

REPORT NO. 1902

**THE DETERMINATION OF BORON IN
ALUMINIUM OF HIGH PURITY**

Director of Division T.W. Steele

Investigators E.B.T. Cook
H. Hoian

Date 15th July 1977

Project 03876

Project Report No. 1

**NATIONAL
INSTITUTE
for
METALLURGY**
200 Hans Strydom Avenue
RANDBURG
2194 South Africa



NATIONAL INSTITUTE FOR METALLURGY

Report No. 1902

**THE DETERMINATION OF BORON IN ALUMINIUM
OF HIGH PURITY**

15th July, 1977

**Investigators E.B.T. Cook
H. Holan**

ISBN 0 86999 386 0

SYNOPSIS

A description is given of the investigations that led to the development of chemical methods for the determination of boron within the range 0,25 to 1,0 p.p.m. in aluminium of high purity. Methods were developed that incorporated fluorimetry, directly in solutions containing aluminium and after separation of boron by liquid-liquid extraction into 2-ethyl-1,3 hexanediol. A published spectrophotometric method, involving extraction of the BF_4^- complex with methylene blue into dichloroethane, was modified for application to aluminium samples. Details of this modified procedure and the fluorimetric-extraction procedure are appended. The precision of the methylene-blue method is about 6 per cent relative and is recommended for precision and speed in preference to the others. Separation of boron by distillation and spectrophotometric determination with curcumin gave low values in comparison with those obtained by the other methods. Agreement between the boron values obtained on the samples tested was good for the fluorimetric and methylene-blue spectrophotometric methods.

SAMEVATTING

Die ondersoek wat gelei het tot die ontwikkeling van chemiese metodes vir die bepaling van boor binne die bestek van 0,25 tot 1,0 d.p.m. in aluminium met 'n hoë suiwerheidsgraad word beskryf. Daar is metodes ontwikkel wat fluorimetrie, regstreeks in oplossings wat aluminium bevat en na die skeiding van die boor deur vloeistof-vloeistofekstraksie in 2-eties-1,3-heksaandiol in, ingesluit het. 'n Gepubliseerde spektrofotometriese metode wat ekstraksie van die BF_4^- -kompleks met metileenblou in dichlooretaan in behels, is gewysig vir toepassing op aluminiummonsters. Besonderhede van hierdie gewysigde prosedure en die fluorimetriese ekstraksieprosedure word aangeheg. Die presisie van die metileenbloumetode is in die orde van 6 persent relatief en word vir presisie en spoed eerder as die ander metodes aanbeveel. Skeiding van die boor deur distillering en spektrofotometriese bepaling met kurkumien het lae waardes gegee vergeleke met dié wat met die ander metodes verkry is. Die ooreenstemming tussen die boorwaardes wat verkry is vir die monsters wat getoets is, was goed vir die fluorimetriese en metileenblou-spektrofotometriemethode.

CONTENTS

1. INTRODUCTION	1
2. EXPERIMENTAL METHOD	1
2.1. TECHNIQUE OF FLUORIMETRIC MEASUREMENT	2
2.2. DIRECT FLUORIMETRIC PROCEDURE	2
2.2.1. Phase Separation in Mixtures of Sulphuric Acid and Diethyl Ether	2
2.2.2. Dissolution of Samples	3
2.2.3. Effect of Aluminium and Mercury	3
2.2.4. Values of Blank Solutions	3
2.3. SEPARATION OF BORON WITH FLUORIMETRIC FINISH	3
2.3.1. Back-extraction	3
2.3.2. Calibration and Values of Blank Solutions	3
2.4. EXTRACTION OF BF_3 COMPLEX WITH METHYLENE BLUE	4
2.4.1. Dissolution of Samples	4
2.4.2. Calibration	4
2.5. BORON BY DISTILLATION	5
3. ANALYSIS OF ALUMINIUM SAMPLES	5
4. DISCUSSION AND RECOMMENDATIONS	6
5. CONCLUSIONS	6
6. REFERENCES	6
Appendix I. The direct fluorimetric determination of boron in aluminium of high purity by the method of standard additions (Laboratory Method No. 5/7)	12
Appendix II. Solvent extraction and fluorimetric determination of boron in aluminium of high purity (Laboratory Method No. 5/8)	14
Appendix III. The methylene blue extractive-spectrophotometric determination of boron in aluminium of high purity (Laboratory Method No. 5/9)	17
Table 1. Comparative results for boron in aluminium of high purity	5

LIST OF ILLUSTRATIONS

Figure 1. Calibration for direct fluorimetric determination of boron	7
Figure 2. Calibration for method of standard additions in direct fluorimetric method	8
Figure 3. Calibration for fluorimetric determination of boron after separation with EHD	9
Figure 4. Calibration for spectrophotometric determination of boron using method of standard additions	10
Figure 5. Calibration for spectrophotometric determination of boron using curcumin	11

1. INTRODUCTION

When aluminium is used as a reducing agent in the production of nuclear-grade zirconium, any boron present is collected in the zirconium. Because boron has an unusually high effective cross-section for the absorption of thermal neutrons, the boron content of this grade of zirconium is required to be less than 0,5 p.p.m. according to the specification of the American Society for Testing and Materials (ASTM). The boron content of the aluminium used in its production should therefore be of the same order of concentration, and a reliable analytical method for the determination of boron at this level is required. The ASTM carmine method¹ for the determination of boron in aluminium within the range 50 to 6000 p.p.m. has been found unsuitable at the 0,5 p.p.m. level. Spectrographic methods have failed as yet because of the lack of suitable boron-free material for the preparation of standards and the lack of chemically analysed standards. Furthermore, mass spectrometric values for two samples of aluminium of German origin were found to differ considerably from the quoted values. For example, in one instance the determined value was about 5 p.p.m. as against a quoted value of less than 0,1 p.p.m.

In the light of what can be regarded only as a paradox when considered in relation to the specification limit of 0,5 p.p.m., alternative procedures must be examined for the determination of boron. These include fluorimetric and spectrophotometric methods applied either direct to solutions containing aluminium, or after a suitable separation of boron from the matrix.

Fluorimetry exhibits high sensitivity^{2,3} for boron, but, as far as is known, it has not been used in the determination of boron in aluminium. Marcantonatos *et al.*⁴ have shown that dibenzoylmethane (DBM) can be used to produce a linear fluorimetric response over the range 0,0005 to 0,0065 p.p.m. of boron. After preliminary investigations at the National Institute for Metallurgy (NIM) had shown that this response was essentially linear in the presence of milligram amounts of zirconium, it was decided to investigate the direct fluorimetric determination of boron in aluminium of high purity by this method. The lower limit of determination by this direct procedure would be determined by the solubility of aluminium sulphate in concentrated sulphuric acid, which is the medium required for fluorimetry. The method of Marcantonatos would also be applied to the determination of boron after it had been separated from the aluminium matrix by liquid-liquid extraction and back-extraction. In this way, the mass of sample used could be higher and the sensitivity of the method could be improved. The separation procedure could indicate whether aluminium interferes seriously in the direct fluorimetric method.

In addition, an extractive-spectrophotometric method in which methylene-blue dye is used (developed by Sudo and Ikeda⁵) for the determination of as little as 0,2 p.p.m. of boron in zirconium would be tested for its applicability to the determination of boron in aluminium samples. If there were little measure of agreement between the results obtained by the two proposed methods, a third alternative would be examined in the form of the classical distillation separation of boron as methyl borate, followed by spectrophotometric determination with curcumin.

2. EXPERIMENTAL METHOD

Marcantonatos *et al.*⁴ determined boron in solutions that contained boron only in the range 0,54 to 6,48 ng per millilitre. For the basic fluorimetric procedure, they added boron in varying concentrations to 0,4 ml of sulphuric acid with a DBM concentration of $3,125 \times 10^{-4}$ M, and heated the mixture to 70°C for 1 hour. After cooling the sulphuric acid solution, they mixed it with small increments of diethyl ether to give a final single phase of 5 ml. They measured the fluorescence at 410 nm, using an excitation wavelength of 385 nm. They reported a variation from linearity of 8,4 per cent for the concentration-absorption relation at the 5 ng/ml level. This indicates that, if the method is applicable to aluminium samples, no better precision can be expected.

Two critical steps in the development of the DBM-boron fluorescing species are the heating at 70°C, and the mixing with diethyl ether. The published results were obtained over a heating period of 60 minutes, and this period was adhered to in the experimental work described here, although there is some evidence from the figures published by Marcantonatos *et al.*⁴ that better reproducibility is obtained by heating for 90 minutes. The mixing step in the present investigation suffered from the intermittent formation of two phases instead of a single sulphuric acid-diethyl ether phase. It is thought that this is associated with the absorption of water by the acid, in spite of the precautions taken (use of a vacuum oven for heating and storage of tubes in a desiccator), particularly as the formation of the two phases was most evident under humid conditions. If water is absorbed during the development

of fluorescence, this can possibly affect the reproducibility of measurements, even when two phases are not apparent.

