HORIBA Scientific

Application Note

Chemistry

ICP-OES

ICP56

High performance analysis of Boron with ICP-OES

Boron is a low abundance element in both the solar system and the Earth's crust. It is concentrated on Earth by the water-solubility of its more natural-occuring compounds, the borate minerals. Such minerals are mined industrially as evaporate ores such as borax and kernite.
Boron is used for several applications in industry. Its main use is in the form of sodium tetraborate pentahydrate for making insulating fiberglass and sodium perborate bleach. Borax is used in detergents formulation and bleaching agents. Boron is also used as a dopant in the semiconductor industry and the high-hardness Boron compounds are used as abrasives.
Boron is also well known for its ability to capture thermal neutron due to its high cross-section and it is then widely used in the nuclear industry where it acts as a shield. In nuclear reactors, boron is used for reactivity control and in emergency shutdown systems. For such applications boron is in the form of borosilicate control rods or as boric acid. Boric acid is also added to the reactor coolant when the plant is shut down for refueling. For such application, monitoring the concentration of boron is more than necessary to prevent any issue.
Boron content of glass used for nuclear waste vitrification has also to be monitored to prevent from any issue as it ensures security of the storage.
Inductively Coupled Plasma – Optical Emission Spectrometry is well suited for boron analysis as it allows reaching low detection limits but main issue is related to memory effects occurring. Since years, it has been reported that high concentration of boron are creating memory effects due to boron that literally sticks on all surfaces which are in contact with the solution or the aerosol. It means the whole introduction system, i.e. tubing, nebulizer and spray chamber, but also the injector of the torch.
This application note evaluates the performance of HORIBA Scientific ICP-OES instruments for boron analysis. Several parameters are evaluated such as sensitivity, linearity, accuracy, repeatability, robustness and memory effects.

Operating conditions

All analyses were done using the ULTIMA 2 ICP-OES. The characteristics of this spectrometer are given in table 1.

Table 1. Characteristics of the ULTIMA 2

Parameters	Specification
Generator	40.68 MHz Solid state, water cooled
Optical system	Czerny Turner (1 m focal length)
Grating	2400 g/mm
Thermoregulation	+32°C
Nitrogen purge	3 L/min
Resolution	< 5 pm in the 120 – 320 nm range (1st order) < 10 pm in the 320 – 800 nm range (2nd order)
Plasma observation	Vertical torch Radial viewing with Total Plasma View*
Introduction system	Inert parallel flow nebulizer Cyclonic glass spray chamber
Pump tubing	Black-black pump tubing for sample Grey-grey pump tubing for drain

** Total Plasma View: measurement of the whole Normal Analytical Zone of the plasma for enhanced sensitivity*

An inert parallel flow nebulizer was used to allow handling high concentrations of boron that may crystallize at high concentration. This nebulizer was associated with a cyclonic glass spray chamber.

The ULTIMA 2 is equipped with the unique fully demountable torch, the 3 mm i.d. alumina injector and the original sheath gas device. The 3 mm i.d. injector increases the residence time of the sample into the plasma leading to enhanced sensitivity and reduced matrix effects while the sheath gas reduces the contact between the injector and the sample, eliminating deposits issues and memory effects.

All plasma parameters, power, gas flows, are optimised to get sensitivity along with long term stability and are given in Table 2.

Table 2. Operating conditions

Parameters	Specification
Power	1100 W
Plasma gas	12 L/min
Auxiliary gas	0 L/min
Sheath gas	0.2 L/min
Nebuliser gas	0.65 L/min
Sample uptake	1 mL/min

All measurements are performed using a 20/80 µm slit combination with 4 seconds integration time for the line and 2 seconds for the background.

Analytical results

Sensitivity

Sensitivity is important as Boron should be analyzed at low concentrations for some samples.

Sensitivity was determined using a 3 points calibration curve: a blank, a 2.5 mg/L standard and a 5 mg/L standard. A blank was then analyzed with 10 replicates. The limits of detection and quatification were calculated using the formulae below:

LOD = 3 x s.d.

LOQ = 10 x s.d.

Where LOD is the limit of detection, LOQ the limit of quantification, s.d. the standard deviation obtained for the blank.

