



TRN: 2A8500304

NIMR - IMAT 10

**A MASS SPECTROGRAPHIC INVESTIGATION OF
THE METHODS FOR OBTAINING QUANTITATIVE
ANALYSES FOR THE MASS BALANCE OF P AND B
THROUGH A SUBMERGED ARC SILICON
SMELTER**

by

**D E C Rogers, D S Jones, J W Wegman,
L Brain and J Van Wamelen**

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Internal Report
MATERIALS CHARACTERIZATION DIVISION

NATIONAL INSTITUTE FOR MATERIALS RESEARCH - CSIR



COUNCIL for SCIENTIFIC and INDUSTRIAL RESEARCH

Pretoria, South Africa

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ROGERS D E C, JONES D S, WEGMAN J W, BRAIN L
AND VAN WAMELEN J

INTERNAL REPORT

MATERIALS CHARACTERIZATION DIVISION
CSI
SEPTEMBER 1983

INDEX

	Page
1. SUMMARY	1
1. INTRODUCTION	2
3. APPARATUS REAGENTS AND CERTIFIED MATERIALS	
3.1 Apparatus	4
3.2 Reagents and chemically certified materials	4
4. METHOD	
4.1 Decontamination of sample in preparation for ultra-trace analyses	6
4.2 Preparation of standard mixtures	7
4.2.1 The liquid doping technique	7
4.2.2 Investigation of the method of liquid doping	7
4.2.3 The solid doping technique	9
4.3 Selection of the powder mix used for pressing the electrodes	12
4.4 The standard Be, and B and P mixtures	14
5. ANALYSIS OF SILICATE STANDARDS AND TWO SiO ₂ SAMPLES	
5.1 Analysis of two certified silicate standards without doping	15
5.2 Analysis of a certified silicate standard doped with Be	15
5.3 Analysis of two certified silicate standards doped with B and P	16
5.4 Sensitivity factors for B, P and Si relative to Be in silica standards	16
5.5 Analysis of silica samples 02 and 03	17
5.6 Comparison of analyses of silica samples 02 and 03 using wet doping and dry doping techniques	17

6.	ANALYSIS OF SILICON	19
7.	ANALYSIS OF COAL ASH, WOOD ASH, ELECTRODE CARBON, CHARCOAL AND PETROLEUM COKE	20
7.1	Analyses of coal and wood	20
7.2	Analyses of electrode carbon, charcoal and petroleum coke	20
7.3	Discussion	
7.3.1	Doping method	21
7.3.2	Matrix Effects	21
7.3.3	Accuracy of these analyses	22
8.	A PRELIMINARY MASS BALANCE OF B AND P AND THE SIGNIFICANCE OF INACCURACIES INHERENT TO THE ANALYSES, ON THE MASS BALANCE	23
9.	CONCLUSION	26

APPENDICES

APPENDIX I	Source decontamination and sample preparation for ultra-trace analyses	27
APPENDIX II	Background levels obtained for RWA-T graphite and Cominco silver powder	28
APPENDIX III	Wet doping procedure for preparation of standard mixtures	29
APPENDIX IV	Ashing procedure for coal and wood ash	31
APPENDIX V	Plate evaluation procedure	32
BIBLIOGRAPHY		34

1. SUMMARY

Mass spectrographic analyses of silica, silicon and silica reducing agents have been made using an arc discharge mass spectrograph. Analyses of certified standards and standard mixtures are given. An evaluation of doping techniques shows that the solid doping technique is satisfactory and that the liquid doping technique leads to significant errors. The amount of liquid dopant absorbed onto the substrate matrix varied from one compound to another and from one matrix to another. Comparison of analyses of solid-doped and undoped certified standards shows that all of the solid dopant is taken up by the sample.

Analysis of silica reducing agents used in the arc reduction furnace shows that the major source of contamination by B and P is likely to be the coal and wood. Silica contains 0.4 ppm of B and 4 ppm of P and is a minor source of contamination. The levels in silicon are about 10 ppm for B and 20 ppm for P. A mass balance on P cannot be made and the missing amount is larger than the inaccuracy of the analysis. For analyses of feedstocks where the smelter outlet fumes are not sampled an accuracy of analysis to a factor of two is sufficient for the analysis of the coal and wood chips.

2. INTRODUCTION

The silicon produced by Samancor Silicon Smelters is of metallurgical grade (99% purity). A mass balance of the two critical elements boron and phosphorous through the smelter is carried out as part of the evaluation of upgrading the arc furnace smelting process for the production of solar grade silicon (99.9970% purity [1]). Previous work on the analysis of Samancor silicon showed the need for an investigation of the methods of obtaining quantitative analyses of boron and phosphorous. They are the two elements which not only are least affected by the methods of unidirectional solidification of silicon by the Bridgman technique [2] but, as impurities, have the most deleterious effects in solar grade silicon. Purity required of metallurgical grade Si for use as solar grade Si is 0.3 ppma for P and B [1].

The purpose of this work was to develop methods for the quantitative analysis of the silicon feedstocks consumed in an arc furnace. In order of priority this entailed the determination of:

- (a) the levels of B and P in silica from the Pietersburg deposit,
- (b) the levels of B and P in metallurgical-grade silicon from a silicon smelter, and
- (c) the amounts of B and P entering the smelter as impurities in the silicon-reducing-agent feedstocks.

The feedstocks and their amount: consumed per tonne of Si produced are given for a typical furnace in Table 1 [3].

