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The Investigation of Boron Measurement Utilizing Varian Vista – MPX Simultaneous ICP-OES with Radial Viewing and CETAC Technologies Ultrasonic Nebulizer

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The ICP-OES technique has many advantages over atomic absorption techniques for the determination of boron (B). The detection limits are low while the linear range is quite broad. However, boron will adhere to glass surfaces in the sample introduction, which increases analysis time because of increased rinse times. Boron is soluble in dilute nitric acid (HNO_3) and in hydrofluoric acid (**HF**). Typically rinse solutions of dilute HF have been used to eliminate boron from the sample introduction system. This poses two additional problems. First, the sample introduction must be inert to HF. Second, most laboratories do not want to use HF for routine analysis due to the potential hazard to the analyst.

This study will investigate using mannitol as a rinse alternative to HF. Mannitol is a less hazardous sugar derivative and a gem diol. A gem diol signifies a compound that has two hydroxy groups on a single carbon. The gem diols are typically unstable and therefore, act as a modifier that scavenges the boron from the sample introduction system. Figure 1 shows the mannitol structure.[1]

Figure 1 - Mannitol Structure
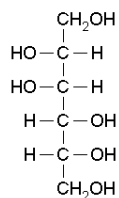
The study will evaluate the rinse time using a 2% mannitol rinse solution for the standard sample introduction system. Boron will be determined in certified standard reference materials. Since ICP-OES is a multi-element technique, nine other elements will also be determined; silver (**Ag**), arsenic (**As**), cadmium (**Cd**), chromium (**Cr**), copper (**Cu**), iron (**Fe**), manganese (**Mn**), lead (**Pb**) and selenium (**Se**). Detection limits, limits of quantitation, recoveries and time of analysis will be presented for B with the standard sample introduction (**SSI**) system and radial viewed plasma. Recoveries of the other nine elements will serve to verify that the mannitol does not enhance or suppress signal. The goal is to keep the multi-element functionality of the ICP-OES technique while speeding up the analysis time by decreasing rinse times.

The second part of the study will investigate the use of an ultrasonic nebulizer (**USN**). The USN is a front-end accessory used to increase sensitivity of analytes on the ICP-OES instrument. The increased sensitivity is due to the fact that the USN is a factor of 5 more efficient than standard pneumatic nebulizers (~ 2% efficient). Figure 2 shows a schematic of a standard USN.

Figure 2 - Schematic of USN
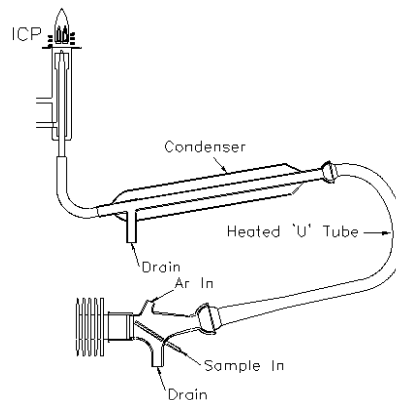
Schematic contributed by CETAC Technologies, Omaha, NE

The ultrasonic nebulizer uses a peristaltic pump to introduce the sample across an oscillating piezoelectric transducer. The oscillations disperse the sample into a fine aerosol, which is swept out of a spray chamber by a flow of argon gas (the nebulizer gas) from the host ICP-OES or ICP-MS instrument.

The aerosol then passes through a heated tube (user programmable from 120° C to 160° C) and an electrothermally cooled condenser (user programmable from – 20° C to + 10° C). An integrated drain pump removes the condensed sample solvent and any excess sample liquid from the spray chamber. After the condenser, dried aerosol particles are swept by the nebulizer to the ICP instrument for analysis.[2] Since the sample is vaporized by the USN, the plasma is primarily an excitation source only.

The challenge of using the USN to achieve low detection limits for B is the system is comprised of all glass/quartz materials. Boron will adhere to these surfaces. Further, B signal decreases by a factor of 15 when desolvated in the ultrasonic nebulizer. It has been proposed that the B does not condense into the aerosol after the heated u-tube. This study evaluates the use of mannitol as a chemical modifier added to each solution in addition to its use as a scavenger in the rinse.

