

Table V.

No.	Sulphide in c.c.	Current amperes.	Volts.	Time,mins.	Tin present grams.	Tin found grams.
1	15	5	11	25	.....	0.2038
2	20	5	9	25	0.4076	0.4077
3	20	5	9	25	0.6114	0.6118
4	21	5	9	25	0.8152	0.8152
5	25	5	9	25	1.0190	1.0235
6	25	5	9	25	1.0190	1.0216
7	25	5	8	30	1.0190	1.0232

The deposit in number 1 was bright and smooth, the others were crystalline but perfectly adherent. The solution gave no test for tin. Up to 0.8 gram, therefore, nothing was occluded, but above that they were always too heavy. Number 5 was washed with carbon bisulphide to remove sulphur, but the weight did not decrease.

From this brief study it may be concluded that tin can be determined in an ammonium sulphide electrolyte rapidly and accurately with the aid of a rotating anode. The deposition of metal is hastened by heating the electrolyte, while polysulphides retard it and their amount should therefore be made as small as possible.

University of Pennsylvania.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## ALKALIMETRIC METHOD FOR THE DETERMINATION OF TUNGSTEN IN STEEL.

BY S. C. LIND AND B. C. TRUEBLOOD.

Received January 24, 1907.

Within the last ten years or more the greatly increasing use of tungsten steels under the name of "self-hardening" or "high speed" steel, and also the astonishing increase in the percentage of tungsten in the same, has been accompanied by the appearance in the literature of a number of new analytical methods for the determination of tungsten. Naturally the object sought has been the simplification of the method as far as possible without too great a sacrifice of accuracy as compared with the standard gravimetric method by precipitation as mercurous tungstate after the removal of carbon, silica, iron oxide, etc., by the several suitable but necessarily tedious operations involved. Strangely, most of these researches have been directed along gravimetric lines, and it may not be amiss to mention some of the more important ones without attempting a complete enumeration. Gravimetric methods have been described by Rodolfo Naumias<sup>1</sup>, George Auchy<sup>2</sup>, who suggests using a constant for the amount

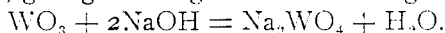
<sup>1</sup> Stahl u. Eisen, 1891, II., 757.

<sup>2</sup> This Journal, 21, 240, 1899.

of  $\text{Fe}_2\text{O}_3$  held by  $\text{WO}_3$  instead of fusing to remove same; P. Kennery<sup>1</sup>, Ibbotson and Beardsley<sup>2</sup>, A. G. McKenna<sup>3</sup>, Wells & Metzger<sup>4</sup>, who find treatment of  $\text{WO}_3$  with HF to remove  $\text{SiO}_2$  allowable but caution against the use of the blast lamp; Rudolph Fieber<sup>5</sup>; L. Campredon and G. Campredon<sup>6</sup>, who apparently independently of Kennery<sup>7</sup>, propose practically the same method; and Friedheim, Henderson and Pinagel<sup>8</sup>.

The only volumetric methods which we have found described in the literature are four in number and will be given brief mention. Otto F. von der Pfordten<sup>9</sup>, proposes reduction of  $\text{WO}_3$  to  $\text{WO}_2$  by means of zinc and 27 per cent. hydrochloric acid, subsequently titrating back with potassium permanganate. He finds the reduction does not take place so readily as in the case of molybdcic acid, and does not recommend the procedure highly. Herting<sup>10</sup> also finds this method unsatisfactory. E. Kuplin<sup>11</sup> gives direction for determining tungsten in steel, making use of the same principle as von der Pfordten, but dissolving the metal in equal parts sulphuric (1.84) and phosphoric (1.70) acids and determining the tungsten by the difference between the reduction value of  $\text{Fe} + \text{W}$ , and that of  $\text{Fe}$  alone, as determined by the Reinhardt method. He publishes no results obtained in this way.

The first mention found of determining tungstic acid alkalimetrically was by Hundeshagen<sup>12</sup>, who found that  $\text{WO}_3$  could be titrated with sodium hydroxide, giving exact agreement according to the formula,



He made no special application of the method to the determination of tungsten in steel.