Table 1: Feedstocks and their consumption per tonne of Si produced from furnace number 1

	tonnes	moisture content of furnace feedstock	moisture content of these samples
SiO ₂ 02 and 03 grade 50/50	2.91	-	<0.1%
Coal unspecified	0.090	3%	3%
Coke unspecified	0.383	4%	1%
Charcoal (Blackwattle 80%, Eucalyptus 20%)	0.754	10%	3%
Wood chips (Pine from Magoebaskloof)	2.22	50%	6%
Electrode (Union Carbide USA)	0.117	-	1%

Each of the feedstocks was sampled systematically over 22 days so that one sample was representative of the whole period. Homogeneity of the sampling technique is critical as each mass spectrographic analysis consumes ~1 mg of sample.

In a similar way the silicon was sampled as it was poured from the furnace with one sample taken to represent 22 days production.

The possibility of upgrading metallurgical silicon to solar grade is dependent upon the purity of the SiO₂ and the levels of impurities presently found in the metallurgical grade Si. Accurate analyses of these two materials are required. Most of the work spent on this project has been on the development of a quantitative method of analysis using internationally certified standard materials and doped mixtures prepared in the laboratory.

3. APPARATUS REAGENTS AND CERTIFIED MATERIALS

3.1 Apparatus

Mass spectrographic analyses are carried out using the Varian MAT SMI-B pulsed DC cathode-arc source mass spectrograph. The operating conditions for the mass spectrograph are shown in Table 3.1. Spectra are recorded on Ilford Q plates.

Table 3.1: Operating conditions of the mass spectrograph

DC arc voltage	300 V
DC arc current	3-5 A
Spark voltage	60 kV
Arc duration	140 μ s
Frequency	30 hz
Vacuum before spark	10^{-4} Pa
Flight path	~ 2 m
Beam line vacuum	10^{-6} Pa
Ion plates	Ilford Q plates

These ion plates are read and interpreted with the NIMR computer controlled microphotometer. The microphotometer is a modified Carl Jena GII microphotometer and the computer is the Motorola based 6800 microprocessor from South West Technical Products, USA. The software used for the quantification of the ion plate blackening is the INTERACT program [3] and is based upon an interactive linearization of the ion-plate response curve using the Hull function [4].

Grinding, mixing and diluting of larger amounts (>1 g) is done with the agate and ball mill of the Fritch Germany, pulverisette model 501. The volume of the vial is ca 200 ml and the diameter of the balls 20 mm. Mixing of small amounts (<1 g) is carried out in the SPEX, USA, Wiglbug 3110-B vibrator. Ultrasonic cleaning is carried out in the Bransonic, USA, B-220-H ultrasonic cleaner using a 10% solution of Decon 75 cleaning agent.

3.2 Reagents and chemically certified materials

Conducting electrodes were made using high purity (99.9999% purity) silver powder supplied by COMINCO, Canada, lot EM5879; and high purity graphite powder (RWA Total) supplied by Ringsdorf-Werke GMBH, West Germany, batch number 727003/00. Electrodes were pressed in polythene electrode moulds (called slugs) at 20 tonnes on the Research and Industrial Instruments Co, 25 tonne press.

Standard solutions for wet doping

Standard solutions were made using distilled water from a still supplied by Baird and Tatlock Ltd, London. A 0.2 g l^{-1} solution of B in water was made by adding 114.4 mg of H_3BO_3 to 200 ml of water. A 0.2 g l^{-1} solution of P in H_2O was made by adding 85.2 mg of $(\text{NH}_4)_2\text{HPO}_4$ to 200 ml of H_2O . The 0.20 g l^{-1} solution of Be was made by diluting a 1 000 ppm solution that was standardized by Mrs Wardale of the Atomic Spectroscopy group.

Standard powder mixtures for dry doping

Standard mixtures containing B, P and Be were made using RWA-T graphite as the diluent. In the first mixture 100 mg of BeO supplied by British Drug Houses, was mixed with 5 g of graphite to give 720 ppm of Be in C. In the second mixture 21.1 mg of 99.8% H_3BO_3 from Merck and 90.7 mg of 99.99% pure $\text{Ca}_3(\text{PO}_4)_2$ from May and Baker, lot 52741, were mixed with 5.00 g of graphite to give a mixture containing 737 ppm B and 3628 ppm P in carbon.

Certified geological standards have been used to test the doping procedure and to provide relative sensitivities for Be, B, P and Si in SiO_2 -like materials. They are BCR-1 and G-2 from the US Geological Survey and SY-2 and SY-3 from the Canadian Certified Reference Materials Project. The certified and uncertified values for the levels of SiO_2 , B, Be and P are given in Table 3.2

Table 3.2: Certified standards used in the analysis of SiO_2 , uncertified values are indicated (?)

Name	BCR-1	SY-2	SY-3	G2
Rock type	basalt	Syenite	Syenite	Granite
SiO_2 level	54.53%	60.10%	59.68%	69.22%
B	4 ppm	85 ppm (?)	110 ppm	2 ppm (?)
P	0.16%	0.19%	0.24%	0.057%
Be	1.6 ppm (?)	23 ppm	22 ppm	2.4 ppm

4. METHOD

4.1 Decontamination and sample preparation for ultra-trace analyses

A major problem of obtaining analyses at trace levels was the reproducibility of the analysis. Exhaustive tests were carried out to eliminate all possible sources of contamination. Several key sources of contamination were identified. They were contamination of the source components that were adjacent to the plasma and at the accelerating potential, and contamination of the specimen as it was being prepared for analysis.

Tests of the source contamination and the equipment used in pressing the electrodes were made using pure graphite and pure silver electrodes. For the same source components the silver electrodes consistently showed higher background levels (up to 30 ppm for S, P, Na, Cl, Fe, Mn, Cr and Sn). These were gradually reduced as the burning of the electrodes coated the source with a silver film. When the background levels remained static despite further coating of the source, the levels were lowest. These levels were measured for B and were 6 ppb in the sample. Replacing the burnt electrode with a new electrode containing silver did not bring back the high background levels and it was concluded that the source was then decontaminated. The apparent difference between the backgrounds for the silver and graphite electrodes can be attributed to the difference in plasma temperature and electrode temperature. The graphite electrodes were burnt in a 3 A arc having a potential drop of ~20 V and the silver electrodes were burnt in a 5 A arc with a potential drop of ~200 V.