Since Marcantonatos *et al.*⁴ worked only with solutions of pure boron, it is necessary to consider the dissolution of aluminium samples, values of the blank solutions, and the effect of aluminium and of any additions used in bringing it into solution.

Agazzi⁶ had been successful in using liquid-liquid extraction to extract boron into a chloroform solution of 2-ethyl-1,3 hexanediol (EHD) from high molarities (up to 6 M) of sulphuric acid. The sensitivity of his method of determination (flame photometry) is inadequate for the levels of boron that are of interest in aluminium of high purity. However, the method appeared to offer a means of separating boron, possibly by back-extraction of the element and then by application of the DBM fluorimetric method for the determination of boron. Of the 23 cations studied, Agazzi⁶ found that only manganese (more than 10 mg), titanium (more than 1 mg), molybdenum (less than 1 mg), and tungsten (less than 1 mg) interfered in the flame-photometric procedure, and they are presumably extracted to some extent. It is unlikely that these elements are present in interfering amounts in the extract obtained after dissolution of high-purity aluminium (1 g or less) because, according to the available data⁷, the total impurities in this material do not exceed 50 p.p.m. Since Agazzi⁶ had found that boron was not extracted from alkaline media into EHD in chloroform, the medium chosen for back-extraction in the present work was sodium hydroxide.

Sudo and Ikedo⁵ had determined boron in zirconium by dissolution of 0,2 g of sample in 3 ml of normal sulphuric acid and 5 ml of hydrofluoric acid (50 g/l), and extraction of the BF_4^- complex with methylene blue into dichloroethane followed by measurement of the absorbance of the extracted dye by spectrophotometry. They observed no serious interference from the elements tested at the levels in which they are present in nuclear-grade zirconium. It was therefore decided to apply this method as published to the determination at NIM of boron in aluminium.

The method chosen for the classical distillation of boron as methyl borate was one⁸ that had been used in the determination of boron in uranium materials down to 0,03 p.p.m. The distillate is collected in a suspension of calcium hydroxide, which, after evaporation of the methanol and addition of sulphuric acid, is heated to fumes of sulphur trioxide. Boron is then determined spectrophotometrically in this medium as the curcumin complex⁸.

2.1. Technique of Fluorimetric Measurement

Marcantonatos *et al.*⁴ used an excitation wavelength of 385 nm and an emission wavelength of 410 nm. As the Fluorimet instrument available at NIM was a filter instrument, an excitation filter with a peak at 375 nm and an interference filter at 410 nm were substituted for the wavelength settings used by Marcantonatos *et al.*⁴.

Because of difficulties experienced in matching the silica fluorimetric cells, a single pair of cells, positioned in the cell compartment in a similar way, was used in measuring the fluorescence difference between the blank solution and each sample and standard solution. The dimensions of these cells were such that the limited volume of solution (about 2 ml) completely covered the slit of the cell compartment. The instrument was adjusted to zero with a reagent blank solution in the cell compartment; this reagent blank solution corresponded to the acid and reagent used in the preparation of the standard boron solution for fluorescence measurement. With the highest boron standard solution in the cell compartment, the coarse and fine gain controls were manipulated to give a scale reading of 100. The fluorescence of the remaining standard, sample, and blank solutions (prepared from the acid used to dissolve the sample) were then measured without disturbance of the setting except during periodic checks for drift.

2.2. Direct Fluorimetric Procedure

2.2.1 Phase Separation in Mixtures of Sulphuric Acid and Diethyl Ether

Marcantonatos *et al.*⁴ prepared a solution for measurement by diluting 0,4 ml of sulphuric acid to 5 ml with diethyl ether. At this ratio, phase separation was often observed; as the fluorescence was evident only in one of the phases, the volume of which varied in a random manner, it was important to eliminate the formation of phases. It was found at NIM that dilution of the same volume of sulphuric acid to 2,5 ml greatly reduced this tendency, although it was not entirely eliminated. By the use of this reduced volume at a DBM concentration of $2,8 \times 10^{-4}$ M in silica tubes and heating at 70°C for 1 hour, it was found possible to construct a calibration graph (Figure 1) in the 1 to 12 ng/ml range, the reproducibility of which compares favourably with the scatter data for calibration reported by Marcantonatos *et al.*⁴.

2.2.2. *Dissolution of Samples*

In the fluorimetric method for boron, it is necessary for the sample to be dissolved in concentrated sulphuric acid. Aluminium does not dissolve in this medium but can be dissolved in dilute sulphuric acid, particularly in the presence of milligram amounts of mercury. After the water had been evaporated off from such a solution and it had been heated to incipient fumes of sulphur trioxide, it was found that the aluminium sulphate could be kept in solution for at least 24 hours. It was, however, necessary to check for possible loss of boron during the evaporation stage. This was done as follows: 500 ng of boron as boric acid was placed in a silica beaker with 50 ml of 10 per cent (v/v) sulphuric acid, and the boron was evaporated off; the solution was heated to boiling point and gently boiled for two hours, the volume being maintained at approximately 50 ml before final evaporation of the solution to fumes of sulphur trioxide and cooling in a desiccator. As a control, 500 ng of boron as boric acid was made alkaline with 2 drops of 0.1 N sodium hydroxide and was evaporated to dryness in a silica beaker, and the salt was dissolved in 5 ml of anhydrous sulphuric acid. No significant difference in fluorescence was found when 0.2 ml of these solutions was compared by the fluorimetric steps described in steps d to i of Section 5.1, Appendix I, and it was concluded that loss of boron during the evaporation of dilute solutions of sulphuric acid to fumes is insignificant.

2.2.3. *Effect of Aluminium and Mercury*

When the direct fluorimetric procedure, described in Section 5 of Appendix I, is applied to sulphuric acid solutions of aluminium sulphate, crystallization of the salt occurs as soon as the acid is mixed with diethyl ether. These crystals have to be separated by a centrifuging step and the clear supernatant solution has to be transferred to a silica fluorescence tube of adequate dimensions to allow the small volume of liquid to be exposed to the full excitation light beam (see step f of Section 5.1, Appendix I). Calibrations in the presence and absence of aluminium (Figure 1) indicate that aluminium suppresses the fluorescence. Consequently, measurements of fluorescence in the samples cannot be referred to standard solutions of pure boron, and it was found necessary to use the method of standard additions for the determination of boron in aluminium samples. The need for several aliquot portions of samples in the method of additions was avoided by the addition of aliquot portions of one sample solution to successive silica tubes containing varying amounts of boron. The boron was added as a solution of boric acid and evaporated to dryness after it had been made alkaline with sodium hydroxide. A typical best-fit curve obtained by this technique is shown in Figure 2.

2.2.4. *Values of Blank Solutions*

All the fluorescence measurements were automatically corrected for the fluorescence of the reagent-blank solution since the instrument was set at zero for the blank solution and at 100 scale divisions for the highest standard. Because mercury and distilled water were added during the dissolution step, the value of the blank solution differed from that in the calibration standards. The blank solution must therefore be measured in relation to the calibration blank, and a correction must be applied for the fluorescence observed.

2.3. Separation of Boron with Fluorimetric Finish

2.3.1. *Back-extraction*

Preliminary tests showed that, when boron was extracted into a solution of EHD in chloroform and back-extracted into 0.05 N sodium hydroxide solution, problems arose with residual EHD in the back-extract. When these back-extracts were evaporated to dryness and the residue was taken up in fuming sulphuric acid, this organic residue suppressed the fluorescence of the DBM-boron complex. This was overcome by wet oxidation of these organic traces by the addition of a few drops of nitric acid to the fuming sulphuric acid. However, it is essential that all traces of nitric acid are eliminated subsequently because even minor amounts of this acid completely suppress the fluorescence of the DBM-boron complex. Details of the procedure that was eventually adopted are given in Appendix II.

2.3.2. *Calibration and Values of Blank Solutions*

Calibrations based on standard solutions taken through the entire procedure in the absence and presence of 1 g of aluminium are depicted in Figure 1. Boron was removed from the solutions of aluminium sulphate that were used for the second calibration by a preliminary extraction into a chloroform solution of EHD, before addition of the boron standards. As in the direct procedure, the precision is better at the higher concentrations of boron. As the extraction procedure permits the use of larger masses of sample, measurements can be restricted to the most significant part of the

DETERMINATION OF BORON IN ALUMINIUM

calibration curve. On a 1 g sample, boron can be determined down to 0,25 p.p.m. with an estimated precision of less than 10 per cent relative to the certified value. No significant difference is apparent in the calibration curves prepared from the data obtained in the presence or absence of aluminium. A correction is made for the fluorescence caused by the boron in the reagent solutions carried through the whole procedure by adjustment of the fluorimeter to zero.

