THE ASSAY OF WOLFRAM CONCENTRATE.

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WOLFRAM is bought and sold on the unit system, taking tungstic oxide as the basis. The average price per unit during the last five years has been 34s. 6d.; the buyers require a minimum of 60 units, although poorer material may be sold, but at a lower price per unit. The necessity for an accurate method of assay of such a valuable product is obvious. As no reliable volumetric method for the estimation of tungstic acid is known, the determination is in all methods made by weighing pure tungstic oxide. Tungstic oxide results from the ignition of either ammonium tungstate, basic mercurous tungstate, or certain organic salts. All three reactions are used in assays. The use of organic salts is so far restricted to the assay of tungsten in alloys, and does not come within the scope of the paper.

Finely powdered wolfram may be decomposed by boiling with strong hydrochloric acid or by boiling with caustic soda solution. With the acid treatment the tungstic acid is liberated and remains undissolved, but with the alkali it passes into solution as tungstate of soda. A preliminary ignition with lime, or calcium carbonate and salt, or calcium carbonate and ammonium chloride, renders wolfram more easily attacked by acids, but may under certain conditions be attended with undesirable complications. Wolfram fused with caustic alkalis or the alkaline carbonates is converted into tungstate of soda or potash, both readily soluble in water.

The use of acid allows of the final determination being made either by ignition of ammonium tungstate or basic mercurous tungstate, but use of alkali necessitates the adoption of the mercury method.

Such reactions are made use of in one or other of the four methods described hereafter, viz. :

1. "Aqua regia-ammonium tungstate" method.
2. "Aqua regia-mercurous nitrate" method.
3. "Soda digestion-mercurous nitrate" method.
4. "Soda fusion-mercurous nitrate" method.

1. "AQUA REGIA-AMMONIUM TUNGSTATE" METHOD, MORE COMMONLY KNOWN
AS THE "AQUA REGIA" METHOD.

To 1 grm. of the finely powdered wolfram in an 8-ounce beaker add about 10 c.c. strong hydrochloric acid, and agitate carefully to prevent caking. Add more acid (about 120 c.c. in all), cover with a clock-glass, and boil briskly till the volume of acid is reduced to about 5 c.c. Allow to cool, add 5 c.c. strong nitric acid, and digest at nearly a boiling temperature for from five to ten minutes. Dilute with water to about 100 c.c., allow to settle, and filter through a 9-cm. filter, wash with water, working so as to obtain as little tungstic acid as possible on the filter. To the beaker add about 10 c.c. distilled water and 10 c.c. dilute ammonia (1 : 1), adding the latter in small quantities down the sides of the beaker. With a rubber-tipped rod remove any deposit from the sides of the beaker into the alkaline liquor, raise to the boil, and stir well (if the suspended matter does not readily subside, boil again until the desired result is attained). Allow to settle, and whilst still hot filter through the original paper into an 8-ounce flask. Wash the beaker two or three times with small quantities of distilled water, decanting each time from any heavy mineral should it be present. Complete the washing of the filter-paper, and reserve the cover-glass, filter-paper, and beaker. Evaporate the solution of ammonium tungstate in the flask to a small volume, transfer carefully to a weighed platinum dish, and continue the evaporation to dryness on a water-bath. Ignite the dish and contents gently at first, and more strongly afterwards. Weigh as tungstic acid.

To the beaker containing the heavy residues add 5 c.c. hydrochloric acid, cover with the original clock-glass, and boil till nearly dry; add a few c.c. of nitric acid, and heat again for ten minutes. Dilute with water, allow to stand till the deposit has subsided, filter through a small paper, and wash beaker and paper several times.

Wash the filter-paper, also the original filter-paper, with a little hot dilute caustic soda solution followed by small washes of distilled water, and collect the alkaline liquors and washings in a beaker. If the clock-glass is stained with tungstic acid, dissolve with a few drops of the soda solution and add to the contents of the beaker. Raise the contents of the beaker to boiling, add about 2 grms. ammonium nitrate, and stir well whilst boiling. Filter through one of the papers previously used, and wash a little. Nearly neutralise the filtrate with dilute nitric acid, add a few c.c. of mercurous nitrate solution, stir well, filter on a small ashless paper, wash, ignite, and weigh as tungstic acid. Add this weight to the weight of the tungstic acid in the platinum dish.

Remarks on the Method.—Fine grinding is essential to success. One grm. is a convenient quantity, but with experience 2·5 grms. may be taken without requiring any modification of the quantities given in the assay.

