Determination of Boron in Fertilizer Materials by ICP-OES

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Why is this important?

- Magruder Check Sample Program **Method Code 165.03** *(Acid Soluble Boron, **ICP**)*
- **14 labs** reported B results by ICP for February **Sample 180211**, *but no Official Method exists?*
- ***No known documented, validated, or commonly shared ICP-OES fertilizer Boron method?***
- **20 labs** reported Boron results by "other" method, so some of these labs might be using or move to an ICP method, if one was published.
- ICP-OES may be used as a "screening" method by some, but would prefer to see method move to official status.
- This presentation is an effort to start a process of documenting and validating a method.

Advantages of B by ICP

- Productivity/speed
- Unattended analysis vs. AOAC **titrimetric** or **spectrophotometric** methods
  - *949.02 Boron (Acid-Soluble) in Fertilizers, Titrimetric Method*
  - *949.03 Boron (Water-Soluble) in Fertilizers, Titrimetric Method*
  - *982.01 Boron (Acid- and Water-Soluble) in Fertilizers, Spectrophotometric Method*
- Broad analytical concentration range is possible
- Limited waste generation

Challenges with B by ICP

- **Boro**silicate composition of glassware, nebulizer, spray chamber and torch are potential sources of Boron contamination
- Can have some carry-over or memory effects
- **Minimum guarantee for product registration *(AAPFCO OP, No 71 p. 45)* = 0.02%**
  - = **0.8 mg / L Boron** with a 1 g sample to 250 ml volume (AOAC 982.01)
- Highest current guarantee is 20% Boron (Na Borate; Solubor/Borax)
  - = **800 mg / L Boron** with a 1 g sample to 250 ml volume (AOAC 982.01)
- Several Boron wavelengths with varying strength/intensity

Why not test B with other Secondary & Trace Metals?

- Its possible, but poses some challenges, especially for low and high concentration samples
- **Borosilicate glassware** – potential contamination from many commonly used glassware sources and less convenient to use Nalgene flasks or other composite materials for all samples and ICP
- Carry-over or memory effects from high concentration samples
  - Need a "scrubber" and longer washout times
- Detection limit concerns for low guarantees
  - With microwave and 0.5 g to 100 ml digestion, a 0.02% Boron guarantee = 1 mg/L (ppm) in solution
  - ICP is very sensitive for B, especially in axial view, but may have contamination and/or carry-over from previous sample(s) impacting accurate recovery of a 1 ppm solution
- Boron is **NOT** part of the new microwave, mixed-acid method, i.e. ***AOAC 2017.02***
- If use AOAC 982.01 extraction, need to matrix match acid strength/type with calibration standards
- For these reasons, we recommend a dedicated ICP-OES method for just Boron

Sample Extraction

- See **AOAC 982.01 B. (a)** :
  - *1 g sample + 40 mL water + 10 ml HCl*
  - *Shake for 20 min*
  - *Bring to 100 ml vol*
- *Use Nalgene bottles for extraction*
- *Use Nalgene volumetric flasks*
- **Modified to accommodate broader range**:

Boron Guarantee	ICP Conc (mg/L)	Recommended Wt *	Volumetric Flask *	Additional HCl
< 0.50%	< 200	4.00 g	100 ml	none
0.50 to 1.00%	100 - 200	2.00 g	100 ml	none
1.00 to 3.00%	100 - 300	1.00 g	100 ml	none
3.01 to 10.00%	75 - 250	0.50 g	200 ml	10 ml
> 10.00%	> 125	0.25 g	200 ml	10 ml

* Assumes top calibration std of 400 ppm B.

Minimum guarantee of 0.02% B = 8 mg/L, well above extraneous contamination and detection levels

Boron "Scrubber"

- *D-Mannitol: $C_6H_{14}O_6$; CAS 69-65-8; Sigma Aldrich, M9546-1KG*
- 1% in wash solution **and** 2% in internal standard solution
  - Reference: *The Investigation of Boron Measurement Utilizing Varian Vista – MPX Simultaneous ICP-OES with Radial Viewing and CETAC Technologies Ultrasonic Nebulizer*
    - *Note: can use with other conventional nebulizers and/or axial view*
  - *Source:* www.teledynecetac.com/Search/Pages/results.aspx?k=boron%20determination
    - *Authors: Christine Rivera (Agilent) and Fred Smith (CETAC)*
- Use a longer rinse time between samples *(i.e. 2 to 3 minutes)* and/or use *"Smart Rinse™"* feature to ensure no carry-over or residual Boron in system