2.4. Extraction of BF_3 Complex with Methylene Blue

Basically, the method involves dissolution of the sample in measured volumes of sulphuric and hydrofluoric acids, followed by solvent extraction of the fluo-boron complex with methylene blue into dichloroethane, and measurement of the resulting absorbance at 657 nm. A significant problem in achievement of the required sensitivity is that of sample dissolution.

2.4.1. Dissolution of Samples

It was found impossible to dissolve, in 3 ml of normal sulphuric acid and 5 ml of hydrofluoric acid (50 g/l), a similar mass of aluminium to that of the zirconium (0,2 g) dissolved by Sudo and Ikeda³. However, when the volume of hydrofluoric acid was doubled, complete dissolution was achieved at room temperature in periods varying from 12 to 24 hours, depending on the size of the aluminium particles. As the concentration of free hydrofluoric acid is unknown and as it influences the extraction of both the F^- and the BF_3 complex of the dye², it is necessary, when the published procedure is used, to match the concentration of free hydrofluoric acid in the samples and standard solutions by dissolution of a similar mass of 'boron free' aluminium in the standard solutions.

2.4.2. Calibration

Because 'boron free' aluminium was not available for the calibration, known masses of boron were added to 0,2 g portions of BCS (British Chemical Standard) aluminium sample no. 198d. This is reputed to have a boron content of less than 0,2 p.p.m., and the absorbance was corrected for boron contributed by the following:

- (1) the standard sample,
- (2) the acids used for dissolution, and
- (3) the small amounts of dye that are extracted as fluo-complexes with methylene blue⁶.

Curve A of Figure 4 shows the calibration for boron, which has been drawn as a calculated best-fit curve and which does not pass through the origin because the corrections listed above have not been made. Curve B of Figure 4 represents the calibration after correction for the absorbance of any fluo-complex of the dye extracted into the dichloroethane had been made. The boron in the acid had to be determined separately and to be subtracted from the determined value for the sample. This arose from the fact that the corrections for (2) and (3) cannot be determined by repetition of the extraction procedure on the acids used for dissolution because the extraction of both the BF_3 and F^- complexes with the dye is influenced by the concentration of free hydrofluoric acid², which is considerably less in the presence of aluminium. Therefore, for the necessary corrections, the following sequence of measurements must be made. Firstly, the absorption due to the fluo-complex of the dye must be measured at the two concentrations of hydrofluoric acid after extraction of the boron in acid and acid plus aluminium. The measurement at the low concentration is required for the correction to the sample absorbances, and that at the higher concentration for the determination of the boron in the acids used for dissolution of the sample. Secondly, the boron in the acid used is obtained by the addition of varying amounts of boron to aliquot portions of acid, and determination of the absorbance of each. After correction for the absorbance of the fluo-complex of the dye (at the high concentration of hydrofluoric acid), the boron in the acid is determined by extrapolation of the calibration curve (method of additions) to the x -axis (absorbance), the negative intercept giving the boron content of the acid. By this rather complex but necessary procedure, corrections (2) and (3) are evaluated, thus enabling the true boron content of the samples to be obtained. The corrections necessary for the boron content of the hydrofluoric acid, and the changes in the absorption of the blank solution of the fluo-methylene blue with the hydrofluoric acid concentration, do not appear to have been taken into account by Sudo and Ikeda³. These corrections need be redetermined only when a new batch of acid or dye is used.

The absorbance contributed by the fluo-complex of the dye³ in the presence and absence of aluminium was determined by a preliminary removal of boron by four successive extractions of the BF_3 complex with methylene blue in dichloroethane, four extractions being considered adequate by Sudo and Ikeda³. Measurement of the absorbance of a fifth extract was then accepted as being due to

DETERMINATION OF BORON IN ALUMINIUM

the fluo-complex only at the two concentrations of free hydrofluoric acid resulting from the presence or absence of aluminium. Reproducibility at the level of greatest interest (0,1 μg in 10 ml of extract) is estimated at 10 per cent relative, and is comparable with the fluorimetric procedure. Consequently, quadruplicate determinations should be done at these levels, and the method of standard additions used. Each addition should be made in duplicate, and a best-fit graph of the average resulting absorbances should be plotted after appropriate corrections. For higher concentrations of boron, the absorbances, corrected for the dye, can be referred direct to this calibration graph provided that the boron content is read from the point where the extrapolated graph cuts the baseline. A correction for the boron content of the acids used must be applied. This is approximately 0,04 μg , which corresponds to 0,2 p.p.m. in a sample.

2.5. Boron by Distillation

The distillation procedure⁸ that has been used for the determination of boron in uranium materials involves dissolution in a distillation flask of the samples in sulphuric acid to which potassium dichromate has been added. Because it is not possible to dissolve aluminium samples by this procedure, 0,5 g of sample was first transferred to a silica beaker containing 5 mg of mercuric sulphate and 20 ml of distilled water, and 5 ml of concentrated sulphuric acid was added. The solution was heated to dissolve the sample, and was finally brought to fumes of sulphur trioxide. The hot solution was transferred to the distillation flask and was rinsed with 5 ml of water, which was added to the flask. Methanol (100 ml) was then added, and the boron was distilled over as methyl borate. Spectrophotometric calibrations for boron by the method described were conducted on pure boron solutions and on similar solutions after distillation. Figure 5 gives the resulting graphs, which indicate a recovery of 78 per cent of the boron distilled. Distillations carried out in the presence of 0,5 g of the BCS 78 aluminium standard gave poorer and variable recoveries (less than 60 per cent). When a solution prepared from a sample of somewhat higher boron content (1 p.p.m.) was subjected to two successive distillations, between 20 and 66 per cent of the boron recovered in the first distillate was recovered in the second. Since aluminium standards with certified boron values were not available at the time, the extent to which boron was recovered from these samples can be assessed only by comparison with values obtained by the other methods described in this report. Incomplete recovery is not unexpected since there is published evidence that boron is not completely recovered by distillation in the presence of aluminium salts^{9,10}, or after a single addition of methanol. There are indications that, if the methanol is added in successive small aliquot portions rather than altogether, the recovery is improved significantly.

3. ANALYSIS OF ALUMINIUM SAMPLES

The two samples selected for determination were supplied by Vereinigte Aluminium Werke Aktiengesellschaft (VAWA), Berlin. The boron in sample VAWA 1 (specified by the manufacturers as being less than 0,1 p.p.m.) was determined by all the methods, whereas the boron in sample VAWA 2 (boron content 1,3 p.p.m.) was determined by the methylene-blue method only. The results are given in Table 1. The value given for boron in BCS 198d by spark-source mass spectrometry was 0,2 p.p.m.

TABLE 1
Comparative results for boron in aluminium of high purity

Method	VAWA 1 Boron, p.p.m.	VAWA 2 Boron, p.p.m.	BCS 198d Boron, p.p.m.
1. Direct fluorimetric, by method of standard additions	1,0 1,1	-	-
2. Fluorimetric, after liquid-liquid separation step	1,2 1,2	-	-
3. Extractive spectrophotometric method with methylene blue	1,35*	3,0	0,60
4. Spectrophotometric method, with curcumin, after separation of boron by double distillation	1,0 0,8	-	-

* Mean of 8 determinations with a precision of 6 per cent relative. Agreement between methods 1, 2, and 3 is reasonably good.
- Not determined.

DETERMINATION OF BORON IN ALUMINIUM

The values obtained by double distillation (Method 4) are variable and have a low bias, thus confirming the incomplete volatilization of boron during distillation. No comparison was possible with data on analysed standards because no aluminium samples with firm values for boron below 1 p.p.m. were available. No real comparison with instrumental methods was undertaken because their calibration is frequently dependent on analysed samples, which, at the low levels being determined, could well suffer from bias. If calibration is not dependent on analysed samples, it is dependent on the use of a boron-free matrix and of reagents that have been almost impossible to obtain.

4. DISCUSSION AND RECOMMENDATIONS

Of the fluorimetric methods examined, the extractive-fluorimetric method probably gives the most reliable results because it involves the removal of the aluminium present. In the direct method, the presence of aluminium appears to depress the fluorescence as well as giving a lower precision of measurement. The extractive method enables larger samples (up to 1 g) to be used, thus increasing the sensitivity of the method. All the fluorimetric methods are time-consuming. The fastest and most precise method is the spectrophotometric method involving extraction of the BF_4^- complex with methylene blue. Once the boron contents of the reagents and distilled water in use have been established, the method is fairly uncomplicated in the hands of a skilled operator. However, its precision at the 0.5 p.p.m. level is probably no better than 10 per cent relative.

