
The Analysis of Trace Elements in Boric Acid by ICP-MS

Application Note

HP 4500 ICP-MS

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Abstract

Until now, the trace analysis of aluminum in boric acid has not been feasible by ICP-MS due to spectroscopic interference by boron oxide and hydroxide. This note describes the use of an ultrasonic nebulizer with membrane desolvator to eliminate both the matrix and water from the sample, thereby removing the interferences. The detection limit obtained for aluminum in 1% boric acid was less than 50 ppt. Detection limits for other elements analyzed using the same procedure were in the single figure ppt range. This approach allows the same ICP-MS to be used for both boric acid

analysis and trace boron measurements without risk of cross-contamination.

Introduction

The analysis of trace elements in boric acid is of interest in the nuclear fuel and production industry, since boron has a high neutron cross-section and is used as a neutron absorber. The determination of impurities in boric acid is difficult because of the high matrix content. Furthermore, until this work, the measurement of aluminum has not been feasible by ICP-MS because of $^{10}\text{B}^{16}\text{O}^1\text{H}$ and $^{11}\text{B}^{16}\text{O}$ interfering with the monoisotopic aluminum peak at mass 27. A unique solution to this involves the use of an ultrasonic nebulizer coupled to a membrane desolvator. Normally this type of sample introduction device cannot be used to measure volatile elements such as boron, since they are lost through the membrane along with the sample matrix. In this case, this limitation of a membrane desolvation device is used to advantage: the boron matrix is purposely removed using the membrane, allowing the analytes alone to be swept into the plasma. Furthermore, oxide and hydroxide interferences are greatly reduced when using a membrane desolvator because the membrane

removes volatile solvent (in this case water) thus decreasing the oxygen loading in the plasma. With less oxygen present, these potential interferences are greatly reduced. The combination of effects allows for the determination of aluminum in boric acid at ppt levels.

Methodology

A standard HP 4500 ICP-MS was used for the study. A U6000AT+ ultrasonic nebulizer with membrane desolvator (CETAC Technologies Inc. Omaha, NE) was used for sample introduction. The sample stream from the desolvator was attached directly to the torch inlet of the HP 4500. Instrument parameters for both systems are shown in Table 1.

The boric acid matrix was prepared by dissolving the appropriate amount of solid boric acid in de-ionized water (Millipore Inc, Bedford MA) to yield a 1% by weight boric acid solution.

The U6000AT+ was optimized by analyzing a 10 ppb Ce solution in 0.1% nitric acid. Flows were adjusted to maximize Cerium signal while minimizing the parent Ce signal at m/z 140. Figure 1 also gives an indication of the observed signal for CeO. A spectrum of the

Table 1. HP 4500 Operating Parameters - Quantitative Analysis

Plasma gas flow rate	16.0 L/min
Aux. gas flow rate	1.0 L/min
Carrier gas flow rate	1.2 L/min(Normal)
RF Power	1300W
Nebulizer	CETAC Technologies U6000AT+
Coolant/membrane/Sweep gas	2 deg C / 160 deg C / 1.5 L/min
Spray chamber	na
Spray chamber temp	na
ICP torch injector	Quartz, 2.5mm injector
Sample uptake rate	2.0 ml/min
Sampling depth	8 mm
Detector mode	Auto
Points/mass	3
Acquisition time/mass	1.0 sec
Acquisition time/sample	47 sec

final signal is shown in Figure 2. The CeO signal at m/z 156 is less than 0.02% of the parent Ce signal at m/z 140 (the normal CeO/Ce ratio of the HP 4500 is 0.5%). Figure 1 also gives an indication of the increase in signal achieved by using the ultrasonic nebulizer. The signal for ^{140}Ce is almost 1MCPS for a 10 ppb solution or 1000 MCPS/ppm. Using a conventional pneumatic nebulizer the HP 4500 usually gives approx. 50 MCPS/ppm. The need for excellent abundance sensitivity can also be seen. Because extremely large signals are exhibited for ppb level contaminants excellent peak shape and abundance sensitivity is needed to ensure that there is no signal overlap from adjacent masses. Figure 1 clearly shows base line resolution of the masses directly adjacent to the large ^{140}Ce signal.