Finally Otto Herting<sup>13</sup> reports that after washing out the acid from the residue of silica and tungstic oxide after solution in aqua regia he was able to titrate directly with normal sodium hydroxide, the tungstic oxide being suspended in hot water. He does not mention any difficulty in removing the ferric salts from the residue of tungstic oxide, nor of getting the latter into solution owing to the dilution of the alkali through the water used for suspending the residue.

<sup>1</sup> Proc. Eng. Soc. of West. Pa., IX, 5, 11; J. Iron and Steel Inst., 1894 I. 614.

<sup>2</sup> Chem. News, 82, 224 (1900).

<sup>3</sup> Proc. Eng. Soc. West. Pa., XVI. No. 4; Chem. News, 82, 67.

<sup>4</sup> This Journal, 23, 356.

<sup>5</sup> Chem.-Ztg. 25, II. 1083, (1901).

<sup>6</sup> Ann. chim. anal. appl. 9, 41 (1904).

<sup>7</sup> loc. cit.

<sup>8</sup> Z. anorg. Chem. 45, 396 (1905).

<sup>9</sup> Ber. 16, 508 (1883).

<sup>10</sup> Z. angew. Chem. 1901, 165.

<sup>11</sup> Stahl u. Eisen, 24, 27 (1904).

<sup>12</sup> Chem.-Ztg. 18, 547 (1894).

<sup>13</sup> loc. cit.

Attracted by the ease with which tungstic oxide is dissolved even by comparatively dilute alkali solutions we conceived the idea, independently of the work of Hundeshagen and of Herting, of dissolving the oxide from the mixture of silica and carbon by means of standard potassium hydroxide and titrating back with hydrochloric acid, using phenolphthalein as indicator. We were soon able to confirm Hundeshagen's statement that the reaction corresponds exactly to that for tungstic oxide as a dibasic acid, but we found great difficulty in freeing the oxide completely from ferric chloride which, of course, interferes with the titration by forming ferric hydroxide at the expense of the alkali. This difficulty in removing the iron is due to the property which tungstic oxide possesses in pronounced degree of packing and clogging a filter so that further washing becomes impossible.

We sought to overcome this obstacle by using suction but this only increased the difficulty and after trying various forms of filters with suction, namely; platinum cone, a Büchner funnel, an asbestos Gooch, and asbestos laid on a bed of coarsely ground glass, we found it necessary to give up suction altogether. The washing is best accomplished by repeated decantation, bringing as little of the precipitate as possible onto the filter until washed iron-free. This is the only time-consuming operation in the whole procedure, and but for it we are convinced that the alkali-method would prove an ideal rapid method for determining tungsten.

In obtaining the results given below, the following procedure was used.

Dissolve 2-10 grms. of the steel in about 30 cc. of nitric acid (1.20), using 1-2 grms. of potassium chlorate to insure complete oxidation of the carbides of tungsten, if the sample prove refractory. Evaporate just to dryness, and repeat the operation, if the digestion of the sample does not seem complete. Finally take up in 15-20 cc. conc. hydrochloric acid, and evaporate nearly to dryness again, then take up as before in a little conc. hydrochloric acid, dilute to 150-200 cc., and boil vigorously for a few minutes and allow the residue consisting of silica and tungstic oxide to settle. The supernatant liquid is then decanted through a filter, and the residue is washed repeatedly with hot 5-10 per cent. hydrochloric acid till the washing gives no test for iron with potassium thiocyanate. After each washing, the precipitate is allowed to settle so that as little as possible of it is brought onto the filter until iron-free. When this is accomplished, washing is continued until free from acid, using a 3-5 per cent. solution of sodium nitrate to prevent the tungstic oxide from passing through the filter in colloidal solution. Transfer the residue and filter to a small Erlenmeyer flask, break up the filter paper into small pieces with a stirring rod, and run in an excess of N/5 potassium hydroxide. If complete solution of the tungstic oxide does not take place at once, stopper the flask

lightly and heat for a few minutes on the steam bath<sup>1</sup>. Finally cool, add a few drops of phenolphthalein and titrate with N/5 hydrochloric acid to disappearance of color. Using 184 as the atomic weight of tungsten. 1 cc. N/5 potassium hydroxide is equivalent to 0.0184 g. of W.