Further analyses are proposed using charged-particle analysis and spark-source mass spectrometry. In addition, analysis of samples VAWA 1, VAWA 2, and BCS 198d is to be repeated in relation to a series of Swiss aluminium standards, which will shortly be available.

5. CONCLUSIONS

Of the four methods examined for the determination of boron in pure aluminium, the fluorimetric procedure combined with a separation step and the extraction-spectrophotometric procedure are considered to be superior to the distillation and direct-fluorimetric approaches, although the results from these last two methods tend to support those obtained by the procedures adopted. The extraction-spectrophotometric method is the most rapid of the methods examined. The precision of the adopted methods is approximately 10 per cent relative, and the values obtained for samples of pure aluminium are reasonably consistent by all four methods.

6. REFERENCES

1. AMERICAN SOCIETY FOR TESTING AND MATERIALS. Annual book of ASTM standards. Part 32. New York, the Society. 1970. pp. 136-138.
2. WHITE, C.E., WEISSLER, A., and BUSKER, D. Fluorimetric determination of microgram quantities of boron. *Analyt. Chem.*, vol. 19, no. 10. 1947. pp. 802-805.
3. BRUCE, T., and ASHLEY, R.W. Spectrofluorimetric determination of boron with carminic acid in neutral solutions. Ontario, Atomic Energy of Canada, Ltd. *Report no. AECL-4446*. Feb. 1973.
4. MARCANTONATOS, M., GAMBA, G., and MONNIER, D. Luminescence determination of boric acid traces. *Helv. Chem. Acta*, vol. 52, fasc. no. 2, no. 59. 1969. pp. 538-543. (In French.)
5. SUDO, E., and IKEDO, S. Spectrophotometric determination of micro amounts of boron in zirconium and zircaloy by solvent extraction. *Bunseki Kagaku*, vol. 17, no. 10. 1968. pp. 1197-1203.
6. AGAZZI, E.J. Extraction-flame photometric determination of boron. *Analyt. Chem.*, vol. 39, no. 2. Feb. 1967. pp. 233-235.
7. ISHIHARA, M., and MUKAI, K. Impurity levels in aluminium as influenced by raw materials and processing methods. *Trans. Metall. Soc. AIME*, vol. 236. Feb. 1966. p. 194.
8. MARTIN, J.R., and HAYES, J.R. Application of ion exchange to determination of boron. *Analyt. Chem.*, vol. 24. 1952. p. 182.
9. RODDEN, C.J. (ed.). *Analysis of essential nuclear reactor materials*. New Brunswick, N.J. U.S. Atomic Energy Commission, New Brunswick Laboratory. 1964. p. 481.

DETERMINATION OF BORON IN ALUMINIUM

Medium : Concentrated sulphuric acid – diethyl ether

Reagent: Dibenzoylmethane

X Calibration for pure boron solutions

⊙ Calibration for boron solutions containing 4 mg of aluminium

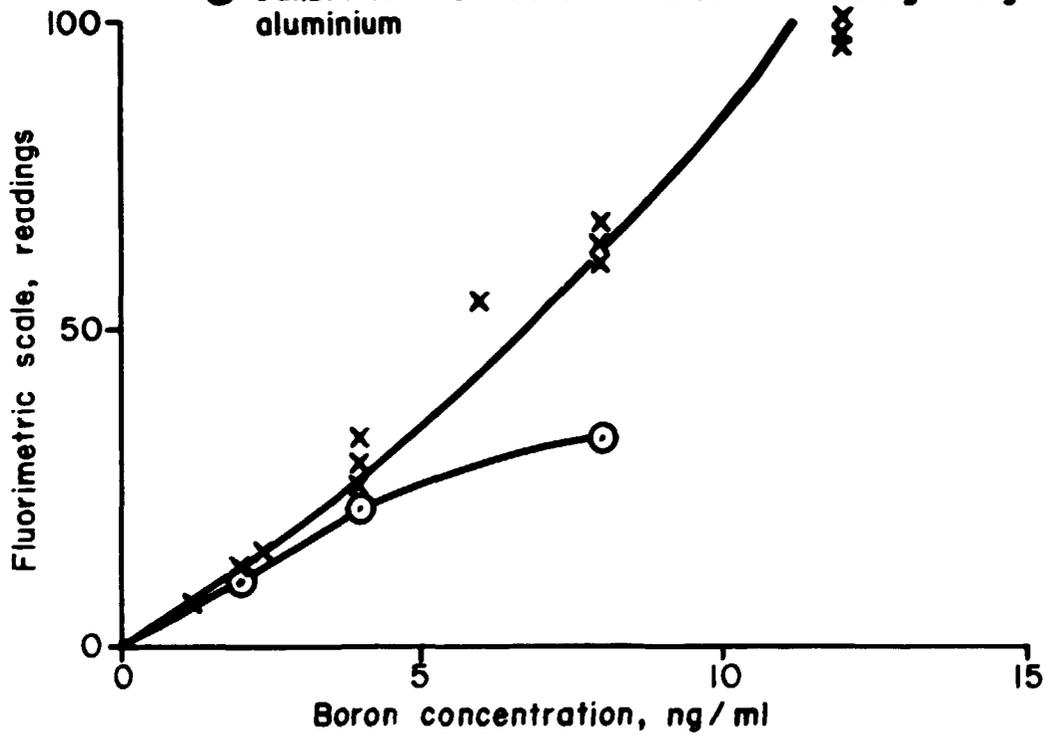
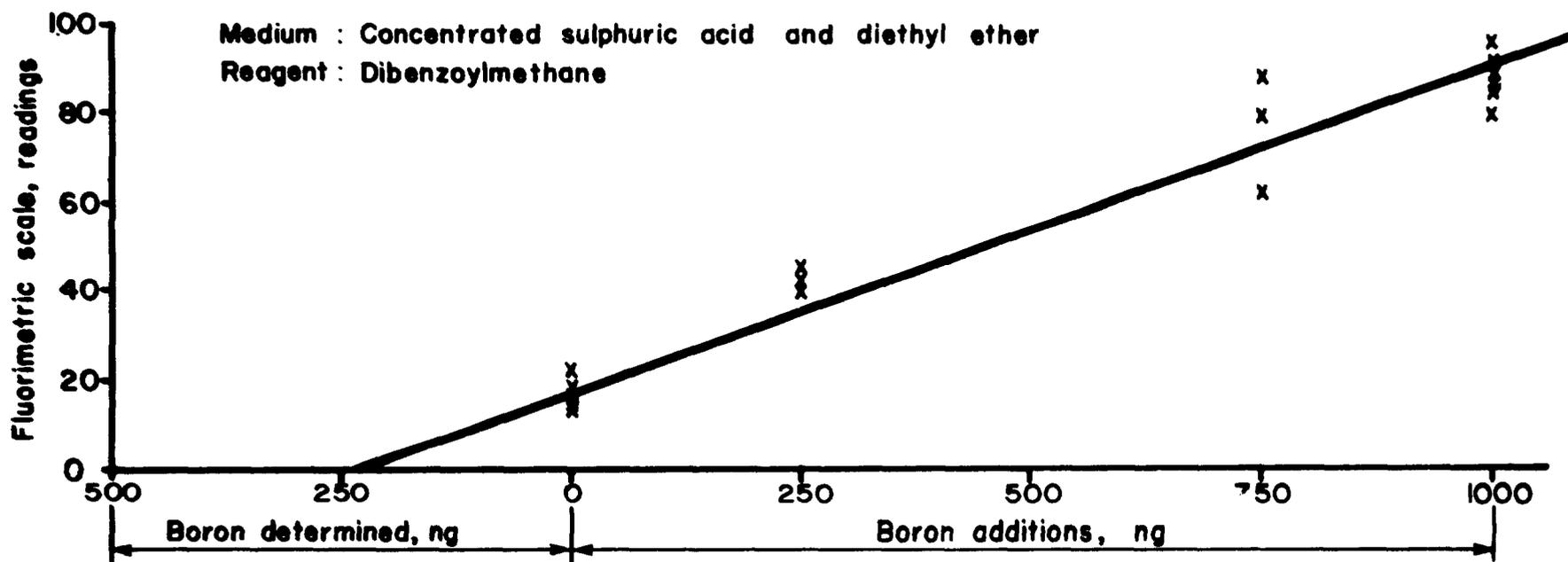


FIGURE 1 Calibration for direct fluorimetric determination of boron



DETERMINATION OF BORON IN ALUMINIUM

FIGURE 2 Calibration for method of standard additions in direct fluorimetric method