ICP-OES Conditions

Torch Configuration	Radial – one piece
Power	1.25 kW
Nebulizer Flow	0.70 L/min
Plasma Gas Flow	15 L/min
Auxiliary Flow	1.5 L/min
Viewing Height	10 mm
Integration Time	30 sec
Instrument Delay/Stabilization	75 sec
Replicates	3

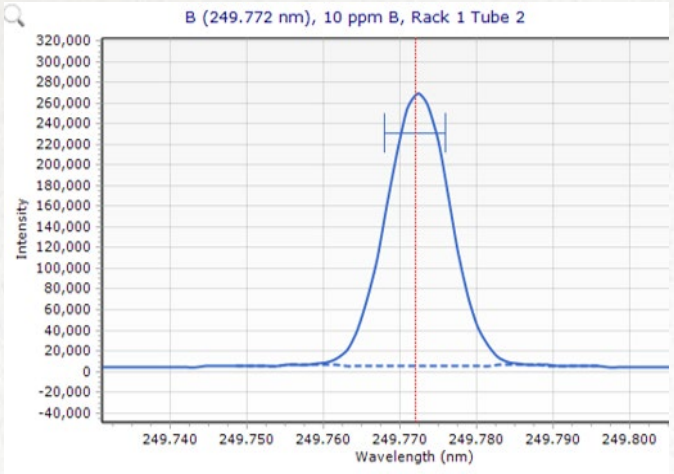
- Two instruments: ***Agilent 720 Axial View*** &

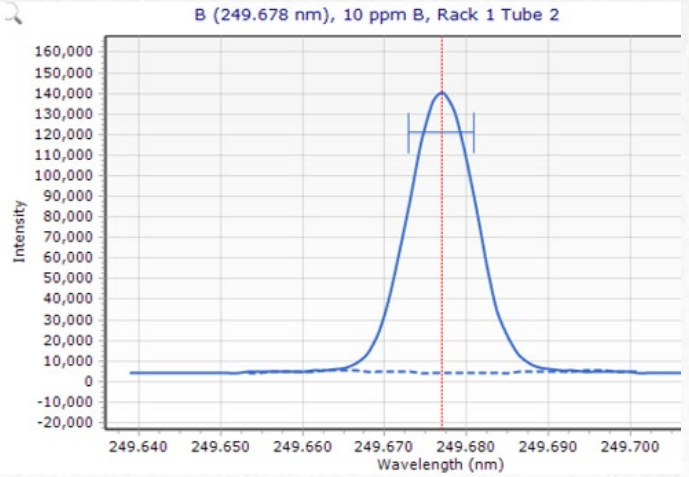
  Agilent 5100 Synchronous/Dual View

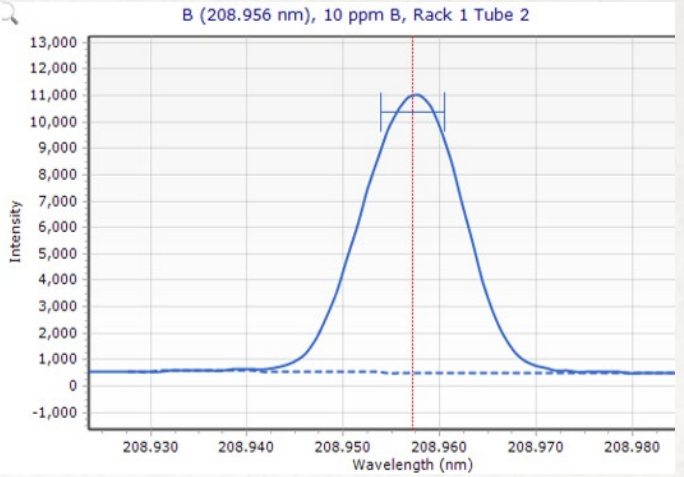
- Wavelengths:
  - 249.772 nm, strongest wavelength, but limited linear dynamic range in axial view
  - 249.678 nm, approximately half the signal of 249.772; good confirmation line and can use to expand the working range.
  - 208.956 nm, about 5% of the signal intensity of 249.772; good for expanding the working range.
  - If necessary, can also use axial view for lowest detection and radial view to expand the working range.
- Conditions listed are from Rivera and Smith study; can use shorter integration times especially with axial view

Relative Intensities for 10 ppm B: *Axial ~ 5X Radial*

- Axial:







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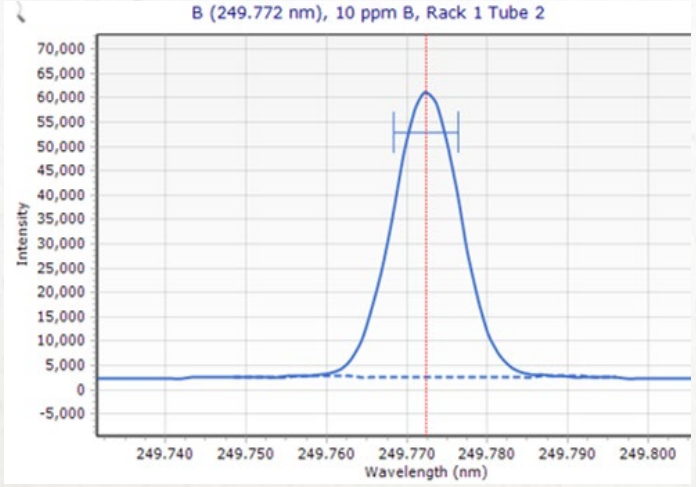
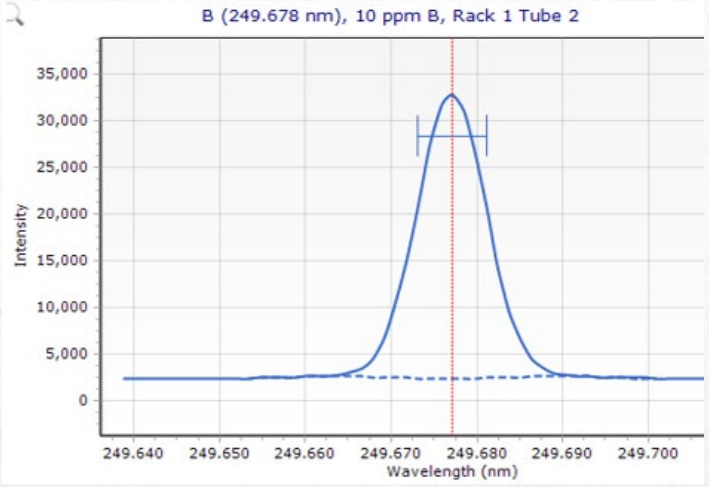
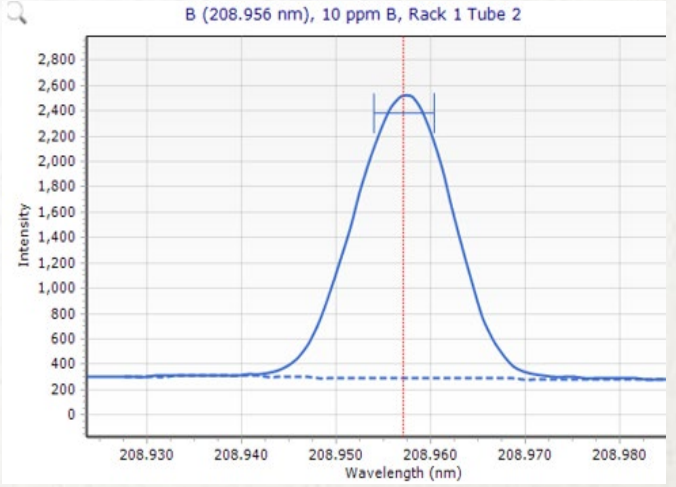






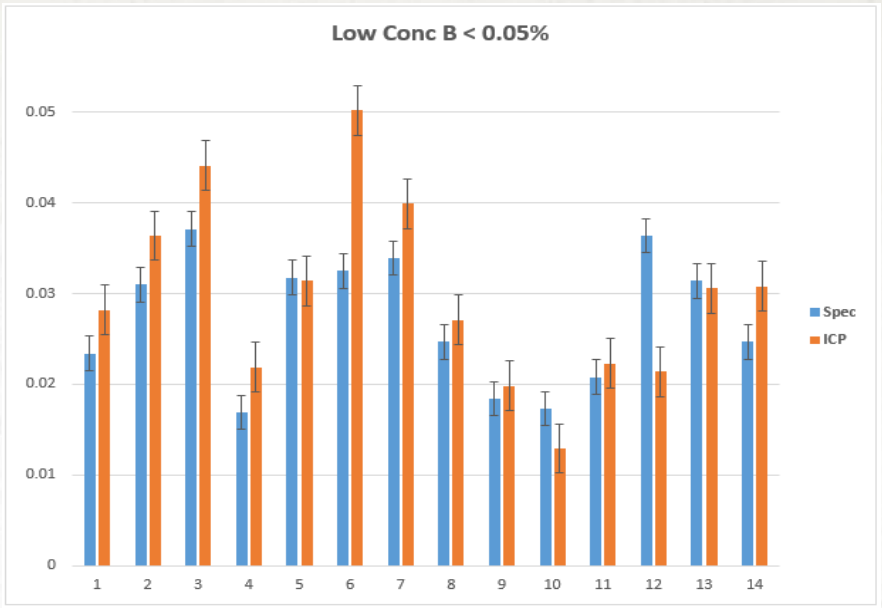
Comparison of ICP-OES Results to Official Method