Detection limits, recovery of standard reference materials, limit of detection and rinse times are reported for B. A comparison of signal with and without mannitol as a modifier is given. Finally, Ag, As, Cd, Cr, Cu, Fe, Mn, Pb and Se values for certified reference materials are reported to verify that the addition of the mannitol will not preclude the determination of other analytes.

Equipment
The instrument used for this study was a Varian Vista – MPX with radial viewing. The Vista – MPX is a simultaneous ICP-OES instrument that uses a thermostatted echelle

polychromator with a mega-pixel CCD detector. The wavelength range is 174 nm to 786 nm. A polyboost option can be used where an additional argon purge is used for wavelengths below 200nm.

The ICP Expert software in conjunction with the mega-pixel chip design uses an auto-integration routine that will optimize the time each pixel is read. As a result, the best sensitivity and the largest linear dynamic range for the selected parameters are achieved.

The standard sample introduction system is a Sturman-Masters inert double-pass spraychamber and a polypropylene v-groove nebulizer with a one-piece torch, 1.4 mm injector. Figure 3 shows the Vista – MPX with the standard introduction system.

Figure 3 - Varian Vista – MPX Simultaneous ICP-OES

The CETAC U-5000AT+ Ultrasonic nebulizer was used for the second part of the experiment (Figure 4). The U5000AT+ has an auto-tuned power supply for stable operation (no adjustment necessary between different sample types) and an efficient desolvation system to prevent solvent overloading of the ICP. Electrothermal cooling is used instead of a recirculating chiller, saving laboratory space and maintenance.[3]

Figure 4 - CETAC U-5000AT+ Ultrasonic Nebulizer

Calibration Standard Preparation
The calibration standards were prepared in a 0.5% HNO_3 matrix. A calibration blank was prepared as well. The stock solution for all analytes was a 100 ppm multi-element mix. Table 1 summarizes the standard concentrations.

Table 1 – Calibration Standard Concentration Summary

Elements	SSI		USN	
Ag, As, B, Cd, Cr,	Std 1	Std 2	Std 1*	Std 2*
Cu, Fe, Mn, Pb, Se	1,000	10,000	20	100

Units = ppb * 0.2% mannitol added to each solution

Six standard reference materials (**SRM**) were purchased from High Purity Standards, Charleston, SC; Tracemetals in Drinking Water, 318820, Certified Wastewater, A324512,

B321210, C232320, D324507 and E323715. The Certified Wastewater standards were purchased in 10 mL aliquots. Each SRM was reconstituted to 1000 mL. A 250 mL aliquot of each preparation and transferred to a low -density polypropylene bottle and 0.5 gms mannitol (Sigma Ultra, St. Louis, MO) was added. These solutions were used for the USN experiment only. SRM B321210 was prepared twice, once according to the prescribed procedure and once with a final dilution to 100 mL. The more concentrated dilution was used in the SSI experiment.

Instrument Conditions
The instrument conditions for the SSI and the USN are summarized in Table 2. The standard Sturman-Masters inert spraychamber was replaced with a smaller glass double-pass spraychamber (Twister). The Twister cyclonic spraychamber is used for high precision analysis as it has a glass baffle added to discourage the flow of large droplets into the plasma. The nebulizer was a Sea Spray with a 2 mL / min uptake rate. The Sea Spray nebulizer is used when the total dissolved solids are > 5% and the particulates are > 75µm. The Twister cyclonic spraychamber and Seaspray nebulizer are products of Glass Expansion, (Pocasset, MA). Regardless of sample introduction system, 2 mg/L yttrium, Y, was added on-line as an internal standard. The tubing between the sample introduction and the torch was a tygon-jacketed tube with an inert flouropolymer (FEP) liner (Fisher Scientific, Pittsburgh, PA.). This polymer will help minimize boron carryover.

