served values are lower than the calculated values, which fact may be attributed to the withdrawal of increased amounts of water vapor at the lower pressures together with a small lag in the humidity recorder. The final observed humidity of 60 per cent is but a rough approximation. No attempt was made to reduce the flow through the flowmeter during the last few minutes of the experiment to approach equilibrium conditions more closely, since for the purpose of this work it was sufficient to determine that the drying efficiency of compressed nitrogen decreases rapidly as the tank pressure decreases.

Table I—Moisture Content of Nitrogen at Atmospheric Pressure after Expansion at 24° C. from High-Pressure Containers in Which Liquid Water Is Present

			RELATIVE	HUMIDITY
TIME AFTER STA	rt Tanf	C Pressure	Obsd.	Caled,
Minutes	Atm.	Lbs./sq. in.	Per cent	Per cent
0	150	2200	1.0	0.66
235	75	1100	2.0	1.32
353	37.5	550	3.4	2.60
411	18.8	275	6.0	5.05
441	9.4	137.5	12.0	9.62
453	4.7	68.8	19.0	17.6
463	2.35	34.4	27.5	29.9
466	1.18	17.2	40.0	45.9
467^{a}	1.0	14.7	44.0	50.0
470ª	0	0	60 a	100.0
^a Approxima	ite.			

Table II contains experimental data obtained with a tank of nitrogen subjected to special manufacturing processes. Integration of these data indicates that even in this case the expanded gas contained 2 grams of water as compared with a total of 4.5 grams in the gas obtained from the tank which was known to contain excess water. Since it seems impossible that these 2 grams of water existed in the vapor phase, one must conclude that the precautions taken to exclude water in the manufacturing processes were insufficient. In this second case, also, the final value of the relative humidity of the gas expanded to atmospheric pressure is only approximate. Since no satisfactory assumption can be made as to the degree of saturation of the gas initially, no significant value of expected relative humidity can be calculated for purposes of comparison. These data, which have been obtained with specially dried nitrogen, make it evident that for most drying purposes the less carefully prepared gas should be nearly as satisfactory as the "dried" gas, provided that the tank is not completely discharged.

Table II—Moisture Content of Nitrogen at Atmospheric Pressure after Expansion at 24° C. from High-Pressure Containers in Which No Liquid Water Is Present

TIME AFTER START	TANK	PRESSURE	Relative Humidity (Obsd.)
Minutes	Atm.	Lbs./sq. in,	Per cent
0	150	2200	0.78
235	75	1100	1.55
353	37.5	550	1.75
411	18.8	275	2.16
441	9.4	137.5	2.75
453	4.7	68.8	3.25
463	2.35	34.4	3.96
466	1.18	17.2	4.65
47 0 <i>a</i>	0	Ō	6.54
a Approvimate			

^aApproximate.

Literature Cited

Bartlett, J. Am. Chem. Soc., 49, 65 (1927).
 Rosecrans, IND. ENG. CHEM., Anal. Ed., 2, 129 (1930).

Determination of Chromium and Vanadium after Oxidation with Potassium Bromate¹

Separate Titration of Chromate and Vanadate in the Same Solution and Application of Method in Steel Analysis

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The determination of chromium by addition of excess arsenious oxide to an acid chromate solution and backtitration with permanganate has been investigated systematically. Good results are obtained in the presence of vanadate, ferric iron, and manganese at various acid concentrations. After chromium has been determined, vanadate can be titrated in the same solution with ferrous sulfate, diphenylbenzidine being used as indicator.

Oxidation of chromium and vanadium to chromate and vanadate, respectively, is effected by use of potassium

A FEW relatively simple methods have been proposed for the titration of vanadium when present with chromium; a review of these has been given in a recent paper by Willard and Young (8). In their important work, these authors oxidize chromium and vanadium by the persulfate method and, after removing the excess of persulfate, titrate the sum of chromate and vanadate with ferrous sulfate either according to the potentiometric or the usual method, in the latter case with diphenyl benzidine as an indicator. Vanadium, when present with chromium, can be oxidized selectively by potassium bromate in the presence of sufficient hydrochloric acid to prevent the oxidation of the chromium. The excess of bromate is removed by boiling with ammonium

¹ Received December 23, 1929.

bromate; the excess bromate is removed by boiling with ammonium sulfate.

The method can be applied to the rapid determination of chromium and vanadium in alloy steels. Tungsten interferes in the titration of vanadium and must be removed.

The time required for the total determination of chromium and vanadium, including dissolving of the steel, is 1 hour or less.

sulfate and the vanadate titrated with ferrous sulfate according to the potentiometric or usual method.

The present writers have tried to simplify the above procedure by applying a reducing agent which would reduce chromate but not vanadate. This was accomplished by using arsenious oxide as a reagent. Since the reduction of the chromic acid takes place rather slowly, an excess of arsenious trioxide is added and this is then titrated back with potassium permanganate. A slight reduction of the vanadate by the excess of arsenious acid would not affect the results since the vanadyl salt would be oxidized again by permanganate. After back-titration with permanganate, the vanadate can be determined with ferrous sulfate according to the directions of Willard and Young (8).

