

Spectrophotometric determination of boron in igneous rocks. Comparison between azomethine-H and 1-1' dianthrimide methods

NARA CORADOSSI, ORLANDO VASELLI

Dipartimento di Scienze della Terra, Università, Via La Pira 4, 50121 Firenze

ABSTRACT. — Boron contents of order of few ppm have been determined by spectrophotometry in silicate rock samples, using different reagents (azomethine-H and 1-1' dianthrimide), to check whether these reagents can be utilized in analysis of complex chemical solutions. The analytical solution was obtained by melting 20-40 mg of the sample with NaOH in crucibles of Pd-Au. This method was used to analyse six international reference standards (G-2, GA, MA-N and GS-N granites, BR basalt and W-1 diabase) and a set of effusive rocks from Vesuvius (Italy) and Fajal and San Miguel (Azores). The boron content of both the international standards and the volcanites obtained with azomethine-H were in all cases higher (by about 25%) than the values obtained with 1-1' dianthrimide. The values obtained for the international standards with 1-1' dianthrimide were in excellent agreement with data reported in the literature. The higher values obtained with azomethine-H are presumably the result of the presence of interfering ions. 1-1' dianthrimide is recommended as the most suitable reagent in spectrophotometric analysis of boron in solutions obtained from geological materials.

Key words: Geochemical method, spectrophotometry, boron, comparison between azomethine-H and 1-1' dianthrimide, igneous rocks.

RIASSUNTO. — Tenori di boro dell'ordine delle ppm sono stati determinati in campioni di rocce silicatiche per spettrofotometria, utilizzando reattivi distinti (azometina-H e 1-1' diantrimide) allo scopo di verificare l'applicabilità degli stessi all'analisi di soluzioni chimicamente complesse. La soluzione analitica è stata ottenuta per fusione di 20-40 mg di campione con NaOH in crogioli di Pd-Au. Il metodo è stato applicato all'analisi di sei standards internazionali (graniti G-2, GA, MA-N e GS-N; basalto BR e diabase W-1) e di una serie di rocce effusive del Vesuvio e delle isole Fajal e San Miguel (Azzorre). I tenori in boro sia negli standards internazionali che nelle rocce effusive, ottenuti con azometina-H risultano sempre superiori (di circa il 25%) rispetto a quelli ottenuti usando la 1-1' diantrimide. Nel caso degli standards internazionali questi ultimi sono in eccellente accordo con i dati della letteratura. Si ipotizza che i valori in eccesso ottenuti con azometina-H siano legati alla presenza di ioni interferenti. Si raccomanda l'uso della 1-1' diantrimide quale reattivo più idoneo nell'analisi spettrofotometrica del boro nelle soluzioni ottenute a partire da materiali geologici.

Parole chiave: Metodologia geochimica, spettrofotometria, boro, confronto azometina-H e 1-1' diantrimide, rocce ignee.

Резюме

В статье, бор был определен в 6 международных стандартах рекомендаций (граниты: G-2, GA, MA-N и GS-N; базальт BR и диабаз W-1) и в некоторых образцах вулканических пород Везувия и о. Фаял и о. Сан-Мигел (Азорские острова).

Образцы расплавили с NaOH в тигле Au-Pd. В растворе, бор был определен с спектрофотометрическим методом. Использовали два разных реагента: азометин-Н и 1-1' диантримид, с такой целью, чтобы были охвачены возможные различия.

Содержания бора международных стандартов, полученные с азометин-Н, оказываются всегда выше рекомендуемых величин, со всей вероятностью по причине интерференции ионов. Наоборот, величины, полученные с 1-1' диантримидом являются совершенно соответствующими с данными научной литературы.

В породах эффузив, величины соответствующие определению с азометин-Н оказываются всегда выше как минимум с 25%-ом в сравнении с тем, которые были получены с 1-1' диантримидом.

Следовательно, параллельное изучение двух реагентов, проведенное в международных стандартах рекомендаций и в образцах вулканических пород показывает что 1-1' диантримид, как реагент, является более пригодным к определению бора в растворах, полученных через плавление с NaOH.

Introduction

The determination of boron in igneous rocks is difficult, because methods which are sensitive, reproducible, and precise enough to reveal traces of it are few. The amounts of boron present in most geological materials are less than 200 ppm.

