

ceases. To the mixture, when cold, ammonia water is added, and the iodine in the zinc and ammonium iodide is estimated exactly as described in the analysis of morphine tetraiodide.¹

For additive iodine 0.1492 gram of the periodide gave 0.0880045 gram iodine, and 0.122 gram gave 0.0727250 gram iodine.

| | Calculated for $C_{28}H_{40}N_2O_5.HI.I_7.$ | Found. |
|---------|--|--------|
| 1 | 59.24 | 59.98 |
| 2 | 59.24 | 59.61 |

For total iodine 0.1313 gram of the periodide gave 0.0890502 gram iodine, and 0.12095 gram gave 0.0818797 gram iodine.

| | Calculated for $C_{28}H_{40}N_2O_5.HI.I_7.$ | Found. |
|---------|--|--------|
| 1 | 67.69 | 67.82 |
| 2 | 67.69 | 67.69 |

CHEMICAL LABORATORY OF THE
UNIVERSITY OF MICHIGAN,
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NOTES ON THE RAPID DETERMINATION OF TUNGSTEN IN STEEL.²

BY GEORGE AUCHY.
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THE rapid method of determining tungsten in steel, generally in use and described in Blair's "Chemical Analysis of Iron," is as follows: Solution of the steel in aqua regia; evaporation to dryness; re-solution in strong hydrofluoric acid containing a little strong nitric acid; dilution and boiling; filtration and ignition of the tungstic oxide contaminated with silica and ferric oxide; elimination of the silica by hydrofluoric acid; ignition and weighing of the tungstic acid and ferric oxide; fusion with sodium carbonate; solution and filtration to determine the ferric oxide. If in this method the final steps—the fusion with sodium carbonate and the determination of the ferric oxide—could be dispensed with, evidently a very considerable saving of time and trouble in the performance of the method would be made; and it has doubtless been observed by many members of the society having occasion to make tungsten determinations in steel, that within the range of their experience the ferric oxide thus carried down with the tungstic acid is constant in amount or nearly so. If this uniformity exists in all steels containing every percentage of tungsten, of course, the determination of

¹ This Journal, 1898, 20, 717.

² Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

this ferric oxide contamination in every particular instance is unnecessary. One of the objects of this paper is to suggest that if members of the society having to do with tungsten in steel, would gather from their note-books, and publish the data representing the amounts of ferric oxide found contaminating their tungstic acid precipitates, the uniformity of these ferric oxide contaminations would no doubt be shown and result in the improvement of the method. The writer's own experience is confined to steels containing 0.20 per cent. to 1.75 per cent. tungsten, and indicates that the ferric oxide contamination is always practically the same within those limits, and that the amount, with four grams steel¹ taken for analysis and with varying amounts of acid present in solution, is about 0.03 per cent. in terms of tungsten. Results follow :

FIVE CC. FREE HYDROCHLORIC ACID PRESENT IN SOLUTION.

| No. | Tungsten. Per cent. | Ferric oxide in terms of tungsten. Per cent. |
|-----|------------------------|---|
| 70 | 1.110 | 0.036 |
| 504 | 0.230 | 0.022 |
| 137 | 1.710 | 0.032 |
| 585 | 0.250 | 0.022 |
| 352 | 0.428 | 0.016 |
| 586 | 0.255 | 0.022 |
| 353 | 0.434 | 0.022 |
| 587 | 0.350 | 0.022 |
| 49 | 1.230 | 0.032 |
| 588 | 0.375 | 0.026 |
| 51 | 1.240 | 0.034 |
| 589 | 0.260 | 0.028 |
| 52 | 1.240 | 0.028 |
| 590 | 0.335 | 0.027 |
| 154 | 1.160 | 0.028 |
| 591 | 0.310 | 0.022 |
| 346 | 0.482 | 0.024 |
| 352 | 0.442 | 0.020 |
| 353 | 0.434 | 0.020 |
| 363 | 0.466 | 0.020 |
| 364 | 0.444 | 0.020 |
| 154 | 1.090 | 0.036 |
| 380 | 0.428 | 0.028 |
| 411 | 0.430 | 0.026 |
| 412 | 0.400 | 0.022 |
| 179 | 1.250 | 0.028 |

¹ 3.9655 grams. Weight of WO_3 multiplied by twenty gives percentage of tungsten in the steel.

