TASMANIA
DEVELOPMENT
AND RESOURCES

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Trace boron in rocks

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OUTLINE

The sample is fused with Na_2CO_3, the boron is then extracted from the HCl acidified filtrate with 2-ethylhexane-1, 3-diol, prior to re-extraction into NaOH solution. Carminic acid reagent is then used to determine the boron spectrophotometrically.

APPARATUS

1. Spectrophotometer or equivalent with 5 cm width cuvettes. AAS spectrophotometer may replace conventional photometer as is done here (fig. 1).
2. (Nalgene, U.S.A.) PTFE separating funnels; 250 mL and 500 mL capacity.
3. Platinum crucibles.
4. ≈ 120 mL capacity polycarbonate plastic bottles with polypropylene caps or equivalent. *cf.* Note 6.
5. ≈ 65 mL capacity, NaOH proof, plastic bottles with caps, or equivalent. *cf.* Note 11.
6. ≈ 70 mL capacity, H_2SO_4 proof, plastic bottles with caps, or equivalent. *cf.* Note 12.
7. 250 mL volume plastic beakers, e.g. PTFE.

SOLUTIONS

1. 20% 2-ethylhexane-1, 3-diol solution in chloroform.
2. 0.05% Carmine Reagent.

   Dissolve 100 mg of carminic acid (No. 211, Merck) in 200 mL of concentrated H_2SO_4 (95–97%).
3. 100 mg/L Boron stock standard solution.

   Dissolve 0.8813 g of recrystallised $Na_2B_4O_7.10H_2O$ to 1000 mL with distilled water.
4. 0.5 N.NaOH.

   2% w/v NaOH; 20 g NaOH in one litre of distilled water.
5. 4N.HCl.

   35% v/v HCl; 350 mL concentrated HCl made up to one litre with distilled water.
6. ≈ 0.1N HCl wash solution.

   0.86% v/v HCl; 8.6 mL concentrated HCl to one litre with distilled water.

METHOD

Fusion

1. Mix 1 g of dry sample with 6 g of Na_2CO_3 in a Pt crucible and cover with 1 g of Na_2CO_3. Run standards and blank also. *NOTE 1*
2. Add a lid and place in a muffle at 500°C. Raise the temperature to 1000°C in steps of 100°C. Keep at 1000°C for a further 30 minutes. *NOTE 2*
3. Cool the crucible and leach the contents with ≈ 32 mL of 35% v/v HCl (4N) in a 250 mL plastic beaker. *NOTES 3 and 4*
4. After dissolving the carbonate adjust the acidity to give a pH of 1 to 2. *NOTE 5*
5. Filter this solution through a Whatman No. 44 paper into a 120 mL polycarbonate plastic bottle marked at 100 mL volume. *NOTES 6 and 7*
6. Wash the residue on the paper with dilute HCl (≈ 0.1N). *NOTE 8*
7. Adjust the pH of the filtrate with HCl/Na_2CO_3 to pH 1 ± 0.5 and the volume to ≈ 100 mL with distilled water. *NOTE 9*

Extraction

8. Pour the 100 mL volume of sample solution into a 250 mL PTFE separating funnel and add 20 mL of ethylhexane-1, 3-diol solution. *NOTE 9*
9. Shake for 120 seconds and collect the organic extract in a 500 mL PTFE separating funnel.
10. Repeat the extraction as at steps 8 and 9 combining the organic extracts into the 500 mL PTFE separating funnel.

11. Add 20 mL of 2% NaOH (0.5N) to the combined extracts.

12. Re-extract the boron from the combined organic extracts, by shaking for 120 seconds.

13. Dilute the NaOH extract to 25 mL, and store in ≈ 65 mL HDPE Nalgene bottles. *NOTE 10*

Colour Development; Samples and Blank

14. Place 2 mL of sample into a ≈ 70 mL capacity, H_2SO_4 proof, plastic bottle. *NOTE 12*

15. Add 2 (two) drops of concentrated HCl.

16. Add 10 mL of concentrated H_2SO_4 and COOL. *NOTE 13*

17. Add 10 mL of 0.05% carmine reagent and mix. *NOTES 14, 15 and 16.*

18. Stand 90 minutes and measure the absorbance at 610 nm using 5 cm width cuvettes, or ALTERNATIVELY

    if 5 cm cuvettes are unavailable use the AAS at 609.5 nm with 5 to 6 cm path length cell, constructed from HC ends, as shown in Figure 1.