Detection and quantification limits obtained are given in Table 3 for a sensitive and a non sensitive line.

Table 3: Detection and quantification limits for Boron

Element	LOD (µg/L)	LOQ (µg/L)
B 206.665	46	153
B 249.678	1.1	3.8

Linearity

Linearity means reduced analysis time as it implies that a single line can be used to cover a wide range of concentration, thus a reduced number of standards can be used.

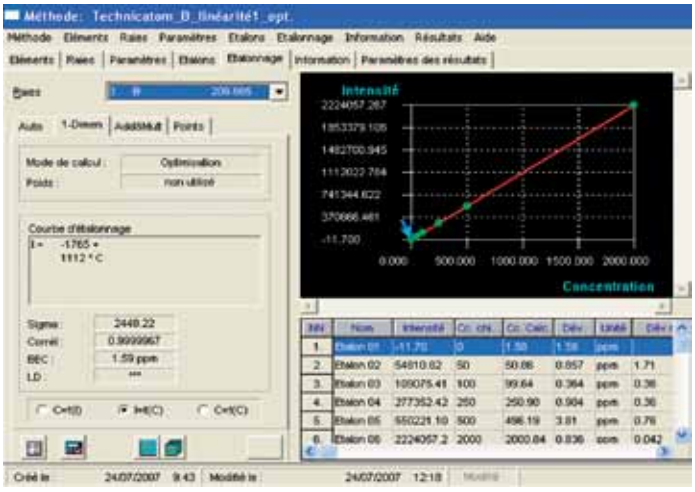
Linearity was evaluated using several calibration standards from 50 to 2000 mg/L. The measurements were done 3 times to check for accuracy of data.

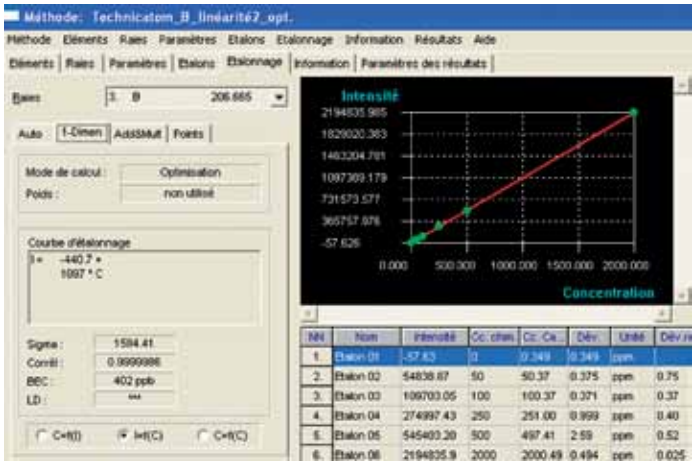
Standards used for calibration are given in Table 4.

Table 4: Standards for linearity evaluation

Elt	Std 0 (mg/L)	Std 1 (mg/L)	Std 2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)	Std 5 (mg/L)
B	0	50	100	250	500	2000

Calibration curves obtained are displayed below. Linear regression was used without any weighting procedure for B 206.665 nm. For B 249.678 nm that is more sensitive, weighting procedure was applied to improve the fitting for low concentrations (weight of $1/\sqrt{c}$ was used, where C is the concentration).