In particular, igneous rocks have only a few ppm of boron. Only a few extremely differentiated acid rocks and some metamorphic rocks reach concentration of

TABLE 1
Analysed samples from Vesuvius (Italy) and Azores

VESUVIUS		
SAMPLE	DEPOSIT TYPE	PLINIAN ERUPTION
VSP 02-04	PUMICE-FALL	POMPEI
VSP 05-12	PUMICE-FALL	AVELLINO
VSP 13-15	PUMICE-FALL	GREENISH
VSP 16-21	PUMICE-FALL	MERCATO
VSP 22-24	PUMICE-FALL	BASAL
VES 39	PUMICE-FALL	POLLENA
AZORES		
SAMPLE	DEPOSIT TYPE	ERUPTIVE CENTRE
AC 01-03	SURGE	CAPELINHOS (*)
AC 31	PUMICE-FALL	CALDEIRA (*)
AC 37	LAVA-FLOW	LA GOA DE FOGO (\$)
AC 44	SURGE	CALDEIRA (*)
AC 63	PUMICE-FALL	POVOAÇÃO (\$)

(*) FAYAL ISLAND; (\$) SAN MIGUEL ISLAND.

1000 ppm or, rarely, a few percent.

In the latter case, boron often forms specific minerals such as tourmaline (TONANI, 1957).

Boron is also relatively concentrated in sea water (4.6 ppm B), while in marine sediments the concentration reaches values slightly higher than 100 ppm. (WALSH, 1985). In fresh water and marine sediments boron is an important indicator of paleosalinity (CURTIS, 1964; WALKER, 1968; COUGH, 1971; CORADOSSI and CORAZZA, 1979).

Understanding the distribution of boron is important in many other fields, such as geothermal systems, plant physiology, agriculture, metallurgy, nuclear power, etc. This justifies the interest that analytical chemists have in finding techniques for determining boron in very different materials.

This paper deals with igneous rocks. The determination of their boron content can be achieved by following two completely different paths: direct analysis of a powdered sample or analysis of a sample in solution. If the physical methods are excluded, the determination of boron in silicate rocks requires several operations which can be divided into three steps: melting, removal of

interfering ions, and determination in the final solution.

The first step is certainly the most critical, because the loss of boron must be avoided. It is well known that boron compounds under hot acid conditions are volatile (FELDMAN, 1961), so that mineral acids and acid solvents cannot generally be used. They can be used when working with special materials such as metals, steels, alloys, and, in geology, with soils and volcanic glasses.

Alkaline fusion is frequently used in the determination of boron in igneous rocks. The most commonly used fluxes are sodium and potassium carbonate (KRAMER, 1955; HAYES et al., 1957; FLEET, 1967; MAURICE, 1968; SCHUCKER et al., 1975; YOSHIMURA et al., 1979). The use of sodium hydroxide (BENNET et al., 1961; SHIMA, 1963) or sodium peroxide (RAFTER, 1950; BELCHER, 1963; AHAMAD KHAN et al., 1980) is quite rare.

The second step of analysis, in the separation of interfering elements, is equally critical, especially when the samples contain only traces of boron. Here too many different techniques can be used, some of which are traditional; like distillation (LUKE, 1955 and 1958; LUKE and FLASCHEN, 1958; SPICER and STRICKLAND, 1958; EBERLE and LERNER, 1960; QUIJANO-RICO, 1968) and centrifugation or filtration (MAURICE, 1968; WOLF, 1971); others are based on extraction (LANZA and BULDINI, 1974; KORENAGA et al., 1980; AZNAREZ et al., 1983 and 1985). Lastly, there are ion-exchange separation procedure (KRAMER, 1955; HAYES et al., 1957; PINON et al., 1968; KOCKEN, 1974; AHAMAD KHAN et al., 1980; HILL and LASH, 1980).

