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A critical review on the determination of boron in various matrices

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ABSTRACT

Boron is an element with a wide range of uses. Boron, which is the main component in boron minerals, is present as a minor component or even a trace component in other sources. Depending on the increase in the boron usage areas, the boron concentrations in environmental samples such as water, soil and air is also increasing. Therefore, it is important to determine boron in such samples accurately and precisely. In order to determine boron in various sample matrices, various analytical methods have been developed and used. This review focuses on the analytical methods for the determination of boron in various sample matrices. This review covers approximately the last four years (2015 - August 2018), offering a critical review of the boron determination by various techniques.

1. Introduction

Commonly found boron minerals in nature are tincal, colemanite and ulexite. The natural sources of boron are due to weathering of rocks, boric acid volatilization from seawater, and volcanic activities. Boron compounds such as boric acid and its sodium salts are used in various industries such as nuclear energy, insulation, metallurgy, borosilicate glass manufacturing, electronics, textile-grade fibreglass, bleaching agent, fire retardants, agricultural fertilizers and herbicides, and ceramic glazes [1]. Boron concentration increases especially in surface waters due to high water solubility of these boron compounds. Main boron compounds are boric acid (H_3BO_3) and metaborate anion $B(OH)_4^-$ in water samples at pH lower than 7 and higher than 10, respectively [2]. Boron concentration in waters depends on the source of the water such as surrounding geology and wastewater discharges. Therefore, strict control of the boron concentration in drinking water in all over the world is required. Boron concentration allowed in drinking water in Turkey is 1 mg/L. [3,4]. Allowable boron concentration is up to 2.4 mg/L according to the WHO guidelines [5] and 1.0 mg/L according to European Union directive [6]. In general, it is accepted that the concentration of boron in drinking-water should be below 0.5 mg/L in the world [6]. It was found that the boron concentration in sea water is between 0.5 to 9.6 mg/L with the mean value of 4.6 mg/L [7]. Boron is generally not present in the atmosphere at significant levels. Some of the atmospheric boron sources are evaporation of sea water, volcanic activities and industrial activities such as mining operations and glass industry.

Boron is both an essential and a toxic element for living organisms such as humans, animals and plants depending on its concentration [2]. There is a narrow margin between useful and harmful concentrations. Boron is necessary to provide the cell membrane function, enzymatic reactions [8] and the utilization of calcium for the human bone structure [9]. When given boric acid or borax to rats, mice and dogs by food or drinking-water, testicular lesions have been observed and no increase in tumor incidence observed in long-term studies [6]. Since boron is only useful at a certain concentration interval, accurate and precise determination of the boron in the samples is very important. Therefore, in the last decades to develop accurate, precise, simple and fast methods have gained considerable interest. Since boron mainly exists in water as boric acid with lower reactivity, the determination is difficult in water especially at lower concentration levels [10].

In recent years, various methods have been proposed for the detection and determination of total boron and also boron isotopes. These methods, including molecular spectrophotometric (UV-Vis spectrophotometric) and atomic spectrometric methods (mass spectrometry (MS), atomic absorption spectrometry (AAS), optical emission spectrometry (OES)), laser-induced breakdown spectrometry, electroanalytical methods and chromatographic methods have been reported [11 -13]. While mass spectrometric methods were mainly used for the determination of isotopic ratio of boron, the others were used for the determination of total boron.