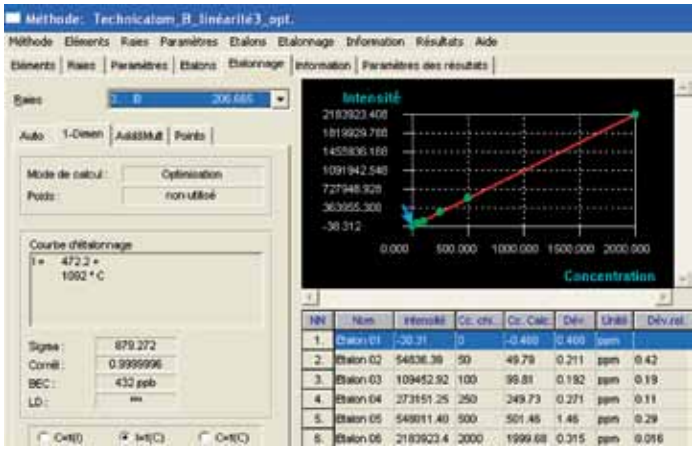
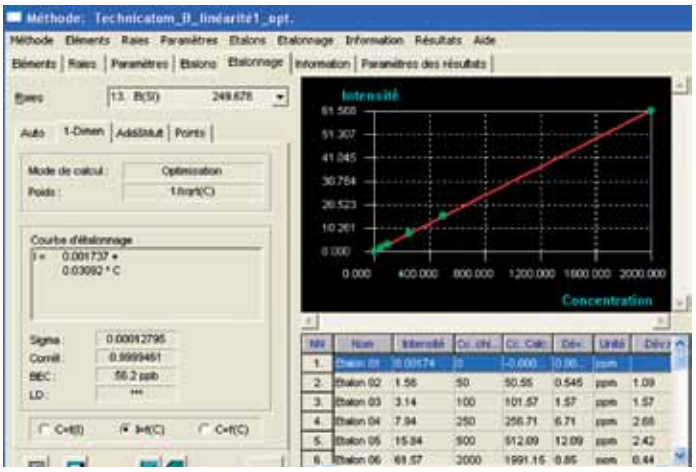
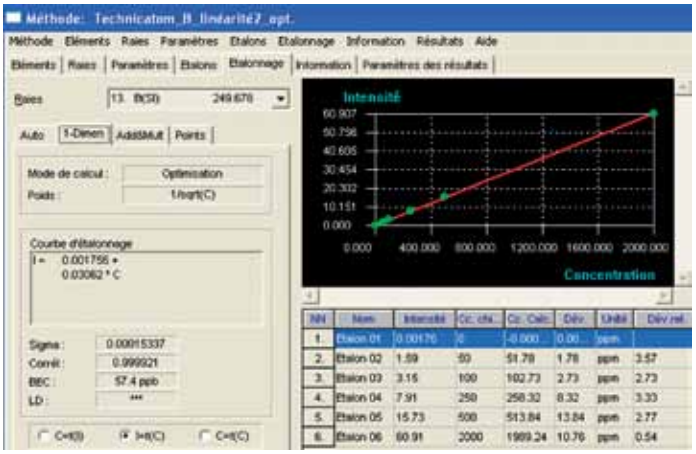


Figure 1: Calibration curves obtained for B 206.665 nm





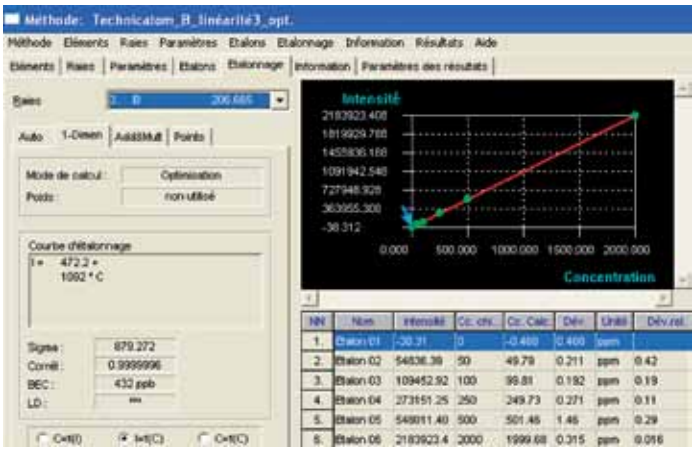


Figure 2: Calibration curves obtained for B 249.678 nm

All correlation coefficient are better than 0.999 for both B 249.678 nm and B 206.665 nm. Residuals are always less than 2% for B 206.669 nm and less than 5% for B 249.678 nm, showing an excellent agreement between given concentrations and calculated concentrations.

Linearity is obtained on a wide range of concentration, proving that analysis of low and high concentrations can be performed on a single line.

Accuracy

For accuracy evaluation, a Reference Material was used, prepared at various concentrations (10, 25, 50, 100, 500 and 1250 mg/L), and analyzed using the calibration curves previously established. To match customer's expectations, the instrument should allow determination of Boron with less than 1% for concentrations lower than 100 mg/kg and less than 0.5% for concentrations less then 100 mg/kg.