    Other instrument conditions; Double beam, Fe line @ 609.5 nm, 3 sec integration time, 0.2 nm slit with burner height ≈ 10 (to support the absorption cell). ZERO on standards blank.

Colour Development; Standards

19. Place 1 mL of 1, 2, 4, 6, 8 µg/mL B standards into ≈ 70 mL capacity plastic bottles together with 1 mL of distilled water.

20. Repeat as for steps 15–18.

NOTES

1. Anhydrous Na_2CO_3 and samples dried as required are used, i.e. dry as received; or dried at 105°C for 1 hour or to constant weight.

2. The lowest temperature possible to give a complete fusion is desirable. Crucibles should be tightly covered and fusion conducted slowly.

3. 32 mL of 35% v/v HCl ≈ 32 mL of 4N.HCl, 6 g of Na_2CO_3 ≈ 32 mL 4N.HCl (53 g Na_2CO_3 ≈ 100 mL of 36.5 w/w % HCl) (or 6 g Na_2CO_3 ≈ 11 × 100/35 ≈ 32 mL of 4N.HCl) (4N.HCl ≈ 35.4% v/v HCl)

4. Heat may be used to hasten the solution but it should be kept to a minimum with the beaker well covered.

5. Whatman pH indicator paper, in the range 1 to 4, is adequate.

6. These are not attacked by the HCl concentrations used in the method. NOTE: Concentrated H_2SO_4 will severely attack them as will the $CHCl_3$ used in the 20% 2-ethylhexane-1, 3-diol solution. [Obtained from Medical Goods Disposable Products; CODE 22410]

7. Quartz or plastic beakers may be used if available.

8. 0.1N HCl is approximately 0.86% v/v.

9. The boron in the 100 mL sample should be in the range 0 to 200 µg, viz. 0 to 2 µg/mL; and as 25 mL is the volume of NaOH extract, the range is 0 to 8 g/mL; cf. standards range 0 to 8 µg/mL

10. Dilute to 50 mL for high boron, i.e. >8 µg/mL in 25 mL.

11. Any plastic container not attacked by 2% NaOH suffices; HDPE Nalgene bottles are suitable.

12. Quartz or plastic beakers may be used if available, not teflon beakers as these are 'sulphonated' by concentrated H_2SO_4. 55 × 42 plastic bottles (≈ 70 mL capacity) with (yellow) caps are ideal, i.e. Medical Specimen bottles obtained from I.V. Plastics 150/002 P/SY. Medical Goods Imbros Pty Ltd, Hobart.

13. This may be done in a water bath (≈ 10°C) if desired. In any case, add the concentrated H_2SO_4 before adding the carmine reagent and keep cooling conditions similar for all samples and standards. Letting cool on the bench before adding the carmine reagent is adequate.

14. Magnetic stirrer may be used; however swirling while adding the carmine reagent is adequate.

15. There is 25% fading of the developed colour in the 1–2 hours interval, i.e. timing of measurements is required for accurate results.

16. (a) There is variable interference from SiO_2 but dependent on the boron concentration. This interference is also independent of the amount of SiO_2. The EXTRACTION method overcomes this. With 0.5 mg/L B; results can be 20% high with 5 to 30 mg/L SiO_2.

    (b) If interference is suspected, 20 to 30 µg of boron may be added to the sample before fusion, besides carrying through an internal standard if extremely accurate work is necessary. Also do the sample without additional boron. (b) should not be necessary, if the EXTRACTION procedure is used, as the organic extraction should not extract SiO_2 in solution (i.e. SiO_2 left after removal of most of the 'precipitated' SiO_2 at the filtration step 5.

    (c) The use of plastic apparatus is imperative. About 20 to 50 µg of boron may be extracted after shaking blank solutions with ethylhexane-1, 3-diol solution for 1–2 minutes in 250 mL glass separating funnels.

    (d) The detection limit of the method depends largely on the purity of the Na_2CO_3 used. (Often 2–3 ppm B in Na_2CO_3).

