of certain complex alloy steels, the application to which of the procedure described, while not discouraged, has not as yet been considered in detail.

Summary.

An oxidimetric determination of Ti and Cr, involving the use of an electrically heated reductor, is described, by means of which these metals may be determined easily and accurately, either alone or together with iron and other metals.

The writer wishes to express his appreciation of the services of A. Ortiz and also of H. B. C. Allison, who performed the test analyses cited and suggested the extension of the procedure to Cr.

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THE PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF CHLORIDES.

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Since the original proposal of the permanganate titration of iron by Marguerite,[1] the method has undergone various modifications. The majority of these changes were made to obviate the high results obtained by titrating in the presence of hydrochloric acid. This error was first pointed out by Löwenthal and Lenssen[2] and later by a number of authors.[3-26] Kessler[4] first called attention to the fact that considerable sulfuric acid, and still better manganese salts, greatly reduced the influence of the hydrochloric acid. Zimmerman[5] then proposed the use of manganese salts for this purpose, claiming as great an accuracy in hydrochloric as in sulfuric acid solutions. Reinhardt[7] next suggested the use of phosphoric acid also, for the removal of the color of ferric chloride to insure a better end point.

The permanganate method, used very largely to-day for the determination of iron in ores, in brief is as follows: Solution of the ore by heating with stannous chloride and hydrochloric acid, completion of the reduction by adding stannous chloride to the hot solution until colorless, dilution, addition of mercuric chloride to remove the excess of stannous salt, addition of the Zimmerman-Reinhardt solution (sometimes known as "preventive solution") containing sulfuric acid, manganese sulfate and phosphoric acid, and titration with permanganate, taking the first recognizable tint of color, permeating the entire solution for a short time, as the end point (inasmuch as the end point is somewhat unstable in the presence of chlorides).

The question which has concerned most of the authors quoted is: Does the Zimmerman-Reinhardt, or similar solution really prevent the action of hydrochloric acid? Birch[23] maintains that the method is only an approximate one. However, the concensus of opinion of the various workers is that, if used in sufficient quantity, it stops practically all, if not all, of the influence of small amounts of hydrochloric acid. Friend[24] says the concentration of hydrochloric acid should not be greater than 0.25 *M*. Jones and Jeffreys[22] find a constant error, which is not obviated by any concentration of hydrochloric acid or manganese sulfate mixture. They recommend a subtraction of this error in each determination. To test this point, a standard solution of ferrous sulfate, containing sulfuric acid, was prepared and its strength determined by permanganate titration in sulfuric acid solution. Equal volumes of this solution were then employed for titration with varied quantities of hydrochloric acid and preventive solution.

General Reagents.

The Reinhardt-Zimmerman solution was made as follows: 160 g. of crystallized manganese sulfate, 330 cc. phosphoric acid (sp. gr. 1.7) and 320 cc. of sulfuric aicd (sp. gr. 1.84) diluted to 2400 cc. It is also designated manganese solution No. 1, to distinguish it clearly from other preventives employed. This solution is in general use for the titration of iron.

Other reagents used in this and other series are as follows: Hydrochloric acid, sp. gr. 1.10; sulfuric acid, sp. gr. 1.40; phosphoric acid, sp. gr. 1.35; mercuric chloride, a saturated solution; stannous chloride, 200 g. $SnCl_2.2H_2O$ and 70 cc. HCl (sp. gr. 1.20) per liter.

The ferric chloride solutions used in each series following series six were analyzed by the use of the Zimmerman-Reinhardt solution called in this paper "manganese solution No. 1." At least one result is given in each series. Where only one result is given it is an average of two or more analyses.

Special reagents for individual series will be described in connection with the series in which they are used.

Volume of Solutions Titrated.

Unless otherwise stated, the volume of the solution after dilution just preceding titration was about 500 cc. In most cases a considerable deviation from this volume is of very little consequence, but for the general purposes of this paper it is important.

Use of Preventives Containing Manganese.

Table I shows very concretely that no correction for an inherent error of the Zimmerman-Reinhardt method is necessary. However, it is easy to conceive a trace of iron in a reagent such as the stannous chloride, which, if used for the reduction of all the iron present, would introduce a fairly uniform error of the nature described by Jones and Jeffreys.[22]

A number of authors recommend a time interval between the addition of the mercuric chloride and manganese sulfate solution. In some cases

Table I.

Series I.—Accuracy of the Zimmerman-Reinhardt Method.

20 cc. of $FeSO_4$ solution = 0.1338 g. Fe. 1 cc. of $KMnO_4$ solution = 0.004386 g. Fe.[1]

Expt. No.	Wt. Fe taken.	Cc. HCl.	Cc. H_2SO_4.	Cc. manganese soln. No. I.	Cc. $SnCl_2$.	Cc. $HgCl_2$.	Wt. Fe. found.	Deviation from H_2SO_4 result.
1	0.1338	..	20	..	....	..	0.1338	....
2	0.1338	..	20	..	....	..	0.1338	....
3	0.1338	..	20	20	....	..	0.1337	−0.0001
4	0.1338	5	..	20	....	..	0.1338	±0.0000
5	0.1338	10	..	20	....	..	0.1337	−0.0001
6	0.1338	10	..	20	....	..	0.1337	−0.0001
7	0.1338	25	..	20	....	..	0.1339	+0.0001
8	0.1338	40	..	20	....	..	0.1351	+0.0013
9	0.1338	5	..	..	....	..	0.1368	+0.0030
10	0.1338	10	..	20	0.06	10	0.1338	±0.0000
11	0.1338	10	..	20	0.10	10	0.1337	−0.0001
12	0.1338	10	..	20	0.20	10	0.1338	±0.0000

even ten minutes[26] is designated. This was investigated by titrating: (1) with a time interval of twenty seconds, (2) of thirty seconds, (3) of ten minutes, using the solutions employed in Table I. In (1) and (2) vigorous stirring with a rather heavy glass rod accompanied the addition of the tin salt and continued until the end of the titration.

Table II.

Series II.—Interval of Time Necessary Just before Titration. 1 cc. $KMnO_4$ = 0.004386 g. Fe. 20 cc. $FeSO_4$ (= 0.13 g. Fe) + 10 cc. HCl + 10 cc. $HgCl_2$ + 20 cc. Mn sol. No. 1 taken.