A decontamination procedure was developed for the preparation of the source and handling of the electrodes during pressing. This is given in Appendix A. The background levels that were obtained for RWA-T graphite are shown in Appendix II.

Whenever an irregular blackening of the plate with exposure was observed for trace analyses, contamination of the source was suspected. There was a correlation between expanding the plasma (i.e. widening the electrode gap) and appearance of contaminants and changes in abundances of the multiply charged ions.

At very low levels (1 ppm and lower) there were often inexplicable changes in levels of some elements. These occurred at exposures about 500 pC. Previous work on the analysis of silicates using silver and carbon electrodes mixtures showed a building up of siliceous dendrites [5] and it is speculated that some fractionation of the sample in the electrodes is associated with these build-ups.

4.2 Preparation of standard mixtures

4.2.1 The liquid doping technique

Initial attempts at preparing standard mixtures were made using the liquid doping technique [6, 7] (see also Appendix III). From the relative abundances of the ions observed on the ion plate, relative sensitivity factors were calculated for Be, B and P in the 00 grade Samancor SiO₂. These are given in Table 4.1. A check of the liquid doping method was made using the certified standard BCR-1. This showed levels of B, Be and P in the expected range. However, when the liquid doping analyses of the SiO₂ sample 00 were repeated a few months later, the analyses were not reproducible to within the precision of the analyses. (This is typically better than 10%.)

Table 4.1: Relative sensitivity correction factors (RSCFa's) obtained from SiO₂ standard mixtures to which 10 ppm aliquots of B, Be and P solutions have been added. Be is the internal standard and has a RSCFa of 1.00

Standard	RSCFa	
	B	P
1	0.30	-
2	0.38	0.66
3	0.25	0.89
4	0.35	0.67
mean	0.32 ± 0.06	0.78 ± 0.1

4.2.2 Investigation of the method of liquid doping

It was suspected that the dopants might not be completely absorbed by the graphite powder and thus four tests dopings were carried out in order to answer the following questions:

(i) How much of the dopants were left on the crucible at the end of the doping procedure?

(ii) How was the doping of the liquid onto the powder affected by the type of powder (there were three powders, C, Ag and SiO₂)?

Aliquots of doping solution containing 200 ppm of dopant were used. Solutions and doping powders were made up to a volume less than 10 ml. The final ratios of the SiO₂, C and Ag powders were the same as the previous analyses. The amount of each element in the electrode mix was calculated from the raw microphotometer reading of the ion plate. From experience with repeated analyses this is, without the use of internal standards, within about 50% of the mean value.

Table 4.2: Test of the liquid doping procedure. Relative amounts of Be, B and P in four SiO₂/C powders

Sample	Be	B	P
undoped, "used" crucible	0.18	0.15	0.44
only graphite doped	0.25	0.29	1.1
only silica doped	0.33	1.0	0.82
graphite and silica doped	1.0	1.0	1.0

In the first test the solutions were doped onto the graphite powder alone. When dry this powder was discarded and the procedure repeated for a SiO₂/C mixture, without cleaning the crucible and using distilled water instead of the dopant aliquots.

For the other three tests clean crucibles were used and doping was made onto graphite, silica and a graphite/silica mixture respectively before making up the Ag/SiO₂/C mixture.

The most notable observations were

- (i) the "carry over" of the dopants onto the quartz crucible, and
- (ii) the preferential doping of B onto quartz. These effects might be explained by the combinations of the electron-accepting nature of B in H_3BO_3 and C in the form of graphite, and the electron-donating nature of both Si and O in SiO_2 .

The results of these tests indicated that wet doping could result in non-quantitative addition to the substrate. For this reason, those analyses carried out using the wet doping technique were not considered reliable.

4.2.3 The solid doping technique

A method of mixing finely powdered samples with the electrode powder was developed from that of Taylor [8]. As initial tests showed inhomogeneity of the powders when special care was not taken when mixing the powders, an evaluation of sample homogeneity and particle sizes required for pulsed DC arc analyses was undertaken. It was found that short exposures were most sensitive to inhomogeneity. This is to be expected as they typically result from the burn of a small amount of electrode material (<1 μ g). Electron micrographs of the powders were taken with a JEOL electron microscope.

An estimate of the minimum particle size and minimum requirement for homogeneity was made from a measurement of the amount of sample consumed in a typical DC arc pulse. This was measured from the change in length of the negatively biased electrode (i.e. the electrode that is consumed relative to the positively biased electrode which in turn remains unchanged in mass). For a 40 nC plate exposure 1.7 mg of a graphite electrode was burnt. This corresponded to a mean reduction in length of 0.25 mm for the 15 mm electrode.