The complete decomposition with the boiling hydrochloric acid takes about one hour, but it is better to continue boiling if the volume of residual liquors is much more than 5 c.c. The addition of nitric acid, with further digestion, is a concession to custom, but it would seem from experiment that in some instances it is unnecessary; for instance, two samples of wolfram gave 71·57 and 75·6 per cent. respectively, using nitric acid, and 71·6 and 75·54 per cent. respectively, using no nitric acid. Departure from custom is not recommended without a more extended series of experiments. In filtering the acid liquors from the tungstic acid, etc., a special wash-water is unnecessary; with water only the filtrate and washings are free from dissolved tungstic acid. The instructions given for effecting the solution of the tungstic acid in ammonia are based on experience; turbid filtrates seldom occur, and the volume of solution for concentration is reduced to a minimum, thereby saving time without sacrificing accuracy. With a turbid filtrate it is better to continue the assay and determine the amount of impurity in the tungstic acid after weighing, as follows: Add sufficient distilled water to cover the tungstic acid in the platinum dish, and about 1 grm. of pure caustic soda. Digest on the water-bath for a few minutes, till all the tungstic acid has dissolved. Wash the contents of the dish into a suitable beaker, add 3 grms. of ammonium nitrate, boil, filter on a small ashless paper, wash, burn, and weigh. Deduct the weight from the original weight of tungstic acid.

The retreatment of the residues from the ammonium tungstate filtrate is the crucial point of the assay; without it concordant results are rare, the residues being seldom free from tungstic acid. Its presence may be due either to unattacked wolfram or to tungstic acid retained by the residues. The former is due to defective powdering, and may be controlled; with experience it is of infrequent occurrence. The retained tungstic acid does not appear to be within the control of the assayer, but proof of its presence is easy. Wolfram is not soluble in cold dilute caustic soda solution, whereas the retained tungstic acid is. Thus in ten recorded assays the quantity of tungstic acid (not including unattacked wolfram), expressed in percentage, extracted from the residues with cold dilute soda solution, was 0·05, nil, 0·55, 0·25, 0·7, 1·57, 1·1, 2·0, 1·1, 1·9, and 0·55 per cent., respectively.

Impurities frequently present in wolfram concentrates are silica and silicates, arsenic as mispickel, titanium, tantalum, niobium, and fluorine as fluorspar.

The presence of silicates and arsenates soluble in hydrochloric acid would give low results, some of the tungsten being dissolved and remaining soluble even in aqua regia. Fortunately such impurities seldom occur.

Arsenic as mispickel does not interfere with the assay; thus, a sample of nearly pure wolfram with no arsenic added gave 75·6 per cent., and with mispickel added, corresponding to 2·5 per cent. arsenic, assayed 75·65 per cent.

Titanium as ilmenite causes the retention of large amounts of tungstic acid in the residues when dissolving out with ammonia.

In an assay of alluvial wolfram concentrate, containing about 10 per cent. TIO_2

as ilmenite (see No. 5 in table), the amount retained by the residue and soluble in weak caustic soda solution was 3.6 per cent. The addition of 0.5 gm. of ilmenite to an assay of a clean wolfram concentrate caused a retention of 11 per cent. Tantalite and columbite do not affect the assay.

The difficulty experienced by some in the decomposition of wolfram has led to various methods being devised. All are somewhat similar in principle—viz., a preliminary ignition with some suitable material is given, the effect of which is to render the wolfram more easily attacked by acids. A brief account of some original work on these lines may be useful, if only to serve as a warning of the possible pitfalls attending the use of such methods.

One gm. of the wolfram is mixed with 0.6 to 0.7 gm. of ammonium chloride and 3.5 grms. of calcium carbonate; the mixture is heated in a platinum crucible (containing a layer of calcium carbonate at the bottom and top of the charge) for five minutes at a low heat, and then for five minutes at full bunsen heat. The fritted mass may be detached from the crucible when cold. It is sufficient then to boil with dilute or strong hydrochloric acid for a few minutes only, to effect complete decomposition. Unfortunately, the ease of attack is the only good feature of the method. Some of the bad points are—(1) The pronounced solubility of the tungsten in the acid liquors; (2) the presence of only small quantities of arsenic very much increases the solubility effect.

It is admissible as an alternative to determine the tungstic acid in the ammoniacal solution by the mercurous nitrate method. The author is indebted to Mr. J. J. Beringer for first acquaintance with the use of this method for the particular purpose.

The details as given below are based on experience.

II. "AQUA REGIA-MERCUROUS NITRATE" METHOD.

Proceed as described in the "aqua regia-ammonium tungstate" method to the sentence (p. 399) ending "wash with water, working so as to obtain as little tungstic acid on the paper as possible." To the beaker add about 15 c.c. distilled water and 5 c.c. of 10 per cent. caustic soda solution; cleanse the cover-glass with a few drops of very dilute solution, and wash into the beaker; run a few c.c. of dilute soda through the filter-paper, and wash with water, collecting filtrate and washings in beaker; rub down any deposit above the level of the liquid in the beaker with a rubber-tipped rod, raise to the boil, add 3 grms. ammonium nitrate, and continue to boil for a minute or so. Allow to settle; filter, and wash with weak ammonium nitrate solution, collecting filtrate and washings in a large-sized beaker. Dilute to about 200 c.c.; acidify with nitric acid first, then neutralise or make faintly alkaline with dilute ammonia. Add sufficient mercurous nitrate solution, and again neutralise with precipitated mercuric oxide; stir well; filter and wash by decantation; finally transfer all precipitate to the paper and complete the washing. Dry, burn, and weigh as tungstic acid. The residues should be again treated with acid, etc., for unattacked wolfram.