No.	Cc. $SnCl_2$.	Time interval.	Wt. of Fe found.
1	0.06	20 sec.	0.1338
2	0.10	20 sec.	0.1340
3	0.10	30 sec.	0.1338
4	0.10	30 sec.	0.1338
5	0.10	10 min.	0.1338
6	0.10	10 min.	0.1340

Series III.—Effect of Speed of Titration. 1 cc. $KMnO_4$ = 0.004836 g. Fe. 20 cc. $FeCl_2$[2] (= 0.1717 g. Fe) 10 cc. HCl taken.

Cc. Mn soln. No. 1.	Time. Min.	Time. Sec.	Wt. Fe found. G.
20	2	30	0.1717
20		45	0.1718
5	2	30	0.1717
5		45	0.1732
3	2		0.1719
3		45	0.1739
2	2	30	0.1729
2	1	45	0.1727
2	1	10	0.1732
2		45	0.1739
2		10	0.1755

These results show that only a short interval of time is necessary between the addition of stannous chloride and mercuric chloride, if the solution is thoroughly agitated.

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[1] This is the average value obtained by checking the solution against electrolytic iron, sodium oxalate and ferrous ammonium sulfate. All the permanganate solutions used in this investigation were standardized in a similar manner.

[2] This solution contained 10 cc. HCl (1.2) per liter.

Speed of Titration.

Many series of analyses have been made in which the influence of the speed of titration was closely watched. In this study the permanganate was added at as nearly a uniform rate as possible until the end point was closely approached and then the titration was finished more slowly. The solutions were stirred vigorously during the entire titration to give uniformity of mixing. Series III is typical of the results obtained.

Another of the several series of analyses was performed using ferrous sulfate as the standard iron solution with analogous results.

The results of Series III seem to justify the conclusion that, if the action of the hydrochloric acid has been offset by a sufficient excess of the preventive, no difference enters except the difference in buret drainage. (See also Series I.) However, if the amount of preventive just sufficient for a good result with considerable hydrochloric acid present in a slow titration be used under the same conditions, except in a faster titration, then more permanganate is required. This confirms the work of Friend.[24]

In the work outlined in the following pages the solutions were stirred thoroughly and the buret allowed to give a uniform flow of permanganate until the end point was nearly approached, then the titration was finished more slowly, as indicated above. About 1 cc. for each 2 seconds was the rate adopted as a convenient basis for comparison of results.

Effect of HgCl in Suspension.

In a large number of titrations, in which an amount of preventive insufficient to stop the action of hydrochloric acid on the permanganate was used, a partial or complete disappearance of the calomel was noticed. This suggested the action of chlorine or hypochlorous acid on the mercurous chloride, thus reducing the concentration of active oxidizing agent in solution and correspondingly lowering the speed of oxidation of ferrous iron, hence requiring more permanganate to complete the reaction. To test this, measured portions of standard ferric chloride solution were acidified with 10 cc. of hydrochloric acid (sp. gr. 1.10), heated, reduced with stannous chloride as usual, and diluted; mercuric chloride was added and the calomel filtered out. To the filtrates were added varying amounts of stannous chloride (40 g. per liter) and the titration was finished as before indicated. No preventive was used in this series. Meineke[11] likewise calls attention to the influence of calomel on the titration.

All the end points were indefinite, becoming more so as the quantity of calomel increased. The first semi-permanent tinge throughout the solution was taken as the end point. These results show that when the hydrochloric acid is allowed to interfere in titration the amount of interference is somewhat proportional to the concentration of calomel in suspension.

TABLE III.

Series IV.—Effect of Suspended Calomel.

Expt. No.	Wt. of Fe taken.	Cc. HCl.	Cc. HgCl.	Excess of $SnCl_2$. Cc.	Wt. of Fe found.
1	0.1930	10	20	1	0.2039
2	0.1930	10	20	1	0.2035
3	0.1930	10	20	2	0.2075
4	0.1930	10	20	3	0.2101
5	0.1930	10	20	3	0.2105
6	0.1930	10	20	5	0.2149

Quantity of Manganese Solution Required.

A series of analyses was made by reducing measured portions of a ferric chloride solution, adding the other reagents as in Series III, but using varying quantities of the manganous sulfate solution mixture. Another series was made keeping the manganous sulfate solution constant. In each determination one drop of stannous chloride was added in excess and the resulting calomel left in suspension.

TABLE IV.

Series V.—Quantity of Manganese Sulfate Soln. Required.

1 cc. of $KMnO_4$ = 0.004887 g. Fe. 20 cc. of $FeCl_3$(=0.2290 g. Fe) + 10 cc. $HgCl_2$ taken.

Cc. HCl.	Cc. manganese soln. No. 1.	Wt. of Fe found.	Comments.	Cc. HCl.	Cc. manganese soln. No. 1.	Wt. of Fe found.	Comments.
5	. .	0.2346	End point unstable	10	20	0.2292	
5	1	0.2331	End point unstable	15	20	0.2290	
5	2	0.2314	End point unstable	20	20	0.2292	
5	3	0.2302	End point more stable	25	20	0.2290	
5	4	0.2299	End point more stable	30	20	0.2292	
5	5	0.2299	End point more stable	35	20	0.2292	
5	6	0.2290	End point good	40	20	0.2299	Part of HgCl dissolved
5	6	0.2287	End point good	50	20	0.2316	Part of HgCl dissolved
5	10	0.2287	End point good	55	20	0.2316	Part of HgCl dissolved
5	20	0.2290	End point good	60	40	0.2297	Part of HgCl dissolved
5	20	0.2290		75	40	0.2302	Part of HgCl dissolved
5	20	0.2290		75	40	0.2302	Part of HgCl dissolved
				120	80	0.2321	All of HgCl dissolved

The lower limit of accuracy under the conditions obtaining is seen to be 6 cc. of manganese solution mixture for five cc. of hydrochloric acid added to the other chlorides present. This amount would probably be somewhat different for varying quantities of ferric chloride and slightly varying with different individuals because of differences in manipulation.

Manganese Solutions with and without Phosphoric Acid.

A manganese sulfate solution containing 160 g. of crystallized salt in 2400 cc. was prepared and used in the following series. (This solution is designated "manganese solution No. 2.")

TABLE V.

Series VI.—Use of H_3PO_4 and H_2SO_4 with $MnSO_4$.