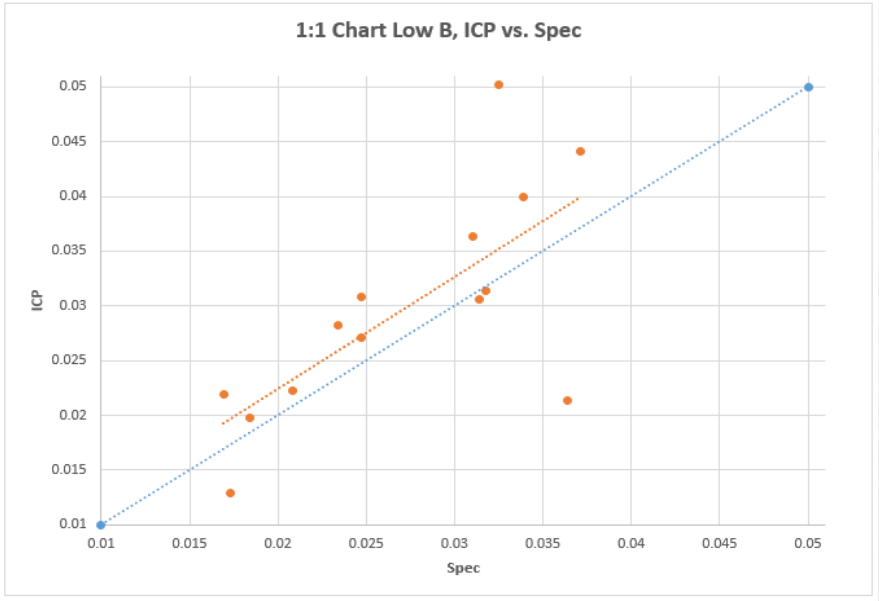
- Official: AOAC 982.01, *Acid-Soluble Boron in Fertilizers, Spectrophotometric Method*
- 18 samples, ranging from 0.0125% to 14.92% B
- t-test (P = 0.05): *overall result were statistically similar*
  - *A few individual samples that were statistically different*
- Slightly higher trend with low Boron concentrations
  - *e.g. 0.025 Spec = 0.025 to 0.030 ICP*
  - *Slightly higher results consistent with Magruder Check Sample data*
  - *ICP may have greater sensitivity than manual spectrophotometer, but this needs to be verified*
  - *Need to ensure source is not from contamination or carry-over*

Data – Low Conc

ICP	Spec
0.0282	0.0234
0.0364	0.0310
0.0441	0.0371
0.0219	0.0169
0.0314	0.0318
0.0502	0.0325
0.0399	0.0339
0.0271	0.0247
0.0198	0.0184
0.0129	0.0173
0.0223	0.0208
0.0214	0.0364
0.0306	0.0314
0.0308	0.0247
1.19	1.10
8.86	9.12
14.64	14.92
3.59	3.37
1.59	1.61

