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Determination of Trace Amounts of Bismuth in Ferrous Alloys by Solvent Extraction Followed by Atomic-absorption Spectrophotometry

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A method is described for the atomic-absorption spectrophotometric determination of 2 to 130 $\mu g\ g^{-1}$ of bismuth in cast irons and stainless steels. From an aqueous solution of an alloy, 2·3 M in hydrochloric acid, 0·09 M in ascorbic acid and 0·2 M in potassium iodide, the bismuth was extracted quantitatively into isobutyl methyl ketone, by shaking the mixture once, while the base elements remained in the aqueous phase. After concentrating it, the organic phase was nebulised into an air - acetylene flame of a Unicam SP90 atomic-absorption spectrophotometer. The standard deviations in the errors from the means for various cast irons and stainless steels were 1·2 and 1·4 $\mu g\ g^{-1}$, respectively. The results of applying the solvent-extraction procedure to twenty-seven other elements of interest to the steelmaker are also reported.

BISMUTH is an undesirable element in stainless steels as even 0·005 per cent. of bismuth reduces the hot ductibility of these steels.[1,2] A rapid and accurate method is therefore desirable for the determination of 0·0001 to 0·01 per cent. of bismuth in ferrous alloys. It was felt that a method with an atomic-absorption spectrophotometric finish might meet these requirements.

The best 1 per cent. absorption value for the determination of bismuth in aqueous solutions by atomic-absorption spectrophotometry with an air - acetylene flame is 0·7 $\mu g\ ml^{-1}$ for the 223·1 nm line.[3] However, with the bismuth hollow-cathode lamps used in our laboratory with the Unicam SP90 instrument, the light output at this wavelength was very low and excessively noisy. It was therefore necessary to use the much more intense bismuth line at 306·8 nm, even although this line was slightly noisy because it falls on the bandhead of the major hydroxyl band in the flame. By damping the output signal from the amplifier the noise was acceptable.

The 1 per cent. absorption value for the determination of bismuth in aqueous solutions in the air - acetylene flame of the Unicam SP90 is 2·0 $\mu g\ ml^{-1}$ with the 306·8 nm line. With 2 g of ferrous alloy in 100 ml of solution this sensitivity corresponds to a bismuth concentration in the alloy of 100 $\mu g\ g^{-1}$. Obviously a direct method is not sensitive enough for the determination of bismuth in the 0·0001 to 0·01 per cent. range. Therefore, it was necessary to use a simple extraction procedure that would enable the bismuth to be extracted from the base elements into an organic phase, which could then be concentrated before nebulisation into the flame of the atomic-absorption spectrophotometer.

Luke[4] has stated that traces of antimony, bismuth, cadmium, copper, indium and lead can be virtually quantitatively extracted from 5 per cent. w/v hydrochloric acid solution containing iodide by a double extraction with isobutyl methyl ketone. Ascorbic acid was added to solutions containing iron(III) to reduce it to iron(II) before adding the iodide. Iron(II), chromium(III) and nickel(II) were retained in the aqueous phase. We have found that by shaking the mixture once bismuth is quantitatively extracted into isobutyl methyl ketone from 2·3 M hydrochloric acid, which is 0·09 M in ascorbic acid and 0·2 M in potassium iodide. The base elements in ferrous alloys are again retained in the aqueous phase.

The basis of a suitable method for the determination of trace amounts of bismuth in ferrous alloys is thus established, as it was possible to concentrate the organic phase to a small volume by distilling off most of the solvent. The bismuth originally present in 2 g of alloy could readily be obtained in 5 ml of isobutyl methyl ketone. The 1 per cent. absorption value for the bismuth iodide complex in isobutyl methyl ketone, when sprayed into the air - acetylene flame of the Unicam SP90 spectrophotometer, was $0.7 \mu g \, ml^{-1}$ of bismuth. This corresponds to $1.8 \mu g \, g^{-1}$ of bismuth in a ferrous alloy, an appreciable improvement on the direct method.

A simple method is described below for the determination of 2 to 130 $\mu g \, g^{-1}$ of bismuth in cast irons and stainless steels.

EXPERIMENTAL

APPARATUS—

Atomic-absorption spectrophotometry was carried out on a Unicam SP90 spectrophotometer fitted with an air - acetylene burner.