Determination of Chromic Acid with Arsenious Oxide under Different Conditions

Spitalsky (7) first made use of arsenious acid in the determination of chromium. In brief, his method of procedure was to add an excess of arsenious oxide to a hydrochloric acid solution of dilute chromate and after 20 to 25 minutes to backtitrate the excess of arsenite with potassium bromate using methyl orange as indicator. Lang (4) determined chromium in a similar manner, titrating the excess of arsenious acid with potassium permanganate in the presence of chloride and a trace of potassium iodide or iodate as catalyst; in the absence of iodide or iodate the reduction of MnO_4^- to Mn^{++} does not take place smoothly at room temperature. Zintl and Zaimis (10) have described the determination of chromium by direct potentiometric titration of chromate with arsenious acid; vanadate is determined in the same solution (after reduction of chromic acid) by titration with ferrous sulfate, the endpoint being found potentiometrically. The same workers have applied a modification of this method to the determination of chromium and vanadium in steel (11). The procedure given necessitates the removal of all except traces of manganese, and preferably iron, before titrating chromate and vanadate with arsenious acid and ferrous sulfate, respectively. The end points are detected potentiometrically; in order that chromic acid may be titrated with arsenious acid, the presence of a few tenths of a milligram of manganese as a catalyst is necessary. Lang and Zwerina (5) have also described a method involving the use of arsenious acid and ferrous sulfate for the direct determination of chromium and vanadium in steel. Chromium is titrated with arsenious oxide potentiometrically in the presence of much manganese and a trace of potassium iodide or iodate.

It would seem advantageous to have at our disposal a simple method by which chromium and vanadium could both be determined by visual titration, not involving the detection of the end points potentiometrically. The development of such a method will be described, especially with reference to its application in the analysis of steel; the influence of various factors which affect the method will be discussed.

An excess of standard arsenious acid is added to an acid solution of chromate and vanadate to reduce chromate to chromic salt; titration of the excess arsenious acid by permanganate gives the amount of chromium present. Vanadium is then determined in the same solution by titration with ferrous sulfate, diphenylbenzidine being used as indicator.

DETERMINATION OF CHROMIUM—Materials Used. Potassium dichromate: 0.1 N solution prepared from recrystallized salt dried at 200° C.

Ammonium metavanadate: 0.025 N solution, standardized by reducing with sulfur dioxide and titrating the hot vanadyl solution with potassium permanganate.

Arsenious acid: 0.1 N solution prepared by weighing out B. of S. arsenic trioxide (99.97%).

Potassium permanganate: 0.1 and 0.025 N solutions, standardized against either sodium oxalate or arsenious oxide. Ferrous sulfate: 0.025 N in approximately 0.1 N sulfuric

acid. Potassium iodide (catalyst): 1/400 N; 1 or 2 drops in

each titration.

Procedure. Varying amounts of dichromate were taken and the acidified solution, having a volume of 50 to 75 cc., was treated with a slight excess of arsenious acid and after standing for 5 to 10 minutes the excess of the latter was titrated with 0.1 N permanganate, 1 or 2 drops of 1/400 N potassium iodide solution being present. The amounts of acid, chloride, iron (as ferric alum), and vanadium (as ammonium vanadate) present are specified in the tables. When iron was present in the solution to be titrated, 5 to 10 cc. of 85 per cent phosphoric acid were always added to give a more easily discernible end point with permanganate. In determinations 40 to 49, Table I, the only chloride present was that introduced with the standard solution of arsenious acid which contained 10 cc. of 12 N hydrochloric acid per liter—i. e., under the conditions of the experiment, the solution to be titrated with permanganate contained approximately the equivalent of 0.25 cc. of 12 N hydrochloric acid.

Table I--Chromate Titrations: Effect of Chloride, Acid Concentration, Ferric Iron, and Vanadate