This is a useful alternative method to the ordinary aqua regia method, and gives

results comparable with it (samples Nos. 1, 2, and 3, in the table). It is most advantageous for the assay of mixed tin-wolfram concentrates.

III. "SODA DIGESTION-MERCUROUS NITRATE" METHOD.

Digest 0·825 gm. of the finely powdered sample with 20 c.c. of a 25 per cent. solution of caustic soda in a porcelain basin on a water-bath for forty-five minutes ; stir well at the commencement to prevent caking ; dilute the extract with water, add a little sodium peroxide, transfer to a 250-c.c. flask, and dilute to 250 c.c. To 200 c.c. of a filtered portion (this will represent 0·5 gm. of the material) transferred to a large flask add nitric acid till acid, and then make alkaline with ammonia. Boil, filter, and wash into a suitable-sized beaker. Add to the filtrate containing the tungsten dilute nitric acid till faintly alkaline, then a solution of mercurous nitrate in slight excess ; again neutralise with precipitated mercuric oxide ; stir well ; allow to subside, filter, and wash, first by decantation, and later when transferred to the paper. Dry, burn in platinum crucible, and weigh as tungstic acid. It is advisable to treat the tungstic acid with a little hydrofluoric acid, ignite, and again weigh. The loss, which is usually small and negligible, represents silica.

Fine grinding of the sample and thorough washing of the mercurous tungstate are both essential to good results. The method gives results comparable with the other methods (see Nos. 1, 4, 5, 7, 8, and 9, in the table).

Titanium as ilmenite, tantalite and arsenic as mispickel, and small quantities of arsenate, do not interfere. Large quantities need no consideration, since they do not occur in practice.

IV. "SODA FUSION-MERCUROUS NITRATE" METHOD.

Fuse 0·625 gm. of the finely powdered sample in a nickel dish with about 1 inch of stick soda and 3 grms. sodium peroxide, at first gently, then more strongly, until the fusion is complete. Pour the molten charge on to a clean sheet of nickel, and when cold transfer both dish and caustic mass to a beaker, and dissolve in water. If the solution is green, add a little peroxide of soda, transfer to a 250 c.c. flask, and make up to volume. Filter, and determine the tungsten in 200 c.c. as described in Method III.

Titanium, tantalum, and niobium, do not interfere. Arsenic, unless in excessive amount, is removed, or practically so, by the tin dissolved in the fusion to such an extent as to be too small to influence the assay.

In the table are set out assay results of a considerable number of samples, from which a comparison of the various methods may be made. It is impossible to make such a series of assays without developing a partiality for one or other method ; of the four methods dealt with, the old aqua regia method (Method I.) has most to commend it. It gives comparable results on amounts varying from 1 to 2·5 grms., whereas the other methods are limited to quantities of about 0·5 gm. All four methods work well in the presence of scheelite.

Samples 9 to 28 inclusive are of interest, inasmuch as there are given both buyer's and seller's assays on a total quantity of about 250 tons, representing a

transaction of considerably over £25,000. The buyer's average assay is 63·58 per cent., the seller's 63·56 per cent.

TABLE OF ASSAY RESULTS.

Sample Number.	Buyer's Assay.	Method I. " Aqua Regia- Ammonium Tungstate."	Method II. " Aqua Regia- Mercurous Nitrate."	Method III. " Soda Diges- tion-Mercurous Nitrate."	Method IV. " Alkaline Fusion-Mer- curous Nitrate.
1	—	55·10	55·05	54·90*	—
2	—	56·90	56·75	—	—
3	—	64·00	63·84	—	—
4	—	66·09	—	65·92	—
5	—	57·10	—	57·00	57·0
6	—	65·90	—	—	65·8
7	—	65·28	—	65·06	—
8	—	63·65	—	63·80	—
9	64·10	64·15	—	64·02	—
10	63·30	63·34	<p><i>Description of Samples.</i></p> <p>1. Spanish wolfram recovered from waste products. 2. Cornish wolfram from lode material. 3, 4, and 6. Alluvial wolfram, locality unknown. 5. Titaniferous alluvial wolfram from Cornwall. 7. Spanish concentrate. 8 to 28 inclusive. Cornish wolfram from lode material.</p>		
11	63·95	63·90			
12	64·77	64·89			
13	63·55	64·00			
14	63·58	63·78			
15	64·10	64·00			
16	63·25	63·10			
17	63·03	62·70			
18	62·75	62·84			
19	63·00	62·65			
20	64·10	63·40			
21	63·80	63·85			
22	63·70	63·85			
23	63·80	63·85			
24	63·80	63·50			
25	64·00	63·80			
26	63·35	63·75			
27	62·75	63·00			
28	62·35	62·25