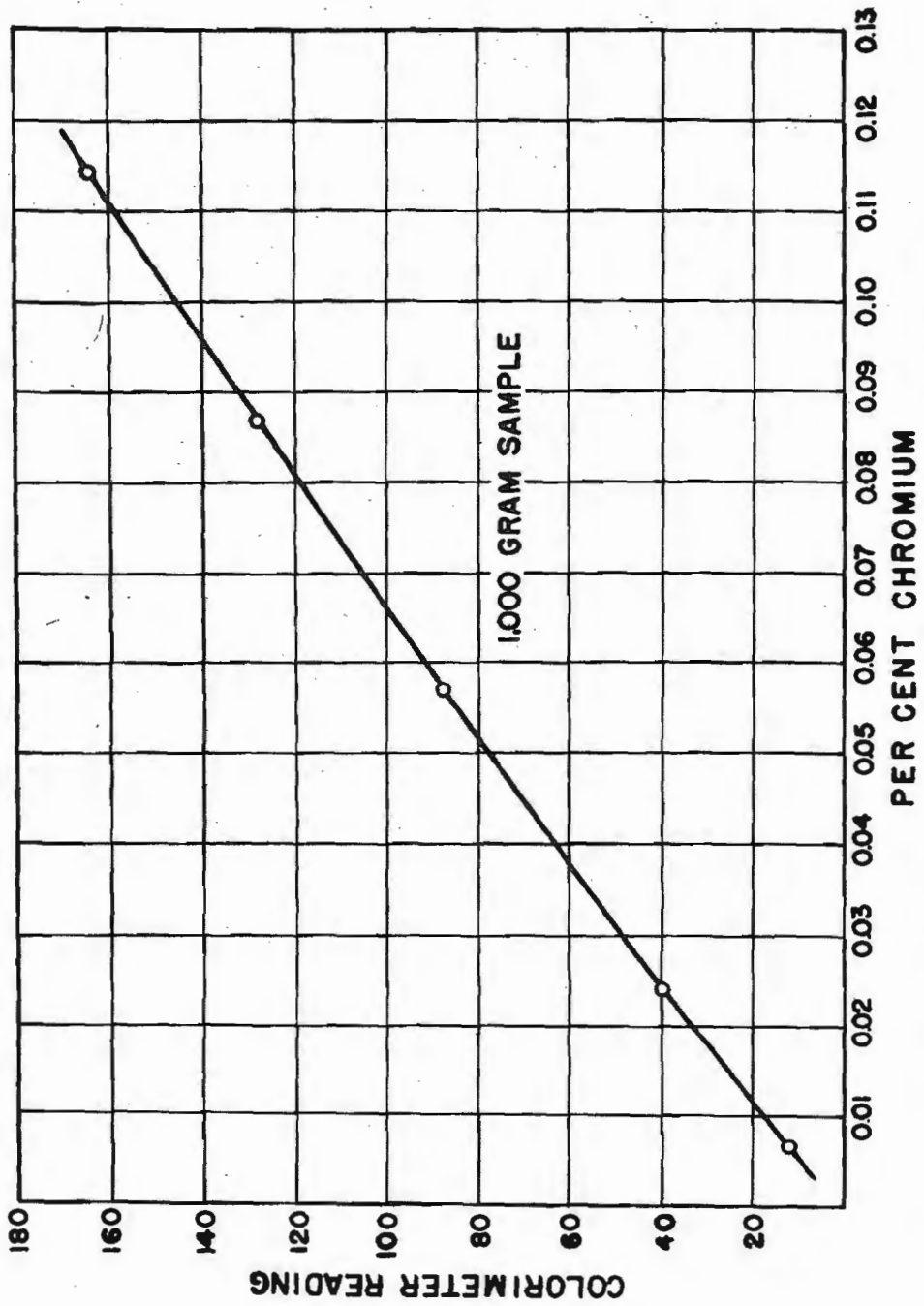


FIG. I. RELATION BETWEEN COLORIMETER READING
AND PER CENT CHROMIUM PRESENT

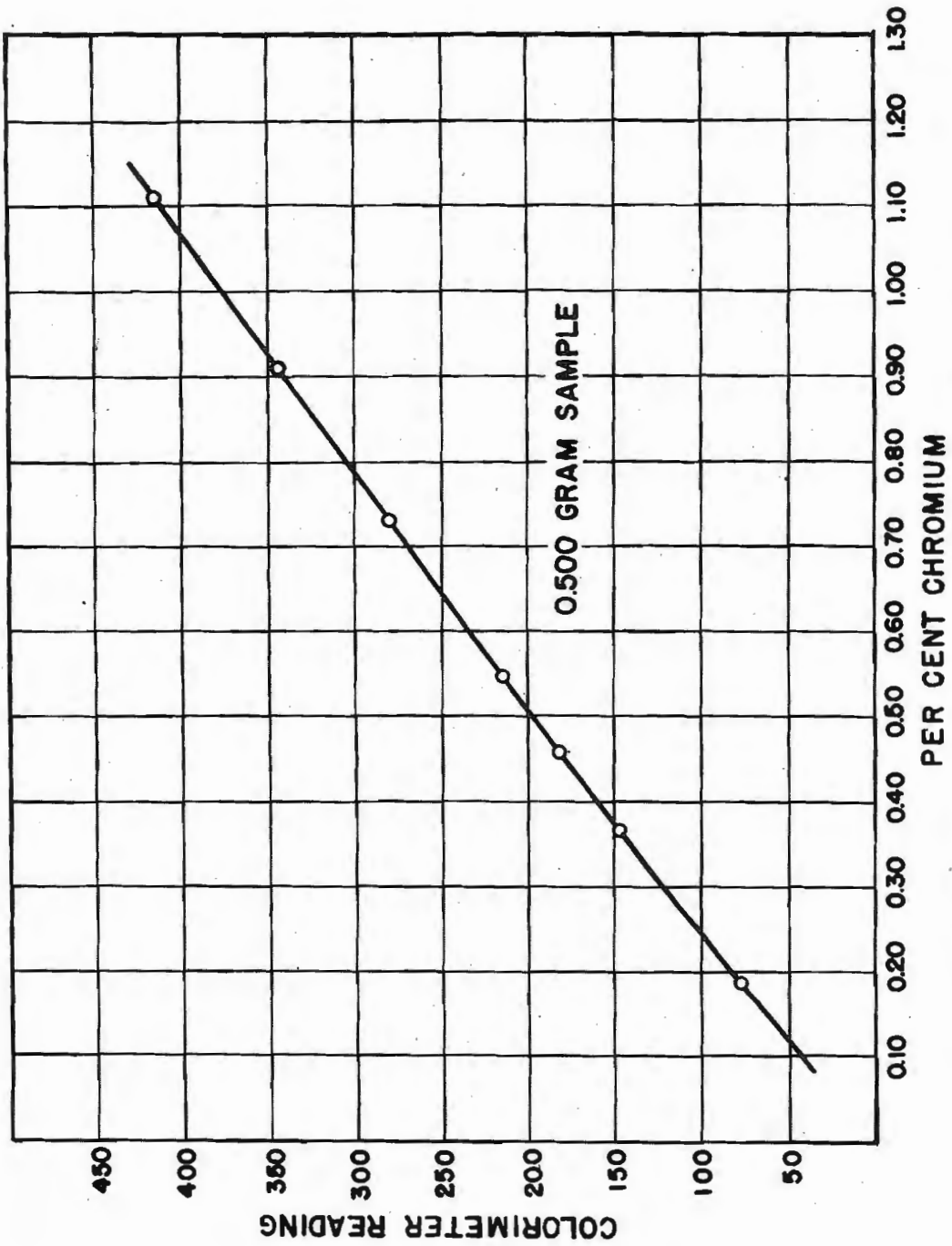


FIG. 2. RELATION BETWEEN COLORIMETER READING
AND PER CENT CHROMIUM PRESENT

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