Examination of the RWA-T graphite as supplied (Figure 4.1) showed typical plate-like particle dimensions of 15 μ m square and less than 1 μ m thick. Assuming that material splashing in the arc typically results in

Figure 4.1

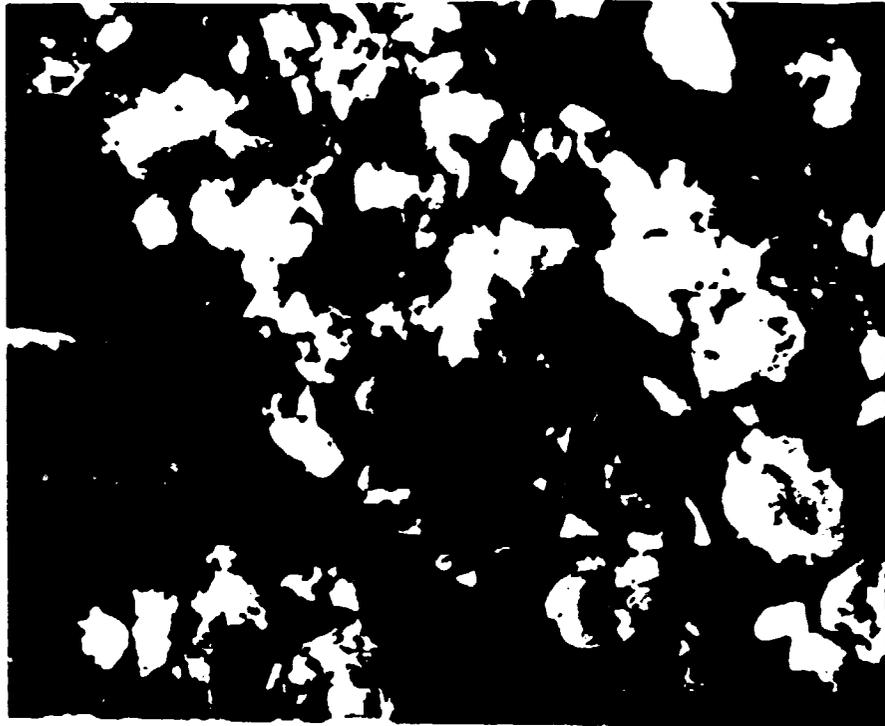


Scale 1 mm \sim 1 μ m

(a) COMINCO silver unground, 100 mesh

(b) RWA graphite unground

Figure 4.2



Scale 1 mm ~1 μ m

BeO powder

each of these particles travelling through the arc twice, one particle is consumed for 10^{-14} C of beam detected. As 140 μ s of burn gives rise to 2×10^{-14} C it is concluded that two particles are consumed in each discharge.

For best mixing, sample particles should be smaller than those of the RWA-T graphite. For BeO powder the size of the larger BeO particles was about 5 μ m diameter (Figure 4.2).

The mixing procedure adopted for these analyses followed that of Taylor [8]. Modifications to this procedure are based on examination of the electron micrograph of RWA-T graphite mixed with BeO for 10 minutes in the ball mill (Figure 4.3). Comparison with Figure 4.1 shows that the graphite cannot be ground finer than supplied and tends to form compacted platelets. A graphite sample mix would therefore hinder grinding of the sample. Dispersing a powder dopant in a graphite powder using a ball mill would not follow the same fracture and compaction mechanism as would be expected for most powder mixtures. Mixing these dopant powders and graphite was done by mixing in 10 successive additions a total of 0.5 g of the graphite in the ball mill for a few minutes each time. Final mixing with Ag was done by shaking in the Wigbug for one minute, turning it around and shaking it one minute the other way.

Inhomogeneity of the mixture was not observed for doping levels in the range 400 ppma to 1 400 ppma in the graphite (this is equivalent to 70 ppma to 200 ppma in the electrode mixture), when a 100 μ s portion of the 140 μ s discharge was analysed for plate exposures higher than 30 pC, and a 40 μ s portion was analysed for plate exposures greater than 5 pC.

4.3 Selection of the powder mix used for pressing the electrodes

As has been indicated above a powder mixture of silver, graphite and sample was used for these analyses. The final ratio of powders was by weight, twenty to three to one respectively. This mixture was established, by trial and error and on the basis of published work [5]. It was selected for its regular burning characteristics and for the precision of results obtained from the microphotometric evaluation of the ion plates.

Figure 4.3



Scale 1 mm ~1 μ m

(a) Mixture BeO and graphite ground for 10 minutes

(b) SiO₂ powder used in these analyses

Burning of the electrodes was at all times carried out so that a constant gap width was maintained along with regular electrode tip shapes. Any variation in tip shape reduced precision of the analyses dramatically. Graphite tip shapes changed rapidly during analyses and for this reason were unsuitable for the precision required of these analyses. Graphite based electrodes were found to develop cork screws and holes, and dramatic changes in spectral composition were observed on the ion plate. Apparent changes in temperature of the plasma (evidenced by changes in distributions of charge states) and changes in instrumental transmission were also observed.

Silver based electrodes burnt well initially, but when mixed with SiO_2 alone later became coated with glassy looking material and ceased to maintain a discharge. Discharge currents could be obtained again temporarily by increasing the potential between the electrodes. These electrodes also tended to give irregular plate exposures (see above section 4.1). It was concluded that the absence of C in the electrode resulted in preferential splashing of the Ag and deposition of unreduced SiO_2 on the electrode surface.

The mixture was typically made up to a final weight of 1.2 g.

4.4 Standard Be and B and P mixtures

Standard mixtures were made according to the method outlined above. The Be and graphite mixture was prepared by mixing 10.0 mg of BeO with 5.00 g of RWA-T graphite to give a Be concentration of 720 ppm. The B and P mixture contained 713 ppm of B and 3 628 ppm of P and was made by mixing 20.4 mg of H_3BO_3 and 90.7 mg of $\text{Ca}_3(\text{PO}_4)_2$ with 5.00 g of graphite. It was found later that the B and P mixture was contaminated by ca. 20 ppm of Be from carry over in the ball mill (see below).