REAGENTS—

Hydrochloric acid, sp.gr. 1·18.

Hydrochloric acid, 2·3 M—Dilute 1 litre of hydrochloric acid, sp.gr. 1·18, to 5 litres with distilled water.

Nitric acid, sp.gr. 1·42.

Hydrofluoric acid, 40 per cent. w/w.

L-Ascorbic acid solution, 16 per cent. w/v—Dissolve 40·0 g of L-ascorbic acid in a little warm 2·3 M hydrochloric acid and dilute the solution to 250 ml with the same acid.

Potassium iodide solution, 2 M—Dissolve 83·0 g of potassium iodide in 2·3 M hydrochloric acid and dilute to 250 ml with the same acid.

These reagents were of analytical-reagent grade.

Bismuth metal was 99·9995 per cent. pure (Koch-Light Laboratories Ltd.). Other metals and salts used were of analytical-reagent grade or Specpure quality (Johnson and Matthey Ltd.).

Isobutyl methyl ketone—General-purpose reagent. Re-distil before use.

Standard bismuth solution A—Dissolve 1·0000 g of bismuth metal powder in 5 ml of about 5 M hydrochloric acid containing 3 drops of concentrated nitric acid. Evaporate the solution nearly to dryness. Add 5 ml of concentrated hydrochloric acid and again evaporate nearly to dryness. Repeat this procedure. Dilute the solution to 1 litre in a graduated flask with 2·3 M hydrochloric acid. Dilute 10 ml of this solution to 100 ml in a graduated flask with 2·3 M hydrochloric acid.

1 ml of solution A ≡ 100 μg of bismuth.

Standard bismuth solution B—Dilute 10 ml of solution A to 100 ml in a graduated flask with 2·3 M hydrochloric acid.

1 ml of solution B ≡ 10 μg of bismuth.

METHOD

DETERMINATION OF BISMUTH IN FERROUS ALLOYS—

Accurately weigh and dissolve, with warming, 2 g of alloy in 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid in a 150-ml Teflon beaker. Add 1 ml of concentrated hydrofluoric acid and simmer the solution gently for 5 minutes. Evaporate the solution nearly to dryness (Note 1). Add 10 ml of concentrated hydrochloric acid and re-evaporate the solution nearly to dryness. Repeat this procedure. Dissolve the solids in warm 2·3 M hydrochloric acid and transfer the solution to a 250-ml graduated flask, washing the beaker with 2·3 M hydrochloric acid. Add 25 ml of ascorbic acid solution to the flask and mix the contents thoroughly, then add 25 ml of potassium iodide solution and dilute the solution to the mark with 2·3 M hydrochloric acid.

Transfer the contents of the flask to a 500-ml separating funnel, rinsing the flask with 5 ml of 2·3 M hydrochloric acid. Add 50 ml of isobutyl methyl ketone to the funnel and shake it vigorously for about 15 s. Allow the layers to separate and transfer the upper organic layer to a 100-ml pear-shaped distillation flask. By using an oil-bath at about 160° C distil

over the solvent until about 2 ml of solution remains in the flask. Transfer this solution to a dry 5-ml graduated flask, wash the distillation flask with a little isobutyl methyl ketone and make the solution in the graduated flask up to the mark with isobutyl methyl ketone.

Nebulise the organic solution containing extracted bismuth in the Unicam SP90 atomic-absorption spectrophotometer, by using the conditions given in Table I, and determine the flame absorbance of this solution with either the meter on the instrument or a recorder attached to it. In either event the output from the amplifier should be damped. The wash solution for the nebuliser is isobutyl methyl ketone (Note 2). Read off the concentration of the bismuth in the alloy from the calibration graph constructed as described below.

NOTES—

1. With cast irons, after the first evaporation nearly to dryness dissolve as much of the solids as possible in warm 2·3 M hydrochloric acid and filter the solution through a Whatman No. 541 paper to remove undissolved carbon. Collect the filtrate in a Teflon beaker and wash the filter-paper with 2·3 M hydrochloric acid. Evaporate the filtrate nearly to dryness, add the first of the 10-ml portions of concentrated hydrochloric acid and proceed with the method.