DETERMINATION OF BORON IN ALUMINIUM

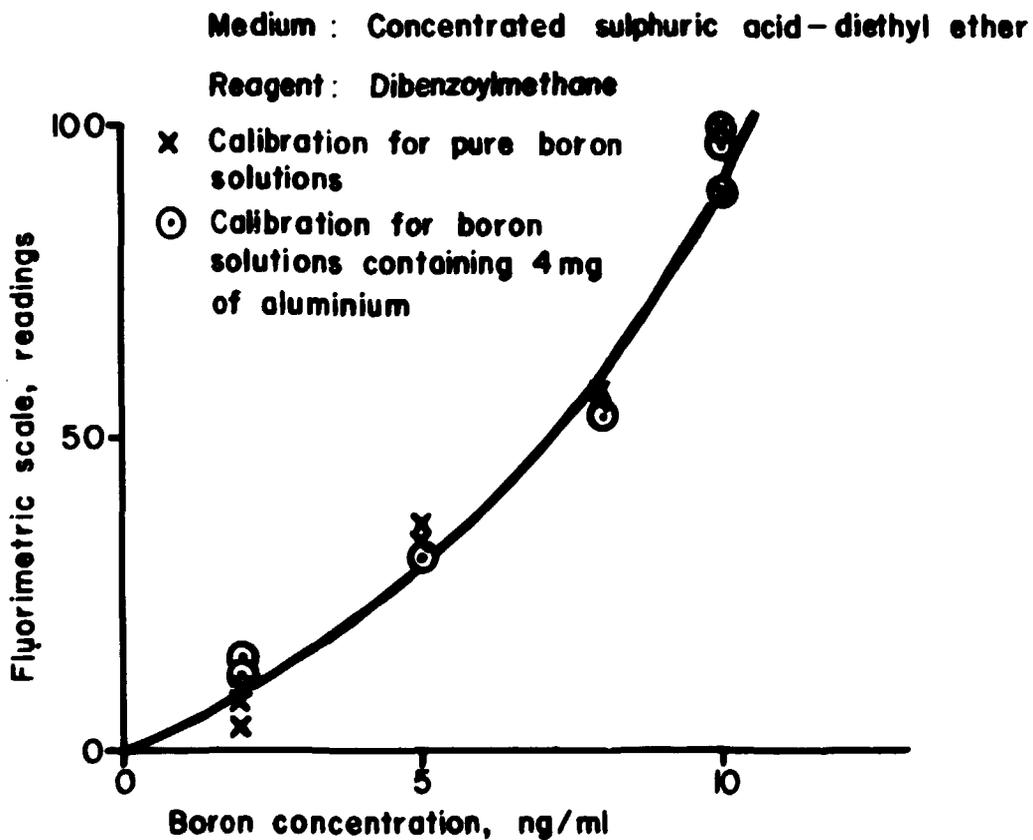


FIGURE 3 Calibration for fluorimetric determination of boron after separation with EHD

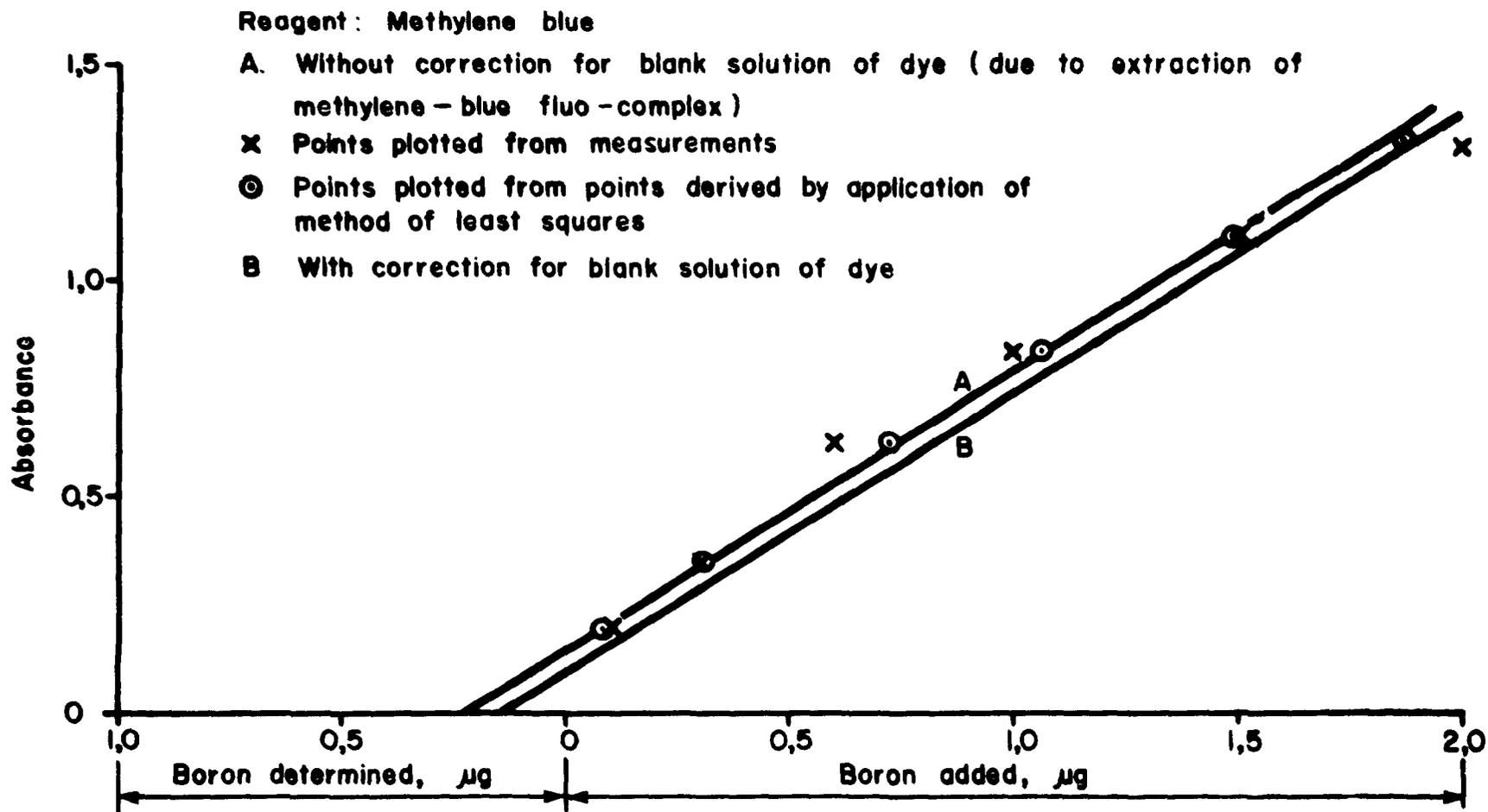


FIGURE 4 Calibration for spectrophotometric determination of boron using method of standard additions