Table 2 - Instrument 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

Results/Discussion
A. SSI
The initial method was optimized with 1% HNO_3 as a rinse solution. The high standard was 10,000 ppb (10ppm) for all of the elements of interest. Three wavelengths were selected for B, 249.772 nm, 249.678 nm and 208.956 nm. Once the wavelengths were calibrated, the instrument rinsed for 60 seconds with 1% HNO_3 rinse and a blank was read. The blank concentration read 100ppb boron at all 3 wavelengths. Twenty blank solutions were read with rinsing in between samples. The boron signal did not decrease noticeably until the 13th blank, which read 34ppb. Further, after 55 minutes, the signal never decreased below 20 ppb. The other nine elemental wavelengths were monitored using the blank solutions as well. All wavelengths exhibited concentrations of not more than (**NMT**) 1ppb for the first blank analyzed after the 10,000 ppb standard except Ag. The silver exhibited memory effects as well. It was concluded that the additional rinse was necessary for B and Ag.

Mannitol (2% solution) was added to the 1% HNO₃ rinse. The first blank solution read after the 10,000 ppb B standard read 10 ppb. After 5 blank readings, the concentration for all B wavelengths was NMT 5 ppb. The Ag still exhibited memory effects with the mannitol added and Silver results were ignored for this portion of the study.

Figure 5 illustrates the calibration curve and in-run precision for the calibration standards. As would be expected, the in-run precision for the three replicates is less than 3%. The ICP Expert software checks each point on the calibration curve to determine how far individual points deviate from the calibration line (of best fit).[4] The Max % error value defines the maximum percent deviation allowed before the calibration is deemed a failure. A good linear calibration will have a Max % error of NMT 5%. The percent error for each standard is NMT 0.2%.

Figure 5 - B Calibration Curve with SSI and 2% Mannitol Rinse
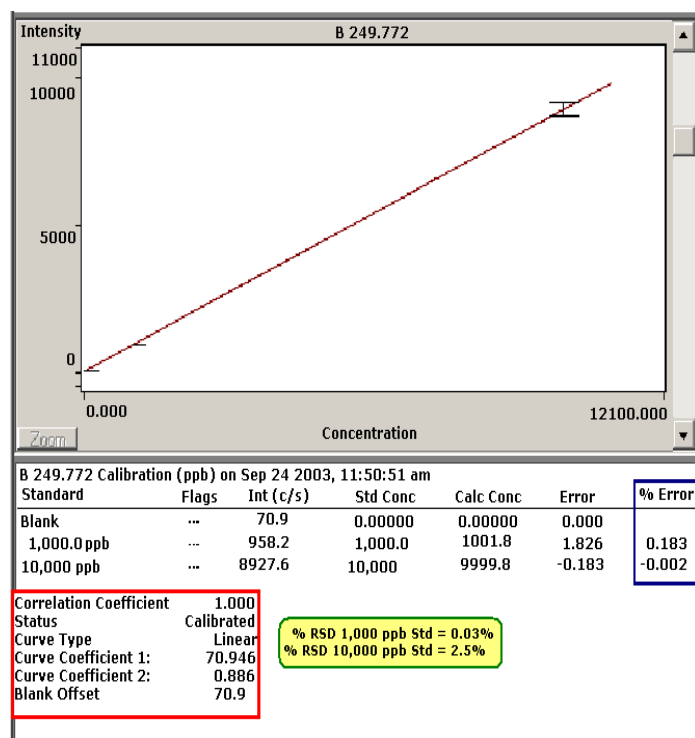
The instrument detection limit, **IDL**, was calculated for B by using the standard deviation of the concentration of the 10 blank solutions (once rinse out was completed) and multiplying by 2.76 (for student t = 99% confidence).[5] The method detection limit was calculated by using the standard deviation of 7 solutions spiked with 100ppb B. The SD was multiplied by 3.14 (for student t = 99% confidence) for the final **MDL** concentration for B.[6] The intensity for the 100 ppb B spiked solution was used to calculate the background equivalent concentration (**BEC**) and the limit of detection (**LOQ**).[5] Table 3 summarizes these calculations for the SSI.