Aggarwal et al. [14] published a review article related to determination of boron isotope ratio ($^{11}B/^{10}B$)

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and boron concentration in various matrices such as soil, water, environmental samples and agricultural samples by mass spectrometric techniques (thermal ionization, inductively coupled plasma and secondary ion mass spectrometry). In this review, mass spectrometric techniques were compared by considering their advantages and limitations, the certified isotopic reference materials available for boron were listed and sample preparation methods for boron were also discussed. It was concluded that MC-ICP-MS was the best for isotope ratio measurements by considering precision and accuracy and N-TIMS was suitable for boron determination at lower boron concentrations. Determination of $^{11}B/^{10}B$ isotopic ratios is also very important in the field of nuclear industry and agriculture. In particular, for enrichment and reactor applications accurate and precise determination of $^{11}B/^{10}B$ isotopic ratios in samples is needed [14]. For this purpose, it is accepted that precision and accuracy of about 0.1% is sufficient. By mass spectrometric techniques, relative precisions better than 0.1% has been achieved for the isotope ratio measurements for 10–50 ng/mL of boron in the solution [14]. Isotopic data for boron also depend on the origin of agricultural products. Because boron is an essential element for vegetation, its determination will help to increase the quality of agricultural products.

In this article, the published papers involving determination of boron and its isotopes in various matrices by various techniques were reviewed. It focuses primarily on the papers related to boron determination. The analytical performances (accuracy, precision, limit of detection, linear working range etc.) of the methods were discussed and compared. The methods have been reviewed under three sub-titles including (i) atomic spectrometric methods, (ii) molecular spectrometric methods, (iii) other methods (electroanalytical, chromatographic etc.).

2. Atomic spectrometric methods

Atomic spectrometric methods have been mostly used for boron determination in the literature recently. In most of the articles, ICP-MS and ICP-OES have been widely used as an analytical technique. In general, ICP-MS is mostly used for determination of $^{11}B/^{10}B$ isotope ratio, while ICP-OES is used for total boron determination. These methods have been standardized and accepted as Turkish Standard for the determination boron together with other elements [15, 16]. In last three years, only one article was published related to determination of boron by atomic absorption spectrometry. Altunay and Gürkan [17] proposed a new cloud-point extraction (CPE) method for the pre-concentration and simultaneous determination of Sb(III) and B(III) by FAAS. The proposed method was based on complexation B(III) with azomethine-H. Cetylpyridinium chloride (CPC) was used as a signal-enhancing agent. Then azomethine-H complex of boron was extracted into the micellar phase of Triton X-114. Linear working range, limit of detection and relative standard deviation were 2.5-600 µg/L, 0.75 µg/L and 1.9-2.3%, respectively for B(III). Recoveries of spiked samples of B(III) were in the range of 99-102%. The method was successfully applied to the determination of B in selected beverage and dairy products.

Kmiecik et al. compared the two reference methods; ICP-MS and ICP-OES for the determination of boron in water samples [7] and the effect of the sample preparation methods on the results was also investigated. Four different sample preparation methods ((i) filtered and acidified, (ii) unfiltered and not acidified, (iii) filtered and not acidified, (iv) unfiltered and acidified were applied and all samples were analysed by both ICP-MS and ICP-OES. Concentrations found by using ICP-MS and ICP-OES were statistically different regardless of sample preparation. The estimated relative standard deviation was lower than 20 % for both methods. Recovery of both methods (accuracy) was found as 80 to 120%. There is a difference between the mean value of the results obtained by ICP-OES and by ICP-MS. The results of ICP-OES was higher than that of ICP-MS. Mean boron concentrations were found as 1.19 mg/L and 2.02 mg/L for filtered and acidified water sample by ICP-MS and ICP-OES, respectively. Some matrix effects and especially high iron concentration were shown as the reason of these differences.

Strkalj and Glavas compared atomic spectroscopic methods for boron determination in the analysis of metallurgical samples [18]. Among the direct reading optical emission spectrometry (OES), the ICP-OES and GF-AAS, they found that OES and ICP-OES were more suitable for metallurgical samples. The authors also studied the effect of sample digestion process on the results and showed that sample preparation in a closed system increase the accuracy of the results.