2. For a detailed account of the spraying procedure, an earlier publication by the authors should be consulted.[5]

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF BISMUTH

Acetylene flow-rate at 7 p.s.i., 1 minute^{-1}	0·9
Compressed air flow-rate at 30 p.s.i., 1 minute^{-1}	5·0
Wavelength for use with bismuth lamp, nm	306·8
Slit width, mm	0·10
Lamp current, mA	6
Distance of centre of light path above burner, mm	9

CALIBRATION GRAPHS—

For alloy samples containing 25 to 125 μg g^{-1} of bismuth weigh 2·00 g of Specpure iron into each of six 150-ml Teflon beakers and treat each sample in a manner identical with that described above for an alloy sample until the solutions are ready to be transferred to 250-ml graduated flasks. To each of six 250-ml graduated flasks add 0, 0·5, 1·0, 1·5, 2·0 and 2·5 ml of bismuth solution A. To each flask add the contents of a Teflon beaker and add the rinsings (2·3 M hydrochloric acid) of each beaker to the appropriate flask. Proceed with the addition of ascorbic acid and potassium iodide, the solvent extraction and the distillation as for an alloy solution but make the final isobutyl methyl ketone solutions up to the marks in 5-ml graduated flasks marked appropriately 0, 25, 50, 75, 100 and 125 μg g^{-1} of bismuth. The flask marked zero is the blank, both for the calibration graph and for the alloy solutions. Nebulise the solutions in the Unicam SP90 by using the conditions given in Table I and obtain a calibration graph by plotting absorbances of the bismuth solutions corrected for the blank *versus* concentration.

For alloy samples containing up to 25 μg g^{-1} of bismuth, the calibration graph is obtained in a similar way, except that 0, 1, 2, 3, 4 and 5-ml aliquots of bismuth solution B are used and the concentrations of bismuth in the final 5-ml volumes of isobutyl methyl ketone solution correspond to 0, 5, 10, 15, 20 and 25 μg g^{-1} of bismuth.

CHECK FOR INTERFERING ELEMENTS—

Only those elements which are extracted with the bismuth could interfere in the method. The extents to which twenty-seven other elements of interest to the steelmaker are extracted from the aqueous phase into the organic phase were therefore determined. Solutions of the metal or a suitable salt were prepared in 2·3 M hydrochloric acid and the composition of the aqueous phase adjusted before extraction to resemble as closely as possible that of a calibration solution but without the bismuth and iron. The concentrations of elements remaining in the aqueous phase were determined by well established atomic and solution absorption spectrophotometric, titrimetric and gravimetric methods. These results, as percentages extracted, are shown in Table II.

TABLE II

EXTENT OF EXTRACTION OF VARIOUS ELEMENTS AS IODIDE COMPLEXES INTO
ISOBUTYL METHYL KETONE

Element		Percentage extracted	Initial concentration in aqueous phase, g per 250 ml	Element		Percentage extracted	Initial concentration in aqueous phase, g per 250 ml
Aluminium	..	0	0·05	Niobium ..	..	0	0·025
Antimony	..	94	0·01	Selenium	..	0*	0·01
Arsenic ..	..	56	0·01	Sulphur ..	..	0	0·01
Bismuth ..	..	100	0·05	Tantalum	..	0	0·01
Calcium ..	..	0	0·05	Tellurium	..	100†	0·01
Cerium ..	..	0	0·01	Thallium..	..	Precipitate	0·01
Chromium	..	0	0·50			formed	
Cobalt ..	..	0	0·50	Tin	..	9	0·01
Copper ..	..	94	0·01	Titanium	..	0	0·05
Lead	..	60	0·01	Tungsten	..	0	0·01
Iron	..	0	2·00	Silver ..	..	Precipitate	0·01
Magnesium	..	0	0·05			formed	
Manganese	..	0	0·50	Vanadium	..	0	0·05
Molybdenum	..	43	0·02	Zinc	..	0	0·02
Nickel ..	..	0	0·50	Zirconium	..	0	0·01

* Cloudy aqueous phase.   † Cloudy organic phase.