1 cc. $KMnO_4$ = 0.004847 g. Fe. 20 cc. $FeCl_3$ (= 0.2101 g. Fe, Experiments 1–15 inclusive) and 20 cc. $FeCl_3$ (= 0.2310 g. Fe, Experiments 16–28 inclusive) + 10 cc. HCl + 10 cc. $HgCl_2$ taken.

Expt. No.	Cc. manganese soln. No. 2.	Cc. H_2SO_4.	Cc. H_3PO_4.	Wt. of Fe found.	Deviation.	Expt. No.	Cc. manganese soln. No. 2.	Cc. H_2SO_4.	Cc. H_3PO_4.	Wt. of Fe found.	Deviation.
1	1	..	..	0.2201	+0.0100	16	..	12	..	0.2375	+0.0065
2	2	..	..	0.2205	+0.0104	17	..	12	..	0.2382	+0.0072
3	3	..	..	0.2167	+0.0066	18	..	..	12	0.2363	+0.0053
4	6	..	..	0.2133	+0.0032	19	..	..	12	0.2375	+0.0074
5	10	..	..	0.2133	+0.0032	20	25	..	..	0.2322	+0.0012
6	15	..	..	0.2128	+0.0027	21	25	..	10	0.2307	—0.0003
7	25	..	..	0.2118	+0.0017	22	25	..	10	0.2307	—0.0003
8	50	..	..	0.2101	+0.0000	23	25	..	..	0.2322	+0.0012
9	50	..	..	0.2104	+0.0003	24	25	..	5	0.2310	+0.0000
10	25	12	..	0.2101	+0.0000	25	25	5	..	0.2312	+0.0002
11	15	8	..	0.2104	+0.0003	26	25	5	..	0.2312	+0.0002
12	10	5	..	0.2133	+0.0032	27	25	5	..	0.2310	+0.0000
13	10	15	..	0.2121	+0.0020	28	25	..	5	0.2310	+0.0000
14	10	30	..	0.2106	+0.0005						
15	10	50	..	0.2123	+0.0022						

This series shows (1) that manganese sulfate without sulfuric or phosphoric acid will prevent the effect of hydrochloric acid on the permanganate, (2) that a less amount of manganese sulfate is required when it is accompanied by sulfuric or phosphoric acids, and (3) that sulfuric and phosphoric acids can be used interchangeably.

On account of the fact shown in Series V, that the phosphoric and sulfuric acids could be used interchangeably, it seemed worth while to make a solution of manganese sulfate in sulfuric acid and test its prevention. Consequently a solution was prepared containing 70 g. of crystallized salt and 300 cc. of sulfuric acid (sp. gr. 1.84) per liter. (This solution is designated "manganese solution No. 3.")

These results show that the use of phosphoric acid is merely a matter of preference. Except in the cases where 40 cc. of hydrochloric acid was present, one solution seemed to be as good as another; however, in the latter case, what difference does exist is in favor of the phosphoric acid. Of course, no such volumes of hydrochloric acid are used in the analysis of iron ores, making this point of less consequence.

A series of analyses was made using manganese chloride solution as preventive, thus eliminating sulfates and phosphates entirely. While the end points were obscure on account of color of the solution, nevertheless comparatively good results were obtained, showing good prevention. In this series (VIII) the following solutions were used: A ferrous chloride solution made by dissolving approximately 25 g. of the crystallized salt

TABLE VI.

Series VII.—Titration without H_3PO_4.

1 cc. $KMnO_4$ = 0.004396 Fe. 20 cc. $FeCl_2$ (= 0.2092 g. Fe) + 10 cc. $HgCl_2$ taken.

Expt. No.	Cc. HCl.	Cc. manganese soln. No. 3.	Wt. of Fe found.	Comments.
1	5	1	0.2123	
2	5	2	0.2112	
3	5	3	0.2105	
4	5	4	0.2098	
5	5	5	0.2101	(Rather heavy HgCl)
6	5	6	0.2098	
7	5	6	0.2096	
8	5	6	0.2096	
9	5	7	0.2092	
10	5	8	0.2092	
11	10	5	0.2105	
12	10	10	0.2092	(Light HgCl)
13	10	10	0.2101	(Rather heavy HgCl)
14	10	15	0.2092	
15	10	15 cc. manganese soln. No. I	0.2092	
16	10	25	0.2090	
17	20	20	0.2090	
18	20	20	0.2092	
19	20	20 cc. manganese soln. No. I	0.2092	
20	40	..	0.2180	
21	40	20	0.2096	Very slow titration
22	40	20 cc. manganese soln. No. I	0.2096	Very slow titration

in a liter of water containing 10 cc. of hydrochloric acid (sp. gr. 1.2); a manganese chloride solution containing 75 g. of crystallized salt and 20 cc. of hydrochloric acid (sp. gr. 1.2) per liter; hydrochloric acid, sp. gr. 1.1. All the titrations were performed somewhat slower than usual, about two minutes being required for each titration.

TABLE VII.

Series VIII.—Manganese Chloride as Preventive.

1 cc. $KMnO_4$ = 0.004836 g. Fe. 20 cc. $FeCl_2$ (= 0.1717 g. Fe) + 5 cc. HCl taken.

Cc. $MnCl_2$.	Cc. manganese soln. No. 1.	Wt. of Fe found.	Cc. $MnCl_2$.	Cc. manganese soln. No. 1.	Wt. of Fe found.
..	20	0.1717	10	..	0.1722
..	20	0.1717	12	..	0.1722
..	..	0.1755	16	..	0.1724
1	..	0.1745	20	..	0.1722
2	..	0.1743	25	..	0.1722
3	..	0.1740	50	..	0.1719
4	..	0.1740	50	..	0.1719
5	..	0.1732	50	..	0.1722
6	..	0.1734	100	..	0.1722
7	..	0.1729	100	..	0.1719
8	..	0.1732	200	..	0.1719

Application of Other "Preventives.".

The role which manganese salts play in preventing the action of hydrochloric acid on the permanganate in titration seemed to warrant a study of other substances to ascertain their action toward prevention.