5. ANALYSIS OF SILICATE STANDARDS AND TWO SiO₂ SAMPLES

5.1 Analysis of two certified silicate standards without doping

Two silicates (SY-2 and SY-3) were analysed to determine the relative sensitivities of Be, B, Si and P. The samples were not doped and were mixed with Ag powder alone. Be is certified for both samples and was taken as the internal standard. The effects of inhomogeneity on the regular fall-off in plate blackening with plate exposure were not observed for SY-2 when the amount of sample consumed for each exposure was as great as that consumed for 0.5 nC exposures taken with the normal discharge sampling interval (100 μ s). For the SY-3 analysis inhomogeneity appeared to be greater and for this reason unsatisfactory readings of P and Si were made. The results of the analyses of SY-2 and SY-3 are shown in Table 5.1

Table 5.1: Sensitivity factors determined for B, P and Si relative to Be in SY-2 and SY-3, assuming RSCFa Be = 1.00

Element	RSCFA			
	SY-2		SY-3	
	Date	29/7/83	3/8/83	8/8/83
Be	1.00	1.00	1.00	1.0
B	0.15(2)	0.18(7)	0.40(6) ⁺	0.15(5)
Si	0.7(7)	*	0.70	*
P	0.47(7)	0.455	0.4	*

* poor data

⁺ contamination suspected

5.2 Analysis of a certified silicate standard doped with Be

The doping mixture containing Be was tested using BCR-1 which has a very small amount of Be. Two specimens were prepared by adding RWA-T graphite containing 720 ppm Be to the rock in the weight ratio one to three. The sensitivity factors were determined for B, P and Si relative to Be and are given in Table 5.2.

Table 5.2: Sensitivity factors for B, Si and P in Be doped BCR-1 assuming RSCFa Be = 1.00

Element	RSCFa	
	first specimen	second specimen
Be	1.0(0)	1.0(0)
B	0.2(45)	0.2(54)
Si	0.61(0)	0.61(6)
P	0.48(1)	0.6*

* Poor data

5.3 Analysis of two silicate standards doped with the B and P mixture

BCR-1 and G-2 were doped with the graphite mixture containing B and P. Analysis of the graphite showed that this mixture was contaminated with Be. It is likely to have come from the agate vial and balls of the milling machine which had been last used for grinding Be O. Taking Si as the internal standard with an RSCFa of 0.61 (see above) the contamination level of Be is ~15 ppm. This level was confirmed in the analysis of G2, assuming a Be sensitivity of 1.00 and a contamination of Be of 19 ppm. The sensitivity factors resulting from this analysis are shown in Table 5.3.

Table 5.3: RSCFa's for Be, B, Si and P in B and P doped BCR-1 and G-2 relative to Be.

Element	RSCFa	
	BCR-1	G2
Be	1.02	1.00
B	0.25(7)	0.17(0)
Si	0.61	0.70(0)
P	0.47	0.43

5.4 Sensitivity factors for B, P and Si relative to Be in silicate standards

Results of the analyses of the undoped silicate standards (Table 5.1) and doped standards (Tables 5.2 and 5.3) show similar sensitivity factors (RSCFa's). It may be concluded therefore that within the accuracy of the results, the doping mixture contains the amounts of B and P that were added and that the sensitivity factors for these elements relative to Be are as given in Table 5.4.

Table 5.4: RSCFa's for silicates taken from the averages of four certified standards

Element	RSCFa
Be	1.0(0)
B	0.19(3) ± 0.03 (6)
Si	0.66(7) ± 0.05(3)
P	0.45(3) ± 0.04

5.5 Analysis of silica samples 02 and 03

Results of the analyses of these silica samples are shown in Table 5.5. Sample 02 was analysed twice and sample 03 once. Be doped RWA-T was added as the internal standard. A background check was made before each analysis and showed background levels much lower than the analytical levels, being 5 ppb for B and 50 ppb for P. Results of these analyses are shown in Table 5.5 using the sensitivity factors determined from analyses of silicate standards.

Table 5.5: Levels of B and P measured in silica samples 02 and 03 (Be is the internal standard at 240 ppm) and RSCFa's of Si

Sample	02	03
Be	240 ppm	240 ppm
B	0.33 ppm	0.55 ppm
P	6 ⁺ ppm	2.7 ppm
Si	2 ⁺ ppm	1.6 ppm

⁺ poor data results quoted correct to one significant figure

Note: There is a difference in sensitivities of silicon in the pure quartz and the rock analyses. This is attributed to the difference in the matrix causing the plasma to burn hotter for pure SiO₂ than SiO₂ in rock.

5.6 Comparison of analyses of silica samples 02 and 03 obtained from the wet doping and dry doping techniques

The results of the wet doping and dry doping methods are compared in Table 5.6. The wet doping method uses standards prepared in the laboratory, while the dry doping method uses internationally certified standards.

It can be seen that the analyses give similar results. Absorbance of the liquid dopants onto the walls of the crucible results in errors as large as half of the B determination.

Table 5.6: Comparison of the analyses using a wet doped standard with the analyses using certified reference materials and a dry doped internal standard (values are in ppm)

Element Sample	B		P	
	dry	wet	dry	wet
SiO ₂ -02	0.33	0.18	6 ⁺	5.5
SiO ₂ -03	0.55	0.44	2.7	2.5

⁺ poor data

6. ANALYSIS OF SILICON

The silicon sample FCE-1 from a spooned sample of furnace number one was analysed by the method of spiking, i.e. without reference to a certified reference material. A portion of the ground sample was collected by passing the fine powders through a 200 mesh cloth. Two specimens were analysed, one weighing 0.152 g to which was added 48.3 mg of the RWA-T graphite doped with 720 ppm of Be and the other weighing 0.161 g to which was added 23.9 mg of the Be doped graphite and 23.7 mg of RWA-T graphite doped with 713 ppm of B and 3 628 ppm of P.

The ratios of the B, P and Si to the Be were measured for both specimens (Table 6.1). The RSCFa's for B, P and Si, and the levels of B and P were obtained from this data. These are shown in Table 6.2.