						Сивом	
No.	Cr Taken	Fe ⁺⁺⁺ Present	V Present	CHLORIDE ADDED	${ m H}_2^{12}{ m sO}_4$	Found	Error
	Gram	Grams	Gram	Cc.	Cc.	Gram	Gram
$\begin{array}{c}1\\2&3&4&5&6\\7&8&9&0\\1&1&2&2&3\\1&1&2&2&3&4\\2&2&2&2&2&2&2\\2&2&2&2&2&2&2\\2&2&2&2&2$	$\begin{array}{c} 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0443\\ 0.0433\\ 0.0433\\ 0.0433\\ 0.0445\\ 0.0445\\ 0.045\\ 0.0$	···· ···· 1.5 1.5 1.5 1.5 1.5 1.5 1.5 1.5	$\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & & $	12 X HCI 10 10 10 10 10 10 10 10 10 10	238 · .55555555555555555555555555555555555	$\begin{array}{c} 0.0426\\ 0.0436\\ 0.0419\\ 0.0445\\ 0.0444\\ 0.0444\\ 0.0444\\ 0.0444\\ 0.0446\\ 0.0446\\ 0.0446\\ 0.0446\\ 0.0429\\ 0.0443\\ 0.0443\\ 0.0443\\ 0.0443\\ 0.0443\\ 0.0443\\ 0.0429\\ 0.0436\\ 0.0429\\ 0.0436\\ 0.0436\\ 0.0434\\ 0.0444\\ 0.0434\\ 0.0444\\ 0.0444\\ 0.0444\\ 0.0444\\ 0.0441\\ 0.0444\\ 0.0444\\ 0.0443\\ 0.0171\\ 0.0171\\ 0.0432\\ \end{array}$	$\begin{array}{c} -0.0019\\ -0.0026\\ 0.0026\\ 0.0000\\ -0.0001\\ -0.0001\\ -0.0001\\ +0.0001\\ -0.0001\\ +0.0001\\ -0.0003\\ -0.0003\\ -0.0003\\ -0.0003\\ -0.0003\\ -0.0003\\ -0.0003\\ -0.0003\\ -0.0003\\ -0.0004\\ +0.0001\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0004\\ -0.0000\\ -0.0001\\ -0.0001\\ -0.0002\\ -0.0002\\ -0.0002\\ -0.0002\\ -0.0002\\ -0.0002\\ -0.0001\\ -0.0002\\ -0.0002\\ -0.0001\\ -0.0002\\ -0.0001\\ -0.0002\\ -0.0001\\ -0.0002\\ -0.0001\\ -0.0002\\ -0.0001\\ -0.0002\\ -0.0002\\ -0.00001\\ -0.0002\\ -0.00001\\ -0.0002\\ -0.0000\\ -0.000\\ -0.$
29 30	$\begin{array}{c} 0.0433 \\ 0.0433 \end{array}$	1.5 1.5	$\begin{array}{c} 0.025\\ 0.025\end{array}$	1 1	$10 \\ 50$	$\substack{0.0433\\0.0431}$	0.0000 - 0.0002
				NaCl Gram			
$31 \\ 32 \\ 33 \\ 34$	$0.0433 \\ 0.0173 \\ 0.0035 \\ 0.0035$	$1.5 \\ 1.5 $	$0.025 \\ 0.02$	$\begin{array}{c} 0.1 \\ 0.05 \\ 0.05 \\ 0.05 \end{array}$	5555	$\begin{array}{c} 0.0432 \\ 0.0173 \\ 0.0030 \\ 0.0030 \end{array}$	-0.0001 0.0000 -0.0005 -0.0005
•-			C	one. 12 N H	ICI		
$\begin{array}{c} 35\\ 36\\ 37\\ 38\\ 40\\ 41\\ 42\\ 43\\ 44\\ 56\\ 47\\ 48\\ 9\\ 50\\ \end{array}$	$\begin{array}{c} 0.\ 0017;\\ 0.\ 0443\\ 0.\ 0445\\ 0.\ 045\\ 0.\ 0$	3 2.0 1.5 0.7 0.6 0.6 0.6	0.025 0.060 0.02 0.025 0.06 0.025 0.025	4 1 10 10 <i>a</i> <i>a</i> <i>a</i> <i>a</i> <i>a</i> <i>a</i> <i>a</i> <i>a</i> <i>a</i> <i>a</i>	525 10 30 20 20 25 10 25 40 	$\begin{array}{c} 0.00177\\ 0.0433\\ 0.0447\\ 0.0445\\ 0.0446\\ 0.0446\\ 0.0446\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0445\\ 0.0444\\ 0.0445\\ 0.0446\\ b\end{array}$	$\begin{array}{c} +0.0004\\ 0.0000\\ +0.0002\\ 0.0000\\ +0.0001\\ -0.0001\\ 0.0000\\ -0.0002\\ 0.0000\\ -0.0003\\ $

^a Chloride from As₂O₃ only. ^b End point could not be distinguished.

Table II shows the influence of time on reduction of chromate with arsenite.

Table II-Influence of Time of Standing before Back-Titration of

	TIME TIME TIME CHROMIUM No. Cr Fe ⁺⁺⁺ V $12 N$ $0F$ Found Error TAKEN Added Added HCl H_2SO_4STAND Found Error Gram Grams Gram Cc. Cc. Min. Gram Gram 1 0.0445 2 25 90 0.0444 -0.0001 2 0.0445 0.5 30 10 0.0446 +0.0001 3 0.0445 0.5 10 10 0.0446 +0.0002							
No.	Cr	Fe+++	v	12 N	12 N	TIME	CHROMIUM	
	TAKEN	ADDED	ADDED	HCI	п2504	SIAND- ING	Found	Error
-	Gram	Grams	Gram	Сс.	 Cc.	Min.	Gram	Gram
1	0.0445			2	25	90	0.0444	-0.0001
2	0.0445			0.5	30	10	0.0446	+0.0001
3	0.0445			0.5	10	10	0.0446	+0.0001
4	0.0445			0.5	30	1 .	0.0445	0.0000
5	0.0445		0.025	0.5	30	180	0.0444	-0.0001
6	0.0445		0.015	0.5	10	1	0.0443	-0.0002
7	0.0445	0.6		0.5	25	15	0.0444	-0.0001
8	0.0433	1.5		1	25	2 1	0.0431	-0.0002
9	0.0433	1.5	0.025	1	5	15	0.0432	-0.0001
10	0.0433	1.5	0.025	1	5	1	0.0434	+0.0001
11	0.0035	1.5	0.025	2	ō	1	0.0033	-0.0002
12	0.0035	1.5	0.025	3	5	2	0.0034	-0.0001
13	0.0173	1.5	0.025	1	25	30	0.0171	-0.0002

The manganous salt present during the determinations given in Table III was added as pure manganous sulfate.