The first class of substances tried were neutral salts. Skrabal[16] has studied the influence of the addition of varying amounts of normal neutral salt solutions in the titration of iron, arriving at the conclusion that these salts do not produce correct results. In this work much stronger solutions are employed, which accounts for somewhat different results. Sodium silicate, borate and tetraborate give some prevention, but the adjustment between the amount of salt and acid to be used was too difficult to give any merit to the procedure. If too much silicate is used the ferrous iron precipitates and if too much sulfuric acid is added the end point is indistinct, overtitration resulting. Sodium sulfate, when used in large enough amounts, gives a good titration. Potassium sulfate is not as effective, probably because of its limited solubility in water. Ammonium sulfate also prevents moderately well with low concentrations of hydrochloric acid and high concentrations of the ammonium salt, but is not as satisfactory as the former two. These observances are in contradiction to the work of Birch,[23] who says that sodium sulfate and magnesium sulfate do not prevent, and that ammonium sulfate is worse than worthless.

TABLE VIII.

Series IX.—$Na_2SO_4.10H_2O$ (250 g. in Liter) as Preventive. 1 cc. $KMnO_4$ = 0.004887 g. Fe. 20 cc. $FeCl_2$ (= 0.1930 g. Fe) + 10 cc. $HgCl_2$ taken.

Expt. No.	Cc. HCl.	Cc. Na_2SO_4.	Wt. of Fe found.
1	25	100	0.1961
2	25	200	0.1961
3	25	200	0.1956
4	25	300	0.1937
5	25	400	0.1930
6	25	400	0.1930
7	25	400	0.1930
8	5	20 cc. Mn soln. No. 1	0.1930

Series X.—K_2SO_4 as Preventive. 1 cc. $KMnO_4$ = 0.004887 g. Fe. 20 cc. $FeCl_2$ (= 0.2290 g. Fe) + 10 cc. $HgCl_2$ taken.

Expt. No.	Cc. HCl.	Cc. $HgCl_2$.	Cc. K_2SO_4.	Wt. of Fe found.
1	5	10	50	0.2297
2	5	10	50	0.2297
3	10	10	50	0.2312
4	15	10	50	0.2331
5	10	10	100	0.2299
6	15	10	100	0.2301
7	20	10	100	0.2326
8.	25	10	200	0.2306
9	25	10	200	0.2304
10	5	10	20 cc. Mn soln. No. 1	0.2290

Another series of results was obtained preceding this series, in which was used a supersaturated solution of sodium sulfate of about twice the strength of the one here employed. A correspondingly less volume of the sulfate solution was necessary for prevention.

In Series X are tabulated the results obtained using a saturated solution of potassium sulfate and from these results it is evident that potassium sulfate solutions do not contain sufficient alkali sulfate for good preventive purposes.

Cady and Ruediger[9] have published a method using mercuric sulfate as reagent to stop the influence of hydrochloric acid. To study the action of this reagent, 300 g. of mercuric sulfate was dissolved in 1400 cc. of water containing 125 cc. of sulfuric acid (sp. gr. 1.84) and the solution applied in Series XI.

TABLE IX.

Series XI.—Mercuric Sulfate as Preventive.

1 cc. $KMnO_4$ = 0.004887 g. Fe. 20 cc. $FeCl_3$ (= 0.2150 g. Fe) + 5 cc. HCl taken.

Expt. No.	Cc. $HgCl_2$.	Cc. $HgSO_4$.	Cc. manganese soln. No. 1.	Wt. of Fe found.	
1	10	10	..	0.2118	
2	..	10	..	0.2167	Indefinite
3	..	15	..	0.2155	
4	10	20	..	0.2167	Indefinite
5	10	25	..	0.2150	
6	..	25	..	0.2150	
7	..	25	..	0.2155	
8	..	35	..	0.2228	Very indefinite
9	10	50	..	0.2297	Very indefinite
10	10	50	..	0.2297	Very indefinite
11	10	..	20	0.2150	

Results 1 to 4, inclusive, show incomplete prevention due to an insufficient quantity of mercuric sulfate. Experiments 5 and 6 were satisfactory. The results obtained in Experiments 8 to 10, inclusive, were decidedly high,

TABLE X.

Series XII.—Potassium and Sodium Acid Sulfates as Preventives.

1 cc. $KMnO_4$ = 0.004887 g. Fe. 20 cc. $FeCl_3$ (= 0.1596 g. Fe) + 10 cc. $HgCl_2$ taken.

$KHSO_4$ = saturated solution.

Expt. No.	Cc. HCl.	Cc. H_2SO_4.	Cc. $KHSO_4$.	Wt. of Fe found.	
1	5	..	..	0.1671	HgCl disappeared
2	5	25	..	0.1618	
3	5	..	25	0.1603	
4	5	..	25	0.1603	
5	5	..	50	0.1598	
6	5	..	50	0.1596	
7	5	25	50	0.1613	
8	5	50	50	0.1637	
9	10	..	25	0.1681	HgCl disappeared
10	10	..	50	0.1600	
11	15	..	50	0.1623	
12	15	..	75	0.1600	
13	20	..	100	0.1613	
14	20	..	125	0.1618	
15	20	..	150	0.1618	
16	20	..	175	0.1628	
17	20	..	200	0.1637	
18	20	..	500	0.1630	
19	5	..	100	0.1596	
20	5	..	100	0.1598	
$NaHSO_4$ = 500 g. per liter.					
1	5	..	25	0.1598	
2	10	..	25	0.1613	
3	10	..	50	0.1603	
4	15	..	50	0.1625	
5	15	..	75	0.1620	
6	15	..	100	0.1623	
7	5	..	20 cc. Mn soln. No. 1	0.1596	

due apparently to the transposition of mercurous chloride to mercurous sulfate by the mercuric sulfate. This point is mentioned in Cady and Ruediger's[9] original paper. The difficulty of adjustment of the quantity of mercuric sulfate to the other variables of an iron determination reduces the value of such a reagent as mercuric sulfate.

Sodium acid sulfate and potassium acid sulfate prevent quite well when the quantity of hydrochloric acid to be counteracted is small. With larger amounts of hydrochloric acid or in the presence of sulfuric acid with the smaller quantities of hydrochloric acid, results are not as good.

Experiments 5 and 6 indicate that about 50 cc. of 50% potassium acid sulfate solution is necessary to stop the detrimental influence of 5 cc. of hydrochloric acid. Experiments 7 and 8 show higher titration results with sulfuric acid than without it. Numbers 19 and 20 indicate that an excess of the potassium acid sulfate does not give a higher value if the

TABLE XI.

Series XIII.—Magnesium and Zinc Sulfates as Preventives.