Table 3 – Summary of IDL, MDL, BEC and LOQ for B with SSI and 2 % Mannitol Rinse

Units = ppb		B 208.95 nm	B 249.68 nm	B 249.77 nm
Blank	SD	6.3	2.5	2.1
	IDL	18	7	6
	Ave.	92.7	101.5	103.7
	SD	5.4	3.7	3.5
100 ppb Soln	MDL	17	12	11
	SBR	149.7	273.0	300.8
	BEC	67	37	33
	RSD	5.8	3.6	3.4
	LOQ	12	4	3.4

The LOQ for these parameters at the primary B wavelengths is about 4 ppb and the BEC was about 30 ppb. Since these are calculated statistics, a final experiment was added running a B solution spiked at 10 ppb. This standard was analyzed 4 times with rinsing in between solutions. Table 4 summarizes these recoveries. Therefore, if a 10 ppb standard must be recovered at ± 10%, the SSI would not meet criteria at this concentration level and additional hardware must be added.

Table 4 – Summary of 10 ppb B Recovery

Units = ppb	B 208.956nm	B 249.678nm	B 249.772nm
10 ppb run1	15	22	25
10 ppb run2	16	22	23
10 ppb run3	11	19	23
10 ppb run4	15	18	23
Average	14	20	23
SD	2.3	2	1

The SRM reported values for B on the SSI are reported in Table 5. The values are an average of 5 analyses of each SRM. All recoveries are in the certified range with the recoveries better than ± 10%. The average sample analysis time is 4 minutes / sample using mannitol as the rinse solution.

Table 5 – SRM Result Summary for B with SSI and 2% Mannitol Rinse

Sample ID	Expected Value	Average		
		B 208.956 nm *	B 249.678 nm *	B 249.772 nm *
SRM 318820	150 μg/L ± 0.5%	142 ± 2.5	148 ± 1.9	150 ± 2.3
SRM B321210	2000 μg/L ± 0.5%	1991 ± 15	1998 ± 20	2005 ± 19
SRM C232320	500 μg/L ± 0.5%	500 ± 11	505 ± 7.2	510 ± 6.5
SRM 324507	1000 μg/L ± 0.5%	1033 ± 12	1040 ± 16	1045 ± 15

*Units for FOUND Values = μg/L ± μg/L

The last part of experiment 1 was to evaluate the effect of mannitol on the other analytes considered. Table 6 summarizes the results for As, Cd, Cr, Cu, Fe, Mn, Pb and Se. The results reported are an average of 5 analyses of the SRM.

Table 6 – SRM Result Summary for Analytes with SSI and 2% Mannitol Rinse

Sample Labels	As 188.980	Cd 226.502	Cr 267.716	Cu 327.395	Fe 239.563	Mn 294.921	Pb 220.353	Se 196.026
SRM 318820	54	9.5	20.3	19.1	87.9	40	-12.6	264
Cert. Value	55	10	20	20	90	40	20	11
%REC	98.5	95.5	101.6	95.4	97.6	100.1	-64.5	239.9
SRM B321210	512	524	2055	2079	2074	2061	2007	525
Cert. Value	500	500	2000	2000	2000	2000	2000	500
%REC	102.5	104.7	102.8	103.9	103.7	103.1	100.4	105.0
SRM C232320	148	160	524	530	535	531	496	163
Cert. Value	150	150	500	500	500	500	500	150
%REC	99.0	106.6	104.7	105.9	107.0	106.2	99.2	108.9
SRM D324507	262	268	1052	1071	1060	1060	1015	266
Cert. Value	250	250	1000	1000	1000	1000	1000	250
%REC	104.8	107.2	105.2	107.1	106.0	106.0	101.5	106.5

Units = ppb

SRM # 318820 was the Trace Metals in Drinking Water standard. The concentrations for the heavy metals, As, Cd, Cr, Cu, Pb and Se were very low. The results for the radial instrument with SSI system for this sample gave recoveries within ± %5 for every analyte with the exception of Pb and Se. Since the Pb and Se recoveries were within ± 10% for the other 3 SRMs, it can be concluded that the 2% mannitol rinse used to scavenge the B from the sample introduction system does not adversely effect the other analyte recoveries. The non-existent recoveries for the Trace Metal Drinking Water SRM were due to the low concentration and not the mannitol. A longer integration time could be used, to try to get the expected recovery for these concentration levels; however, the solutions were run on the USN instead.

