The Volumetric Determination of Tin in Titanium and its Alloys

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Procedures have been established for the determination of tin in titanium and its alloys. For alloying amounts, the method involves the direct reduction of tin with hypophosphite and volumetric determination with potassium iodate. Tests with solutions containing known amounts of titanium, tin and other metals indicate that recovery is satisfactory for amounts of tin above 0·2 per cent. and that no interference is caused by likely alloying metals. The recommended procedure is simple, rapid and particularly suitable for control analysis. No difficulty has been experienced in applying the method to a wide range of titanium - tin alloys.

For impurity amounts of tin below 0·2 per cent., a modification is necessary and it involves the preliminary separation of tin as sulphide in the presence of a carrier and then by reduction with hypophosphite and volumetric determination of the separated tin. Experiments have proved that recovery of tin is satisfactory for amounts as small as 0·002 per cent.

Titanium alloys containing tin and aluminium are of increasing importance when higher creep resistance is required, and consideration has therefore been given to the determination of tin in the presence of large amounts of titanium.

When this investigation was commenced, no published methods were available and a review of possible methods indicated that the hypophosphite reduction procedure[1,2] offered the most promising approach. Subsequently, however, Norwitz and Codell[3] recommended a method for alloying amounts of tin in titanium alloys based on the preliminary separation of tin as sulphide, but they found that copper and molybdenum (above 0·5 per cent.) interfered with the determination. A later method,[4] in which tin is reduced directly by iron powder, is stated to be ineffective in the presence of copper, and chromium and vanadium at concentrations above 5 per cent. definitely interfere.[5]

The experimental work described in this paper has led to the development of a rapid and direct method for tin in titanium - tin alloys, and reference is made to a modification suitable for the determination of tin present as an impurity in titanium metal.

Experimental

Effect of titanium—

During preliminary tests on the reduction of tin in the presence of titanium and diluted hydrochloric acid (1 + 1), the addition of sodium hypophosphite resulted in the formation of a dense flocculent precipitate. However, it was found that, when the solution was boiled, the precipitate dissolved to leave a clear pale-blue solution in which, after cooling, the reduced tin could be titrated with potassium iodate and the starch - iodine end-point easily observed.

Further tests on solutions containing the equivalent of 0·2 or 0·5 g of titanium with various amounts of tin added, indicated that the recovery of tin by the proposed method was satisfactory over the range of 0·1 to 25 per cent., as shown by the results in Table I.

Effect of other metals—

From previous work on copper-base alloys,[2] it was known that aluminium, iron, lead, manganese and nickel do not interfere with the volumetric determination of tin, and interference by precipitated arsenic, selenium and tellurium can be avoided by filtration. As titanium - tin alloys usually contain aluminium, confirmation was obtained of the non-interference of up to 10 per cent. of aluminium. In addition, possible interference by other metals likely to be present in titanium alloys, namely chromium, molybdenum or vanadium, was determined for a series of solutions containing the metal under investigation with 1 to 10 per cent. of tin and the appropriate amount of titanium to bring the total sample weight to 0·2 g. In addition, the effect of copper and tungsten, which may be present as impurities, was studied and the results of these tests are given in Table II.

TABLE I

RECOVERY OF TIN ADDED TO SOLUTIONS CONTAINING TITANIUM

Tin added		Tin recovered,
g	%	%
In presence of 0·2 g of titanium—		
Nil	Nil	Nil
0·0010	0·50	0·49
0·0020	1·00	1·00
0·0030	1·50	1·42
0·0050	2·50	2·45
0·0100	5·00	4·90
0·0200	10·00	9·98
0·0500	25·00	25·00
In presence of 0·5 g of titanium—		
Nil	Nil	Nil
0·0005	0·10	0·12
0·0010	0·20	0·20
0·0015	0·30	0·26
0·0025	0·50	0·49
0·0050	1·00	1·03
0·0100	2·00	2·00
0·0250	5·00	4·97