1 cc. $KMnO_4$ = 0.004847 g. Fe. 20 cc. $FeCl_3$ (= 0.2283 g. Fe) + 10 cc. $HgCl_2$ taken.
$MgSO_4$ solution = $MgSO_4.7H_2O$ — 500 g. per liter.

Expt. No.	Cc. HCl.	Cc. $MgSO_4$.	G. Fe found.	
1	5	..	0.2283	20 cc. Mn soln. No. 1 added
2	5	50	0.2283	
3	5	50	0.2285	
4	10	50	0.2293	HgCl partially disappears
5	10	100	0.2297	
6	10	150	0.2293	HgCl partially disappears
7	10	200	0.2293	HgCl partially disappears
8	15	50	0.2297	HgCl partially disappears
9	20	50	0.2327	HgCl partially disappears
10	25	50	0.2346	HgCl partially disappears
11	10	..	0.2366	HgCl disappears entirely

1 cc. $KMnO_4$ = 0.005309 g. Fe. 20 cc. $FeCl_3$ (= 0.2283 g. Fe) + 10 cc. $HgCl_2$ taken.
$ZnSO_4$ soln. = 500 g. $ZnSO_4.7H_2O$ per liter.

1	5	..	0.2283	20 cc. Mn soln. No. 1 added
2	5	..	0.2378	
3	5	20	0.2296	
4	5	25	0.2293	
5	5	50	0.2293	
6	5	100	0.2293	
7	5	200	0.2291	
8	25	100	0.2325	HgCl disappears
9	25	200	0.2304	HgCl partially disappears
10	10	50	0.2293	
11	15	50	0.2309	
12	15	100	0.2393	
13	20	125	0.2309	
14	20	200	0.2309	
15	20	250	0.2291	

amount of hydrochloric acid remains the same. However, in numbers 13 to 18 inclusive, in which the amount of acid was 20 cc., the potassium bisulfate gave a progressively higher titration as its concentration was increased. Sodium acid sulfate showed somewhat the same kind of deportment. These acid sulfates while possessing preventive powers do not have this quality to a sufficient degree to make them suitable for an accurate titration of iron.

Magnesium sulfate and zinc sulfate produce decided effects in checking the influence of hydrochloric acid, the former being more efficient than the latter.

Scrutiny of Table XI shows good results in only two cases when magnesium sulfate was used, *e. g.*, Experiments 2 and 3, in which only 5 cc. of hydrochloric acid was added. In the zinc sulfate series all the results were too high. Almost identical volumes of permanganate were required for 5 cc. of hydrochloric acid within a range of 25 to 200 cc. of the zinc sulfate solution. A somewhat analogous set of figures was obtained for 10 cc. of hydrochloric acid within a range of 50 to 200 cc. of the magnesium sulfate. These results show a tendency toward prevention, which, nevertheless is not sufficient for practical application in titrating iron.

Chromium and ferric sulfates were found to have no value as preventives of the high results due to the action of hydrochloric acid on permanganate. High concentrations of chromium were naturally impossible on account of the color imparted to the solution.

TABLE XII.

Series XIV.—Potassium Phosphate Mixtures as Preventives.

K_3PO_4 solution = 500 g. K_3PO_4 per liter.

20 cc. $FeCl_3$ = 0.2031 g. Fe + 10 cc. $HgCl_2$ taken.

1 cc. $KMnO_4$ = 0.004887 g. Fe.

Expt. No.	Cc. HCl.	Cc. H_3PO_4.	Cc. K_3PO_4.	Cc. H_2SO_4.	Wt. of Fe found.
1	5	..	..	..	0.2031[1]
2	5	..	..	..	0.2028[1]
3	5	..	..	..	0.2031
4	5	..	..	..	0.2055
5	10	..	..	..	0.2160[2]
6	25	..	..	..	0.2189[2]
7	50	..	..	..	0.2180[2]
8	5	..	10	30	0.1906[3]
9	5	..	10	30	0.2048
10	5	..	10	30	0.1899[3]
11	5	..	10	30	0.2053
12	5	30	10	..	0.2031
13	5	30	10	..	0.2033
14	5	30	10	..	0.1891[2]
15	10	30	10	..	0.2031
16	5	30	20	..	0.2004
17	25	30	10	..	0.2072
18	25	50	20	..	0.2051
19	25	50	30	..	0.2009
20	25	75	30	..	0.2026
21	25	100	30	..	0.2031
22	25	200	30	..	0.2031
23	25	200	..	..	0.2063
24	5	..	..	..	0.2031
25	5	..	..	..	0.2033

[1] 30 cc. manganese soln. No. 1 added.

[2] HgCl dissolved almost completely.

[3] Added K_3PO_4 before the acid (H_3PO_4 or H_2SO_4) + 50 cc. manganese soln. No. 1 added.

Mixtures of tri-potassium or disodium phosphate and phosphoric acid were found to produce excellent prevention.

Experiments 1, 2, 3, 24, 25 are titrations with "manganese sulfate solution No. 1." Experiments 8, 10, 14, show the influence of adding the alkaline phosphate before the acid. In all likelihood some of the iron is precipitated as ferrous phosphate in these cases, yielding low results. Experiments 16, 19, 20, indicate an insufficiency of acid to keep the ferrous phosphate from forming. Experiments 12, 13, 15, 21, 22, show that when the proper adjustment of phosphoric acid and potassium phosphate is obtained correct results follow. A proportion of not less than three volumes of 1–1 phosphoric acid to 1 volume of 50% K_3PO_4 gives the best results. A solution containing 500 g. of tripotassium phosphate (or its equivalent in dipotassium phosphate) and 1500 cc. of phosphoric acid (sp. gr. 1.7) diluted to two liters can be used instead of the separate reagents. Twenty cc. of this solution will stop the action of 5 cc. and 60 cc. will suffice for 25 cc. of hydrochloric acid (sp. gr. 1.10).

In Series XIII a saturated solution of $Na_2HPO_4.12H_2O$ was employed.

TABLE XIII.

Series XV.—Disodium Phosphate Mixtures as Preventives.

20 cc. $FeCl_3$ = 0.2280 g. Fe + 10 cc. $HgCl_2$ taken.

1 cc. $KMnO_4$ = 0.004887 g. Fe.