TEN CC. FREE HYDROCHLORIC ACID PRESENT IN SOLUTION.

| No. | Tungsten. Per cent. | Ferric oxide in terms of tungsten. Per cent. |
|-----|------------------------|---|
| 179 | 1.25 | 0.028 |
| 49 | 1.25 | 0.028 |
| 51 | 1.25 | 0.030 |
| 52 | 1.27 | 0.030 |
| 70 | 1.00 | 0.028 |
| 137 | 1.65 | 0.032 |
| 154 | 1.10 | 0.034 |
| 179 | 1.22 | 0.042 |
| 70 | 1.08 | 0.022 |
| 352 | 0.384 | 0.020 |
| 353 | 0.396 | 0.020 |
| 70 | 1.100 | 0.026 |
| 179 | 1.230 | 0.026 |
| 352 | 0.396 | 0.028 |
| 353 | 0.390 | 0.030 |

More accurately speaking, the amount of ferric oxide contamination lies between 0.02 and 0.03 per cent. for the lower percentages of tungsten and between 0.03 and 0.04 per cent. in steels containing from 1.00 to 2.00 per cent. tungsten. In these tests the ferric oxide in the sodium carbonate used for fusion was found and deducted. Also regard was had for the fact that the weight of the crucible is sometimes slightly affected by the fusion.

Professor Arnold in his "Steel Works Analysis" directs that the tungstic acid be washed with very dilute hydrochloric acid till quite free from iron; and omits the sodium carbonate fusion for the determination of the iron. In the above tests the tungstic acid precipitates were washed seven times with hot hydrochloric acid (1 : 20) and three times with alcohol (1 : 4) filling the filter each time. In one case only 0.10 per cent. tungsten carried down 0.012 per cent. ferric oxide, in terms of tungsten, not washed out by this procedure.

The determination of silicon in tungsten steels is most conveniently made along with that of the tungsten.

PRECAUTIONS IN TUNGSTEN DETERMINATIONS.

Authorities do not agree in considering the completeness of the tungstic acid separation to be affected by the acidity of the liquid from which it separates. For instance, in Blair's

“Chemical Analysis of Iron,” the dry residue after the dehydration of the silica is directed to be taken up with an amount of strong hydrochloric acid sufficient for the purpose (about forty cc. for four grams steel, and ten cc. for one gram), and then, without any previous evaporation or neutralization, diluted, boiled, and filtered. In Arnold’s “Steel Works Analysis,” on the contrary, the liquid is directed to be evaporated to a bulk of five cc. before dilution and filtration. Another point that does not seem to be generally appreciated is that evaporation to dryness and dehydration of silica from nitric acid solution does not always cause complete separation of the tungstic acid, although such an evaporation and dehydration from hydrochloric acid solution will separate all the tungstic acid. In Blair’s description of the standard method the evaporation and dehydration is made in nitric acid solution.¹ In Arnold’s method the evaporation and dehydration from nitric acid solution is also made, but is followed by a second evaporation to dryness from hydrochloric acid solution, the explanation being made that several evaporations to complete dryness are necessary to insure the complete separation of the tungstic acid on account of its solubility in hydrochloric acid.

With regard to these two points it is the writer’s experience that the completeness of the tungstic acid separation is dependent upon the smallness of the amount of acid present in the liquid ; and frequently also upon whether the previous evaporation and dehydration has been made from nitric or from hydrochloric acid solution. The amount of acid in the liquid from which the tungstic acid is filtered should be as little as possible ; and the preceding evaporation to dryness and dehydration of silica should be made in hydrochloric and not in nitric acid solution, in which case only one such evaporation to complete dryness is necessary. The best procedure seems to be : Solution of the steel in dilute nitric acid (taking four grams of the steel); evaporation to first appearance of a scum on the surface of the liquid ; addition of thirty to forty cc. strong hydrochloric acid ; evaporation to dryness and heating on the hot plate; re-solution in forty cc. strong hydrochloric acid ; evaporation to first appearance of scum ; taking up with five cc. strong hydrochloric acid diluted to twenty cc. with water,

¹ In his rapid method the evaporation and dehydration is made from *aqua regia* solution.

and heating ; addition of twenty-five to thirty cc. of hot water ; and filtration.

The failure of a complete separation of tungstic acid by evaporation to dryness from nitric acid solution is perhaps due to the absence of aqua regia—aqua regia perhaps being necessary to a complete oxidation to tungstic acid. Blair, in fact, in his rapid method, dissolves the steel in aqua regia, and also takes up the dry residue with aqua regia containing, however, an unusual proportion of hydrochloric acid. But this theory is rather discredited by the fact that in Arnold's process no aqua regia is formed, the heating for the dehydration of the silica being carried to the point of decomposition of nitrates, and yet all the tungsten is obtained.

The following results illustrate the necessity for the two precautions just considered.

| No. | 5 cc. HCl present. | 10 cc. HCl present. | 40 cc. HCl present. |
|-----|---|---|---|
| | Total bulk 50 cc. Tungsten. Per cent. | Total bulk 100 cc. Boiled before filtration. Tungsten. Per cent. | Total bulk 100 cc. Boiled before filtration. Tungsten. Per cent. |
| 70 | 1.11 | 1.10 | 1.05 |
| 137 | 1.71 | 1.67 | 1.59 |
| 352 | { 0.442 0.428 | 0.396 | 0.290 |
| 353 | { 0.434 0.434 | 0.390 | 0.320 |
| 49 | { 1.24 1.23 | 1.24 | |
| 51 | 1.24 | 1.25 | |
| 52 | { 1.25 1.24 | 1.27 | |
| 154 | 1.16 | 1.09 | |
| 179 | { 1.26 1.25 | 1.23 | |