Table III-Determination of Chromium in Presence of Manganese,

	<u>^-</u>	Fe + + +	v	Mn ++		Acu	>	Сняс	MIUM
No.	TAKEN	Pres- ent	PRES- ENT	Pres- ent	12 N HC1	12 N H ₂ SO ₄	H ₃ PO ₄ (85%)	Found	Error
	Gram	Grams	Gram	Gram	Cc.	Cc.	Cc.	Gram	Gram
1	0.0441			0.005	1	10	10	0.0439	-0.0002
2	0.0433	1.5		0.005	1	25		0.0431	-0.0002
3	0.0433	1.5	0.05	0.007	1	$\frac{25}{6 N}$	• •	0.0431	-0.0002
4	0.0441			0.050	11	15	10	0.04385	-0.00025
5	0.0441	2.5		0.050	0.5	20	10	0.0436	-0.0005
6	0.0441	2.5	••	0.070	0.5	30	10	0.0435	-0.0006

Discussion of Results. The reduction of dichromate by arsenious acid is fairly rapid. In solutions which are 1 normal (or more) in acid, the reduction is complete in 1 minute if 1 or 2 cc. of excess arsenious acid are added (Nos. 4, 6, 10, and 11, Table II). The presence of chloride is necessary in the back-titration of arsenious acid with permanganate: in the absence of chloride, even when catalyst is present. the results of the titration are low. These observations confirm in some respects the observations of Lang (4). The amount of chloride that need be added, however, is small, as little as 0.05 to 0.1 gram in 50 cc. being sufficient (Nos. 31 and 32, Table I). Even at chloride concentrations as high as 1 or 2 normal a good end point is obtained with permanganate; increasing the chloride concentration much above this gives a fleeting end point. Varying the acidity of the solution from 1 normal to more than 6 normal has no effect on the results within experimental error. Iron and vanadium are without influence. Experiment 5 in Table II shows that no interference by vanadate occurs even if the excess of arsenious trioxide is titrated back after 3 hours' standing. When iron is present in large amounts, phosphoric acid should be added in order that a sharp end point may be obtained with potassium permanganate.

When large amounts of manganese are present in solution with chromic acid, a brownish color appears in the solution soon after the addition of a little arsenious acid in spite of the presence of the catalyst, potassium iodide, and has a tendency to persist, especially when iron is present, after a slight excess of arsenious acid has been added. After standing for a short time (usually less than 1 minute) with a slight excess of 0.1 Narsenious acid, the murky color of the solution disappears and the normal bluish green color appears. When potassium iodide is not present as catalyst, the brown color due to trivalent manganese disappears only with extreme slowness after addition of excess arsenious acid. The addition of a trace of potassium iodide is, therefore, unconditionally necessary in the presence of manganese.

The color change in titrating with permanganate is from bluish green to blue. A deepening of the color indicates the end point. The results given in the tables have not been corrected for the color effect of the chromic salt; the excess of permanganate required to give a perceptible end point in the colored solution under the conditions described (40 mg. chromium in 100 cc., etc.) corresponds to a correction of about +0.1 mg. chromium in the amount found. The end point can easily be detected with an accuracy of a drop of 0.1 Npermanganate. The observation of the end point is incomparably better than in cases where the reduction is accomplished with ferrous sulfate instead of arsenious trioxide in the presence of vanadate. It is for this reason that the writers prefer this procedure to that described by Hamner (1) and ecommended by the Bureau of Standards for routine analysis (February 7 1922).

Knop (3) has recently described the use of several new oxidation-reduction indicators in titrations with permanganate. The applicability of two of these, Eriogrün B and Setopalin, to the detection of the end point in the titration of excess arsenious acid with permanganate for the determination of chromate was tested. One-half a cubic centimeter of a 0.1 per cent solution of each indicator, respectively, was added to the acid solution (1 or 2 N) of chromic salt containing arsenious oxide; titration was then made with 0.025 N permanganate. The end point thus obtained (color change from green to bluish) was more distinct than that with permanganate alone, but the relatively high acidity of the solution evidently is detrimental to the full utility of the indicators. At lower acidities (below 0.5 N) both indicators are very useful. The general procedure for the titration of chromate and vanadate will be described later.

Determination of Vanadate by Titration with Ferrous Sulfate with Diphenyl Benzidine as Indicator

A brief study was made of the method of determining vanadic acid by titration with ferrous sulfate using diphenylbenzidine as indicator according to the procedure given by Willard and Young (8).

Titrations of vanadic acid were made at a volume of 50 to 100 cc. with 0.025 N ferrous sulfate which had been standardized against potassium permanganate. Vanadium was present as ammonium vanadate. The concentration of the diphenylbenzidine indicator used was 0.1 per cent in concentrated sulfuric acid. Sodium acetate was added in the form of the trihydrate. (Table IV)

In agreement with the results of Willard and Young (8), it was found that the color change at the end point in the titration of vanadic acid in the absence of sodium acetate was slow, although good results could even then be obtained if

Table IV-Titration of Vanadate

	v	Cr	Fe ^{+ + +}	0.1 N	ACID PR	ESENT	SODIUM ACE-	Diphenyl- benzidine	TIME BEFORE	VANAD	IUM
	Taken	PRESENT	Present	Added	$6 N H_2 SO_4$	H ₃ PO ₄	TATE Added	ADDED (0.1%)	TITRAT- ING	Found	Error
	Gram	Gram	Grams	Cc.	Cc.	Cc.	Grams	Cc.	Min.	Gram	Gram
1	0.0280				5	5	5	0.8	5	0.0278	-0.0002
2	0.0280		• • •		5	10	5	0.6	0	0.0278	-0.0002
3	0.0280				5	õ	0	0.5	0	0.0278	-0.0002
4	0.0280				5	5	8	0.5	ð	0.0278	-0.0002
5	0.0280				10	ō	8	0.5	õ	0.0279	-0.0001
6	0.0280				10	ð	8	0.5	ā	0.0279	-0.0001
7	0.0280	• •	1.5		10	5	8	0.5	5	0.0278	-0.0002
8	0.0280	• •	1.5		10	5	0	0,5	0	0.0279	-0.0001
9	0.00224		1.5		10	10	0	0.5	0	0.00233	+0.0009
10	0.00224		1.5		10	10	0	0.5	0	0.00229	+0.00003
11	0.00224		1.5		10	10	10	0.5	5	0.00210	-0.00014
12	0.00224		1.5		5	10^{a}	12	0.5	5	0.00216	-0.0008
13	0.00224		1.5		5	5^a	12	0.5	5	0.00213	-0.00011
14	0.00224	0.03			5	10	8	0,5	5	0.00221	-0.00003
15	0.00224	0.03	1,5		5	10	8	0.5	5	0.0022 +	0.0000
16	0.00224	0.03		0.1	5	10	8	0.5	5	0.0022	0.0000
17	0.00224	0.03	1.5	0.1	5	10	8	0.5	5	0.0022	0.0000
18	0.00224	0.03	1.5	0.5	5	10	8	0.5	3	0.0218	-0.00006

 $^a~2$ cc. 12 N HCl also present.