Expt. No.	Cc. HCl.	Cc. Na_2HPO_4.	Cc. H_3PO_4.	Wt. of Fe found.	Expt. No.	Cc. HCl.	Cc. Na_2HPO_4	Cc. H_3PO_4.	Wt. of Fe found.
1	5	50	100	0.2280	8	50	50	100	0.2292
2	10	50	100	0.2280	9	60	50	100	0.2292
3	15	50	100	0.2284	10	100	50	100	0.2292[1]
4	20	50	100	0.2282	11	5	5	10	0.2287
5	25	50	100	0.2280	12	5	10	20	0.2280
6	30	50	100	0.2280	13	5	20	40	0.2278
7	35	50	100	0.2282	14	5	20 cc. manganese soln. No. 1	. .	0.2280

This series shows excellent prevention, even 35 cc. of hydrochloric acid being taken care of nicely, and 50–100 cc. did not produce an error such as one might anticipate.

The phosphoric acid and sodium phosphate may be combined into one solution by preparing as follows: Solution of 500 g. of disodium phosphate in 1000 cc. of phosphoric acid and 500 cc. of water then dilution to 2000 cc. Thirty cc. is a sufficient quantity for 10 cc. and 100 cc. are enough to offset the action of 25 cc. of hydrochloric acid.

Cerium sulfate gives excellent prevention of the hydrochloric acid interference. In fact it works as effectively as manganous sulfate when its efficiency is measured on the basis of gram equivalents. 20 g. of $Ce_2(SO_4)_3.8H_2O$ were dissolved in 250 cc. of water to be used in the following series:

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[1] End point unstable.

TABLE XIV.

Series XVI.—Cerium Sulfate as Preventive. 20 cc. $FeCl_3$ (= 0.2291 g. $FeCl_3$) + 10 cc. $HgCl_2$ taken. 1 cc. $KMnO_4$ = 0.004887 g. Fe.

Expt. No.	Cc. HCl.	$Ce_2(SO_4)_3$ soln. Cc.	Wt. of Fe found.
1	5	10	0.2309
2	5	20	0.2291
3	5	20	0.2293
4	5	20	0.2293
5	10	20	0.2299
6	7	20	0.2293
7	5	25	0.2293
8	5	35	0.2288
9	5	50	0.2288
10	5	20 cc. Mn soln. No. 1	0.2291

Series XVII.—Cerium Sulfate Mixture[1] as Preventive. 20 cc. $FeCl_3$ (= 0.1571 g. Fe) + 10 cc. $HgCl_2$ taken. 1 cc. $KMnO_4$ = 0.004887 g. Fe.

Expt. No.	Cc. HCl.	$Ce_2(SO_4)_3$ soln. Cc.	Wt. of Fe found.	Comments.
1	5	5	0.1583	
2	5	10	0.1570	Slow titration
3	5	10	0.1579	Rapid titration
4	5	15	0.1572	Rapid titration
5	5	25	0.1572	Rapid titration
6	10	20	0.1574	Slow titration
7	20	20	0.1614	Rapid titration
8	20	35	0.1572	
9	5	20 cc. Mn soln. No. 1	0.1571	

Thus it is to be seen that $Ce_2(SO_4)_3$ is very effective in stopping the detrimental nature of hydrochloric acid on permanganate, its value being commensurate with $MnSO_4$.

Theoretical.

A number of explanations have been offered to explain the function of manganese salts in the iron titration with permanganate. Volhard[35] explains the action by assuming the formation of tetravalent manganese (MnO_2) which then oxidizes the ferrous iron more rapidly than it does hydrochloric acid. Wagner[49] assumes the intermediate formation of $FeCl_2.2HCl$ in the absence of manganese sulfate, which oxidizes very rapidly, consuming more permanganate than is required for ferrous iron. Zimmerman[5] suggested that, in absence of manganese salts, the iron is converted into a peroxide which is unstable and at once forms ferric iron and oxygen, the latter acting upon the hydrochloric acid. Manchot[60] explains the action by assuming the formation of "primary oxides" of the peroxide nature, but which tend to revert immediately to oxides of a lower state of oxidation. According to this theory oxidation caused by oxygen forms FeO_2; by permanganate, chromic acid, hydrogen peroxide, etc., Fe_2O_5; and with hypochlorous acid, FeO_3. Hence the reaction is assumed to go somewhat as follows: Oxygen forms FeO_2, FeO_2 oxidizes FeO to Fe_2O_3, Mn_2O_7 oxidizes FeO to Fe_2O_5 with the formation of MnO_2, the MnO_2 then oxidizes FeO to Fe_2O_3. If the hydrochloric acid is too

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[1] A solution of mixed earth sulfates when analyzed was found to contain 65 g. $Ce_2(SO_4)_3.8H_2O$ + 200 cc. H_2SO_4 per liter. This solution was used as was the cerium sulfate of the preceding series.

strong then the Fe_2O_5 reacts with the HCl, liberating chlorine. Birch[23] suggests the formation of $MnCl_3$, which in turn has a greater tendency to oxidize ferrous iron than hydrochloric acid. This last assumption seems to warrant a more general consideration than has been accorded to it. While hydrated manganese peroxide can be assumed to exist for a brief space of time in the hydrosol condition, yet $MnCl_4$ has not been definitely proven to exist in such a solution. The same argument can be applied to a theory requiring assumptions of FeO_2, FeO_3, Fe_2O_5.

Pickering[36] has shown that when manganese dioxide is treated with hydrochloric acid manganese sesquichloride results. A number of other authors have studied the formation of trivalent manganese in solution, especially sulfuric, hydrochloric, hydrofluoric, and phosphoric acids and alkaline cyanides, a number of trivalent salts and double salts being separated from such solutions. (See references under heading, "Theoretical.") Meyer[59] has recently pointed out the definiteness of these compounds in acid solutions and also shows that even when potassium manganicyanide hydrolyzes a trivalent manganihydroxide results. Schilow[61] has explained the reaction of potassium permanganate with oxalic acid on the basis of the intermediate formation of trivalent manganese. Skrabal[16] outlines the oxalic acid oxidation and also that of manganese in alkaline solution through the formation of manganese of the valence of three. Muller and Koppe[64] point out an error in the titration of manganese by the permanganate method in the presence of fluorides due to the formation of MnF_3 and $2KF.MnF_3$.