Table 6.1: Ratios of B, P and Si to Be in FCE-1 silicon

	Doped 240 ppm Be	Doped 107 ppm Be, with B and P
Be	1.00	1.00
B	5.78×10^{-2}	1.332
Si	890.4	2.150
P	3.60×10^{-2}	1.319

Table 6.2: Analysis of silicon sample FCE-1

	RSCFa	Level
Be	1.0	-
B	0.66	11 ppm
Si	1.5	100%
P	1.1	26 ppm

7. ANALYSIS OF COAL ASH, WOOD ASH, ELECTRODE CARBON, CHARCOAL AND PETROLEUM COKE

Semi-quantitative analyses were carried out on coal ash, wood ash, electrode carbon, charcoal and petroleum coke. Analyses were made using the same electrode mix as that in the SiO_2 and Si analyses with Be as the internal standard. The coal and wood chips were ashed and the other three samples were analysed directly.

7.1 Analyses of coal and wood

Samples were ashed by a modified method of Willis [9] (see Appendix IV). From 5 g of coal powder taken directly from the sample bottle 0.42 g of ash was obtained. The coal ash was mainly SiO_2 and the semi-quantitative analysis was carried out using the microphotometer and sensitivity factors (RSCFa's) found for silicate standards. To 0.050 g of the Be doped graphite was added 0.150 g of coal ash. The results of the analyses are shown in Table 7.1

Table 7.1: Semi-quantitative determination of B and P in coal ash and wood ash. Analyses are given in ppm unless indicated otherwise. Levels in coal are calculated assuming all the B and P remains in the ash.

Element	coal ash	coal	wood ash	wood
B	978	82	1 197	7.2
Si	47%	4.0%	1.1×10^4	65
P	3.9%	0.33%	7.1×10^3	43

The wood chips yielded 0.030 g of ash from 5.0 g of wood taken directly from the sample bottle. To 0.027 g of the ash as added 0.050 g of the Be doped graphite. The sample contained very little SiO_2 and for the semi-quantitative analysis the sensitivities obtained from silicon were used for the microphotometer determined abundances.

7.2 Analysis of electrode carbon, charcoal and petroleum coke

These samples were analysed without ashing by mixing with Be doped graphite and Ag powder. Semi-quantitative analyses were made with the micro-

photometer using the Si matrix sensitivity factors. The results of these analyses are shown in Table 7.2.

Table 7.2: Semi-quantitative determination of B and P in electrode carbon, charcoal and petroleum coke. All values are in ppm

	electrode carbon	charcoal	petroleum coke
B	1.9	1.5	1.0
Si	1.4×10^3	890	380
P	11	30	3.3

7.3 Discussion

7.3.1 Doping method

The agreement between the sensitivity factors for P and Si relative to Be for the doped (BCR-1) and undoped (SY-2 and SY-3) standards indicates that the doping method for the internal standard is correct. Agreement of the sensitivity factors for B, P and Si relative to Be for the doped (BCR-1 and G-2) and undoped (BCR-1, SY-2 and SY-3) mixtures indicates that the doping method for preparation of a chemical standard is also correct.

7.3.2 Matrix effects

The large difference between the sensitivity factors for Si in the rock and silica analyses (see Tables 5.4 and 6.2) is apparently due to the nature of the electrode mixture, i.e. it is a matrix effect. The electrode compositions in atomic abundance for the SiO₂ analyses are 0.05 sample, 0.025 graphite and 0.2 silver, and for the Si analyses 0.03 sample, 0.025 graphite and 0.2 silver. Other sensitivities are approximately the same but a difference in sensitivity by a factor of three is observed for Be. This matrix effect is not due to the major components of the electrode (C and Ag) as both mixtures are almost identical, and it must therefore be due to the chemical nature of the sample.

A good indication of the sensitivity of the analysis to the matrix can be seen in the RSCFa's for B in the four certified silicates (Table 7.5).

Summary of the sensitivities (RSCFa's) for analyses of
certified silicate materials

Rock type	Basalt			Syenite			Granite	
Standard	BCR-1			SY-2			SY-3	G-2
Specimen	Doped Be-1	Doped Be-2	Doped B and P	Undoped 1	Undoped 2	Undoped 3	Undoped	Doped B and P
Be	1.0(0)	1.0(0)	1.0(2)	1.0(0)	1.0(0)	1.0(0)	1.0	1.00
B	0.2(45)	0.2(54)	0.25(7)	0.15(2)	0.18(7)	0.40(6) [†]	0.15(5)	0.17(0)
Si	0.61(0)	0.61(6)	0.61	0.71(7)	*	0.70	*	0.70(0)
P	0.43(1)	0.6*	0.47	0.47(7)	0.45(5)	0.4*	*	0.43

* poor data

† likely to be contaminated

brackets are placed around digits of significance greater than the standardized values

Clearly these are matrix effects as they are reproducible (and greater than the error on analysis of different specimens of the same sample) and show greatest variation between rock types.

Table 7.5: Summary of the sensitivities (RSCFa's) for analyses of certified silicate materials

Rock type	Basalt			Syenite			Granite	
Standard	BCR-1			SY-2			SY-3	G-2
Specimen	Doped Be-1	Doped Be-2	Doped B and P	Undoped 1	Undoped 2	Undoped 3	Undoped	Doped B and P
Be	1.0(0)	1.0(0)	1.0(2)	1.0(0)	1.0(0)	1.0(0)	1.0	1.00
B	0.2(45)	0.2(54)	0.25(7)	0.15(2)	0.18(7)	0.40(6) ⁺	0.15(5)	0.17(0)
Si	0.61(0)	0.61(6)	0.61	0.71(7)	*	0.70	*	0.70(0)
P	0.43(1)	0.6*	0.47	0.47(7)	0.45(5)	0.4*	*	0.43

* poor data

+ likely to be contaminated

brackets are placed around digits of significance greater than the standardized values

Analyses of pure SiO₂ and rock SiO₂ also show a matrix effect (see Tables 5.4 and 5.5) and it is possible that the use of certified silicate standards are not adequate for highest accuracy analyses. A better method is spiking the sample with well tested doping mixtures.