Lithium was added to all samples (10 mg/L Li) and used as internal standard to correct for small drifts and improve accuracy.

Results obtained are presented in Tables 5 and 6 below for the 2 selected lines. For improved accuracy, low concentrations (lower than 50 mg/L) are determined using B 249.678 nm and weighted fit with calibration standards ranging from 50 to 250 mg/L. For high concentrations, B 206.665 nm was used with unweighted calibration and standards ranging from 50 to 2000 mg/L.

Table 5: Results for low Boron concentrations with B 249.678 nm

Theoretical conc (mg/L)	Measured conc (mg/L)	SD (mg/L)	RSD (%)	Specification
10	9.99	0.05	0.54	9.9 - 10.1
25	25.05	0.09	0.36	24.75 - 25.25
50	49.97	0.26	0.53	49.5 - 50.5

Table 6: Results for high Boron concentrations with B 206.665 nm

Theoretical conc (mg/L)	Measured conc (mg/L)	SD (mg/L)	RSD (%)	Specification
100	99.79	0.50	0.50	99 - 101
500	501.64	2.76	0.55	497.5 - 502.6
1250	1250.78	7.31	0.58	1243.75 -1256.25

Excellent accuracy is obtained for both B 249.678 nm and B 206.665 nm lines, meeting expectations.

Repeatability

To evaluate the repeatability, the 50 mg/L and 250 mg/L standards were analyzed 10 times using 5 replicates with rinse between each sample. A stability test over 1 hour is then obtained.

Results obtained are displayed in Table 7 for 50 mg/L using B 249.678 nm and in Table 8 for 250 mg/L using B 206.665 nm.

Table 7: Repeatability test for 50 mg/L using B 249.678 nm

-	Sample	Time	-	Conc (mg/L)	RSD (%)
B 249.678	50 mg/L	15:42		49.6	0.4
	50 mg/L	15:47		49.6	0.6
	50 mg/L	15:51		49.5	0.4
	50 mg/L	15:56		50.3	0.5
	50 mg/L	16:01		50.3	0.3
	50 mg/L	16:05		50.2	0.3
	50 mg/L	16:10		49.7	0.3
	50 mg/L	16:15		49.5	0.3
	50 mg/L	16:19		49.6	0.5
	50 mg/L	16:28		49.9	0.2
	50 mg/L	16:33		49.9	0.6
			Mean	**49.8**	**0.4**
			SD	0.3	
			RSD%	**0.6**	

Table 8: Repeatability test for 250 mg/L using B 206.665 nm

-	Sample	Time	-	Conc (mg/L)	RSD (%)
B 206.665	250 mg/L	17:26		250.8	0.5
	250 mg/L	17:32		249.5	0.4
	250 mg/L	17:39		250.6	0.4
	250 mg/L	17:46		251.8	0.2
	250 mg/L	17:53		250.6	0.6
	250 mg/L	17:59		250.6	0.5
	250 mg/L	18:06		248.2	0.4
	250 mg/L	18:13		248.4	0.6
	250 mg/L	18:20		248.3	0.5
	250 mg/L	18:27		248.7	0.5
			Mean	**249.8**	**0.5**
			SD	1.3	
			RSD%	**0.5**	

Excellent repeatability was obtained on both short and long term with all RSDs lower than 0.7% over 1 hour. RSDs of each measurement are also lower than 0.7% showing the stability of each measurement and then the ability of the spectrometer to stabilize within few seconds after introduction of the sample into the introduction system.

Robustness

The robustness was evaluated as the capability of the spectrometer to give a concentration over a long period of time, with natural variations of measurement conditions (temperature of the laboratory…). The 50 mg/L standard was then analyzed just after calibration and then measured again after 1 hour, 2 hours, 4 hours and 4.5 hours without any recalibration.

Results are given in Table 9 for both B 249.678 nm and B 206.665 nm.