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					ACIDITY	,	Conditi	ons of V Litratio	ANADIUM	Chr	OMIUM	VANAI	DIUM
No.	Cr Taken	V Taken	Fe Present	H ₂ SO ₄ (6 N)	H3PO4	HCl (concd.)	Sodium acetate added	Diphenyl- benzi- dine (0.1%)	Time of stand- ing	Found	Error	Found	Error
	Gram	Gram	Grams	Cc.	Cc.	Cc.	Grams	Cc.	Min.	Gram	Gram	Gram	Gram
1	0.0433	0.00224		5	10	2	10	0.5	3 - 5	0.0434	+0.0001	0.00238	+0.00014
2	0.00346	0.0280	: : :	õ	10	2	10	0.5	3-5	0.00338	-0.00008	0.02787	-0.00013
3	0.0433	0.0280	1.0	o p	10	2	15	0.5	3-5	0.0430	-0.0003	0.0282	+0.0002
4	0.0433	0.0280	1.5	5	10	20	12	0.5	0-0	0.0432	-0.0001	0.0281	± 0.0001
0	0.0433	0.0112	1.0	5	10	2	12	0.5	0-0	0.0432	-0.0001	0.00248	± 0.0001
9	0.0433	0.00224	1.5	5	10	2	12	0.5	3-5	0.0430	-0.0003	0.00240	+0.0001
\$	0.01732	0.00224	3.0	Š	10	5	10	0.5	3-5	0.01724	-0.00008	0,00340	+0.00004
ä	0.01732	0.00224	1.5	5	10	2	10	0.5	3-5	0.01730	-0.00002	0 00235	+0.00011
10	0 01732	0.0280	1.5	5	10	$\tilde{2}$	1 10	0.5	3-5	0.01728	-0.00004	0.02794	-0.00006
īĭ	0.0433^{a}	0.00224	1.5	5	īő	$\overline{2}$	iŏ	0.5	3-5	0.0430	-0.0003	0.00248	-0.00024

Table V-Simultaneous Determination of Chromate and Vanadate

 a In this determination 5 mg. Mn $^{++}$ were present.

care was exercised in addition of reagent near the end point. It is advisable, however, to add sufficient sodium acetate to react with the sulfuric and hydrochloric acid present; approximately 5 grams of NaC₂H₃O_{2.3}H₂O can be allowed for each cubic centimeter of concentrated sulfuric acid and 1.5 grams for each cubic centimeter of concentrated hydrochloric acid. In the calculation of the results given in Table IV, the volume of ferrous sulfate was corrected for the indicator blank by adding 0.03 cc. to the volume of 0.025 N ferrous sulfate used for each 0.1 cc. of 0.1 per cent diphenylbenzidine solution added, this being the value given by Willard and Young (8). In agreement with the statement of these authors it was found that, in the presence of tungstic acid, the blue color of diphenylbenzidine does not appear and the titration of vanadium is rendered impossible.

It appears that more than traces of arsenious acid partially reduce vanadate on standing (compare determinations 16, 17, and 18, Table IV).

Combined Determination of Chromate and Vanadate

In the determinations of both chromium and vanadium the solution had a volume of 50 to 75 cc. and contained the amounts of chromate, vanadate, ferric alum, acid, and chloride indicated in Table V; 1 or 2 drops of 1/400 N potassium iodide were always added at the beginning. Tenth-normal arsenious acid was added from a buret until the color of the solution became bluish green; then a few cubic centimeters were always added in excess. After having stood for a few minutes, the excess of arsenious acid was titrated with 0.025 Npermanganate and from this volume the amount of chromium present was found. One drop of 0.1 N arsenious acid was then added to reduce any small excess of permanganate that might be present. After addition of the amounts of sodium acetate trihvdrate and 0.1 per cent (in concentrated sulfuric acid) diphenylbenzidine given in the table, the solution was allowed to stand for the length of time indicated. The titration of vanadium was then made by slowly adding 0.025 Nferrous sulfate until the blue color of the liquid changed to green. In the calculation of the quantity of vanadium present, the indicator correction was assumed to be 0.03 cc. 0.025 N ferrous sulfate per 0.1 cc. 0.1 per cent diphenylbenzidine, this correction being added to the volume of 0.025 Nferrous sulfate actually used.

From the results in Table V it may be concluded that the following general procedure will give satisfactory results.

STANDARD SOLUTIONS REQUIRED—Arsenious acid: 0.1 N, preferably prepared by weighing out 4.947 grams of pure arsenic trioxide and dissolving in 40 to 80 cc. of 1 N sodium hydroxide and diluting nearly to 1 liter. Hydrochloric acid is added until the solution is neutral or slightly acidic and finally the solution is made up to exactly 1 liter. If pure arsenic trioxide is not at hand, an approximately 0.1 N solu-

tion is prepared from the best product and standardized against permanganate. The solution of arsenious acid to be standardized should be about 1 normal in hydrochloric acid; 1 or 2 drops of 1/400 N potassium iodide are added. Potassium permanganate is run in (not too rapidly) until the faintest pink tinge appears in the liquid. The end point is excellent.