To test our method we used it to determine tungsten in a sample of chrom-tungsten steel containing about 24 per cent. of tungsten and 4 per cent. of chromium. Tungsten was also determined in a mixture of carbides obtained from this same steel, and in a sample of impure tungstic acid. For comparison, gravimetric determinations of tungsten were made according to the method described by A. A. Blair<sup>2</sup>, consisting in dissolving in nitric acid (1.2), evaporating to dryness, taking up in hydrochloric acid, boiling and filtering. The precipitate was washed free from iron and acid, ignited to remove carbon, treated with hydrofluoric acid to remove silica, fused with sodium carbonate and the solution filtered, made slightly acid with nitric acid, boiled to remove carbon dioxide and neutralized with mercuric oxide. The tungsten was then precipitated with mercuric nitrate, and after ignition weighed as tungstic oxide.

### Percentage of Tungsten.

I.		II.		III.	
In "Zenith Steel A" <sup>3</sup>		In Sample of Tungstic Acid.		In Mixed Carbides from "Zenith Steel A"	
Alk.	Grav.	Alk.	Grav.	Alk.	Grav.
24.19	24.16	69.47	69.66	56.78	57.29
24.01	24.30	68.93	69.87	57.57	57.07
24.21	23.90	69.11	—	—	—
23.80	24.13	69.37	Av. 69.76	Av. 57.17	Av. 57.18
24.18	—	—			
24.11	Av. 24.12	Av. 69.22			

Av. 24.08

It may be mentioned here that no difficulty was experienced in dissolving the above sample of chrom-tungsten steel in nitric acid, aided by potassium chlorate, without the necessity of a fusion as suggested by Herting<sup>4</sup> in a similar steel. And we think it possible that this simpler method of digestion may be generally applicable.

The above, procedure, as will be seen, takes no precautions in regard to silica, and the results on the steel analyzed for tungsten are perhaps not a fair test of the tendency of silica to produce an error in the alkalimetric

<sup>1</sup> In this process care must be taken not to introduce free alkali from the glass. Either well steamed flasks or those of Jena glass should be used.

<sup>2</sup> Blair's Analysis of Iron and Steel, 2nd Ed. p. 192.

<sup>3</sup> This steel was rendered soft enough for cutting by annealing for 10 hours at 900°. In some cases, even a lower temperature may be necessary. In case annealing is not convenient, repeated quenching from red heat may be employed, the steel becoming so brittle it can be broken in an iron mortar.

<sup>4</sup> loc. cit.

titration, as the steel contained only about 0.1 per cent. of silicon. But it seems improbable that higher silicon would seriously affect the results from the following considerations. In the first place no especial effort is made to dehydrate the silicic acid nor to prevent its passing directly into the filtrate. Secondly, of the silica remaining with the  $WO_3$  only a small quantity is likely to be dissolved by N/5, potassium hydroxide, and that which is dissolved, the hydrolysis of potassium silicate being very high, would hardly be able to displace the end point far in titrating back with acid.

It is our opinion that the foregoing procedure might be used to good advantage, in laboratories where a large number of tungsten determinations are continually made, but that for occasional determination, the labor of preparing the normal solutions, and in becoming acquainted with the method would perhaps not justify its preference to the gravimetric methods.

It gives us pleasure to express our indebtedness to Prof. E. D. Campbell for his interest and helpful suggestions in this work.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## THE COLORIMETRIC DETERMINATION OF TITANIUM.

BY JAMES H. WALTON, JR.  
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Several investigators have shown<sup>1</sup> that in an alkaline solution which contains an excess of hydrogen peroxide titanium is not precipitated, but remains in solution. It occurred to the writer that this soluble compound of titanium might be formed by heating substances containing titanium with sodium peroxide.

In order to test this idea, about one gram of pure, dry titanium dioxide was intimately mixed with five grams of sodium peroxide in an iron crucible. The two substances had scarcely been mixed, when, without any application of heat, they began to react with each other forming little fused lumps and evolving considerable heat. On dissolving the fusion in water, filtering, and acidifying with sulphuric acid, it was evident from the reddish color of the solution that a considerable portion of the titanium dioxide had been changed to the soluble form. It was necessary to heat to the fusing point in order to bring all of the titanium into solution in this way. A sample of titanium iron ore was completely decomposed by fusion with sodium peroxide. On dissolving the fusion in water, filtering and acidifying, the usual test for titanium was obtained.

Several experiments were also carried out in which the titanium diox-

<sup>1</sup> Classen, Ber. 21, 370 (1888); Walker, this Journal 20, 513 (1898).