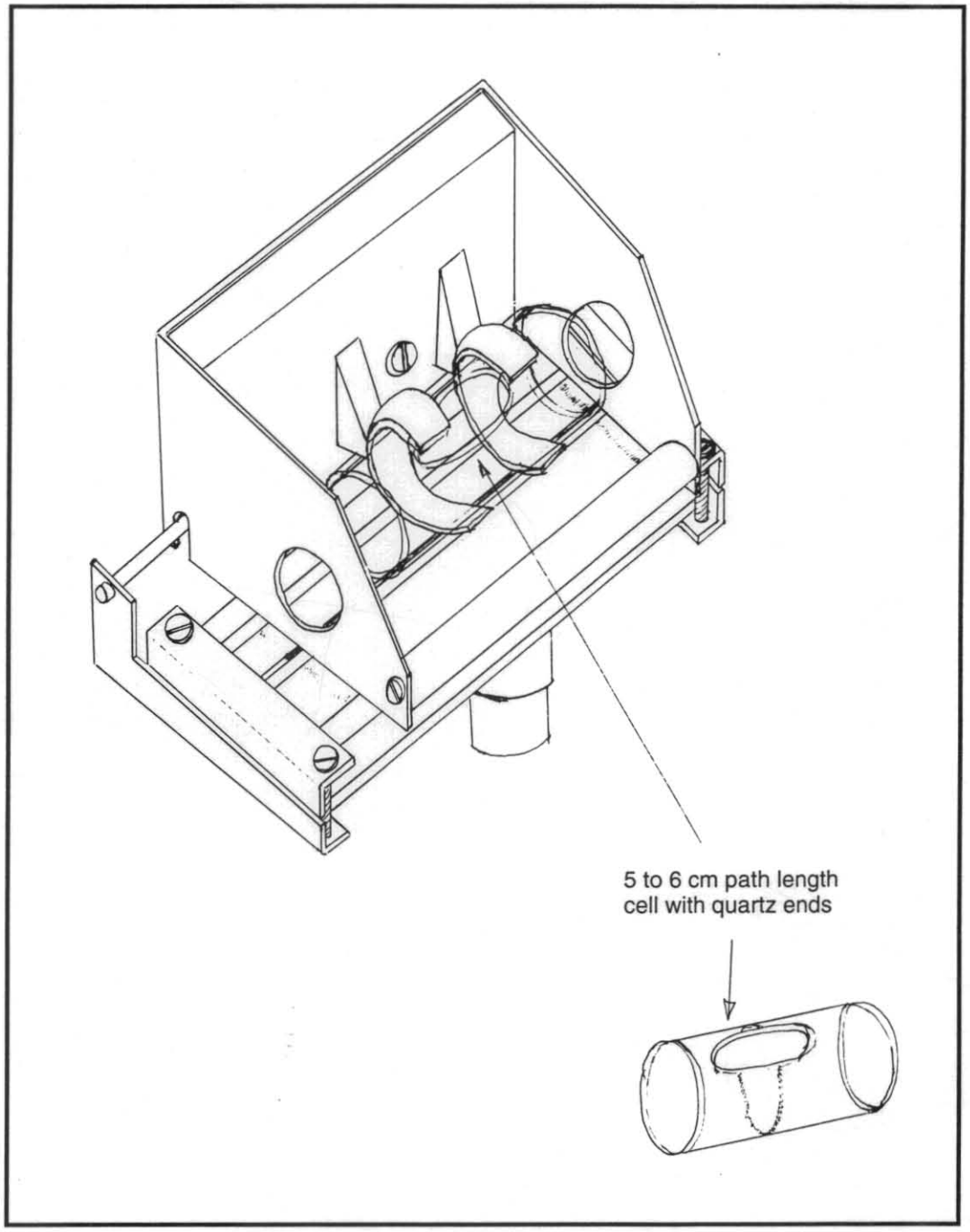
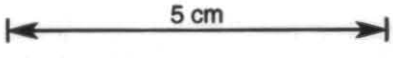


Figure 1



(e) Boron in the concentration range 1 to 1000 ppm may be routinely done.

EXAMPLE CALCULATION

Straight boron in H_2O standards (from $Na_2B_4O_7.10H_2O$)

1 mL of 1, 2, 4, 6, 8 µg/mL B plus) cf. 2 mL
1 mL of H_2O per standard) SAMPLES
→ 22 mL H_2SO_4/ Carmine
10 mL 10 mL

µg B	Blank	1	2	4	6	8
mg/L	0	0.5	1	2	3	4
Abs + Blk	0.000	0.099	0.182	0.391	0.568	0.774
Abs	0.000	0.099	0.182	0.391	0.568	0.774

ZEROED on Blank.
[cf. BOOK 21, 26-10-92]

CONCLUSION

The combination of the extraction procedure with the carminic acid colour procedure allows samples with varying matrix composition to be done satisfactorily, *cf.* example calculation and appended results (Table 1 *Analyst*, March 1985, Vol. 110 p. 285).