Potassium permanganate: 0.025 N, standardized against pure arsenious acid or pure sodium oxalate.

Ferrous sulfate: 0.025 N in approximately 0.1 N sulfuric acid.

DETERMINATION OF CHROMATE-The solution in which chromium and vanadium are to be determined may conveniently have a volume of 100 cc. and should not contain more than 0.05 or 0.075 gram of chromium in this volume. The acidity of the solution should be at least 1 normal; 1 or 2 cc. of concentrated hydrochloric acid, or its equivalent, should be present, as well as 1 or 2 drops of 1/400 N potassium iodide. In case iron is present 5 to 10 cc. of 85 per cent phosphoric acid must be added. Standard arsenious acid is slowly run into the solution of chromate and vanadate from a buret until the color becomes bluish green; a few cubic centimeters in excess are then added. In case much manganese is present, the appearance of the bluish green color may take some time. Therefore, 5 minutes should elapse between the addition of arsenious acid and the beginning of the back-titration with permanganate; in most cases when the quantity of manganese present is small, it is sufficient to allow the solution to stand for 1 or 2 minutes to effect complete reduction of chromate. The excess of arsenious acid is now titrated by slowly running in potassium permanganate; the end point is indicated by a sudden deepening in color of the green chromic solution to bluish green. The end point may be recognized to within 1 or 2 drops of 0.025 N permanganate without difficulty if not much more than 0.05 gram of chromium is present per 100 cc.

DETERMINATION OF VANADATE—To remove a possible slight excess of permanganate, 1 drop of arsenious oxide is added. Vanadium is now determined essentially according to the directions of Willard and Young. Approximately 5 grams of sodium acetate trihydrate are added for each cubic centimeter of concentrated sulfuric acid present (including also the sulfuric acid of the indicator to be added) and 1.5 grams for each cubic centimeter of 12 N hydrochloric acid, and thereafter 0.5 to 1.0 cc. of 0.1 per cent diphenylbenzidine (in concentrated sulfuric acid). The solution is allowed to stand for 5 minutes and is then titrated slowly with 0.025 Nferrous sulfate. Special care should be taken to add the ferrous sulfate dropwise near the end point. The color change is from blue to green or bluish green, the change being sharper the less chromium is present in solution. To correct for the indicator blank add 0.03 cc. for each 0.1 cc. of diphenylbenzidine indicator present to the volume of 0.025 N ferrous sulfate used in the titration. In case tungstic acid is present, it must be removed before vanadate can be titrated with diphenylbenzidine as indicator (8).

Oxidation of Chromic and Vanadyl Salts with Potassium Bromate

The oxidation of chromic salts to chromic acid and vanadyl salts to vanadic acid can be effected by the use of potassium persulfate as oxidizing agent, and this is the reagent ordinarily used in determining the sum of chromium and vanadium in steels $(\mathcal{Q}, \mathcal{G}, \mathcal{G})$. In the present investigation the possibility of using potassium bromate as the oxidizing agent was studied. Potassium bromate has already been utilized by Willard and Young (8) as a reagent for the oxidation of vanadyl salts to vanadic acid in hydrochloric acid solution without affecting chromic salts.

In the experimental work to be described, the oxidation of chromium was carried out in a solution acidified with sulfuric

a 100-cc. portion of chromic and vanadyl salts (obtained by reducing dichromate and vanadate with sulfur dioxide) containing the stated amounts of acid and manganese (as manganous sulfate) with 2 grams of pure potassium bromate. In determinations 1 to 6 boiling with potassium bromate was continued for 10 minutes, in determinations 7 to 18 for only 5 minutes. Five grams of ammonium sulfate were then added to the solution; after most of the bromine had been boiled out, 10 cc. of 1 N hydrochloric acid were added and boiling was continued until starch-iodide paper was no longer colored. After cooling, chromate and vanadate were determined as already described. In all cases when iron was present enough additional phosphoric acid was added after oxidation to make the total amount present about 10 cc. of 85 per cent acid. After the addition of 2 drops of 1/400 N potassium iodide and a small excess arsenious acid (usually only a few cubic centimeters), the solution was allowed to stand 3 to 5 minutes or until it was bluish green with no murky color, which would be due to trivalent manganese.

Table VI-Oxidation of Cr⁺⁺⁺ and VO⁺⁺ with Potassium Bromate and the Determination of Chromium and Vanadium according to the Proposed Method