DETERMINATION OF BORON IN ALUMINIUM

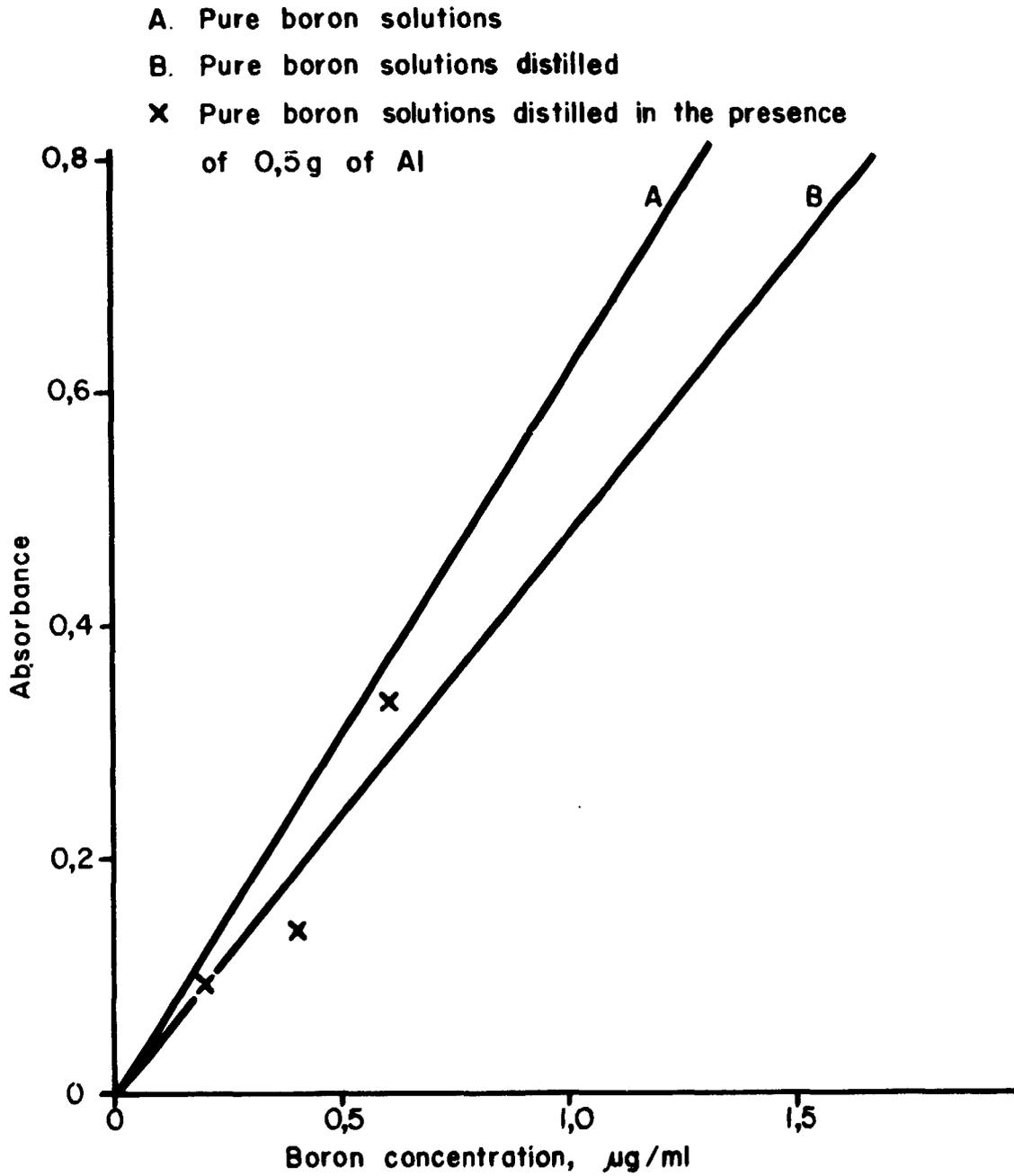


FIGURE 5 Calibration for spectrophotometric determination of boron using curcumin

DETERMINATION OF BORON IN ALUMINIUM

APPENDIX I

E.1. Boron

E.2. Aluminium, boron in

THE DIRECT FLUORIMETRIC DETERMINATION OF BORON IN ALUMINIUM OF HIGH PURITY BY THE METHOD OF STANDARD ADDITIONS (LABORATORY METHOD NO. 5/7)

1. OUTLINE

The sample is dissolved in a measured volume of dilute sulphuric acid and evaporated to incipient fumes of sulphur trioxide. An aliquot portion of this solution is mixed with an equal volume of dibenzoylmethane (DBM) in sulphuric acid and heated *in vacuo* for 75 minutes at 70°C. After being cooled in a desiccator, the solution is mixed with diethyl ether and diluted to volume, and its fluorescence is measured by the method of standard additions.

2. APPLICATION OF THE METHOD

The method is applicable to aluminium samples of high purity in the boron concentration range 0.4 to 1 p.p.m. The coefficient of variation of the method is estimated as being about 10 per cent.

3. REAGENTS

Use A.R.-grade reagents and double-distilled water for their preparation.

(1) **Dehydrated Sulphuric Acid**

Transfer 250 ml of Merck's p.a. grade of acid to a silica beaker and heat to strong fumes. Cool and store in a desiccator.

(2) **Dibenzoylmethane (DBM) Solution, 0.125 g/l**

Transfer 0.0025 g of Fluka A.G. 'purum' DBM to a dry 100 ml polythene bottle. Add 20 ml of dehydrated sulphuric acid and shake to dissolve. Keep tightly stoppered in a desiccator. Prepare afresh each day.

(3) **Sulphuric Acid, 20 per cent (v/v)**

To a 1-litre polythene bottle previously marked at the 1-litre level, add 700 ml of distilled water. From a polythene measuring cylinder add 200 ml of Merck's p.a. grade sulphuric acid, mix, and cool to room temperature. Dilute to volume and mix.

(4) **Diethyl Ether**

May and Ba'er peroxide-free with a water specification of not more than 0.15 per cent.

(5) **Mercuric Sulphate**

Merck's G.R. reagent

(6) **Sodium Hydroxide, Normal Solution**

Transfer 0.1429 g of H_3BO_3 to a 500 ml polythene bottle, place on a top-loading balance, and, after counterpoising, add 500 g of water. Shake to dissolve the boric acid. This solution contains 50 μ g of boron per millilitre. By similar appropriate mass dilutions in 100 ml polythene bottles, prepare two standard solutions having concentrations of 10 ng/ml and 20 ng/ml respectively. (Use a graduated polypropylene pipette for measuring the respective volumes to be diluted.)

4. APPARATUS

(1) **Fluorimeter**

Baird Atomic Fluorimet.

DETERMINATION OF BORON IN ALUMINIUM

- (2) **Lamp**
FM102. Spectral range 300 to 400 nm.
- (3) **Excitation Filter**
OXI band-filter peak at 365 nm.
- (4) **Emission Filters**
OBIO band filter peak at 400/420 nm, 410 nm interference filter.
- (5) **Fluorimetric Cells**
7,7 by 76,8 mm cylindrical silica cells marked at the 2,5 ml level.
- (6) **Fluorimetric Cells**
7,2 by 52 mm cylindrical silica cells with file mark to orientate cell with corresponding mark on cell-holder.
- (7) **Stoppers**
Polypropylene stoppers wound with Teflon tape to fit fluorimetric cells.

5. PROCEDURE

Take through the whole procedure a blank solution containing similar amounts of sulphuric acid and mercuric sulphate.

- a. Transfer a catch mass of 0,25 g (weighed to within 0,0001 g) of aluminium to a 250 ml silica beaker. Add 2 mg of HgSO_4 and 50 ml of 20 per cent (v/v) sulphuric acid, using a polypropylene measuring cylinder. Cover with a polypropylene cover, heat to boiling, and boil gently until all the metal has dissolved. Remove the cover and evaporate until fumes of sulphur trioxide are just apparent. Transfer immediately to a desiccator and cool to room temperature.
- b. Prepare a set of calibration solutions as follows. Take three silica fluorimetric tubes for each sample, and, to the appropriate sample tubes, add 1, 2, and 3 times the estimated boron content of each sample. Add 2 drops of 0,01 N sodium hydroxide solution to each tube, place the tubes in an air oven at 50°C , and evaporate to dryness. Remove the tubes, and, to each set of three tubes, add 0,2 ml of sample solution. To an additional dry tube, add a further 0,2 ml aliquot portion of sample solution to serve as a reagent + sample reference solution.
- c. Transfer 0,2 ml of the sample and blank solutions to similar tubes.
- d. Add 0,2 ml of dibenzoylmethane solution to all the tubes, mix by tilting and rotating the tubes, and place them under vacuum in an oven at 70°C . Maintain at this temperature for 75 minutes. Transfer immediately to a desiccator and cool to room temperature.
- e. With minimum exposure to the atmosphere, remove each tube and, while stirring with a platinum wire, add small increments of diethyl ether, cooling between successive additions. Finally dilute to 2,5 ml, mix well, and insert the stopper. Centrifuge the samples containing aluminium in order to compact the crystals of aluminium sulphate that form at the bottom of the tubes on the addition of ether.
- f. Transfer the reagent blank solution and the highest standard solution to short (7,2 by 52 mm) fluorimetric tubes. Clean the outside of the tubes by dipping them into a beaker of diethyl ether. Before inserting the tube into the fluorimeter cell compartment, drain the excess ether onto a tissue pressed to the bottom of the tube.
- g. With the reagent + sample reference solution in the cell compartment, turn the cell so as to orientate the marks on the cell and the compartment. Adjust the 'zero-gain' control knob to read zero on the scale. With the highest standard in the compartment and the cell similarly orientated, adjust the 'fine-gain' to read 100 on the scale. If necessary, switch the 'coarse-gain' to the appropriate setting required to achieve the adjustment of zero to 100 scale divisions between the blank solution and the standard. Check these two settings several times.
- h. Using the same fluorimetric cell as was used for the highest standard, take readings for the three spiked sample solutions. Repeat the measurements for each set of sample solutions. Drain the cell as well as is possible between measurements but do not wash, and conduct the measurements in sequence from those of highest to those of lowest boron concentration.
- i. Plot a graph of the amounts of boron added to the sample against the fluorescence readings, and interpolate the boron content of the sample by projecting a line from the best fit for these points and the sample reading on the y-axis to the base line.

APPENDIX II

E.1 Boron
E.2 Aluminium, boron inSOLVENT EXTRACTION AND FLUORIMETRIC DETERMINATION OF BORON
IN ALUMINIUM OF HIGH PURITY
(LABORATORY METHOD NO. 5/8)

1. OUTLINE

The sample is dissolved in dilute sulphuric acid. Boron is extracted into a chloroform solution of 2-ethyl-1,3 hexanediol (EHD) and back-extracted into 0,05 N sodium hydroxide solution. The back-extract is evaporated to dryness, and the salts are dissolved in sulphuric acid. Residual organic materials are wet-oxidized with nitric acid, and, after complete elimination of this acid, boron is determined by a fluorimetric method involving dibenzoylmethane (DBM) as the fluorescing agent.