When potassium permanganate is added to a manganese solution containing an excess of phosphoric acid a deep red to violet coloration is obtained; when added to a manganese solution with hydrochloric acid in excess a greenish brown to black solution results; when added to a manganese sulfate solution in the presence of an excess of sulfuric acid a deep red to purple color is imparted to the solution. Solutions of this nature contain manganese sesquisalts. The possibility of tetravalent manganese being present at ordinary temperatures in significant quantity is apparently quite remote. While very small amounts may be present, practically all attempts to prepare salts in which manganese has the valence of four from such solutions have been negative—only trivalent salts crystallizing from them. More confirmation seems to be necessary to establish the existence of tetravalent manganese in even small quantity in these acid solutions. However, if tetravalent manganese is present the mechanism of the reaction to be later described would partially be explained through medium of its formation and the fundamental idea of prevention of the chlorine or hypochlorous acid formation remains the same.

In the presence of hydrochloric acid these manganese sesquisalt solutions have a tendency to preserve the oxidation value of the solution; in other words, prevent the rapid loss of chlorine or hypochlorous acid. This preservation can be shown in open beakers qualitatively in a striking manner by adding 10 cc. of 0.1*N* permanganate to 50 cc. of 50% manganese sulfate solution containing 10 cc. of concentrated hydrochloric acid and to 50 cc. of water containing a like volume of the acid. In a moderately short time the second solution loses its chlorine in sufficient quantity to become much lighter in color than the first and in a few hours becomes completely colorless, but the solution containing the manganese maintains its color for weeks. Two such solutions in duplicate were prepared August 15 at 9 A.M. Both gave a decided odor of chlorine. At 9 A.M., the following day, the two solutions containing the manganese were still brownish black, but the two without the manganese were practically colorless. On September 5, the two containing the manganese were light brown and on November 18, the color still persisted and a few cc. of the solution gave an evolution of iodine when potassium iodide was added. Water was added from time to time to replace what was lost by evaporation.

In the titration of iron in hydrochloric acid solution it has been shown that manganous and cerous salts used in moderate amounts, and certain acid phosphate and sodium sulfate solutions, prevent the loss of chlorine or hypochlorous acid during titration and enable correct results to be obtained in the presence of hydrochloric acid. Evidently the reactions of these preventives involve two different types of effects. One effect is transposition from chloride to salts of another acid by the mass action of the preventive. The other effect is the formation of an intermediate compound or compounds which have the capacity to oxidize the ferrous iron, preventing the loss of chlorine. In a preventive one or the other effect may be in predominance. In the case of sodium sulfate the first effect is the larger, but some manganese is in solution due to the products of reaction and must exert some influence. In the case of manganese sulfate and sulfuric acid we have both effects with the second the larger, a mixture of sesquichloride and sulfate being produced as intermediate products. When manganese sulfate, phosphoric acid and sulfuric acid are employed, the opportunity for a larger number of sesquisalts to be formed is increased correspondingly, with the same effect as that produced by the more simple mixtures. With manganese chloride as preventive, the intermediate sesquimanganese chloride gives the only effect toward prevention. In these cases the reactions may be represented by the following equations:

(1) (In part), $2KMnO_4 + 10FeCl_2 + 16HCl = 2KCl + 2MnCl_2 + 10FeCl_3 + 8H_2O$

(2) (In part), $2KMnO_4 + 8FeCl_2 + 16HCl = 2KCl + Mn_2Cl_6 + 8FeCl_3 + 8H_2O$

(3) $Mn_2Cl_6 \rightleftarrows 2MnCl_2 + Cl_2$
(4) $Cl_2 + FeCl_2 = FeCl_3$ (slow)
(5) $Mn_2Cl_6 + 2FeCl_2 = 2FeCl_3 + 2MnCl_2$ (more rapid than 4)

The permanganate oxidizes a considerable portion of the iron according to equation (1). However, some Mn_2Cl_6 is formed, equation (2). This sesquichloride is unstable and has a tendency to decompose, liberating chlorine (3). The smaller the amount of manganese present the more rapid is this decomposition; the larger the amount of manganese the greater the tendency to retard the evolution of chlorine. The chlorine oxidizes the ferrous iron slowly (4). Manganese sesquichloride oxidizes ferrous iron much more rapidly than does free chlorine (5). Hence, if the reaction represented by equation three is forced to proceed toward the left by the addition of manganese chloride, preserving the initial character of the Mn_2Cl_6, the loss of oxidation effect due to chlorine evolution may be prevented and the final reaction follows the theoretical value (1).

When the Reinhardt-Zimmerman, Mixer-DuBois, or other solution of similar nature is employed the first list of reactions takes place partially, but the larger portion of the reaction occurs through the medium of some other acid than hydrochloric—usually phosphoric or sulfuric. In case of sulfuric acid this portion of the reaction can be thus illustrated:

(6) $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O$
(7) $2KMnO_4 + 8FeSO_4 + 8H_2SO_4 = K_2SO_4 + 4Fe_2(SO_4)_3 + Mn_2(SO_4)_3 + 8H_2O$
(8) $Mn_2(SO_4)_3 + 2FeSO_4 = 2MnSO_4 + Fe_2(SO_4)_3$

When cerium sulfate is used for the prevention:

$$(8a)\ \begin{cases} Mn_2(SO_4)_3 + 2Ce_2(SO_4)_3 = 2Ce(SO_4)_2 + 2MnSO_4 \\ 2Ce(SO_4)_2 + 2FeSO_4 = Fe_2(SO_4)_3 + Ce_2(SO_4)_3 \end{cases}$$

When phosphoric acid is used the reaction probably occurs through the medium of acid phosphates, involving corresponding changes of valences.

Analysis of Iron Ores with Various Preventives.

A number of iron ores were analyzed using the solutions heretofore described: (*a*) sodium sulfate, (*b*) potassium phosphate and phosphoric acid, (*c*) sodium phosphate and phosphoric acid, (*d*) manganese sulfate and sulfuric acid, (*e*) manganese sulfate, phosphoric and sulfuric acids, (*f*) cerium sulfate and sulfuric acid. The sample in each case was decomposed by heating with about 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and sufficient stannous chloride solution to almost reduce all of the iron. After complete solution of the iron, the reduction was finished by adding stannous chloride drop by drop to the hot solution until one drop just made it colorless, then one drop was added in excess. After dilution to about 500 cc., 10 cc. of mercuric chloride was added all at once with vigorous stirring. One of the preventives above noted was added and the iron titrated. The results from four representative ores are listed below.