Palma et al. [19] compared ICP-OES and azomethine-H UV-Vis methods for the determination of boron in leachate samples from sanitary landfills and groundwater. The two methods were evaluated by considering their analytical characteristics and applicability. It was found that precision and accuracy of Azomethine-H UV-Vis method were better than those of ICP-OES. However, differences between these two methods were not significant statistically by evaluating F-test and t-test up to 10 mg/L of the boron in various matrix. For routine analysis UV-Vis method based on the formation of azomethine-H complex method was suggested.

Yamamoto et al. investigated the optimum conditions for the determination of boron using GF-AAS [20]. The GF-AAS method had poor sensitivity due to insufficient thermal dissociation of boron compounds such as its oxides and carbides. Therefore, to increase sensitivity and decrease molecular absorption chemical

Table 1. Boron (^{11}B) determination by mass spectrometry.

Method	Sample	LOD	RSD,%	Linear range	Relative error, %	Refs.
LA-MC-ICP-MS	Roman glasses	-	0.03	-	-	21
ICP-MS	Silicon carbide	0.010 µg/g	-	-	0.053	22
ICP-MS	Geochemical reference materials	0.135 ng/mL	-	1 - 400 µg/g	below 10	23
ICP-MS	Tooth enamel		0.2			24
ICP-oa-TOFMS	Uranium-silicon-aluminium compounds	0.7 µg/L	-	-	0.08 for isotope ratio (^{10}B/^{11}B)	25
SI-MS	Silicate glass	-	0.15 (1 ng/g B)	-	-	26
ID-ICP-MS and MC-ICP-MS	Vegetation samples	-	0.036	-	-	27
MC ICP-MS	Foraminiferal shells	-	0.052	-	-	28
LA-MC-ICP-MS	Paleoproterozoic borate deposits	-	-	-	-	29
LA-MC-ICP-MS	Mica, pyroxene, and serpentine	-	2.88 to 3.31	-	-	30
ICP-MS	Foodstuffs	LOQ: 0.200 mg/kg	-	0–10 µg/L	Below -10	31
PTI-MS	Natural samples, gypsums	-	-	-	0.02	32
MC-ICP-MS	Carbonate Samples	-	0.04	25-125 ng/g	-	33
MC-ICP-MS	Small sample-size geological materials	-	0.035 for 10 ppb B		-	34
MC-ICP-MS	Pore water	-	0.024	50-300 µg/L	0.201	35

Table 2. Summary of analytical parameters of boron determination by optical emission spectrometry.

Method	Sample	LOD	RSD, %	Linear range	Relative error, %	Refs.
ICP-OES	Steel	-	-	-	1.9 – 5.3	36
ICP-OES	Silicon carbide	0.25, 0.50 and 1.2 µg/g	-	-	-	37
DCArc-OES	Geochemical samples	1 µg/g	4.57	-	-	38
MP-AES	Turkish red wine and white wine	0.08 µg/mL	-	up to 10 mg/mL	2 – 6 (recovery, 94%-102%)	39
ICP-OES	High-purity nickel	0.21 µg/g	-	-	-	40
ICP-OES	ductile iron	-	-	-	-	18
ICP-OES	Leachate samples from sanitary landfills and groundwater	0.25 mg/L	2	0 – 7.0 mg/L	8.54 for calibration method -3 for standard addition	19
MP-AES ICP-OES	Biosludge 1	0.001 mg/L 0.001 mg/L	2.4 1.8	0.0–2.0 mg/L	<6.5	41
ICP-OES	Natural samples, gypsums	0.006 mg/L	3.6	-	96–103% (Recovery)	42
ICP-OES	Uranium fuel samples	0.05 µg/g	9			43
MP-AES	Organic compounds	-	-	-	0.3	44
ICP-OES	Bşological sample	-	<2	-	99% (recovery)	45
ICP-OES	High silicon matrices	-		-		46
ICP-OES	Salt	0.006 mg/L	1.93-3.37	-	106.00% (recovery)	47
GD-OES	Fast breeder reactor components		<5	-	-	48
ICP-OES	Mineral fertilizer	-	7.1	-	-	49

modification was widely used. By using chemical modifiers pyrolysis temperature may be increased to about 1200 ºC which provides atomization of boron compounds by thermal dissociation. Yamamato et al. investigated the effects of different GF-AAS instruments and chemical modifiers on the boron absorbance. Ca, Fe, Cu, Si and Dy were tested as chemical modifiers. Iron nitrate was found as optimum reagent and used as chemical modifier. Under the optimum conditions the limit of detection was found as 0.0026 mg/L.

