

Highly Sensitive and Specific GC-MS/MS Method for the Analysis of Boron in Drinking Water and Other Beverages

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Introduction

Boron (B), an essential trace element, can prevent osteoarthritis and osteoporosis and helps maintain bone and joint functionality. However, increased exposure to B in animal models has demonstrated a negative impact on development and reproduction. Crop models have also demonstrated adverse effects on root and shoot growth under field conditions. The World Health Organization suggests drinking water to contain no more than 0.5 ppm B with a suggested daily intake of 18 mg or less. US EPA has not set a maximum exposure limit for B. Herein is presented a specific and sensitive GC-MS/MS method for the analysis of Boron in tidal river water.

Why GC-MS/MS analysis of Boron?

Boron is typically analyzed by ICP-OES because of the high sensitivity of the technique; however, metals such as Fe, Ni, Mn and Ti can greatly interfere with the emission spectrum of B so separation of B is required from these metals. Previous work by Zeng *et al.* have demonstrated a quick and simple derivatization of boric acid with triethanolamine. The derivatized boron complex was analyzed quantitatively by GCMS in SIM mode. While their approach was sufficient for drinking water, it could not be applicable for boron analysis in more demanding matrices such as soil or vegetable extracts. The selectivity of the MS/MS technique would allow for elimination of coeluting isobaric matrix ions that would result in false positives or enhancements in quantitation in SIM.

Experimental

GC Conditions

Oven Program
100 °C for 0.7 min
then 35 °C/min to 280 °C for 1 min

MMI Inlet (He)
Mode: Pulsed Splitless
Injection Volume: 1 µL
Temperature Program
105 °C for 0.1 min
then 300 °C/min to 280 °C for 0 min

Transfer Line 280 °C

Column #1
HP-5MS 15 m x 250 µm x 0.25 µm {19091S-431UI}
Flow: 1 mL/min
Post Run: -10.435 mL/min, 1 min

Column #2
HP-5MS 15 m x 250 µm x 0.25 µm {19091S-431UI}
Flow: 1.2 mL/min
Post Run: 10.983 mL/min, 1 min

Run Time 6.6429 min

MRM conditions

El, source 260 °C

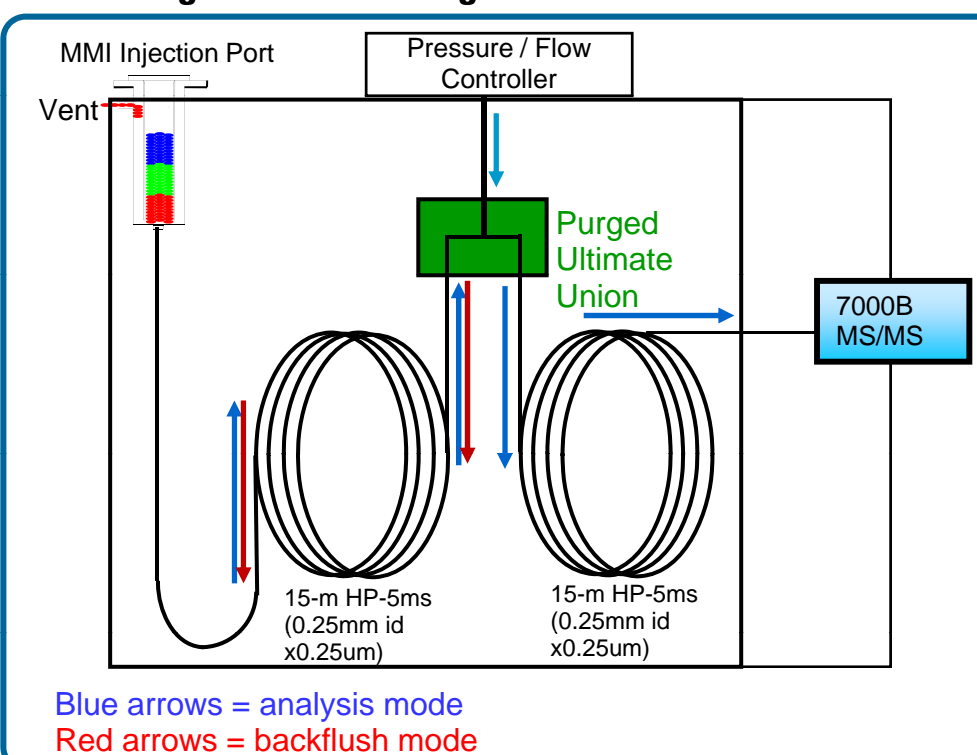
Name	Precursor	Product	Dwell	Collision Energy
TEB	126	98	150	20
TEB	126	86	150	25

The GC-MS/MS analysis of the boron complex was performed on the Agilent 7890A GC coupled to a 7000B triple quadrupole mass spectrometer. The 7890A GC was equipped with a multimode inlet (MMI) and an auxiliary electronic pneumatic control with a purged ultimate union to provide backflush capability. The MMI is a large volume programmable temperature vaporization injector that can also be used as a standard split/splitless injector using the same S/SL liners. Cool injection with a rapid thermal ramp was performed for enhanced response.