In the above tests the filtrates from the tungstic acid of the first column of results were tested for tungstic acid by evaporation to complete dryness with aqua regia. None was found in any test. In the above tests, the evaporations to dryness and the dehydrations of the silica were all made from hydrochloric acid solutions ; but in the following determinations they were made from nitric acid solutions.

| No. | Tungsten present. Per cent. | Tungsten found. Per cent. |
|-----|--------------------------------|------------------------------|
| 70 | 1.11 | 1.08 |
| 179 | 1.26 | 1.15 |
| 352 | 0.440 | 0.384 |
| 353 | 0.434 | 0.396 |
| 70 | 1.11 | 1.00 |
| 137 | 1.71 | 1.65 |
| 154 | 1.16 | 1.10 |
| 179 | 1.26 | 1.22 |

But ten cc. hydrochloric acid instead of five cc. were present in the solution ; and the lowness of the results may have been partly due to that fact. Comparing results obtained under like conditions as regards the amount of acid present we have :

| No. | 10 cc. HCl present. Evaporation and dehy- dration from HCl solution. | 10 cc. HCl present. Evaporation and dehy- dration from HNO ₃ solution. |
|-----|--|---|
| | Tungsten. Per cent. | Tungsten. Per cent. |
| 70 | 1.10 | 1.08 |
| 179 | 1.23 | 1.15 |
| 137 | 1.68 | 1.65 |
| 352 | 0.396 | 0.384 |
| 353 | 0.390 | 0.396 |
| 70 | 1.10 | 1.00 |
| 154 | 1.09 | 1.10 |
| 179 | 1.23 | 1.22 |

In No. 79 the filtrate from the tungstic acid (1.15 per cent. tungsten) was found to contain 0.10 per cent. tungsten.

Phosphorus in Tungsten Steels.

In Arnold's "Steel Works Analysis" the operator is directed to separate and filter tungstic acid before determining phosphorus. In Blair's "Chemical Analysis of Iron" this is not specified and it is therefore, perhaps, to be inferred that phosphorus is to be determined as usual. The following tests were made, using the volumetric method :

| No. | P after separating and filtering tungstic acid. Per cent. | P as usual; yellow precipitate stood less than 2½ hours. Per cent. | P as usual; yellow precipitate stood over night. Per cent. | P carried down by the tungstic acid in the first column of results. Per cent. |
|-----|--|---|---|--|
| 154 | 0.016 | 0.017 | | 0.0007 |
| 179 | 0.025 | 0.026 | 0.029 | 0.0007 |
| 70 | 0.017 | 0.018 | 0.024 | 0.0007 |
| 137 | 0.020 | 0.023 | | 0.0009 |
| 70 | 0.017 | 0.018 | | |
| 70 | 0.017 | 0.016 | | |
| 70 | 0.017 | 0.018 | | |
| 154 | 0.016 | 0.018 | | |
| 179 | 0.025 | 0.025 | 0.032 | |
| 179 | 0.022 | 0.024 | | |

This indicates that in very low phosphorus steels at least, the determination may be made as usual, provided the yellow precipitate is not allowed to stand more than two and one-half hours. Also in neutralizing with ammonia, no excess must be used or tungstic acid will precipitate with the ferric oxide and remain undissolved by the nitric acid added to clear the solution. But the tendency seems to be toward higher results.

Ferrotungsten

is usually analyzed by roasting, followed by solution, filtration, fusion, and evaporation with acid. The writer, with a sample containing 35.25 per cent. tungsten, obtained low results by this method (twenty-nine and thirty per cent.), doubtless because only a single fusion was made, but had no difficulty when using the same method as for tungsten steels, except that aqua regia was used for a solvent.¹ The ferrotungsten apparently could not be completely decomposed by this means. A bright metallic residue was left, consisting, however, of almost pure tungsten, and readily oxidizing to tungstic oxide by ignition after filtration. In this procedure the preparatory roasting of the ferrotungsten is, of course, unnecessary. The ferric oxide and other contamination seems to be variable; in nine determinations of five different ferrotungstens, it ranged from 0.28 per cent. to 1.60 per cent.

LABORATORY OF THE KEYSTONE SAW WORKS,
PHILADELPHIA, PA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE
UNIVERSITY.]

THE ABSORPTION OF METHANE AND ETHANE BY FUMING SULPHURIC ACID.²

BY R. A. WORSTALL.

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APPARENTLY one of the most firmly established facts has been that marsh-gas and its homologues are not acted upon either by fuming nitric or by fuming sulphuric acids. The indifference of methane and ethane to all reagents, especially to

¹ The metal being treated first with strong nitric acid and heated, and the strong hydrochloric acid then added by degrees.

² Read by title before the New York meeting of the American Chemical Society, December 28, 1898.