REFERENCE

TROL, G.; SAUERER, A. 1985. Determination of trace amounts of boron in geological samples with carminic acid after extraction with 2-Ethylhexane-1, 3 diol. *Analyst*. 110:283–286.

[22 November 1993]

Samples Reg. No.	No.	Wt	pH 1 ± 0.5 HCl Vol	0.5N NaOH Vol	B Abs	µg B/ 22 mL	µg/g B	Given ppm B
DTS-1	1	1	100	25	Contaminated 0.401/0.398	4.15	?52	≈ 10
SO-3	2	1			0.205/0.202	2.106	26	22
SY-2	3	1			0.666/0.663	6.91	86	88 ± 5
SY-3	4	1			0.816/0.813	8.47	106	107 ± 12
Blank	5	-			0.003/0.000	-	-	-
920245	6	1			0.018/0.015	0.15	≈ 2, <5	-
920246	7	1			0.798/0.795	8.32	104	-
920247	8	1			0.525/0.522	5.44	68	-
920248	9	1	100	25	0.444/0.441	4.59	57	-

µg/g = µgB/22 mL × 25/2
or µg/g = mg/L × 100 × 25/100

APPENDIX 1

Boron content (ppm) of 14 international samples compared with literature values (from Trol and Sauerer, 1985)

Table 1. Boron content (p.p.m.) of 14 international reference samples compared with literature values

Reference sample	Reported values	Mean	Analytical method*	Reference
ZGI-TB	83, 87, 76, 86	83	FYJ	This work
		92†	OOS, OOJ	1
		118†	OOS	2
ZGI-GM	9, 7, 5, 7, 7	7	FYJ	This work
		13†	OOS, OOJ, OOR	1
		11†	OOS	2
SY-2	92, 92, 93, 95, 104	95	FYJ	This work
	33		ODS	3
	77		OOS	3
	178		OOO	3
	110		OVS	3
	95		FYJ	3
	83		BVS	3
	84		OVS	3
	87		FOS	4
MAG-1	132, 139, 140	137	FYJ	This work
	159, 163, 147, 131, 156, 177	155	OOS	5
		130†	OOS	5
	128		OOR	6
	138		FOS	4
SDC-1	13, 15, 20, 16	16	FYJ	This work
	10.8, 10.0, 12.8, 10.6, 10.1, 10.0	10.7	OOS	5
		30†	OOS	5
DTS-1	9, 12, 9, 9, 10, 10	10	FYJ	This work
	<10, <10, <10, <10, <10, <10	(<10)‡	OOS	5
		5	OOO	1
	<10	<10	OOS	2
		20†	OOO	5
		5†	OOO	5
	<20, <8.0, <0.7		OOS	7
SCo-1	71, 76, 63, 78, 79	73	FYS	This work
	75.7, 102, 89.1, 83.4, 90.1, 88.9	93.2	OOS	5
		70†	OOS	5
		64.4†	OOR	5
	72.1		OOR	6
BHVO-1	2, 3, 2, 1, 3	2	FYJ	This work
	<10, <10, <10, <10, <10, <10	(<10)‡	OOS	5
	0		OOS	5
	2.3		OOR	6
	<5		FOS	4
SGR-1	41, 37, 43	40	FYJ	This work
	65.0, 57.2, 53.6, 67.0, 53.7, 56.2	58.8	OOS	5
		29.8†	OOS	5
	50.4		OOR	6
NIM-G	5, 6, 8, 6	6	FYJ	This work
		10†	OOO	1
ASK-1	12, 19, 12, 15, 13	14	FYJ	This work
	20, 20, 10	17	OOS	8
ASK-2	125, 130, 123, 118, 125	124	FYJ	This work
	160, 150, 150	153	OOS	8
BCS-375	9	—	FYJ	This work
BCS-376	7	—	FYJ	This work

* To describe the analytical methods we have used a three-letter code, as given by Abbey *et al.*[3]:
Sample pre-treatment:
B pelletisation;
F fusion, sintering;
O not used or not specified.
Separations:
D fractional distillation;
V bulk volatilisation;
Y solvent extraction;
O not used or not specified.
Final measurement:
J absorptiometric;
S spectrographic;
O not specified;
R radiometric, neutron activation.
† Only an average value was reported.
‡ These values were given in parentheses in the original paper.