The third step is determination of boron in analytical solution. The best known and most used reagents, capable to give coloured complexes with it, are: *curcumin* (LUKE, 1955; COURSIER et al., 1955; DUCRET, 1957; LUKE, 1958; LUKE and FLASCHEN, 1958; SPICER and STRICKLAND, 1958; EBERLE and LERNER, 1960; HAYES and METCALFE, 1962; GREENHALGH and RILEY, 1962); *1-1' dianthrimide* (ELLIS et al., 1949; BREWSTER, 1951; CODELL et al., 1953; DANIELSSON, 1959; MAURICE, 19689; GUPTA and BOLTZ, 1971); *carminic acid* (ROSENFELD and SELMER-OLSEN,

1979; AHAMAD KHAN et al., 1980; AZNAREZ et al., 1983 and 1985; TROLL and SAUERER, 1985); and *azomethine-H* (CAPELLE, 1961; SHANINA et al., 1967; BASSON et al., 1969; WOLF, 1971; JOHN et al., 1975; SCHUCKER et al., 1975; YOSHIMURA et al., 1979; KRUG et al., 1981; AZNAREZ and MIR, 1985; BENCINI, 1985).

The purpose of the present study is to seek a simple, and rapid colorimetric method of boron analysis, applicable to igneous rocks and capable of providing results as precise and reproducible as those of usually used methods. The analytical method devised was tested either on a set of international reference standards and on a set of effusive rocks containing boron in relatively wide concentration range.

The following rocks, which have different chemical and petrographical characters were chosen: G-2, GA, MA-N, and GS-N granites, BR basalt, and W-1 diabase. The method was then applied to a group of volcanic rocks from Vesuvius (Italy) and volcanoes on Fajal and San Miguel (Azores). These rocks are composed of pumice-falls from Vesuvius belonging to various Plinian-type eruptions (LIRER et al., 1973; DELIBRAIS et al., 1979; SANTACROCE, 1983; ROSI and SANTACROCE, 1983) and of pumice-falls, surges, and lava-flow from various eruptive centres on Fajal and San Miguel; for the description of the latter rocks, see VASELLI (1985) and CAPACCIONI et al. (1986). In Table 1 are reported the analyzed samples from Vesuvius and Azores.

Experimental techniques

1. Generalities on fusion procedure and organic reagents

The use of sodium hydroxide, which is available in boron-free pellets, turns out to be essential for three important reasons: small quantities of sample can be used (20-40 mg); sample dissolution is rapid (10-15 minutes); and dissolution does not effervesce while being measured with the spectrophotometer.

The choice of the organic reagent with which to complex the boron present in solution is also important. In the course of

this project we tested two reagents: azomethine-H and 1-1' dianthrimide. Azomethine-H is a sensitive reagent whose results are highly reproducible but it is insuitable because it is affected by interference effects of many other elements.

Instead, 1-1' dianthrimide is sensitive, highly reproducible, and also very selective with respect to boron. In other words, the centrifugation which the sample undergoes after it is melted is sufficient to remove interfering ions.

2. Material used

3-ml Pd-Au crucibles; Schott Ceran protection plate for heating samples over Bunsen burner; 50-ml transparent fused silica dishes; steam bath; 50-ml polyethylene test tubes; centrifuge; 10-ml volumetric flasks; 20-ml polyethylene containers; 5-ml transparent fused silica test tubes; Socorex 811-821 micropipettes (50-200 μ l, and 200-1000 μ l); Socorex bottle top with dispenser with adapters; Philips PYE UNICAM SP6-350 spectrophotometer; 1-cm glass cells.

3. Reagents

Sodium hydroxide in pellets (BDH, art. 30167)

Azomethine-H solution: 0.9 azomethine-H (SIGMA) and 2 g L(+) ascorbic acid (C. ERBA), diluted in 100 ml of twice-distilled water.

Masking-buffer solution: 250 g ammonium acetate (MERCK, art. 1116), 17.5 g EDTA tetrasodium salt (SIGMA) and 10 g NTA-acid disodium salt (SIGMA, art. N-0128) diluted in 400 ml glacial acetic acid (MERCK, art. 63), and 150 ml of twice-distilled water.

1-1' dianthrimide solution: 25 mg 1-1' dianthrimide (MERCK) in 50 ml sulfuric acid $d = 1.84$. Sulfuric acid (MERCK, art. 731), $d = 1.84$. Water distilled twice by fused silica device.