average=

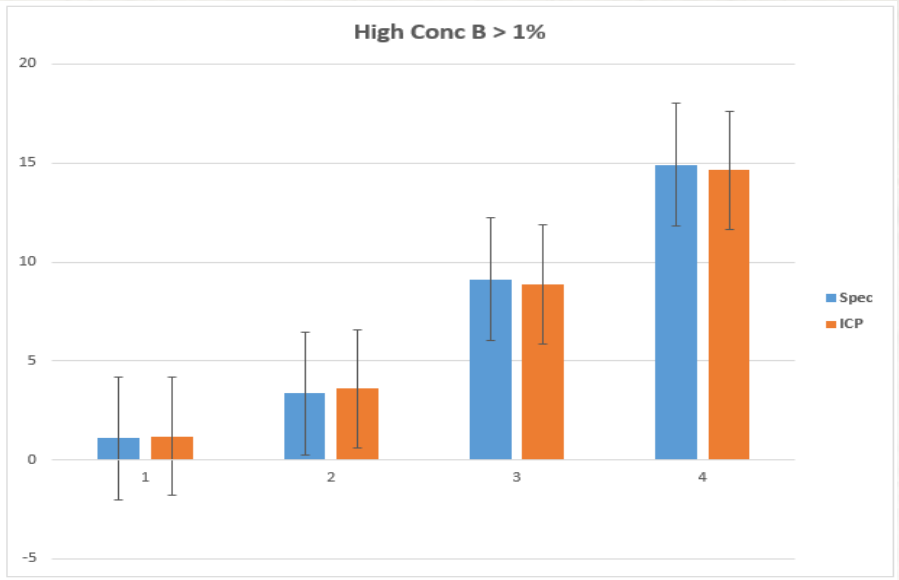


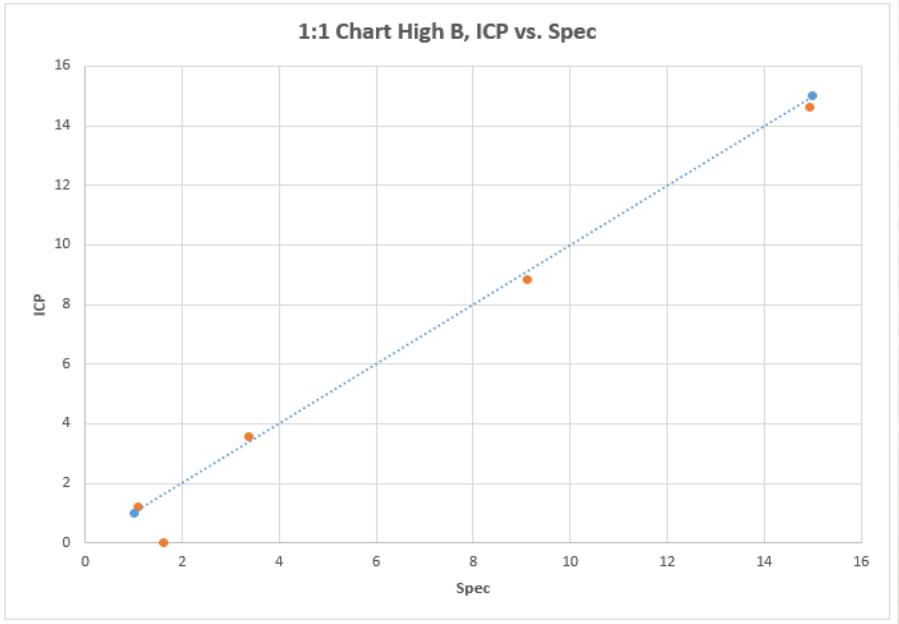


Data – High Conc

ICP	Spec
0.0282	0.0234
0.0364	0.0310
0.0441	0.0371
0.0219	0.0169
0.0314	0.0318
0.0502	0.0325
0.0399	0.0339
0.0271	0.0247
0.0198	0.0184
0.0129	0.0173
0.0223	0.0208
0.0214	0.0364
0.0306	0.0314
0.0308	0.0247
1.19	1.10
8.86	9.12
14.64	14.92
3.59	3.37
1.59	1.61

average=





Accuracy

QC Material	Method	Consensus/Content	Proposed Method	% Recovery
Magruder 170411	Spectrophotometric	0.2467 +/- 0.0449	0.2544%	102.96%
	ICP	0.2745 +/- 0.0449		92.68%
Boric Acid	Reagent Grade	17.48%	17.89%	102.34%

- Would need more materials for a method validation study, but recoveries for known or consensus materials are good

Recommendation

- Solicit method information from other labs testing B by ICP-OES for comparison to candidate method
- Proposed method parameters and preliminary results are sufficient to start a SLV *(Single Lab Validation)* study
- Conduct a SLV study and publish in JAOAC
- If results meet acceptance criteria, then conduct a full collaborative study
- With the *Magruder Check Sample Program*, it may be possible to use that venue to collect collaborative study data

Conclusion

- Boron determination by ICP-OES offers processing efficiencies that save time and effort
- Preliminary results are within the consensus standard deviation range for Magruder Check Samples
- Results are statistically similar with AOAC 982.01
  - Further investigation of some individual samples may be warranted
- Several labs using some derivation of an ICP method, but very limited external documentation
- Method is a good candidate for SLV and further Collaborative study
- More work is needed, but preliminary results are very encouraging

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