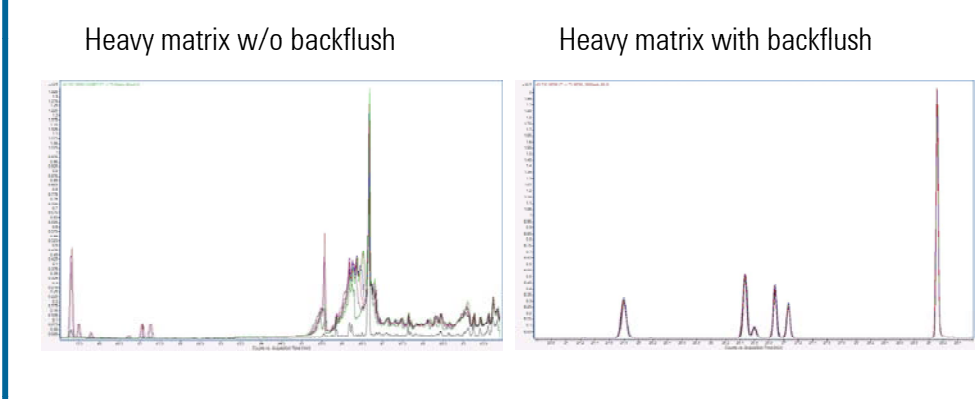
The backflush capability allows for reversal of carrier gas flow at a specified time in the method. This allows for rapid elimination of heavy, nonvolatile matrix components- typically near the head of the column- out the split vent in the injector. This preserves the integrity of the column stationary phase, keeps the ion source clean, improves spectral quality and speeds up the analysis since prolonged bakeout is not required to eliminate the nonvolatile matrix components. The backflush had a substantial effect on reducing the matrix carryover and retention time stability of the boron complex spiked in vegetable matrix.