Standard boron solution (100 μ g ml⁻¹B): 0.4406 g sodium tetraborate (RIEDEL de HAËN) in 0.5 lt of twice-distilled water. This was the stock solution from which a solution containing 10 μ g ml⁻¹B was prepared before each determination. From this latter were prepared solutions with concentrations

varying between 0 and 1 $\mu\text{g ml}^{-1}\text{B}$.

Analytical methodology

1. Solution preparation

20-40 mg of the powdered sample, dried at 110°C, was weighed directly in a Pd-Au crucible. Two to three pellets of sodium hydroxide were added (total weight 200-300 mg), the crucible was then placed on the Schott Ceran plate and the mixture melted over a Bunsen burner. Six to seven samples could be melted simultaneously by using this system. After 10-15 minutes the reaction reached completion; the crucible was brought to red heat for 10-15 seconds and then allowed to cool. The fusion cake was dissolved in a few ml of twice-distilled water over a steam bath. The solution and precipitate (made up essentially of Fe and Al hydroxides) were transferred to a polyethylene test and centrifuged for 30 minutes. The solutions thus obtained were transferred to fused silica dishes and evaporated over the steam bath. The highly alkaline environment keeps boron from being lost during this step, as confirmed by experimental evidence (BRAMAN, 1978). The evaporation was continued until the salts began to precipitate, and the mixture was then put into a 10-ml volumetric flask and diluted to volume with twice-distilled water. The solution was transferred to a polyethylene container.

2. Determination of boron with azomethine-H

Although azomethine-H is the most widely used reagent for the determination of boron in water, biological materials, and soils, it is rarely used on geological materials, because of the interfering effects by the complex silicate matrix. The interfering ions can be removed; for example, by passing the solutions under examination through ion-exchange columns (YOSHIMURA et al., 1979) or adding a masking-buffer solution, made up of the mixture of EDTA-NTA acid (WOLF, 1971; SCHUKER et al., 1975). We carried out the determination of boron following the second method.

The solutions with known concentrations of boron and the samples were treated as

follows: 2-ml of the masking buffer solution and 1-ml of the azomethine-H solution were added to 2-ml samples of the solutions to be measured and the mixtures were swirled for a few minutes. After one hour, the solutions were transferred to 1-cm glass cells and the absorption spectra were measured with a Philips PYE UNICAM SP6-350 spectrophotometer (415 nm).

3. Determination of boron with 1-1' dianthrimide

For the determination of boron by means of 1-1' dianthrimide, as made in previous geochemical studies (CORADOSSI and MARTINI, 1965; CORADOSSI, 1975; CORADOSSI et al., 1984), we followed the methods developed by ELLIS et al., (1949).

The standards and sample solutions were prepared as follows: 2-ml of sulfuric acid ($d = 1.84$) and 0.5-ml of 1-1' dianthrimide solution were added to 0.3-ml samples of the test solutions in transparent fused silica test tubes. The solutions were then left to change color over a steam bath at 90°C for one hour. After they had cooled, the solutions were transferred to 1-cm glass cells and colour intensities were measured with a Philips PYE UNICAM SP6-350 spectrophotometer (625 nm).

Discussion of results

Table 2 gives the boron concentrations of the international reference standards G-2, GA, MA-N, GS-N, BR and W-1 obtained with azomethine-H and 1-1' dianthrimide. For comparison, Table 2 also gives the values reported by GOVINDARAJU (1984) and VITTOZ et al., (1987), using different techniques. As may be seen, 1-1' dianthrimide method gives results in good agreement with literature data. The determinations carried out, for example, on granite GA (recommended value 20 ppm B) give an average value of 21.7 ppm B, with a standard deviation of 1.2 ppm and a relative error of 5.6%. The mean value of 37 ppm of the GA granite using azomethine-H (22 alkaline fusions and 48 spectrophotometric measurements) is off by 85% with respect to the average value (20 ppm) reported by GOVINDARAJU (1984). The standard deviation

TABLE 2

Boron content (in ppm) in 6 international reference rock standards determined by azomethine-H and diathrimid methods