Table 9: Robustness results for the 50 mg/L standard

-	Sample	Time	-	Conc (mg/L)	RSD (%)
B 206.665	50 mg/L	15:05		50.0	0.4
	50 mg/L	16:12		49.5	0.4
	50 mg/L	17:13		50.0	0.4
	50 mg/L	18:54		50.0	0.5
	50 mg/L	19:34		49.5	0.4
			Mean	**49.8**	**0.4**
			SD	0.3	
			RSD%	**0.5**	

-	Sample	Time	-	Conc (mg/L)	RSD (%)
B 249.678	50 mg/L	15:05		50.3	0.5
	50 mg/L	16:12		50.5	0.3
	50 mg/L	17:13		50.1	0.5
	50 mg/L	18:54		49.8	0.5
	50 mg/L	19:34		49.6	0.2
			Mean	**50.1**	**0.4**
			SD	0.4	
			RSD%	**0.7**	

RSDs obtained on 4.5 hours for Boron analysis show excellent robustness of the method, ensuring quality of the results over hours.

Memory effects

As Boron is known for memory effects and issues with rinsing time, it was mandatory to include it in the study as it will affects the analysis time and the accuracy of the results.
A calibration was done using a blank and a 250 mg/L standard. A 2000 mg/L sample was then analyzed during 2 minutes and the calibration blank was then measured every 2 minutes until it reaches the initial calibration blank value. For this test, the most sensitive line was used.

Rinsing was done using acidified water without any other reagent. It is reported than mixtures of ammonia and D-Mannitol help to reduce rinsing time with creation of a complex of Boron with D-Mannitol in Ammonia. However, such mixtures imply higher stabilization time due to the stabilization of the spray chamber that is necessary between acid samples and ammonia. Careful optimization of amounts of reagents is also required as the formation of the complex may continue if too high amounts are used, inducing a bias on the result.

The results obtained are displayed in the Table 10 and Figure 3.

Table 7: Repeatability test for 50 mg/L using B 249.678 nm

B 249.678	Sample	Time	Net Intensity	Comments
	Blank	15:52	1048.788	I_0: Calibration blank value
	250 mg/L	15:55	2833394.048	250 mg/L standard
	Blank	15:59	1243.536	Calibration blank value after 250 mg/L standard and reduced rinsing time
	2000 mg/L	16:24	21063757.938	2000 mg/L Boron sample
	Blank	16:26	6469.925	
	Blank	16:35	1621.799	
	Blank	16:37	1378.476	
	Blank	16:40	1236.595	
	Blank	16:42	1116.513	
	Blank	16:44	1046.264	
	Blank	16:47	1030.333	$I < I_0$
	Blank	16:49	1033.233	
	Blank	16:51	1032.072	

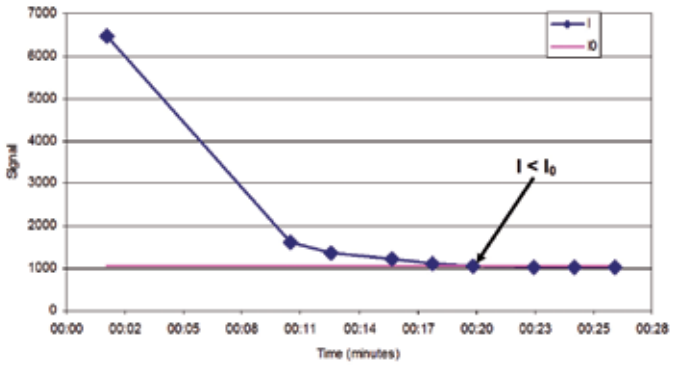


Figure 3: Rinsing time for Boron using B 249.678 nm line

Only 20 minutes are necessary to rinse the system and reach the calibration blank value after the analysis of a 2000 mg/L Boron sample. This performance is possible due to the reduced sample path between the spray chamber and the torch and also thanks to the original sheath gas device that insulates the aerosol of the spray chamber from the inner walls of the injector.

Conclusion

The performances obtained with the ULTIMA 2 ICP-OES spectrometer for Boron analysis are excellent. Unrivaled sensitivity and linearity are achieved thanks to the optical quality of the monochromator, the PMT detection device and the radial viewing mode with Total Plasma View allowing the measurement of the whole Normal Analytical Zone. The combination of this high quality optics and the introduction system design with a reduced path between the spray chamber and the plasma as well as the original sheath gas device allows exceptional performances in terms of accuracy, repeatability, robustness and memory effects.

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