B. USN

The experimental design for the addition of the USN did not include addition of mannitol to each solution. The mannitol was used only in the rinse solution. Further, since the USN gives a factor of 10 lower detection for most elements, the calibration curve was lowered to 100 ppb and 1000 ppb.

1. 2% Mannitol as RINSE Only

The calibration standard concentrations for the USN experiment were lowered by a factor of 10 (since the USN will automatically give a factor of 10 better sensitivity due to the superior nebulization efficiency of the accessory compared to the SSI). A simple check to verify the calibration range was done by comparing the intensity of the 1,000ppb low standard on the SSI experiment to the intensity of the 1,000 ppb high standard on the USN. Theoretically the USN intensity should be at least a factor of 10 greater. This was true for all of the analytes except B. The B signal was **REDUCED** by a factor of 7. Table 7 compares the Ssi and USN intensity values for B, Cd and Fe.

Table 7 – Comparison of Intensity Values Between SSI and USN with 2% Mannitol Rinse

Element	Std Conc.	Intensity SSI	Intensity USN
B 249.772	1,000	750	113
Cd 214.439	1,000	300	3942
Fe 216.187	1,000	210	2900

Units = ppb

The mannitol was added as a modifier to each solution to correct for the B loss believed to be in the condenser of the USN. The signal for the 1,000 ppb standard increased to 7300 counts with the addition of 0.1% mannitol to the standard. The optimum amount of mannitol was determined. A comparison of signal was done by preparing standards in 0.1% mannitol, 0.2% mannitol and 0.3% mannitol. Table 8 shows the comparison.

Table 8 – Optimization of Mannitol Concentration for B Signal Using B 249.772 nm Wavelength

10 replicates 1,000 ppb Std	Mannitol Concentration		
	0.1%	0.2%	0.3%
Mean Intensity	7252.3	9524.8	8791
%RSD	2.8	2.14	2.14

The 0.2% mannitol gave the best intensity and good % RSD.

The experiment proceeded with 0.2% mannitol added to each solution and a 2% mannitol rinse between samples. Mannitol is a very dense sugar derivative. As the USN desolvated all of the solutions, the mannitol particles were carried into the torch, causing clogging of the injector tube.

2. Rinse Solution Evaluation

Since it was essential to the B signal to have the mannitol added to the solutions, the rinse solution needed to be changed. Two solutions were evaluated, a diethanolamine mixture (diethanolamine with ammonia and hydrazine) and tartaric acid. The diethanolamine mixture is commonly used as a cleaning solution for nuclear power plants where lithium borohydrate is used with the reactors. Tartaric acid was evaluated as it is listed in a B solubility table.

Both solutions worked equally well, however, the plasma was more easily stabilized after the tartaric acid rinse compared to the diethanolamine mixture. It was also determined from these experiments, that 1000 ppb B was too high a concentration to use for the USN. The rinse times and stabilization times were in excess of 15 minutes. Therefore, the calibration curve was lowered to 20 ppb low standard and 100 ppb high standard. The rinse time was now 4 minutes / sample. With total analysis time of 7 minutes / sample.

The 1% tartaric acid rinse was prepared using 20 gms of tartartic (Mallenckrodt, St. Louis, MO) and diluting to 500 mL.

Table 9 summarizes the IDL, MDL and LOQ for the USN portion of the experiment.

Table 9 – Summary of IDL, MDL and LOD for B Using USN and 1 % Tartaric Acid

Units = ppb		B 208.95 nm	B 249.68 nm	B 249.77 nm
Blank	SD	0.5	0.23	0.23
	IDL	1.5	0.7	0.6
10 ppb Soln	Ave.	10.6	11.5	11.2
	SD	0.53	0.49	0.57
	MDL	1.7	1.5	1.8
	SBR	12.3	18.7	19.5
	BEC	8.2	5.3	5.1
	RSD	5.0	4.3	5.1
	LOQ	1.2	0.7	0.8

The LOD for the USN experiment was 0.8 ppb for the primary B wavelength. The working range should include a 10 ppb standard with good recovery. Table 10 summarizes the 10 ppb standard recoveries. The recovery range for the average results is 104% to 110%.