REFERENCE STANDARDS	\bar{B} ppm (*) AZOMETHINE-H	(1)	(2)	\bar{B} ppm (*) 1-1'DIANTHRIMID	(1)	(2)	\bar{B} ppm (\$) (1984)	\bar{B} ppm (+) (1987)
G-2 (granite)	14	2	4	3.15	2	4	2	2.3±1.3
GA (granite)	37.5	22	48	21.7	7	22	20	
MA-N (granite)	57.5	3	6	16	3	8	17	
GS-N (granite)	21.5	4	8	12.3	4	8		
BR (basalt)	26.3	2	4	10.5	1	2	10	
N-1 (diabase)	22	5	7	12	6	8	13	12.5±1.3

(*) THIS WORK; (1) NUMBER OF ALKALINE FUSIONS WITH SODIUM HYDROXYDE; (2) NUMBER OF SPECTROPHOTOMETRIC MEASUREMENTS; (\$) GOVINDARAJU (1984); (+) VITTOZ ET AL. (1987).

TABLE 3

Boron content (in ppm) in volcanic rock samples from Vesuvius (Italy) and Azores

SAMPLE	\bar{B} ppm AZOMETHINE-H	(1)	(2)	\bar{B} ppm 1-1'DIANTHRIMID	(1)	(2)
VES 39	129	36	55	91	4	8
VSP 02	186	1	2	74	1	2
VSP 04	106	4	7	75	1	2
VSP 05	265	1	2	201	1	2
VSP 07	248	7	15	195	2	4
VSP 08	294	1	2	195	2	4
VSP 09	223	1	2	178	1	2
VSP 10	240	1	2	145	1	2
VSP 11	215	1	2	168	1	2
VSP 12	123	2	4	100	2	3
VSP 13	113	4	10	63	2	4
VSP 14	109	1	2	81	1	2
VSP 15	134	1	2	105	1	2
VSP 16	324	7	13	201	2	4
VSP 17	282	2	4	181	1	2
VSP 19	336	1	2	286	1	2
VSP 20	307	5	10	200	2	4
VSP 21	261	2	4	206	2	3
VSP 22	295	2	4	173	1	2
VSP 23	112	1	2	51	1	2
VSP 24	85	2	4	40	2	3
AC 01	26	4	8	7	2	4
AC 02	30	4	8	8	2	4
AC 03	39	4	8	8	2	4
AC 31	54	4	8	10	2	4
AC 37	30	4	8	9	2	3
AC 44	38	4	8	11	2	4
AC 63	51	4	8	12	2	4

(1) NUMBER OF ALKALINE FUSIONS WITH SODIUM HYDROXYDE; (2) NUMBER OF SPECTROPHOTOMETRIC MEASUREMENTS.

TABLE 4

Comparison between the azomethine-H method and the diathrimid method for all analyzed samples (S.D., Cv% and t-test). For further explanation see text

CONCENTRATION RANGE (ppm B)	NUMBER OF SAMPLES	\bar{x} (B ppm)	S.D.	Cv%	t, obt.	t critical value 5%	t critical value 1%
0 - 25	13	22.6	18.6	82.2	5.97	2.06	2.80
25 - 100	8	95.7	39.6	41.4	3.95	2.14	2.98
100 - 300	13	227	56.0	24.7	3.83	2.06	2.80

is 6.3 ppm and the relative error 16.5%. These results indicate that azomethine-H is unsuitable for the method proposed, because the centrifugation and addition of a masking-buffer solution are insufficient to eliminate the interference of the ions present in the solution.

Table 3 gives the concentrations of boron in 21 pumice falls from various Plinian-type eruptions of Vesuvius and in 7 volcanic rocks from Fajal and San Miguel (Azores), as determined with azomethine-H and 1-1' dianthrimide. As observed for the standard rocks, the concentrations determined with azomethine-H are always at least 25% higher than those obtained with 1-1' dianthrimide.

To summarize, the tests we carried out with the two reagents on the international reference rock standards and the volcanic rocks indicate that 1-1' dianthrimide is a more suitable reagent for determination of boron in solution obtained by fusion with sodium hydroxide. The high sensitivities which can be reached with this procedure mean that determinations may be extended to rock with a few ppm of boron.

Acknowledgments. — The present research was partially supported by Italian C.N.R. (Centro Studi per la Mineralogia e la Geochimica dei Sedimenti). We thank Professor M. Martini and Doctor B. Capaccioni for kindly giving us the pumice-fall samples from Vesuvius.