7.3.3 Accuracy of these analyses

As can be seen from Table 7.5 precision of the analytical method is in the range 2% to 20%. Accuracy of the analysis is determined by the suitability of standards. Suitable certified reference standards are not available (see discussion above). The doping method is accurate to within the precision of the analyses and sample contamination and instrumental backgrounds are not significant. Accuracy of the analyses have not been measured. The most accurate analyses have been obtained for Si and SiO₂ and these are expected to be within about 50%. Accuracies of the analyses of the other feedstocks, with the exception of the wood chips (see below), are expected to be within a factor of 2.

8. A PRELIMINARY MASS BALANCE FOR B AND P AND THE SIGNIFICANCE OF INACCURACIES INHERENT TO THE ANALYSES, ON THE MASS BALANCE

From the previous discussion of the results of the analyses of the various feedstocks it is clear that the ability to calculate a mass balance for the furnace is dependent upon the absolute accuracy of the analyses, e.g. analyses of SiO_2 , and the representativeness of the analyses of the materials consumed and produced by the furnace, e.g. coal.

Moisture contents of the feedstocks differ from those of the samples analysed. The moisture contents of the feedstocks were supplied and those of the samples were determined using ASTM standard test methods D2961-74 for coal and D143 for wood. Moisture contents are shown in Tables 1 and 8.1.

Ash analyses of the wood chips and coal were made as the raw materials could not be analysed directly. There is therefore the possibility that B and P could be driven-off in gaseous forms during the pyrolysis.

The levels of B and P found in standard materials can be taken as guides to those expected in wood and coal. The three South African coal standards now being prepared by MINTEK for certification have P in the range 0.01% to 0.1%. The level of 0.3% found in this analysis is similar to that of the SA coal containing most P. Levels of B in coal are not certified in any coal standards. It does not appear that P is driven off in the ashing process for coal. NBS certified wood materials have P levels between 0.1% and 0.2% and B levels about 25 ppm. As the analyses of the wood ash gives 20 ppm of P and 4 ppm of B in the undried wood it appears that pyrolysis of the wood does drive off the B and P. (Analysis of the charcoal also shows low levels of B and P. It was however prepared from different types of wood.) Wood should be analysed after an acid digestion using by a wet doping technique modified from that tested here (see above).

The effect of the silicon feedstocks on the purity of the silicon can be estimated. Assuming that each material is equivalent in its contaminating characteristic, i.e., wood chips contribute to contamination in the Si the same way as does electrode carbon. The contribution of each feedstock to the final level in Si is calculated in Table 8.1

Table 8.1: Summary of analyses of silicon feedstocks and an estimate of the sources of contamination in the silicon spoon sample. Concentrations are given in ppm unless indicated otherwise.

Material	These levels		Moisture content feed- sample stock	Consumption feed- stock sample	Estimated con- tribution to Si spoon sample			
	B	P			B	P		
SiO ₂ *	0.4	4	<0.1%	<0.1%	2.9	2.9	1.2	12
Coal	80	0.3%	3%	3%	0.090	0.090	7	0.03%
Charcoal	1.5	30	3%	10%	0.754	0.70	1	20
Wood chips	7.2	43	6%	50%	2.22	1.17	8	50
Petroleum coke	1.0	3.3	1%	4%	0.383	0.371	0.4	1
Electrode material	1.9	11	1%	0%	0.117	0.116	0.2	1
TOTAL AMOUNT ADDED							20	400
Si	11	26	<0.1%	<0.1%	1		11	26

* Average of O2 and O3 grade

** The samples that were analysed had lower moisture contents than the actual feedstocks (see Table 1).

A similar study has been carried out by Dow Corning Corporation [1]. A comparison of the levels obtained from the feedstocks can be seen in Table 8.2. The levels in electrode material and wood chips differ significantly. As discussed above it is expected that the method of pyrolysis of the wood is not satisfactory, and the higher values reported for the Dow analyses of electrode material would be in agreement with these analyses if there is, as is suspected, an error in labelling a table in that report [1].

Table 8.2: Comparison of B and P levels in Si from Samancor silicon feedstocks and Dow Corning feedstocks (Unless indicated otherwise levels are given in ppm)

	SiO ₂	coal	charcoal	wood chips	petroleum coke	electrode material	Si
B							
Dow	8	35	not used	<19	<12	10	15
Samancor	0.4	80	1.5	7	1	2	11
P							
Dow	<16	0.1%	not used	600	13	60	33
Samancor	4	0.3%	30	43	3.3	11	26

The amount of B and P added to the furnace is greater than that found in the silicon (see Table 8.1). Coal and wood chips are the greatest sources of B and P. Assuming these feedstocks have been analysed with an accuracy within a factor of two, the amount of B found in the refined silicon is a little low, but within the expected range. The amount of P is very much less than the amount added (by a factor of ten) and it is probably being lost as a gas. Analysis of deposits at the gas outlet of the Dow furnace [1] showed high concentrations of B and P; more P and B was found. These two observations support the finding that both B and P are being driven out from the furnace.

9. CONCLUSION

Analyses have been carried out to the accuracies necessary for an evaluation of the materials used in the submerged arc silicon smelter. Highest accuracy is obtained for the analyses of SiO_2 and Si. It is found that sensitivity depended upon matrix and that best accuracy should be obtained with standards nearly identical to the analyte. Accurate standards are made by the solid doping technique. Using this method background levels for B of 6 ppb and for P of 50 ppb are obtained. These restrict quantitative analytical detection limits to levels above 20 ppb for B and 150 ppb for P.