TABLE XV.

Series XV.—Analyses of Iron Ores with Various Preventives.

Ore No.	Sample No.	Wt. of sample. G.	Preventative.		% Fe found.	Ore No.	Sample No.	Wt. of sample G.	Preventative.		% Fe found.
			Kind.	Volume. Cc.					Kind.	Volume. Cc.	
20	1	0.5000	*a*	200	65.91	26	1	0.7000	*a*	200	35.60
20	1	0.5000	*b*	30	65.96	26	1	0.7000	*b*	30	35.71
20	1	0.5000	*c*	30	65.96	26	1	0.7000	*c*	30	35.64
20	1	0.5000	*d*	15	65.91	26	1	0.7000	*d*	20	35.64
20	2	0.5000	*d*	15	66.07	26	1	0.7000	*e*	20	35.64
20	1	0.5000	*e*	15	66.07	26	1	0.7000	*f*	30	36.68
20	2	0.5000	*e*	15	65.96	43	1	0.8000	*a*	200	33.80
20	1	0.5000	*f*	25	65.96	43	1	0.8000	*b*	25	33.77
20	2	0.5000	*f*	25	65.98	43	2	0.8000	*b*	25	33.84
21	1	0.4000	*a*	200	57.44	43	3	0.8000	*b*	25	33.84
21	1	0.4000	*b*	25	57.44	43	1	0.8000	*c*	30	33.81
21	2	0.4000	*b*	25	57.50	43	2	0.8000	*c*	30	33.86
21	1	0.4000	*e*	25	57.41	43	1	0.8000	*d*	20	33.83
21	1	0.4000	*f*	30	57.52	43	2	0.8000	*d*	20	33.94
						43	1	0.8000	*e*	20	33.85
						43	2	0.8000	*e*	20	33.79
						43	1	0.8000	*f*	20	33.87

Discussion of the End Point.

The end point in the titration of iron is more stable in sulfuric and phosphoric than in hydrochloric acid solutions. In the last named the pink tinge imparted to the solution, showing a slight excess of permanganate, is more fleeting. While the addition of the preventives enumerated allows a correct iron analysis to be made within the range of error expected of such an analysis, nevertheless when the permanganate is added in excess, as at the end of the titration, a fading effect becomes more or less marked. On this account an analyst accustomed to the iron titration in hydrochloric acid solution calls the first slight tinge of color permeating the entire solution the end point. The tinge is much lighter than the tint in sulfuric or phosphoric acid solutions free from hydrochloric acid. This difference is at least partially due to the difference in color of the sesquichloride and sulfate and phosphate solutions. This variance in stability may account for some of the conflicting analyses heretofore published.

The end point in the titration of ferrous to ferric sulfate in the presence of sulfuric acid and in the absence of hydrochloric acid is almost as clean cut in the ordinary iron analysis as in phosphoric acid solution. Analysts recognize this fact in the standardization of permanganate against ferrous ammonium sulfate and metallic iron, in which case the end point is much more clear than in the regular titration of iron ores in the presence of suspended calomel even when phosphoric acid is added. However, this much must be said, if phosphoric acid is added by an analyst to give what to his eye seems to be a clearer end point in the analysis of the iron containing product, then the analyst who is having trouble with this color change must, to be consistent, add phosphoric acid in standardization if he standardizes the permanganate against an iron containing standard.

One gram of iron present as ferric sulfate with a little free sulfuric acid in a volume of 400–500 cc. gives a recognizable color change with 0.04 cc. of tenth normal permanganate. Of course this coloration is not red or pink, but it is a distinct change of color. Twice the above amount of permanganate gives a very decided coloration. These observations were naturally made against a white background. A moderate amount of experience with the iron titration allows a very sharp end point with moderate amounts of iron (up to about 0.6 g. metal) without the presence of a decolorizing influence, however, when a large amount of iron (over 0.6 g. metal) is to be titrated the addition of phosphoric acid is to be recommended, although, with care, larger amounts can be titrated with accuracy. With smaller amounts the addition of the phosphoric acid is optional with the analyst. Since ordinarily the amount of iron present in the solution being titrated is about 0.3 g. or less it seems to the author that the use of a decolorizer is unnecessary.

Summary.

(1) Correct results are obtained with a mixture of manganese sulfate, sulfuric acid and phosphoric acid for the prevention of the action of hydrochloric acid on permanganate. The use of phosphoric acid in the presence of considerable sulfuric acid in a volume of 400–600 cc. has very little tendency to decolorize the solution, inasmuch as the sulfate solution is practically colorless, except when titrating large amounts of iron. Hence, the elimination or use of phosphoric acid with the sulfuric acid and manganese sulfate is largely a matter of individual preference rather than a fundamental difference in the analysis.

(2) When a titration runs too high, the amount of variance from the true value is dependent on the amount of mercurous chloride present in suspension as well as on the concentration of hydrochloric acid.

(3) Certain neutral sulfates and acid phosphate mixtures react with hydrochloric acid and prevent the latter from causing high results in the iron titration. The acid phosphate solutions are especially serviceable.

(4) Cerous sulfate shows the same deportment in the titrating solution as manganese sulfate.

(5) Sodium sulfate, acid phosphate mixtures, manganese sulfate with sulfuric acid, manganese sulfate with phosphoric acid, or with both acids, can be applied to iron ore analyses. The use of cerous sulfate, while effective, is as yet prohibited on account of the present cost of the chemical.

(6) The prevention of the various reagents studied may be considered of two types: (1) conversion to salts of other acids than hydrochloric by the mass action of the preventor, and (2) the formation of intermediate compounds, which in turn oxidize ferrous to ferric iron with or without the first type being effective at the same time.

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See also the references under the title "Experimental."

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A NITROGEN GENERATOR.

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A form of generator for producing oxygen-free nitrogen from air, which has some advantages over those hitherto commonly used, has been devised by the writer and has been in constant use for over a year in this laboratory. The absorbing medium for oxygen is the well known copper-ammonium carbonate combination. What novelty there is consists in the continuous circulation of the solution through the copper column in the absorption vessel by means of an air-lift actuated by the incoming air current.

The nitrogen obtained by this means is so far free from oxygen that an incandescent tungsten wire is not oxidized even in a rapid current of the gas. Experience shows this to be a test of great delicacy. As a matter of security, however, it has been usual to add a tube of hot copper to the