REFERENCES

- AHAMAD KHAN S., STONE M., BAWDEN M.G. (1980) - A rapid improved colorimetric method for the microdetermination of boron in silicate rocks and minerals by use of carminic acid. *Rev. Roumanie Chim.* 25, 9-10, pp. 1433-1442.
- AZNAREZ J., BONILLA A., VIDAL J.C. (1983) - Spectrophotometric and fluorimetric determination of boron in soils, plants, and waters by extraction with 2-methylpentane-2,4-diol in isobutyl methyl ketone. *Analyst* 108, pp. 368-373.
- AZNAREZ J., FERRER A., RABADAN J.M., MARCO L. (1985) - Extractive spectrophotometric and fluorimetric determination of boron with 2, \rightarrow 2, \rightarrow 4-trimethyl-1, 3-pentanedial and carminic acid. *Talanta* 32, 12, pp. 1156-1158.
- AZNAREZ J. MIR J.M. (1985) - Spectrophotometric determination of boron. *Analyst* 110, pp. 61-64.
- BASSON W.D. BÖHEMER R.G., STANTON D.A. (1969) - An automated procedure for the determination of boron in plant tissue. *Analyst* 94, pp. 1135-1141.
- BELCHER C.B. (1963) - Sodium peroxide as a flux in refractory and mineral analysis. *Talanta* 10, pp. 75-81.
- BENCINI A. (1985) - Applicabilità del metodo dell'azometina-H alla determinazione del boro nelle acque naturali. *Rend. Soc. It. Mineral. Petr.* 40, 1, pp. 311-316.
- BENNET H., EARDLEY R.P., THWAITES I. (1961) - Apparent loss of iron during fusion of silicate materials with sodium hydroxide in nickel crucibles. *Analyst* 86, pp. 135-136.
- BRAMAN R.S. (1978) - Boron. In Kolthoff I.M. and Elving P.J. eds., *Treatise on analytical chemistry*. Part. II: Analytical chemistry of inorganic and organic compounds. 10, pp. 3-88, J. Wiley & Sons, New York.
- BREWSTER D.A. (1951) - Colorimetric determination of boron in aluminium with 1-1' dianthrimide. *Anal. Chem.* 23, 12, pp. 1809-1811.
- CAPACCIONI B., GIANNINI L., MARTINI M. (1986) - Triggers of explosive processes as suggested by volatile distribution in pyroclastic products. *Per. Miner.* 55, pp. 123-129.
- CAPELLE R. (1961) - Microdosage colorimétrique du bore en milieux aqueux, au moyen de réactifs à groupement azoïque ou imine dérivés des acides H et K. *Anal. Chim. Acta* 24, pp. 555-572.
- CODELL M., NORWITZ G. (1953) - Colorimetric determination of small amounts of boron in titanium alloys. *Anal. Chem.* 25, 10, pp. 1446-1449.
- CORADOSSI N., MARTINI M. (1965) - Contributo allo studio geochimico delle acque di Montecatini Terme. *Rend. Soc. It. Min. Petr.* 21, pp. 67-90.
- CORADOSSI N. (1975) - Il boro nei depositi alluvionali e nelle acque del frume Cecina (Toscana). *Rend. Accad. Naz. Lincei, Ser. 8*, 59, pp. 465-474.
- CORADOSSI N., CORAZZA E. (1979) - Boron geochemistry at the Miocene/Pliocene boundary. Initial Reports Deep Sea Drilling Project 47, Part 1, Washington (U.S. Government Printing Office), pp. 553-555.