Table 10 – Summary of Recovery for 10 ppb B with USN

Units = ppb	B 208.956	B 249.678	B 249.772
10 ppb 1	10.7	11.6	11.8
10 ppb 2	9.7	11.2	11.2
10 ppb 3	10.3	11	10.9
10 ppb 4	10.8	10.7	10.5
10 ppb 5	10.5	10.5	10.5
Average	10.4	11	11
SD	0.42	0.43	0.54

The result summary for the 5 SRMs for B is listed in Table 11. All of the B recoveries were within the certified range and had calculated recoveries within ± 10%. The results reported are an average of 5 analyses for each SRM.

Table 11 – Result Summary SRM for B, 0.2% Mannitol Modifier with Tartaric Acid Rinse - USN

Sample ID	Expected Value	Average B 208.956 nm *	B 249.678 nm *	B 249.772 nm *
SRM #A324512	50 µg/L ± 0.5%	53 ± 2.1	52 ± 1.8	51.6 ± 1.7
SRM #B321210	200 µg/L ± 0.5%	211.5 ± 2.4	203.5 ± 2.8	202.5 ± 3.1
SRM #C232320	500 µg/L ± 0.5%	532 ± 1.9	512 ± 2.1	506.7 ± 1.9
SRM #D324507	1000 µg/L ± 0.5%	1076 ± 1.7	1031 ± 1.4	1021 ± 1.3
SRM #E323715	25 µg/L ± 0.5%	26.1 ± 0.24	25.1 ± 0.2	24.8 ± 0.1

*Units for FOUND Values = µg/L ± µg/L

Finally, the last data set shows recovery for the other analytes. Using the mannitol as a modifier and lowering the calibration curve standard concentrations, made the conditions favorable for Ag determinations also. The results in Table 12 summarize all of the additional analytes. The percent recoveries for most elements were within ± 4%. The average was calculated for 5 analyses of each SRM.

Table 12 – Result Summary of All Analytes Using USN, 0.2% Mannitol Modifier and 1% Tartaric Acid Rinse

Sample Labels	Ag 328.068	As 188.980	Cd 226.502	Cr 267.716	Cu 324.754	Fe 261.187	Mn 257.610	Pb 220.353	Se 196.026
SRM A324512	9.8	9.4	10.0	49.5	50.0	50.1	50.3	49.3	10.3
Cert. Value	10	10	10	50	50	50	50	50	10
%REC	98.0	94.2	99.7	98.9	99.9	100.1	100.7	98.7	103.3

Table 12 – Result Summary of All Analytes Using USN, 0.2% Mannitol Modifier and 1% Tartaric Acid Rinse

Sample Labels	Ag 328.068	As 188.980	Cd 226.502	Cr 267.716	Cu 324.754	Fe 261.187	Mn 257.610	Pb 220.353	Se 196.026
SRM B321210	51.0	50.2	50	199	200	200	204	201	51
Cert. Value	51	50	50	200	200	200	200	200	50
%REC	100.0	100.5	100.6	99.7	100.2	100.2	102.2	100.6	103.0
SRM C232320	154.7	153.2	152	500	503	505.4	507.8	507.4	154.1
Cert. Value	150	150	150	500	500	500	500	500	150
%REC	103.1	102.2	101.5	100.0	100.6	101.1	101.6	101.5	102.8
SRM D324507	255	252	249	990	997	996.7	1006.1	1014.0	259.9
Cert. Value	250	250	250	1000	1000	1000	1000	1000	250
%REC	101.9	101.0	99.6	99.0	99.7	99.7	100.6	101.4	104.0
SRM E323715	4.7	4.3	25.2	25.1	25.2	24.7	25.3	24.7	5.2
Cert. Value	5	5	25	25.0	25.0	25	25	25	5
%REC	94.3	86	100.8	100.4	100.8	98.8	101.2	98.7	103.1

Units = ppb

Table 13 summarizes the IDL and MDL for the nine other elements of interest using SSI and USN. The average results are for the low concentration standard used for each experiment, 100ppb and 10 ppb for SSI and USN respectively. The %RSD is the precision of this low concentration standard analyzed 7 times.