Table 3. Summary of analytical parameters of boron determination by molecular spectroscopic methods.

Method	Sample	LOD	RSD, %	Linear range	Relative error, %	Refs.
Azomethine-H UV-Vis	Leachate samples from sanitary landfills and groundwater	20 mg/L	1	0 – 10.0 mg/L	2.51	19
UV-Vis based on the boron–pyridoxine complex	Freshwaters	0.76 mg/L		0 – 8 mg/L		50
UV-Vis carminic acid assay	Oilfield water	0.16 mg/L	5	0 - 420 mg/L		51
HR-CS-GF-MAS	Water	-	0.13 - 0.5	-	0.15	52
Azomethine-H UV-Vis	Tap water, ocean water and eye drops	0.10 mg/L	<3%	0.35 - 3.0 mg/L	Recoveries 102% (for eye drops), 94% (for drinking water) and 93% (for ocean water)	53
UV-Vis carminic acid assay	Produced water					54
UV-Vis carminic acid assay	Oilfield water	0.3 mg/L	4.2	0-40.0 mg/L		55
Fluorimetric method	Water	0.11 ng/L		0-40 nM	Recovery 86.9 to 93.2%.	8

Some analytical parameters of the methods on boron determination given in published papers by mass spectrometry and optical emission spectrometry between 2015 and 2018 are summarized and given in Table 1 and Table 2, respectively.

3. Molecular spectrophotometric methods

Most of the molecular spectrophotometric methods for boron determination are based on the measuring molecular absorbance of boron complexes such as its azomethine-H, curcumin and carminic acid complex in UV-Vis ranges. The Azomethine-H method is the most widely used UV-Vis method due to its simplicity, sensitivity and fast application. Some fluorescent boron complexes have been obtained and used for fluorimetric boron determination [11]. However, in the period of 2015 – 2018 only one article was published about fluorimetric method [8]. The published papers on boron determination by molecular spectrometric methods in this period were discussed and some analytical parameters are summarized in Table 3.

3. Other methods

Boron was also determined by methods other than atomic and molecular spectroscopic methods. These are electroanalytical methods, chromatographic methods, nuclear methods and laser-induced breakdown spectroscopy (LIBS).

As one of the electroanalytical method, Liv and Nakiboğlu [2] proposed a voltammetric boron determination method in water and steel samples. They applied differential pulse voltammetry with a disposable pencil graphite electrode as working electrode and Ag/AgCl/KCl (3 M) electrode as reference electrode. The oxidation of tiron in the boron-tiron complex at pH 7.5 (phosphate buffer) was used for the determination. The effects of supporting electrolyte type and concentration, pH and ionic strength on the determination were investigated. Under the optimized conditions the LOD (3s) and percent relative standard deviation were found as 84 µg/L and 4.6% (for 1 mg B/L (N = 7)), respectively. The accuracy was given as recovery values. Recoveries were found as 90% - 103% for water samples and 94% - 108% for steel samples. Samples were also analyzed by ICP-OES and the results were compared. It was found that there is not statistically significant difference between them. Same authors [56] described another voltammetric method for determination of boron. In this method the poly xylenol orange-modified and oxidized pencil graphite electrode were used. The oxidation peak of tiron at +0.86 V at pH 8 (phosphate buffer) was used again for voltammetric determination. The LOD and LOQ were found as 28 and 83 µg/L, respectively. The RSD% was 4.89% for 0.2 mg/L boron. Linear working range was 83 to 900 µg/L. Boron could be determined in tap water, drinking water and eye lotion samples at the recoveries of