The mass balance of B and P in the silicon smelter has been calculated and found to be in quantitative agreement with a previous observation [1] that only part of the impurities are trapped in the silicon; the remainder is exhausted in the gas. A larger amount of phosphorous is lost as a gas. A higher accuracy of analysis would only be required when a fuller understanding of the chemistry leading to exhaustion of these gases was known and a measure of the composition of these gases was made.

APPENDIX I

SOURCE DECONTAMINATION AND SAMPLE PREPARATION FOR ULTRA-TRACE ANALYSES

STEP NO.

1. Remove
 - Source box
 - Electrode holders
 - Cover plate
 - Focussing cup
2. Abrase with emery paper
3. Etch in HNO_3 (65%) at room temperature for 0.3 h
4. Rinse in distilled water
5. Wash in fresh decon (10% solution) in the ultrasonic bath
6. Rinse three times in fresh distilled water in the ultrasonic bath (to remove the DECON)
7. Dry in air
8. Clean a new slug (electrode mould) (steps 5 to 7)
9. Clean the stainless steel filling-tool (steps 5 to 7)
10. Clean debris from inside the source vacuum housing using a tissue wet with a volatile nonpolar solvent e.g. petroleum ether
11. Press the graphite (or silver) electrodes in a cleaned press. (The press should be free of loose particles.) Break off the tips of the electrodes that were in contact with the press walls
12. Reassemble the source. Align the cup with the Z-focal plane using a screw driver blade

APPENDIX IIANALYSIS OF HIGHEST PURITY RINGSDORFF GRAPHITE (RWA-TOTAL) WITH A MAXIMUM
PLATE EXPOSURE OF 2 nC

Mass Spectrograph		Certificate RWA-T (series IV/37/393)
B	40 ppba	<10 ppba
P	<10 ppba	-
Al	100 ppba	-
Si	10 ppba	40 ppba
F	<10 ppba	-
Be	<10 ppba	-

APPENDIX III

WET DOPING PROCEDURE

This method was used for the analyses of the Samancor SiO₂ samples and gave results with a reproducibility better than 4% (average).

1. Weigh out the required amount of substrate to be doped into a porcelain crucible (volume >20 ml).
2. Add 5 ml of high purity acetone to the substrate (or sufficient volume to adequately cover the substrate). This step is merely to "wet" the material to be doped and to dilute the standard solution to make sufficient volume available to impregnate the whole surface of the sample.

3. Pipette the appropriate volume of the standard solution(s) into the acetone.

CAUTION: Pipettes are generally calibrated to allow for the small drop of solution left in the pipette when the vacuum is released. DO NOT therefore, blow out the remaining solution because the volume dispensed will be inaccurate.

4. Gently stir the substrate and solution in the crucible to mix. Be careful not to spill any of the solution in the crucible! Use a clean nickel spatula for stirring.
5. Place the crucible on the hot plate. Position the infra-red lamp about 20 cm from the crucible to aid evaporation of the acetone. If the lamp is positioned too close to the crucible sputtering results when the acetone boils.
6. When the acetone has evaporated, place the crucible in the oven overnight to dry the sample completely.
7. Before making the electrode, make sure that the dried contents of the crucible are thoroughly mixed (in a shaker in the balance room downstairs). This is to ensure that there are no localised spots of concentrated dopant on the substrate.

CALCULATION OF DOPING LEVELS FOR THE WET DOPING PROCEDURE

This is perhaps best illustrated by an example.

PROBLEM

To dope silicon with 200 ppm of beryllium 200 ppm phosphorous and 200 ppm boron (all by weight).

METHOD

Weigh out exactly 1 g of silicon previously powdered to <200 mesh. Add the acetone as described under "doping procedure". Add to the silicon 1 ml of beryllium, boron and phosphorous standard solutions which should contain 200 μ g of each element respectively per 1 ml of solution. Proceed as under "doping procedure".

APPENDIX IV

ASHING PROCEDURE FOR COAL AND WOOD ASH

The sample was weighed and placed in a crucible in a oven. The temperature was increased in steps and kept at the final temperature until constant weight was obtained.

Temperature/ °C	Duration/hours
100	2
200	2
300	2
400	2
500	2
550	until constant weight is obtained

APPENDIX V

METHOD FOR QUANTITATIVE EVALUATION OF ION PLATES

Ion plates were evaluated with the Hull function [4] linearization of the ion plate response curve. It is plotted against the log of the plate exposure. It was found that considerable variation in the analysis could be obtained if a fixed routine for evaluating the plates was not followed. The greatest variation in the analyses is likely to occur when there is poor data (i.e. a poor correlation coefficient for the first order least squares fit) and when the number of data points is less than six.

The method that was followed was based on experience using good data.

- STEP 1 Determine the instrumental error in the background correction (see reference 4).
- STEP 2 Plot the Hull function for all the data in the range ± 2 of the Hull function.
- STEP 3 Examine the gradient of the least squares fit. It should be 1.30 ± 0.05 for Be^+ and B^+ and 1.00 ± 0.05 for Si^+ and P^+ . If it is not the expected gradient, examine the scatter of the points with a view to discarding doubtful data and obtaining the expected gradient. If a good plot cannot be obtained then the data is probably not suitable for the analysis. As a last resort data can be plotted by hand.
- STEP 4 If a large number of points are out of the range ± 2 of the Hull function then the saturated transmission correction term can be employed. Considerable care should be taken using this term as it can significantly alter the gradient. If few points are available then it is best to determine this term for an ion at a similar m/z , which shows a good spread of dark and grey images.

STEP 5 The precision of the plate evaluation is reflected by the correlation coefficient. When sample inhomogeneity occurs it is possible that the correct interpretation will show the poorest correlation coefficient, say 0.97, but have a gradient closest to that expected.

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