- CORADOSI N., MARTINI M., PINARELLI L. (1984) - On boron content in products of explosive volcanism. *Rend. Soc. It. Min. Petr.* 39, pp. 465-470.
- COUGH E.L. (1971) - Calculation of paleosalinities from boron and clay mineral data. *Bull. Amer. Assoc. Petrol. Geol.* 55, pp. 1829-1837.
- CURTIS C.D. (1964) - Studies on the use of boron as a paleoenvironmental indicator. *Geochim. Cosmochim. Acta* 28 (7), pp. 1125-1137.
- DANIELSSON L. (1959) - A study of the conditions for the determination of boron with dianthrimide. *Talanta* 3, pp. 138-146.
- DELIBRAIS G., DE PAOLA G.M., ROSI M., SANTACROCE R. (1979) - La storia eruttiva del complesso vulcanico Somma-Vesuvio ricostruita dalle successioni piroclastiche del Monte Somma. *Rend. Soc. It. Min. Petr.* 35, pp. 411-438.
- DUCRET L. (1957) - Séparation et dosage de traces de bore dans le silicium. II. Nouvelle méthode de séparation et de dosage de traces de bore. Application au dosage du bore dans le silicium. *Anal. Chim. Acta* 17, pp. 213-219.
- EBERLE A.R., LERNER M.W. (1960) - Determination of boron in beryllium, zirconium, thorium and uranium. *Anal. Chem.* 32 (2), pp. 146-149.
- ELLIS G.H., GATES ZOOK E., BAUDISH O. (1949) - Colorimetric determination of boron using 1-1' dianthrimide. *Anal. Chem.* 21 (11), pp. 1345-1348.
- FELDMAN C. (1961) - Evaporation of boron from acid solutions and residues. *Anal. Chem.* 33 (13), pp. 1916-1920.
- FLEET M.E. (1967) - Spectrophotometric method for determining traces amounts of boron in rocks and minerals. *Anal. Chem.* 39 (2), pp. 253-255.
- GOVINDARAJU K. (1984) - Special Issue of *Geostandard Newsletter*. Vol. VIII.
- GREENHALGH R., RILEY J.P. (1962) - The development of a reproducible spectrophotometric curcumin method for determining boron, and its application to sea water. *Analyst* 87, pp. 970-976.
- GUPTA H.K.L., BOLTZ D.F. (1971) - 1-1' dianthrimide as a reagent for the spectrophotometric determination of boron. *Anal. Lett.* 4 (3), pp. 161-167.
- HAYES G.R., HILL W.H., WOLSON J.D. (1957) - Applications of anion exchange resins to the determination of boron. *Anal. Chem.* 29 (5), pp. 829-832.
- HAYES M.R., METCALFE J. (1962) - The boron-curcumin complex in the determination of trace amounts of boron. *Analyst* 87, pp. 956-967.
- HILL C.J., LASH R.P. (1980) - Ion chromatographic determination of boron as tetrafluoroborate. *Anal. Chem.* 52, pp. 24-27.
- JOHN M.K., CHUAH H.H., NEUFELD J.H. (1975) - Application of improved azomethine-H method to the determination of boron in soils and plants. *Anal. Lett.* 8 (8), pp. 559-568.
- KOCKEN R.L. (1974) - Potentiometric determination of boron in borosilicates glasses. *Anal. Chim. Acta* 71, pp. 451-457.
- KORENAGA T., MOTOMIZU S., TOEI K. (1980) - Improved extraction method for the spectrophotometric determination of trace amounts of boron in river waters with 1,8-dihydroxynaphthalene-4 sulphonate and removal of the excess of reagent. *Analyst* 105, pp. 955-964.
- KRAMER H. (1955) - Determination of boron in silicates after ion exchange separation. *Anal. Chem.* 27 (1), pp. 144-145.
- KRUG F.J., MORTATTI J., PESSENDA L.C.R., ZAFATTO E.A.G., BERGAMIN H. (1981) - Flow injection spectrophotometric determination of boron in plant material with azomethine-H. *Anal. Chim. Acta* 125, pp. 29-35.
- LANZA P., BULDINI P.L. (1974) - Spectrophotometric determination of trace of boron in silicon by means of solvent extraction. *Anal. Chem. Acta* 70, pp. 341-350.
- LIRER L., PESCATORE T., BOOTH B., WALKER G.P.L. (1973) - Two-plinian pumice-fall deposits from Somma-Vesuvium, Italy. *Geol. Soc. Am. Bull.* 84, pp. 759-772.
- LUKE C.L. (1955) - Determination of traces of boron in silicon, germanium, and germanium dioxide. *Anal. Chem.* 27 (7), pp. 1150-1153.
- LUKE C.L. (1958) - Determination of traces of boron in nickel. *Anal. Chem.* 30 (8), pp. 1405-1408.
- LUKE C.L., FLASCHEN S.S. (1958) - Photometric determination of traces of boron in silicon after separation by hydrothermal refining technique. *Anal. Chem.* 30 (8), pp. 1408-1409.
- MAURICE J. (1968) - Dosage colorimétrique du bore total des minéraux, des roches et des sols au moyen du 1-1' dianthrimide. *Ann. Agron.* 19 (6), pp. 699-704.
- PINON F., DESON J., ROSSET R. (1968) - Propriétés de la résine échangeuse d'ion spécifique du bore Amberlite XE 243. *Bull. Soc. Chim. Franç.* 8, pp. 3454-3461.
- QUIJANO-RICO M. (1968) - Méthodes rapides à très haute sensibilité pour la détermination du bore et du lithium dans les météorites pierreuses et dans les roches. In « Dosage elem. état traces roches autres sust. miner. natur. ». *Actes Colloq.*, Ed. Cent. Nat. Rech. Sci., Paris, pp. 367-380.
- RAFTER T.A. (1950) - Sodium peroxide decomposition of minerals in platinum vessels. *Analyst* 75, pp. 485-492.
- ROSENFELD H.J., SELMER-OLSEN A.R. (1979) - Spectrophotometric determination of trace amounts of boron in solution containing large amounts of nitrate. *Analyst* 104, pp. 95-100.
- ROSI M., SANTACROCE R. (1983) - The A.D. 472 « Pollena » eruption: Volcanological and petrological data for this poorly-known, plinian type event at Vesuvius. *J. Volcan. Geotherm. Res.* 17, pp. 249-271.
- SANTACROCE R. (1983) - A general model for the behaviour of the Somma-Vesuvius complex. *J. Volcanol. Geotherm. Res.* 17, pp. 237-248.
- SCHUCKER G.D., MAGLIOCCA T.S., YAO SIN-SU (1975) - Spectrophotometric determination of boron in siliceous materials with azomethine-H. *Anal. Chim. Acta* 75, pp. 95-100.
- SHANINA T.M., GEL'MAN N.E., MIKHAILOVSKAYA V.S. (1967) - Quantitative analysis of heteroorganic compounds. Spectrophotometric determination of boron. *Zhurn. Anal. Khim.* 22 (5), pp. 782-787.
- SHIMA M. (1963) - Geochemical study of boron isotopes. *Geochim. Cosmochim. Acta* 27 (8), pp. 911-913.
- SPICER G.S., STRICKLAND J.D.H. (1958) - The determination of microgram and submicrogram amounts