98.72, 100.53, and 100.14%, respectively. In another voltammetric study, Kajiwara et al. [57] used the ternary system for the determination of boric acid, salicylaldehyde (SA) and H-acid (HA). In this study, the voltammetric determination of boron using 5-fluorosalicylaldehyde (F-SA) was optimized. Using this method boron concentration could be determined within only 5 min with a LOD of 0.03 mg/dm^3 and a recovery ranges between 97-100%. Calibration graph equation was $\Delta I(\mu A) = 1.075C - 0.400$ ($R^2 = 0.999$), where C is the boric acid concentration in mg/dm^3.

In the period of 2015-2018, three papers were published about chromatographic boron determination. One of them was published by Raut et al. [58]. This method was based on the pyrohydrolysis extraction of boron and its determination in paraffin waxes borated with H_3BO_3 and B_4C with ion chromatography. Wax samples were mixed with U_3O_8 to accelerate the extraction of boron and to prevent the sample from flare up. Pyrohydrolysis was carried out at 950 °C. The recovery of B was found above 98%. Boron was separated as boron-mannitol anion complex in ion chromatography. Linear working range and LOD (S/N = 3) and reproducibility were found as 0.1 - 50 ppm, 5 ppb and 5%, respectively. Bita et al. [59] describe the simultaneous determination of boric acid (BA) and calcium fructoborate (CFB) in dietary supplements by a new high-performance thin-layer chromatographic (HPTLC) method. HPTLC silica gel G 60 F-254 precoated glass plates and 2-propanol-water 8:2 (v/v) were used as the stationary phase and mobile phase, respectively. The two boron-based compounds could be separated with the Rf values of 0.83 ± 0.01 (BA) and 0.59 ± 0.01 (CFB). The linear working ranges for BA and CFB were 0.2-0.8 µg/band and 1-4 µg/band, respectively. The LOD and LOQ values were 0.05 and 0.16 µg/band for BA and 0.27 and 0.83 µg/band for CFA, respectively. The accuracy expressed as recovery was 98-102%. In the next article, simultaneous determination of B, Cl and Mo as micronutrients [60] in plant samples by an ion chromatography (IC) method was described. A gradient elution with D-mannitol and NaOH was used. Analytes were separated by pyrohydrolysis. The linear calibration graph was obtained for B between 0.05 and 1 mg/L ($r^2 = 0.992$). The LOD for B was found as 19 µg/L. The proposed IC method was successfully applied for the analysis of real samples.

Several articles related to other spectroscopic methods such as laser-induced breakdown spectroscopy (LIBS) [61], nuclear activation analysis [62,63] has been applied for boron determination. Li et.al proposed a LIBS as a fast and accurate analytical method for boron determination [61]. In that study, LIBS-LIF was used for determining boron in nickel-based superalloys and steels. In the experiment, plasma was generated by a 532 nm laser for boron with a pulse energy of 60 mJ. Then, the 249.68/249.77 nm wavelength-tunable optical parametric oscillator laser (OPO laser) was focused onto the plasma at 2 µs later. Boron could be determined with a very high sensitivity. The LOD of boron in nickel-based superalloys and steels were found as 0.9 ppm and 0.5 ppm, respectively. It was shown that LIBS-LIF is suitable for boron detection in practice [61]. Guo et al. [64] proposed LIBS method to accurately and rapidly determine high boron content. In this method, molecular emission was used as an alternative method for boron content analysis. Boron monoxide (BO) radicals were determined by laser-induced radical fluorescence (LIBS-LIRF). Vibrational ground state excitation (LIRFG) and vibrational excited state excitation (LIRFE) modes were applied to measure BO radicals and compared. It was found that LIRFG achieved better sensitivity with a limit of detection of 0.0993 %(m/m). However, it was found that the LIRFE was more accurate [64].