TABLE II

EFFECT OF METALS ON THE RECOVERY OF TIN

Metal	Amount of metal present		Titanium present		Tin present		Tin recovered,
	g	%	g	%	g	%	%
—	Nil	Nil	0·180	90·0	0·0200	10·00	9·98
Aluminium	0·02	10·0	0·178	89·0	0·0020	1·00	1·01
Chromium	0·02	10·0	0·178	89·0	0·0020	1·00	1·01
	0·02	10·0	0·160	80·0	0·0200	10·00	9·96
	0·06	30·0	0·120	60·0	0·0200	10·00	9·94
Vanadium	0·02	10·0	0·178	89·0	0·0020	1·00	1·01
	0·02	10·0	0·170	85·0	0·0100	5·00	5·04
	0·02	10·0	0·160	80·0	0·0200	10·00	9·98
	0·06	30·0	0·120	60·0	0·0200	10·00	9·97
Molybdenum	0·02	10·0	0·178	89·0	0·0020	1·00	1·01
	0·02	10·0	0·170	85·0	0·0100	5·00	4·99
	0·02	10·0	0·160	80·0	0·0200	10·00	9·99
	0·06	30·0	0·120	60·0	0·0200	10·00	9·97
Copper	0·001	0·5	0·197	98·5	0·0020	1·00	1·02
	0·001	0·5	0·179	89·5	0·0200	10·00	10·05
	0·002	1·0	0·178	89·0	0·0200	10·00	10·27
	0·010	5·0	0·170	85·0	0·0200	10·00	10·33
Tungsten	0·004	2·0	0·196	98·0	Nil	Nil	Nil
	0·004	2·0	0·194	97·0	0·0020	1·00	1·00
	0·004	2·0	0·186	93·0	0·0100	5·00	5·01
	0·008	4·0	0·192	96·0	Nil	Nil	Nil
	0·008	4·0	0·190	95·0	0·0020	1·00	1·01
	0·008	4·0	0·182	91·0	0·0100	5·00	4·99
	0·008	4·0	0·172	86·0	0·0200	10·00	9·97

The results indicated that up to 30 per cent. of chromium, molybdenum and vanadium had no effect on the determination of tin in the range of 1 to 10 per cent. A slight yellowish pink colour was noted in the presence of molybdenum, but the end-point could be easily detected. Addition of copper resulted in some fading of the end-point with consequent over-titration to the extent that 5 per cent. of copper introduced a positive error of 0·3 per cent. on 10 per cent. of tin. However, in commercial practice, only impurity amounts of copper are encountered and, as indicated in Table II, amounts as large as 0·5 per cent. had no appreciable effect.

With tungsten, a deep-blue solution was produced on reduction with sodium hypophosphite, but the end-point could still be discerned and the recovery of tin was satisfactory.

METHOD

REAGENTS—

Potassium iodate solution, 0·02 N—Dissolve 0·7134 g of potassium iodate and 10 g of potassium iodide in water. Add 25 ml of sodium hydroxide solution (about 0·05 *N*) and dilute to 1 litre.

1 ml ≡ 1·187 mg of tin (theoretical value).

Standardise the solution against a known amount (about 0·04 g) of high-purity tin in the presence of 0·160 g of pure tin-free titanium by the recommended procedure.

Mercuric chloride solution, saturated—Dissolve 6 g of mercuric chloride in 100 ml of boiling water, allow to cool and decant from the crystals formed.

Starch solution, 1 per cent.—Make a paste of 1 g of soluble starch with cold water, pour it into 80 ml of boiling water, boil the solution for a few minutes, cool and dilute to 100 ml. This solution should be freshly prepared.

PROCEDURE—

For tin contents exceeding 0·5 per cent., weigh 0·2 g of sample and, for 0·2 to 0·5 per cent., weigh 0·5 g of sample; transfer it to a 100-ml beaker. Add 30 ml of dilute sulphuric acid (1 + 4) and warm gently to assist solution (see Note). Maintain the level of solution by the addition of water. When the reaction ceases, cool and oxidise with a slight excess of nitric acid, sp.gr. 1·42, added dropwise, and heat again until tin is dissolved. Evaporate to fumes of sulphur trioxide, cool, and transfer to a 500-ml conical flask, using about 50 ml of water.

Add 50 ml of hydrochloric acid, sp. gr. 1·18, 1 ml of saturated mercuric chloride solution and 5 g of sodium hypophosphite. Insert a rubber bung provided with a delivery tube leading into 40 per cent. w/v sodium bicarbonate solution and boil the sample solution gently for 15 minutes. Cool to room temperature with the outlet of the delivery tube maintained below the surface of the bicarbonate solution. Add 2 g of potassium iodide, replace the rubber bung and delivery tube with an ordinary rubber bung or glass stopper, shake until the iodide has dissolved, add about 5 ml of starch solution and titrate with standard 0·02 *N* potassium iodate solution to the characteristic starch - iodine blue end-point.

Calculate the tin content of the sample.