2. APPLICATION OF THE METHOD

The method is applicable to the determination of boron in aluminium of high purity in the range 0,2 to 1,5 p.p.m. The coefficient of variation of a single fluorimetric determination is estimated to be about 10 per cent.

3. REAGENTS

Use A.R.-grade reagents, and double-distilled water for their preparation.

3.1. Reagents for the Separation Procedure

- (1) **Sodium Hydroxide Solution, 0,1 M**
Transfer 4 g of sodium hydroxide to a 1-litre polythene bottle and dissolve in 1 litre of distilled water.
- (2) **Sodium Hydroxide Solution, 0,05 M**
Transfer 2 g of sodium hydroxide to a 1-litre polythene bottle and dissolve in 1 litre of distilled water.
- (3) **2-Ethyl-1,3 Hexanediol (EHD) Solution, 5 per cent Boron-free**
Transfer 12,5 ml of the reagent (British Drug Houses laboratory grade) to a 1-litre polythene bottle. Add 237,5 ml of chloroform and 250 ml of 0,1 M sodium hydroxide solution. Stopper and shake for 2 min. Decant most of the aqueous phase, and pour the contents of the bottle into a polythene beaker. Decant as much of the remaining aqueous phase as possible and return the chloroform solution to the bottle. Wash by shaking with 500 ml portions of distilled water, and repeat the decantation until the washings have a pH value of 7 to 8 (use pH paper). Finally, use polythene separating funnels to remove the residual aqueous phase, and transfer the solution to a glass reagent bottle. (Borosilicate glass must not be used.)
- (4) **Sulphuric Acid, sp.gr. 1,84**
Merck's p.a. grade.
- (5) **Sulphuric Acid, about 0,05 M**
Add 1,3 ml of concentrated acid to 500 ml of distilled water in a polythene bottle and mix.
- (6) **Nitric Acid, sp.gr. 1,40**
Merck's p.a. grade
- (7) **Mercuric Sulphate**
Merck's p.a. grade

3.2. Reagents for the Fluorimetric Procedure

Use A.R.-grade reagents and double-distilled water for their preparation.

- (1) **Dehydrated Sulphuric Acid**
Transfer 250 ml of Merck's p.a. grade of acid to a silica beaker and heat to strong fumes. Cool and store in a desiccator.

DETERMINATION OF BORON IN ALUMINIUM

- (2) **Dibenzoylmethane (DBM) Solution, 0,125 g/l**
Transfer 0,0025 g of Fluka A.G. 'purum' dibenzoylmethane to a dry 100 ml polythene bottle. Add 20 ml of dehydrated sulphuric acid and shake to dissolve. Keep tightly stoppered in a desiccator. Prepare afresh each day.
- (3) **Sulphuric Acid, 20 per cent (v/v)**
To a 1-litre polythene bottle previously marked at the 1-litre level, add 700 ml of distilled water. From a polythene measuring cylinder, add 200 ml of Merck's p.a. grade sulphuric acid, mix, and cool to room temperature. Dilute to volume and mix.
- (4) **Diethyl Ether**
May and Baker peroxide-free with a water specification of not more than 0,15 per cent
- (5) **Mercuric Sulphate**
Merck's G.R. reagent
- (6) **Sodium Hydroxide, Normal Solution**
Transfer 0,1429 g of H_3BO_3 to a 500 ml polythene bottle, place on a top-loading balance, and, after counterpoising, add 500 g of water. Shake to dissolve the boric acid. This solution contains 50 μ g of boron per millilitre. By similar appropriate mass dilutions in 100 ml polythene bottles, prepare two standard solutions having concentrations of 10 ng/ml and 20 ng/ml respectively. (Use a graduated polypropylene pipette for measuring the respective volumes to be diluted.)

4. APPARATUS

- (1) **Fluorimeter**
Baird Atomic Fluorimet.
- (2) **Lamp**
FM102. Spectral range 300 to 400 nm.
- (3) **Excitation Filter**
OX1 band-filter peak at 365 nm.
- (4) **Emission Filters**
OB10 band-filter peak at 400 to 420 nm, 410 nm interference filter.
- (5) **Fluorimetric Cells**
7,7 by 76,8 mm cylindrical silica cells marked at the 2,5 ml level.
- (6) **Fluorimetric Cells**
7,2 by 52 mm cylindrical silica cells with file mark to orientate cell with corresponding mark on cell-holder.
- (7) **Stoppers**
Polypropylene stoppers wound with Teflon tape to fit fluorimetric cells.

4.2. Apparatus for the Separation Procedure

- (1) **Polythene Separating Funnels**
Gradplex plastic ware of 125 ml capacity made by XLON, England.
- (2) **Beakers**
Vitreosil of 250 ml capacity.

5. PROCEDURE PRIOR TO MEASUREMENT

- Carry a blank solution, containing all the reagents, through the entire procedure.
- a. Transfer 1 g of aluminium to a 250 ml silica beaker.
 - b. Add 8 mg of mercuric sulphate and 60 ml of water.
 - c. Using a polythene measuring cylinder, carefully add 15 ml of concentrated sulphuric acid.
 - e. Cover the beaker with a polythene (or silica) lid and maintain at boiling point, occasionally agitating the contents, until the sample is entirely dissolved (for about 1 hour).
 - f. Cool to room temperature.
 - g. Transfer the sample to a 125 ml polythene separating funnel and dilute to about 60 ml.
 - h. Add 30 ml of 5 per cent EHD and shake for 5 min. Transfer the organic phase to a similar separating funnel, and shake with 30 ml of 0,05 M sulphuric acid for 2 min.
 - i. Rinse the original funnel once with a few millilitres of 0,1 M sodium hydroxide, and three times with distilled water.
 - j. Transfer the organic phase to this funnel, add 10 ml of 0,05 M sodium hydroxide solution, and back-extract boron by shaking for 5 min.

DETERMINATION OF BORON IN ALUMINIUM

- k. Discard the organic phase, and wash the back-extract twice by shaking for 2 min with 25 ml of chloroform.
- l. Transfer the aqueous phase to a 250 ml silica beaker.
- m. Rinse the funnel with a few millilitres of distilled water and add to the beaker.
- n. Evaporate the solution to dryness, exercising care during the final stage to avoid spattering.
- o. From a polythene pipette, add 10 ml of sulphuric acid (sp.gr. 1,84) and heat to fumes.
- p. Add 3 drops of nitric acid (sp.gr. 1,40) to the fuming sulphuric acid and continue fuming for 1 min. Cool.
- q. Rinse the walls of the beaker with distilled water to wash off traces of nitric acid, and again heat to fumes of sulphur trioxide and fume for 1 min.
- r. Cool and repeat this step.
- s. Finally transfer the beaker to a desiccator and cool to room temperature.

6. FLUORIMETRIC DETERMINATION

Determine the boron on quadruplicate aliquot portions (0,2 ml).

- a. Transfer 0,2 ml of the sample and blank solutions to sets of silica fluorimetric tubes.
- b. Add 0,2 ml of dibenzoylmethane solution to all the tubes, mix by tilting and rotating the tubes, and place them under vacuum in an oven at 70 °C.
- c. Maintain at this temperature for 75 minutes.
- d. Transfer immediately to a desiccator and cool to room temperature.
- e. With minimum exposure to the atmosphere, remove each tube and, while stirring with a platinum wire, add small increments of diethyl ether, cooling between successive additions.
- f. Finally dilute to 2,5 ml, mix well, and insert the stopper.
- g. Centrifuge the samples containing aluminium in order to compact the crystals of aluminium sulphate that form at the bottom of the tubes on the addition of ether.
- h. Transfer the reagent blank solution and the highest standard solution to short (7,2 by 52 mm) fluorimetric tubes.
- i. Clean the outside of the tubes by dipping them into a beaker of diethyl ether.
- j. Before inserting the tube into the fluorimeter cell compartment, drain the excess ether onto a tissue pressed to the bottom of the tube.
- k. With the reagent + sample reference solution in the cell compartment, turn the cell so as to orientate the marks on the cell and the compartment.
- l. Adjust the 'zero-gain' control knob to read zero on the scale.
- m. With the highest standard in the compartment and the cell similarly orientated, adjust the 'fine gain' to read 100 on the scale. If necessary, switch the 'coarse gain' to the appropriate setting required to achieve the adjustment of zero to 100 scale divisions between the blank solution and the standard. Check these two settings several times.
- n. Using the same fluorimetric cell as was used for the highest standard, take readings for the three spiked sample solutions.
- o. Repeat the measurements for each set of sample solutions.
- p. Drain the cell as well as possible between measurements but do not wash, and conduct the measurements in sequence from those of highest to those of lowest boron concentration.
- q. Plot a graph of the amounts of boron added to the sample against the fluorescence readings and interpolate the boron content of the sample by projecting a line from the best fit for these points and the sample reading on the y-axis to the base line.