Only antimony, arsenic, copper, lead, molybdenum, tellurium and tin are extracted with bismuth from the aqueous phase and, with the exceptions of copper and molybdenum, these elements seldom occur in cast irons and steels in amounts greater than 0·5 per cent. Such alloys can contain up to 1 per cent. of copper and 5 per cent. of molybdenum. For each of the elements capable of being extracted, 250 ml of solution were prepared, which contained 1·4 g of iron, 0·4 g of chromium, 0·2 g of nickel, 100 μg of bismuth and 10 mg of the element except for copper (20 mg) and molybdenum (100 mg). The solutions were also 2·3 M in hydrochloric acid, 0·09 M in ascorbic acid and 0·2 M in potassium iodide. These solutions were treated by the above method and the amounts of bismuth in the 5-ml volumes of isobutyl methyl ketone determined from the calibration graph. In all instances the amount of bismuth thus determined was 100 μg. This showed that there was no interfering effect from any of the seven elements that are extracted wholly or in part with the bismuth.

RESULTS

Both calibration graphs were straight lines passing through the origin. At no time in this study did the blank solutions contain bismuth.

TABLE III

RESULTS FOR THE ANALYSIS OF SIMULATED SOLUTIONS OF STAINLESS STEELS

Base elements, per cent.			Bismuth content by addition, μg g^{-1}	Bismuth content found,* μg g^{-1}
Iron	Chromium	Nickel		
70	20	10	100	99, 99, 100, 100
70	20	10	50	50, 50, 50, 50
70	20	10	25	25, 25, 25, 25
70	20	10	5	5, 5, 5, 5
70	20	10	2·5	3, 2·5, 2·5, 2·5
60	30	10	100	101, 103, 101, 101
60	30	10	50	49, 49, 50, 51
60	30	10	25	26, 25, 26, 25
70	10	20	100	101, 99, 101, 102
70	10	20	50	50, 50, 50, 50
70	10	20	25	25, 25, 25, 25

* All of these results were obtained by using the recorder.

The results for the analysis of twelve solutions prepared to simulate 2-g samples of stainless steels are shown in Table III. The base elements were of Specpure quality. For

these "stainless steels" the standard deviation in the errors from the actual contents was $0.8\ \mu g\ g^{-1}$. The results for the analysis of four normal stainless steels are presented in Table IV. For these alloys the standard deviation in errors from the means was $1.4\ \mu g\ g^{-1}$. Finally, the results for the analysis of nine cast irons are presented in Table V. For these samples the standard deviation in the errors from the means was $1.2\ \mu g\ g^{-1}$.

TABLE IV

RESULTS FOR THE DETERMINATION OF BISMUTH IN NORMAL STAINLESS STEELS

Sample number	Nominal bismuth content, $\mu g\ g^{-1}$	Bismuth content found, $\mu g\ g^{-1}$
1	<10	7, 7, 5, 5, 5,* 5*
2	45	47, 47, 47, 47, 43,* 43*
3	60	62, 62, 63, 63, 66,* 64*
4	100	104, 103, 102, 103, 106,* 104,* 107*

* These results were obtained with the meter; others with the recorder.

TABLE V

RESULTS FOR THE DETERMINATION OF BISMUTH IN CAST IRONS

Sample	Bismuth content from B.C.I.R.A.,* $\mu g\ g^{-1}$	Bismuth content found,† $\mu g\ g^{-1}$
D1	85	83, 82, 81, 81
D2	130	132, 131, 130, 130
D3	16	15, 14, 15, 16
D4	65	62, 63, 61, 60
D5‡	180	186, 184, 184, 184
D6	85	82, 81, 86, 86
D7	19	20, 22, 22, 21
D8	63	60, 61, 59, 59
D9	90	90, 92, 92, 93

* These results were obtained by cathode-ray polarography after solvent extraction.[6]
† All of these results were obtained with the meter.
‡ The sample analysed consisted of 1 g of D5 *plus* 1 g of Specpure iron.

DISCUSSION

The above results are considered to be satisfactory. It seems likely that the method could also be used with slight modification for the determination of antimony in ferrous alloys.

It might be thought unnecessary to add iron to the bismuth solutions used in preparing the calibration graph, but when iron was absent the calibration graph for bismuth had a slightly steeper slope. A possible explanation is that dehydroascorbic acid produced by the reaction of ascorbic acid with iron(III) is partly extracted into the organic phase and has a slight depressive effect on the flame absorbance of bismuth solutions. For this reason the bismuth solutions, which are to be extracted, should also contain iron.

REFERENCES

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