NOTE—

Alternatively, the sample may be dissolved in 50 ml of hydrochloric acid, sp.gr. 1·18, in a 500-ml conical flask. This method of solution has the advantage that evaporation to fumes of sulphur trioxide is avoided, but care is necessary to avoid loss of hydrochloric acid, and the drillings must be finely divided.

APPLICATION OF PROPOSED VOLUMETRIC METHOD

The proposed procedure was applied to the determination of tin in a number of experimental titanium - tin alloys nominally containing from 5 to 27·5 per cent. of tin. The results, shown in Table III, indicate that the method provides reasonably reproducible figures.

TABLE III

APPLICATION OF THE METHOD TO TITANIUM - TIN ALLOYS

Alloy mark	Nominal tin content, %	Tin content by volumetric method, %
A	5·00	4·56, 4·55
B	7·50	7·52, 7·49
C	10·00	9·54, 9·34
D	12·50	12·60, 12·30
E	17·50	17·12, 17·38
F	21·80	21·75, 21·81, 21·67
G	22·50	22·48, 22·75
H	25·00	24·83, 24·79
I	27·00	26·77, 26·94
J	27·50	27·45, 27·45, 27·45

DETERMINATION OF SMALL AMOUNTS OF TIN IN TITANIUM—

Experience indicated that, with a sample weight of 0·2 g, the proposed direct method was only suitable for amounts of tin in excess of about 0·5 per cent. By increasing the sample weight to 0·5 g, amounts as small as 0·1 per cent. could be determined, but the end-point became increasingly difficult to detect.

For amounts of tin smaller than about 0·2 per cent., a modification involving the separation, or concentration, of tin was considered advisable. A tentative method was drawn up in which a larger weight of sample (up to 10 g) was used, with a single precipitation of tin as sulphide in the presence of added cadmium to act as a carrier. Preliminary tests were made to ascertain if the separated tin could be titrated with 0·005 *N* iodate, particularly in the presence of any small amounts of titanium that might remain owing to incomplete separation.

Various amounts of tin in increments from 0·1 to 10 mg were titrated with 0·005 *N* iodate both in the absence of titanium and in the presence of 10 to 50 mg of titanium. The end-points were satisfactory and the results, which are shown in Table IV, indicate that recovery of tin was sufficiently accurate, provided at least 10 mg of titanium were also present. Accordingly, in the proposed method, the addition of 10 mg of titanium is recommended just before the reduction with hypophosphite.

TABLE IV

EFFECT OF TITANIUM ON DETERMINATION OF SMALL AMOUNTS OF TIN, 0·005 *N* IODATE BEING USED

Titanium present in solution, mg	Tin taken, mg	Tin determined, mg	Difference, mg
Nil	0·10	0·12	+ 0·02
	0·20	0·11	− 0·09
	0·50	0·47	− 0·03
	1·00	0·34	− 0·66
	10·00	7·95	− 2·05
	10·00	7·49	− 2·51
10	0·10	0·12	+ 0·02
	0·20	0·22	+ 0·02
	0·50	0·50	Nil
	1·00	1·02	+ 0·02
	10·00	9·98	− 0·02
20	10·00	9·94	− 0·06
50	10·00	10·04	+ 0·04

As it had been proved that amounts of tin as low as 0·1 mg could be reduced by hypophosphite and then determined satisfactorily by titration with 0·005 *N* iodate, the full procedure, including the sulphide separation, was applied to a series of solutions containing titanium and the equivalent of 0·002 to 0·05 per cent. of tin. Ammonium citrate was added

TABLE V

RECOVERY OF SMALL AMOUNTS OF TIN FROM SOLUTIONS CONTAINING TITANIUM AND COPPER

Weight of titanium, g	Tin added, %	Tin recovered, %
(*a*) *In absence of copper*—		
1·0	0·05	0·050
2·0	0·05	0·051
2·0	0·02	0·020
5·0	0·0040	0·0039
10·0	0·0040	0·0039
10·0	0·0020	0·0018
10·0	0·0020	0·0017
(*b*) *In presence of copper equivalent to* 0·1 *per cent.*—		
1·0	0·10	0·098
2·0	0·050	0·049
5·0	0·020	0·020
5·0	0·010	0·010
10·0	0·0020	0·0020

to prevent precipitation of titanium hydroxide during neutralisation of the excess of acid with ammonia solution and 10 ml of diluted sulphuric acid (1 + 1) per 400 ml were added before the precipitation of tin by hydrogen sulphide. The modification for small amounts of tin under 0·1 per cent., as detailed later, was found to be reasonably convenient and the results (see Table V (*a*)) were sufficiently accurate to a lower limit of 0·002 per cent.