_	0		T1.	24	Acid F	RESENT	CHRO	DMIUM	VANAI	DIUM		
No.	Taken	TAKEN	PRESENT	PRESENT	H ₂ SO ₄ (concd.)	H ₃ PO ₄ (85%)	Found	Error	Found	Error		
	Gram	Gram	Grams	Gram	Cc.	Cc.	Gram	Gram	Gram	Gram		
1 2 3 4 5 6 7 8 9 10 11 12 13	$\begin{array}{c} 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ 0,0441\\ \end{array}$	0.0112	1.0 2.5 2.5	$\begin{array}{c} 0.004\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.010\\ 0.010\\ 0.010\\ 0.005\\ 0.025\\ 0.035\\ 0.005\\ 0.005\\ \end{array}$	3338311123352	$ \begin{array}{r} 10 \\ 10 \\ 10 \\ 10 \\ 4 \\ 5 \\ 5 \\ 2 \\ 2 \\ 1 \\ 5 \\ 3 \\ 2 \\ 1 \\ 3 \\ 3 \\ 2 \\ 1 \\ 3 \\ 1 \\ $	$ \begin{array}{c} 0.0435\\ 0.0435\\ 0.0434\\ 0.0433\\ 0.0433\\ 0.0435\\ 0.0439\\ 0.0439\\ 0.0442\\ 0.0442\\ 0.0441\\ 0.0439\\ 0.0440\\ 0.0439\\ 0.0438\\ \end{array} $	$\begin{array}{c} - \ 0,\ 0006\\ - \ 0,\ 0006\\ - \ 0,\ 0007\\ - \ 0,\ 0008\\ - \ 0,\ 0006\\ - \ 0,\ 0002\\ - \ 0,\ 0002\\ + \ 0,\ 0000\\ - \ 0,\ 0,\ 000\\ - \ 0,\ 0,\ 0,\ 0,\ 0,\ 0,\ 0,\ 0,\ 0,\ 0$	 0.0112	0.0000		
14ª 15 16 17ª 18	$\begin{array}{c} 0.0441 \\ 0.0441 \\ 0.0176 \\ 0.0882 \\ 0.0176 \end{array}$	$\begin{array}{c} 0.0112 \\ 0.0112 \\ 0.0112 \\ 0.0280 \\ 0.0280 \\ 0.0280 \end{array}$	$2.0 \\ 2.0 \\ 2.0 \\ 2.0 \\ 2.0 \\$	$\begin{array}{c} 0.050 \\ 0.050 \\ 0.040 \\ 0.050 \\ 0.050 \\ 0.050 \end{array}$	3 2 2 3	$10 \\ 5 \\ 4 \\ 10 \\ 3$	$ \begin{array}{c} 0.0442 \\ 0.0438 \\ 0.0175 \\ 0.0882 \\ 0.0176 \end{array} $	$\begin{array}{c} +0.0001 \\ -0.0003 \\ -0.0001 \\ 0.0000 \\ 0.0000 \end{array}$	$\begin{array}{c} 0.0110\\ 0.0110\\ 0.0112\\ 0.0282\\ 0.0281\end{array}$	$\begin{array}{r} -0.0002 \\ -0.0002 \\ 0.0000 \\ +0.0002 \\ +0.0001 \end{array}$		

^a Vol. 200 cc. instead of 100 cc.

and phosphoric acids. At low acid concentrations the oxidation is so slow that it is not conveniently applicable. It was found, however, that small amounts of manganese greatly increased the speed of the reaction, since in the presence of phosphoric acid the trivalent (and quadrivalent) forms of manganese catalyze the oxidation of chromic salts to chromic acid. After the oxidation has been completed, it is necessary to destroy all excess of bromate and to decompose the manganic phosphate still present. For this purpose ammonium sulfate was used. The higher oxidation states of manganese are quickly reduced to Mn⁺⁺ in hot solution, but it was found that a complete decomposition of bromate at 100° C. was difficult to attain after a moderate period of boiling even though the presence of manganese is decidedly favorable. Thus, after boiling for 15 minutes with about 3 grams (excess) ammonium sulfate in the presence of 3 cc. of concentrated sulfuric acid and 10 cc. of phosphoric acid and 5 to 10 mg. of Mn⁺⁺ in 100 cc., the solution still contained enough bromate to give an error of about +0.5 mg. in the amount of chromium found. It was found, however, that, after most of the bromate had been destroyed by boiling for a few minutes with ammonium sulfate, the last traces could be eliminated by adding a small amount of hydrochloric acid. If 5 grams ammonium sulfate were added to a solution containing 5 cc. of concentrated sulfuric acid, 5 to 10 cc. of phosphoric acid (85 per cent), and 1 cc. of concentrated hydrochloric acid with 1 gram of potassium bromate, no bromate was left after boiling for 10 to 15 minutes (methyl orange test).

The results recorded in Table VI were obtained by oxidizing

Note—At the Minneapolis meeting of the AMERICAN CHEMICAL SOCIETY September, 1929, H. H. Willard described the favorable properties of 70 per cent perchloric acid as an oxidizing agent. In concentrated solution chromium and vanadium can be oxidized to chromic acid and vanadic acid, respectively, by boiling with perchloric acid. After the completion of the oxidation, the perchloric acid need not be removed; by simply diluting with water its oxidizing properties practically disappear and it will not interfere in the titration of chromate and vanadate. In this way it may be possible to avoid the use of potassium bromate entirely. See also Lichtin, IND. ENO. CHEM., Anal. Ed., **2**, 126 (1930).

It will be seen that, when the acidity is high, the amount of chromium found is too low. This may be attributed to the decomposition of chromic acid by boiling with Cl⁻ in the presence of the amounts of acid given. Decreasing the acid concentration improves the results. It had been the original intention to maintain a rather high concentration of phosphoric acid in the solution during oxidation to prevent the precipitation of manganese dioxide, which dissolves rather slowly when boiled with ammonium sulfate. In the presence of smaller amounts of phosphoric acid (2 to 5 cc. per 100 cc. of solution) there is more or less precipitation of manganese during the 5-minute period of boiling required for oxidation, depending upon the amount of manganese present. When ammonium sulfate is added and the liquid boiled, manganese dioxide will be dissolved by the combined action of ammonium ion and phosphoric acid. Only when 50 mg. or more of manganese are present is complete solution of manganese dioxide effected with difficulty at phosphoric acid concentrations of 3 or 4 cc. per 100 cc. The hydrochloric acid added to decompose the residual bromate will, of course, also attack manganese dioxide.