- of boron. Part. I. Absorptiometric determination using curcumin.* Anal. Chim. Acta 18, pp. 231-239.
- TONANI F. (1957) - *La distribuzione del boro nelle intrusioni granodioritiche toscane del Monte Capanne (Isola d'Elba) e dell'Isola del Giglio.* Atti Soc. Tosc. Sc. Nat., Ser. A, 64, pp. 206-236.
- TROLL G., SAURER A. (1985) - *Determination of trace amounts of boron in geological samples with carminic acid after extraction with 2-ethylhexane-1,3-diol.* Analyst 110, pp. 283-286.
- VASELLI O. (1985) - *Studio geochimico di prodotti piroclastici alcalini. Due esempi: Isole Azzorre e Vesuvio.* Thesis, University of Florence.
- VITTOZ P., OLIVER R.A., VIVIER G., KERR S.A., HOYLER F. (1987) - *Determination of B, Sm and Gd in twenty-three geological reference materials by neutron-capture prompt gamma-ray activation analysis (PGAA).* Geostand. Newslett. 11 (1), pp. 43-47.
- WALKER C.T. (1968) - *Evaluation of boron as a paleosalinity indicator and its application to offshore prospects.* Amer. Ass. Petrol. Geol. Bull. 52 (5), pp. 751-766.
- WALSH J.N. (1985) - *Determination of boron at trace levels in rocks by inductively coupled plasma spectrometry.* Analyst 110, pp. 959-962.
- WOLF B. (1971) - *The determination of boron in soil extracts, plant materials, composts, manures, water and nutrient solutions.* Soil Sci. Plant. Anal. 2 (5), pp. 363-374.
- YOSHIMURA K., KARIYA R., TARUTANI T. (1979) - *Spectrophotometric determination of boron in natural waters and rocks after specific adsorption on Sephadex gel.* Anal. Chim. Acta 109, pp. 115-121.