Any copper present would be co-precipitated as the sulphide and, if in sufficient concentration, would interfere subsequently with the end-point. Some tests were carried out in which copper, equivalent to 0·1 per cent., was added to a further series of solutions containing titanium together with the equivalent of 0·01 to 0·10 per cent. of tin. In these tests, tin was separated from the combined sulphide precipitate with ammonium sulphide and subsequently determined in the copper-free solutions. The results, shown in Table V (*b*), indicate that this additional step effectively eliminated the interference by copper and its use is recommended when the presence of copper is known or suspected from the colour of the sulphide precipitate.

Modified procedure for tin contents below 0·2 per cent.

Reagents—

Titanium sulphate solution—Dissolve 0·5 g of pure tin-free titanium in 30 ml of dilute sulphuric acid (1 + 4), cool and dilute with water to 50 ml.

Potassium iodate solution, 0·005 N—Transfer 25 ml of 0·02 *N* potassium iodate (see p. 660) to a 100-ml calibrated flask and dilute to the mark with water,

1 ml ≡ 0·297 mg of tin (theoretical value).

Cadmium sulphate solution—A 10 per cent. solution of cadmium sulphate, $3CdSO_4.8H_2O$, in water.

Procedure—

Dissolve the recommended weight of sample in the appropriate amount of dilute sulphuric acid (1 + 4), as follows—

Tin present, %	0·05 to 0·2	0·02 to 0·05	0·005 to 0·02	< 0·005
Weight of sample, g	1	2	5	10
Dilute sulphuric acid (1 + 4) required, ml	50	100	200	300

Warm gently to assist solution and maintain the level of the solution by the addition of water. Oxidise with a slight excess of nitric acid, sp.gr. 1·42, added dropwise, and then boil for 2 to 3 minutes to remove nitrous fumes and ensure dissolution of tin. Dilute to about 300 ml, add 2 ml of cadmium sulphate solution and 5 g of ammonium citrate (10 g for the 10-g sample). Neutralise with diluted ammonium hydroxide (1 + 1), using methyl red as indicator, acidify with 10 ml of diluted sulphuric acid (1 + 1) and dilute to 400 ml. Warm to 80° C and pass hydrogen sulphide through the solution for 30 minutes.

Set the solution aside at room temperature for at least 4 hours, then collect the precipitate on a Whatman No. 42 filter-paper and wash it once with cold water containing a small amount of hydrogen sulphide (see Note). Dissolve the precipitate from the filter-paper with 50 ml of warm hydrochloric acid, sp.gr. 1·18, into a 500-ml conical flask, wash the filter-paper with 50 ml of water, add 1 ml of titanium sulphate solution, 1 ml of saturated mercuric chloride solution and 5 g of sodium hypophosphite. Reduce the tin as described in the method for tin in titanium alloys and finally titrate with 0·005 *N* potassium iodate.

Calculate the tin content of the sample.

Note—

At this stage it will be apparent if a significant amount of copper is present. If it is known or suspected that the amount of copper is greater than about half the tin content, dissolve the tin sulphide through the paper with 10 ml of warm diluted ammonium sulphide (1 + 1) into a 500-ml conical flask. Wash the copper sulphide residue with 50 ml of water containing hydrogen sulphide. Add 50 ml of hydrochloric acid, sp.gr. 1·18, to the filtrate and then 1 ml of titanium sulphate solution, 1 ml of saturated mercuric chloride solution and 5 g of sodium hypophosphite, and continue as described above.

Conclusions

The direct volumetric method described on p. 660 is satisfactory for the determination of more than 0·2 per cent. of tin in titanium metal and alloys. Other alloying elements likely to be present, such as aluminium, chromium, iron, manganese, molybdenum and vanadium, and also impurity amounts of copper and tungsten, cause no interference; consequently the

method has definite advantages over other published methods[4,5] in which copper, molybdenum and vanadium interfere.

After solution of the sample, the proposed procedure for alloying amounts of tin takes only about 30 minutes and, being simple and direct, it can be recommended particularly for routine control analysis. The method has now been in use in a routine laboratory for over 2 years and no difficulties have been encountered, even when used by inexperienced personnel.

For amounts of tin less than 0·2 per cent., preliminary sulphide separations are recommended, followed by reduction and volumetric determination of tin. This modified procedure obviously increases the operational time, but experiments have proved that it is satisfactory for tin contents as low as 0·002 per cent.

References

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