7. CALIBRATION

- a. Using a graduated polythene pipette, transfer 1, 2, 5, 4, and 6 millilitres of standard boron solution (1 ml \equiv 250 mg of boron) to a series of four 250 ml silica beakers.
- b. Prepare another silica beaker for the blank determination of the solution.
- c. Transfer 8 mg of mercuric sulphate to each beaker, add 30 ml of water and, with a polythene measuring cylinder, add 15 ml of concentrated sulphuric acid. Cool.
- d. Proceed as described in Section 5.g, onwards, but take duplicate aliquot portions (0,2 ml) for the fluorimetric determination only.
- e. Draw a calibration graph of boron concentration against measured fluorescence in terms of arbitrary scale readings, and determine the boron content of the sample with reference to this calibration.

DETERMINATION OF BORON IN ALUMINIUM

APPENDIX III

E.1 Boron E.2 Aluminium, boron in

THE METHYLENE-BLUE EXTRACTIVE-SPECTROPHOTOMETRIC DETERMINATION OF BORON IN ALUMINIUM OF HIGH PURITY (LABORATORY METHOD NO. 5/9)

1. OUTLINE

The sample is dissolved at room temperature in precisely measured amounts of sulphuric and hydrofluoric acids. After the solution has been transferred to a polypropylene separating funnel, BF_3 is extracted into dichloroethane as a complex with methylene blue and the boron is determined spectrophotometrically on this extract.

2. APPLICATION OF THE METHOD

The method is applicable to the determination of boron in aluminium of high purity at levels from 0,25 p.p.m. upwards by the method of standard additions. Because of the scatter of individual results at this level, quadruplicate determinations should be conducted on the sample, and the standard additions should be made in duplicate. The result should be assessed by extrapolation of the best-fit graph drawn through all the points plotted. For boron concentrations of more than 1 p.p.m., the absorbances can be referred direct to a calibration graph. At the 1 p.p.m. level, the precision of the method is estimated as being of the order of 10 per cent relative.

3. REAGENTS

Use only polypropylene measuring devices and containers for the preparation and storage of reagents. Use only one source of distilled water in a single polythene container of 10 to 25 litres capacity for the preparation of reagents and samples, and for calibration. Clean all the apparatus by washing successively with tap water, demineralized water, and distilled water. All the reagents are of A.R. grade unless otherwise specified.

(1) Hydrofluoric Acid, 50 g/l

Transfer 100 ml of acid (Merck's Art. 334 grade, 48 to 50 per cent) to a polypropylene container marked at the 1-litre level. Dilute to volume and mix.

(2) Sulphuric Acid, Boron-free

Pour approximately 100 ml of Merck's acid (sp.gr. 1,84) into a platinum dish, and, using a platinum wire, mix with 5 ml of hydrofluoric acid. Heat to strong fumes of sulphur trioxide and continue fuming for 15 min.

(3) Sulphuric Acid, Normal

Add 13,5 ml of boron-free sulphuric acid to 100 ml of water contained in a polythene bottle marked at the 500 ml level. Dilute to the mark and mix.

(4) Methylene Blue Solution, 0,001 M

Transfer 0,8897 g of Merck's microscopic-grade methylene blue boron (M.W. 355,89) to a 250 ml plastic bottle. Add 250 ml of water and shake until dissolved. Dilute 25 ml of this solution to 250 ml in a similar bottle.

(5) 1,2-Dichloroethane

Merck's grade, Art. 954

(6) Standard Boron Solution

Transfer 0,1429 g of H_3BO_3 to a 500 ml polythene bottle, place on a top-loading balance, and, after counterpoising, add 500 g of water. Shake to dissolve the boric acid.

1 ml \equiv 50 μg of B.

Prepare a solution with a boron concentration of 0,1 $\mu\text{g}/\text{ml}$ by similar appropriate mass dilutions.

DETERMINATION OF BORON IN ALUMINIUM

4. APPARATUS

- (1) **Separating Funnels**
125 ml polypropylene funnels supplied by XLON of England.
- (2) **Centrifuge Tubes**
15 ml polypropylene.
- (3) **Plastic Squeeze Bottle**
Polythene, fitted with a polythene delivery tube.
- (4) **Suction Tube**
Made by cutting off about 15 cm of a 10 ml graduated polypropylene pipette.

5. PROCEDURE FOR SAMPLES CONTAINING 0,25 TO 1,0 p.p.m. OF BORON

- a. Transfer ten 0,2 g (\pm 0,0002 g) portions of finely divided aluminium sample (Note 1) to 100 ml beakers.
- b. To six of the beakers add, by means of a graduated pipette, duplicate (Note 2) additions of 1,3 and 5 ml of standard boron solution (1 ml \equiv 0,1 μ g of boron).
- c. Using similar pipettes, to each beaker add 10 ml of 50 g/l hydrofluoric acid and 3 ml of normal boron-free sulphuric acid.
- d. Cover with a polypropylene cover, and stand at room temperature until the samples have dissolved (for periods of 12 to 24 hours depending on the degree of comminution of the sample).
- e. Transfer the solutions to 125 ml separating funnels and dilute to 20 ml, using a polythene squeeze-bottle as specified in (3) of Section 4.
- f. Using graduated pipettes, add 3 ml of 0,001 M methylene-blue boron solution and 10 ml of 1,2-dichloroethane, and shake for 1 min. Allow the phases to separate, transfer all of the lower organic phases to 15 ml centrifuge tubes, and centrifuge for 5 min.
- g. Discard the aqueous phases, and thoroughly rinse the funnels successively with ethanol, demineralized water, and distilled water.
- h. Carefully draw off any supernatant aqueous layers by means of a suction tube (specified in (4) of Section 4) attached to a vacuum system.
- i. Return the organic phases to the funnels and wash the tubes with 5 ml portions of distilled water, adding this to the funnels.
- j. Shake for 1 min and allow the phases to separate for 15 min.
- k. Drain the organic layers into the original tubes and centrifuge for 5 min.
- l. Draw off the supernatant aqueous layers as before, and measure the absorbances of the organic extract in a 1 cm cell at 657 nm against pure 1,2-dichloroethane.
- m. Correct these absorbances by the absorbance found for the extraction blank solution, determined as described in step n.
- n. Determine the absorbance of the extraction blank as follows. Transfer, in quadruplicate, 0,2 g portions of the same sample, or a similar sample with a boron content of less than 1 p.p.m. (e.g., BCS standard 198d), to 100 ml beakers and repeat the procedure described in steps a to f, but discard the organic extracts instead of transferring them to centrifuge tubes. Repeat the extractions three more times with 10 ml portions of 1,2-dichloroethane, discarding the extracts each time (Note 3). Repeat the extraction once more, drain all the extract into a 15 ml centrifuge tube, and centrifuge for 5 min. Continue with the procedure described in steps g to l, and measure the absorbance due to the fluo-complex of methylene blue. Correct the absorbances found for the extracts from the sample and for those from the sample + 'standard-addition' solutions by the average absorbance value found here.
- o. Plot a best-fit graph (using the method of least squares) of the average absorbance values of the sample and 'standard-addition' extracts against the increments of boron concentration. By extrapolation of the graph to the base line, determine the boron content of the aluminium sample plus the boron contributed by the reagents. Apply a correction for the boron in the reagents, which is determined as described in step p.
- p. Repeat the whole extraction and spectrophotometric procedure described in steps a to o for the reagents without aluminium, adding, in duplicate, 2 and 3 millilitres of standard boron solution (1 ml \equiv 0,1 μ g of boron) to six of the reagent solutions. Determine the boron content of the reagents as described in step o.

DETERMINATION OF BORON IN ALUMINIUM

6. NOTES

1. Once the corrections for the fluo-methylene blue complex formed in the blank solution and for the boron in the acid have been established, it is then only necessary to prepare 4, not 10, aliquot portions per sample.
2. The method is not precise enough to rely on single measurements for the sample solutions and for the sample solutions to which measured volumes of boron have been added. The specified number of repeated determinations are recommended. For boron concentrations of more than 1 p.p.m., duplicate determinations should be adequate; standard additions are not required provided that a calibration graph prepared as described in the procedure is available, and the boron content of the reagents has been determined.
3. The purpose of these preliminary extractions is the elimination of any boron contributed by the aluminium and reagents. This boron must be eliminated before the absorbance due to the extraction of the fluo-complex with methylene blue can be determined under the exact acid concentrations prevailing in the sample solutions. This determination has to be repeated in the subsequent determination of the boron content of the acids because there is a considerable difference between the free hydrofluoric acid content when aluminium is present and that when it is absent.