PGAA was proposed for the determination of boron and hydrogen in raw materials, the crucibles, and the solidified blocks (ingots) used for manufacturing of multicrystalline silicon for solar cells [62]. The materials were analyzed with various methods based on neutron activation analysis. Distribution of boron in the ingots was successfully described with a Scheil curve. It was also shown that PGAA is suitable for bulk analysis. The detection limit of this method was found as ng/g order for boron.

5. Conclusion

This critical review focuses on the boron determination by various techniques. Among them optical emission spectrometry (OES) and mass spectrometry (MS) are still the most favorable methods. Inductively coupled plasma was mostly used as an excitation source in optical emission spectrometry for the determination of boron. A few papers were appeared involving other sources such as glow discharge (GD), DC arc and microwave plasma (MP). Different mass spectrometric methods such as inductively coupled plasma orthogonal acceleration time of flight mass spectrometry, isotope dilution inductively coupled plasma mass spectrometry, multi-collector inductively coupled plasma mass spectrometry, laser ablation multi collector inductively coupled plasma mass spectrometry, positive thermal ionisation mass spectrometry, secondary ion mass spectrometry, thermal ionisation mass spectrometry have been applied for the determination of boron. In general, while OES was used for the total boron determination MS was widely used for the determination of isotope ratio of boron ($^{11}B/^{10}B$) in various sample matrices. Only one paper was published related to FAAS detection and GF-AAS detection. It can be concluded that trace boron cannot be determined directly by FAAS. It should be separated and/or preconcentrated from the sample matrix before FAAS detection. In GF-AAS method, without chemical modification boron determination is very difficult due to less atomization of boron compounds. It is needed to increase pyrolysis temperature by using suitable chemical modifiers. Few papers were published about chromatographic and voltammetric methods. Studies about spectrophotometric and spectrofluorometric boron determination methods still continue for routine analysis. LIBS seems as the future method for the determination of boron. Almost all elements in any physical form can be determined simultaneously by LIBS rapidly. Sample preparation is simple and nearly nondestructive [61]. Determination of light elements, such as boron, carbon, phosphorus and sulfur in various samples can be performed by LIBS.

In order to prevent matrix interferences and/or to enhance sensitivity of a method some pretreatment procedures have been applied in most techniques before determination of boron. Most of the pretreatment procedures involve preconcentration and/or separation procedures such as solid phase extraction, liquid-liquid extraction, dispersive liquid-liquid microextraction, ion-exchange method and cloud-point extraction [17, 24,42,43,59,65-69].

Abbreviations

CPE: Cloud point extraction

DCArc-OES: Direct current arc - optical emission spectrometer

FAAS: Flame atomic absorption spectrometry

GD-OES: Glow discharge optical emission spectrometry

GF-AAS: Graphite furnace atomic absorption spectrometry

HPTLC: High-performance thin-layer chromatography

HR-CS-GF-MAS: High-resolution continuum source grapite furnace molecular absorption spectrometer

ICP-OA-TOFMS: Inductively coupled plasma orthogonalacceleration time of flight mass spectrometry

ID-ICP-MS: Isotope dilution inductively coupled plasma Mass Spectrometry

LA-MC-ICP-MS: Laser ablation multi collector inductively coupled plasma mass spectrometry

LIBS: Laser-induced breakdown spectroscopy

LIBS-LIF: Laser-induced breakdown spectroscopy assisted by laser-induced fluorescence

LOD: Limit of detection

LOQ: Limit of quantification

MC-ICP-MS: Multi-collector inductively coupled plasma mass spectrometry

MP-AES: Microwave plasma-atomic emission spectrometry

PGAA: Prompt gamma activation analysis

PTI- MS: Positive thermal ionisation mass spectrometry

RSD: Relative standard deviation

SI-MS: Secondary ion mass spectrometry

UV-Vis: Ultraviolet-visible spectrophotometry

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