April 15, 1930

Determination of Chromium and Vanadium in Steel

The results of the analyses of different steels given in Table VII were obtained by the following recommended procedure:

For steels containing chromium to the extent of 1 per cent a 2- to 3-gram sample is taken and for higher contents correspondingly less. The weighed sample is transferred to a 250-cc. Erlenmeyer flask; 25 cc. water are added and then 1.5 cc. of concentrated sulfuric acid for each gram of steel, allowing 1 to 2 cc. in excess, and 3 or 4 cc. of 85 per cent phosphoric acid. To hasten solution of the steel, the liquid is boiled. When solution is complete, sufficient concentrated nitric acid is added dropwise to oxidize iron to the ferric condition; about 1 cc. per gram of steel is sufficient. The solution is now boiled to expel the oxides of nitrogen and sufficient water added to make the total volume approximately 100 cc. One or two grams of pure potassium bromate are then added and the solution is boiled for 5 minutes. Five grams of ammonium sulfate are cautiously added in small portions to the solution (which should again have been brought to approximately 100 cc.); the solution is boiled until most of the bromine has been expelled. Then 10 cc. of 1 N hydrochloric acid are added and boiling is continued until starchiodide paper is no longer colored. After cooling to room temperature, 5 to 8 cc. of 85 per cent phosphoric acid and 1 to 2 drops of 1/400 N potassium iodide are added; 0.1 N arsenious acid is run in slowly from a buret until the color of the solution has become bluish green and finally 2 to 3 cc. in excess. The analysis is then continued as described above for the combined determination of chromate and vanadate.

Table VII shows that the proposed method gives satisfactory results.

Table VII—Analyses of Bureau of Standards Steels according to the Proposed Method

STEEL	BUREAU OF VAL	STANDARDS LUES	VALUES BY MET	VALUES BY PROPOSED METHOD		
	Chromium	Vanadium	Chromium	Vanadium		
30	Per cent 1.35	Per cent 0.21	Per cent 1.343	Per cent 0.220		
3 0 °	1.044	0.21	1.333 1.005	0.214		
3 0 b	1.01 b 1.03	0.208	0.998 0.99	$\begin{array}{c} 0.212 \\ 0.206 \end{array}$		
32	0.89	•••	$\begin{array}{c} 0.930\\ 0.941 \end{array}$	0.018		

^a Persulfate oxidation. ^b Permanganate oxidation.

Literature Cited

- (1) Hamner, Met. Chem. Eng., 17, 206 (1917).
- (2) Kelley and Conant, J. IND. ENG. CHEM., 8, 719 (1916).
- (3) Knop, Z. anal. Chem., 77, 125 (1929).
- (4) Lang, R., Z. anorg. allgem. Chem., 152, 205 (1926).
- (5) Lang, R., and Zwerina, Z. Elektrochem., 34, 364 (1928).
- (6) Lundell, Hoffman, and Bright, IND. ENG. CHEM., 15, 1064 (1923).
- (7) Spitalsky, Z. anorg. Chem., 69, 179 (1911).
- (8) Willard and Young, IND. ENG. CHEM., 20, 764 (1928).
- (9) Willard and Young, Ibid., 20, 769 (1928).
- (10) Zintl and Zaimis, Z. angew. Chem., 40, 1286 (1927).
- (11) Zintl and Zaimis, Ibid., 41, 543 (1928).

The Testing of Automotive Rubber Parts Assembled under Compression

Part I-Deflection under Compression

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Present-day test specifications on automotive rubber parts are not only incomplete and misleading, but entirely lacking in uniformity. This is particularly true of compression and permanent-set tests on automotive mechanical rubber parts assembled under compression. Consequently, an effort has been made to show the urgent need for unification of such methods.

Data are presented in Part I to show that high tensile is no criterion of relative resistance to compression set and that hardness is not a measure of deflectability. In addition, deflection and permanent set under compression are greatly influenced by the size and shape of the

I N KEEPING with the rapid strides in the automobile industry, an almost endless variety of rubber mechanical goods is being used in motor-car manufacture. As a result there has arisen a great variety of tests and test specifications, many of which are worthless for evaluating the parts under consideration. In fact, some of these specifications, particularly those requiring compression- and permanent-set tests, are often defeating the purpose for which they were

¹Received July 3, 1929; revised paper received December 2, 1929. Presented before the Division of Rubber Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929. test piece, the method of cutting the sample, the gage and methods of measuring it, and condition and kinds of surfaces in contact with the test piece.

Compression and compression-set testing equipment are discussed, and some newly designed laboratory equipment is described. One piece of apparatus, the compressetometer, has been found extremely useful in making deflection, hysteresis, and set tests. These tests may be performed under constant load or constant distortion. The constant-load (spring) compression-set clamp is suggested as a suitable laboratory standard for permanentset testing under compressive loads.

written. The authors of these specifications have either presupposed a uniformity in testing equipment and details of tests, and hence have very briefly stated the tests, or else, through a lack of appreciation of the many factors influencing the results, have failed to include such important details as size of test piece, gage, etc. Consequently many inferior stocks may pass these specifications if the testing conditions are carefully chosen. There are generally other requirements, such as tensile, elongation, etc., to preclude the possibility of passing certain very low-grade stocks, but even these requirements do not offer an absolute safeguard against inferior quality, for a very high tensile, for example, does not