Table 13 – Summary of IDL and MDL for Additional Element - SSI and USN

	Ag 328.068nm	As 188.980 nm	Cd 226.50 nm	Cr 267.72 nm	Cu 324.75 nm	Fe 261.187 nm	Mn 257.610 nm	Pb 220.353 nm	Se 196.026 nm
SSI									
IDL	NA	19	0.8	3.9	2.3	2.7	0.3	31	42
MDL	NA	21	8.6	6.9	8.8	7.3	7.9	19	20
Average	NA	108	105	104	111	103	105	79	126
%RSD	NA	6.3	2.6	2.1	2.5	2.3	2.4	7.8	5.0
USN									
IDL	0.09	3.5	0.08	0.18	0.20	0.24	0.02	1.6	3.7
MDL	0.22	0.69	0.30	0.35	0.35	0.28	0.32	0.71	0.89
Average	10	8.9	10	10	11	9.9	10	10	9.5
%RSD	0.69	2.5	0.94	1.1	1.0	0.90	0.98	2.2	3.0

Conclusions

The goals for the investigation of boron measurement in this study were numerous such that the study was broken down into 2 parts, boron with the standard sample introduction and boron with the USN. The goals for the SSI were:

- Find an easy to use rinse solution for the SSI on an ICP-OES to replace HF.
- Ensure that the rinse solution will not adversely affect recovery of additional elements of interest.
- Reduce analysis time by using typical rinse times and not extended rinse times.

The use of the gem diol, mannitol accomplished the above goals such that the analysis time was 4 minutes/sample. The recoveries of the SRM solutions were not degraded by the addition of mannitol to the rinse solution for any of the elements of interest.

Part two of the study evaluated increasing the sensitivity of the B by using a CETAC Technologies U – 5000AT+ as an accessory to the Vista – MPX with radial viewing. The goals are summarized as follows:

- Evaluate mannitol as a modifier for B to recover signal from the USN.
- Find a suitable rinse solution for the USN to replace the mannitol due to torch clogging.
- Reduce analysis time and increase sensitivity for all analytes of interest.

The above tasks were easily accomplished so that the analysis time was 6 minutes/sample with 1% tartaric acid rinse and 0.2% mannitol added to each solution. SRM recoveries for all analytes were within ± 10% even at the low ppb concentrations.

Therefore, the Vista – MPX with radial viewing and the CETAC Technologies USN can be used to successfully quantitate low concentration analytes with a few sample preparation modifications.

References:

1. Department of Polymer Science, Univ of Southern Mississippi, Macrogalleria Glossary copyright 1995,1996.

2. CETAC U-5000AT $^+$ Ultrasonic Nebulizer, Improving Trace Element Detection in Liquid Samples for ICP-AES and ICP-MS, July 2003, p 6.

3. CETAC U-5000AT $^+$ Ultrasonic Nebulizer, Improving Trace Element Detection in Liquid Samples for ICP-AES and ICP-MS, July 2003, p 2.

4. Varian, Inc., ICP Expert Software Help Version 3.0.2.0, 3/28/2002, Section Standards page – Multi-Cal Parameters, MAX% ERROR, © 2001 Varian Australia Pty Ltd ACN 004 559 540.

5. IUPAC, Analytical Chemistry Division, Commission on Spectrochemical and Optical Procedures for Analysis, Nomenclature, symbols, units and their usagein spectrochemical, analysis_II. Data interpretation, Spectrochem. Acta part B33 (1978) pp. 242 – 245.

6. Definition and Procedure for the Determination of the Method Detection Limit 1, 40 CFR – Chapter I – Part 425, Appendix C. (1988) pp. 1-6.