Experimental

GC configuration showing back flush flows



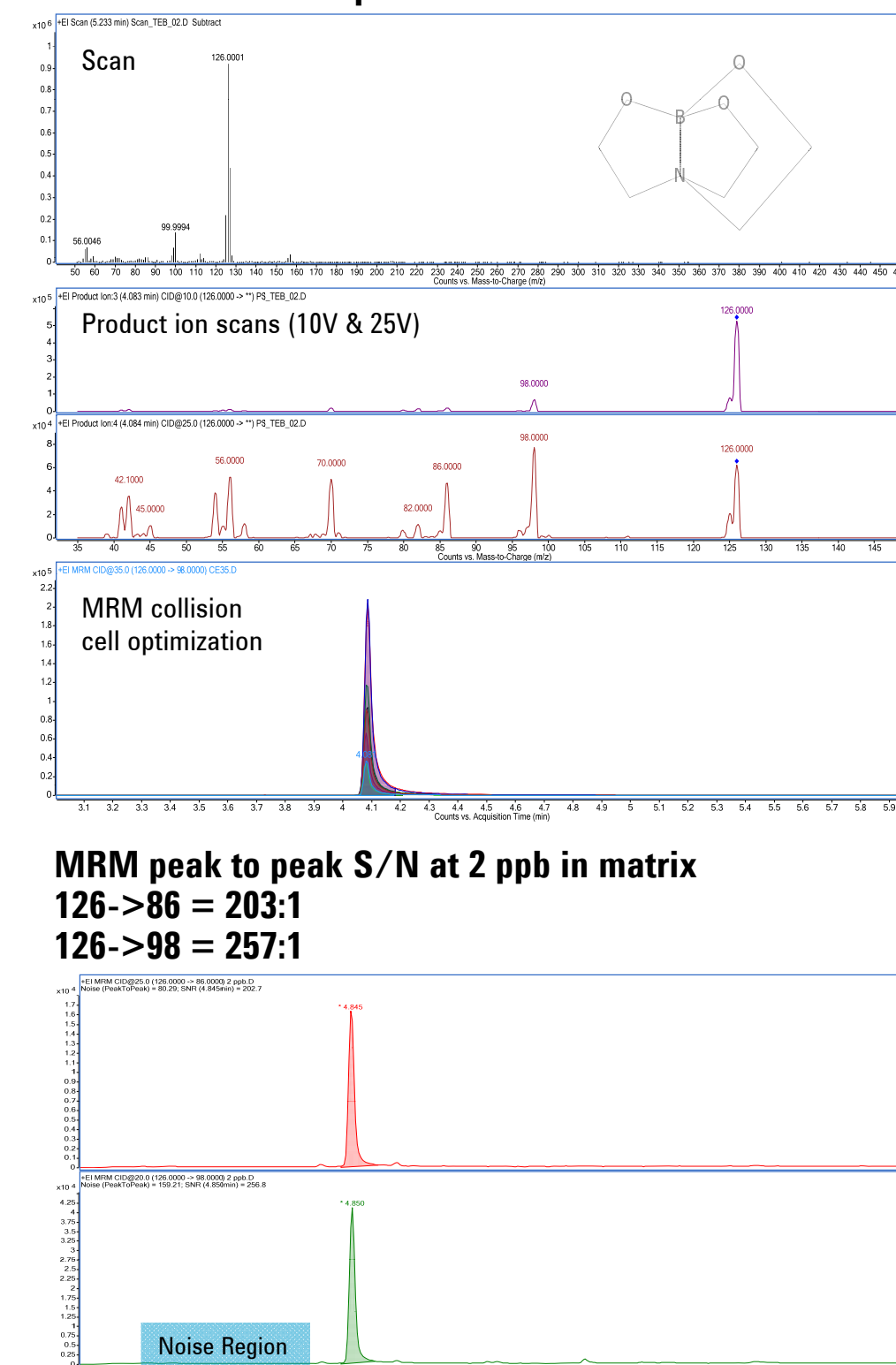
Backflush



Multi-Mode Inlet MMI



MRM method Development



MRM peak to peak S/N at 2 ppb in matrix
126->86 = 203:1
126->98 = 257:1

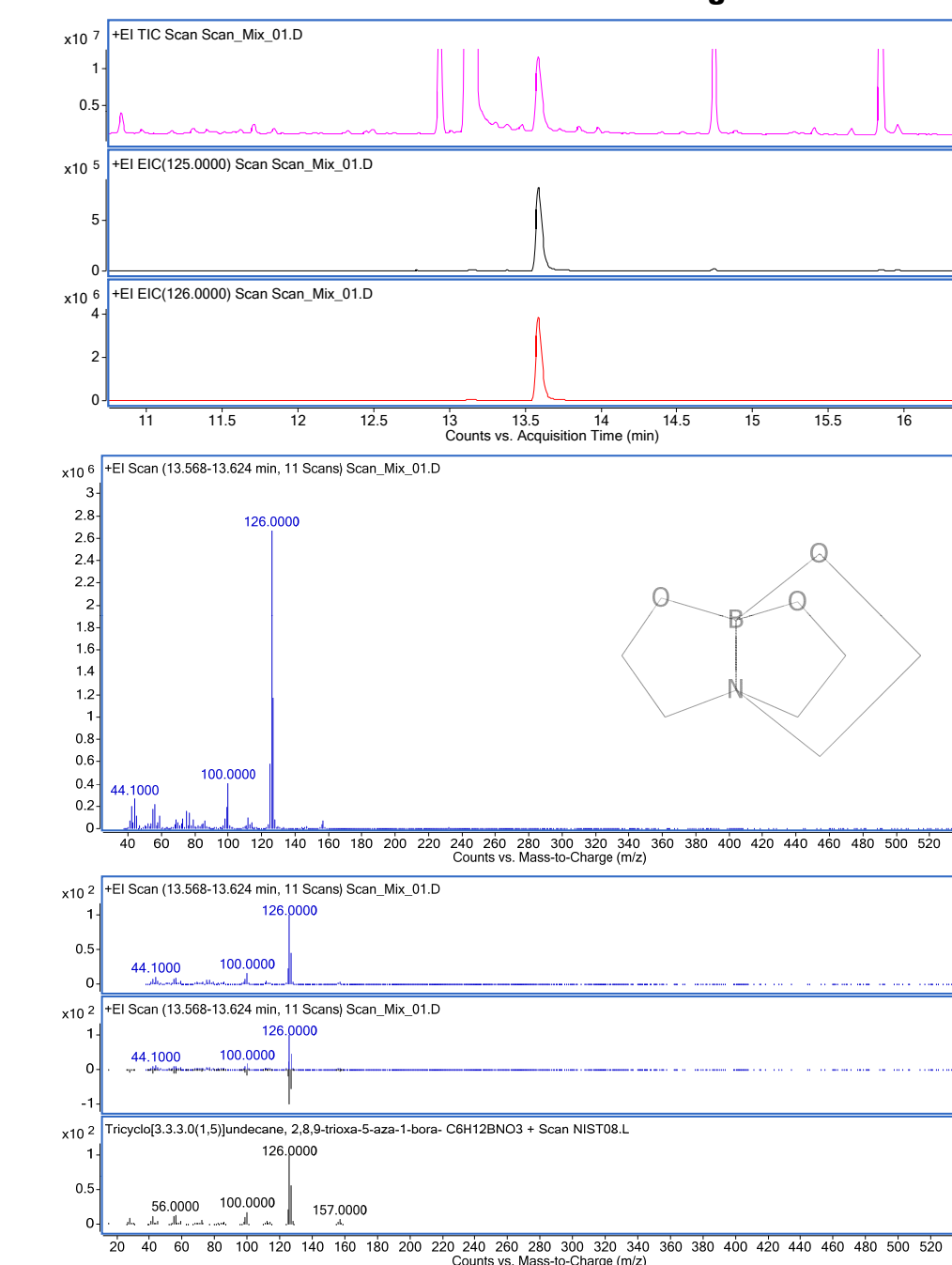
Sample Preparation and Analysis

Samples of commercially bottled tomato based vegetable juice were purchased. Known sample volumes were filtered and evaporated to dryness. For derivatization, 1 ml of a 0.5% (wt/v) ethanolamine in acetonitrile was added to the dry samples and heated for 1 hour at 50 C. Samples were dried and reconstituted with ethyl acetate prior to injection.

Separate calibration standards were prepared in ethyl acetate and an LOQ of 2ppb was achieved with the MS/MS method in standard and 15ppb in matrix. These results are substantially lower than the literature results found by GCMS-SIM (80ppb LOQ) and ICP-OES (150ppb LOQ).

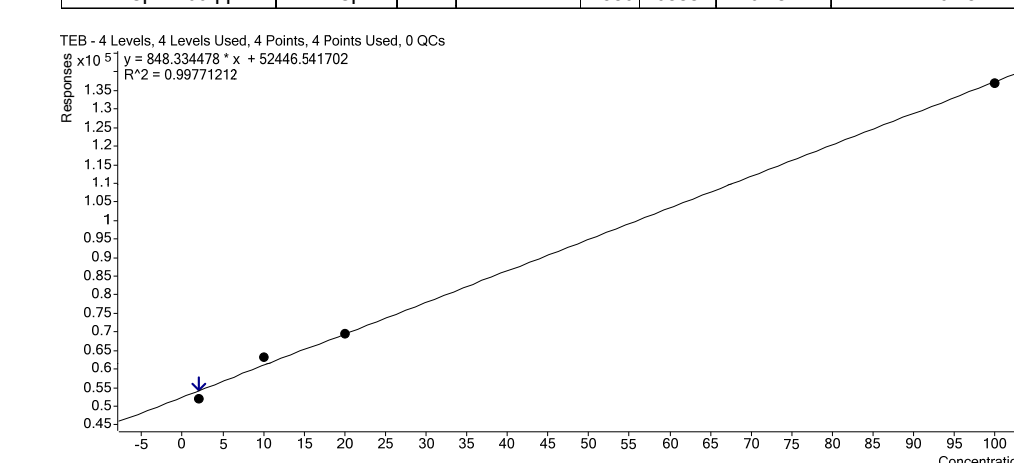
Results and Discussion

ID of derivatized boric acid from drinking water



Batch Quantification

Sample Data File	Type	TEB Method		TEB		Qualifier (126.0 -> 86.0)	
		Level	Exp. Conc.	RT	Resp.	Final Conc.	Ratio
2 ppb.D	Cal	1	2	4.850	51902	0.00	40.28
10 ppb.D	Cal	2	10	4.850	63171	12.64	40.06
20 ppb.D	Cal	3	20	4.845	69637	20.26	41.01
100 ppb.D	Cal	4	100	4.845	137056	99.74	40.79
Matrix.D	MatrixBlank						
Matrix Spike 15 ppb.D	MatrixSpike			4.850	49074	18.31	40.31
Matrix Spike 30 ppb.D	MatrixSpike			4.850	80392	32.94	40.35
Matrix Spike 60 ppb.D	MatrixSpike			4.850	105331	62.34	40.45



Conclusions

Under aqueous conditions, elemental boron is in the form of boric acid and borate ions. Recently, it was demonstrated that a rapid and simple GC-MS experiment can measure boric acid in drinking water to with LOD and LOQ of 40 ppb and 80 ppb, respectively. In many cases, MS/MS processes can lower detection limits found in SIM through MRM reactions that discriminate the analyte from matrix interference. Water can be considered a fairly clean matrix and S/N values compare in SIM versus MRM. However, the residual vegetable juice matrix interferes with SIM analysis and affects quantitative results. In matrix, a lower detection limit approaching 2 ppb or better was achieved via MRM on the tandem mass spectrometer through improvement in overall S/N. Detection limits were driven further through the implementation of cold, splitless injection. Chromatography and spectral data were improved with the implementation of column backflush technologies.

Bibliography

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