Results

Figure 1 shows the instrument detection limits for various elements in 1% boric acid solution. While these detection limits are excellent, they are all limited by elemental contamination in the *blank* boric acid solution. Most of the detection limits are well under 10 ppt. The highest detection limit is exhibited by Iron at 67 ppt because of interference from ArO. Aluminum exhibits a detection limit of 41 ppt, several orders of magnitude better than can be achieved with out using the membrane desolvator.

Detection limits were calculated using the standard deviation from a *blank* 1% boric acid solution analyzed 10 different times multiplied by three. A 500 ppt multi-element solution in the

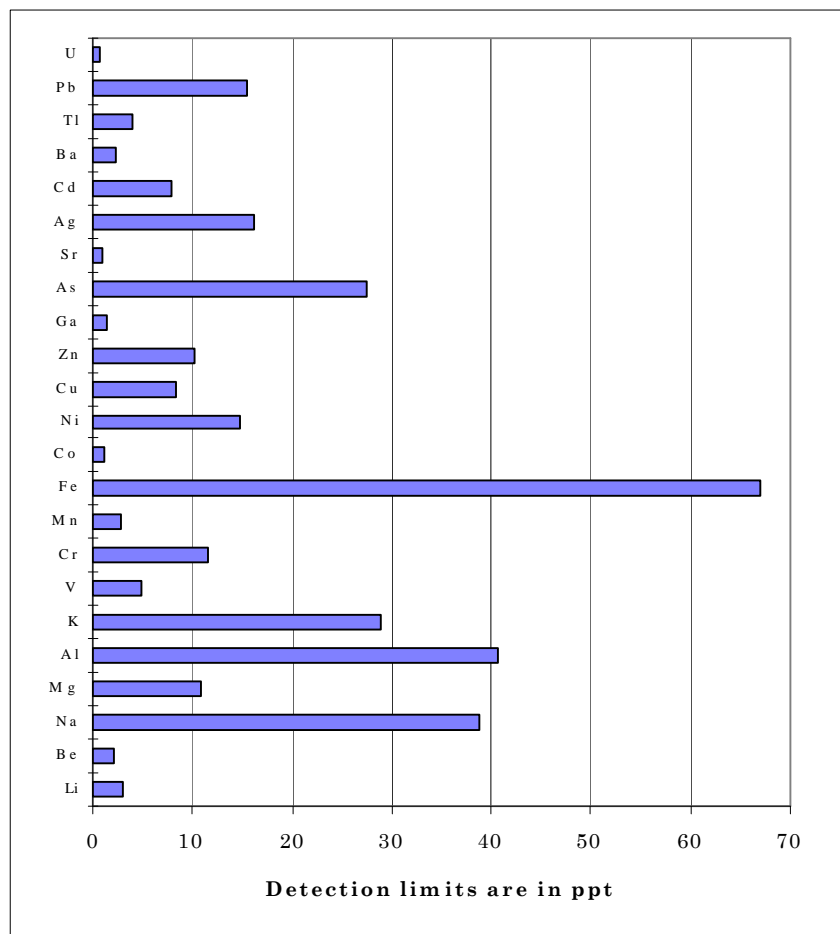


Figure 1. Instrument Detection Limits for Elements in 1% Boric Acid (DLs are based on the standard deviation of 10 blank replicates and the response level from a 500 ppt spike).

boric acid matrix was used to calculate detection limits. It should also be remembered that this matrix would need to be diluted $\times 10$ to be run routinely with a conventional nebulizer, with a subsequent degradation in detection limits for all elements.

Figure 3 shows the standard addition curve generated when 100ppt and 500ppt spikes of Aluminum in the 1% boric acid solution were measured. The concentration of Aluminum determined by standard addition is 0.16 ppb. The precision of both the 100 and 500 ppt spikes is good for ultrasonic nebulization at less than 3% RSD.

The instrument was extremely stable considering the high concentration of boron introduced to the system. Over a thirty minute time period (30 replicate analyses) the signal precision for the 500 ppt spike solution was better than 5% RSD for all elements studied. During the 30 minute analysis the 1% boric acid solution was continuously aspirated through the system.

Conclusion

Analysis of impurities in boric acid is simplified by the use of a membrane desolvator. Removing both water vapor and the boron matrix eliminates boron oxide formation allowing for aluminum determinations at the ppt level. The use of the membrane desolvator also improves the detection limits for iron, calcium and potassium compared with conventional pneumatic nebulizers operating under normal plasma conditions.

Finally, another important benefit in using the membrane desolvator

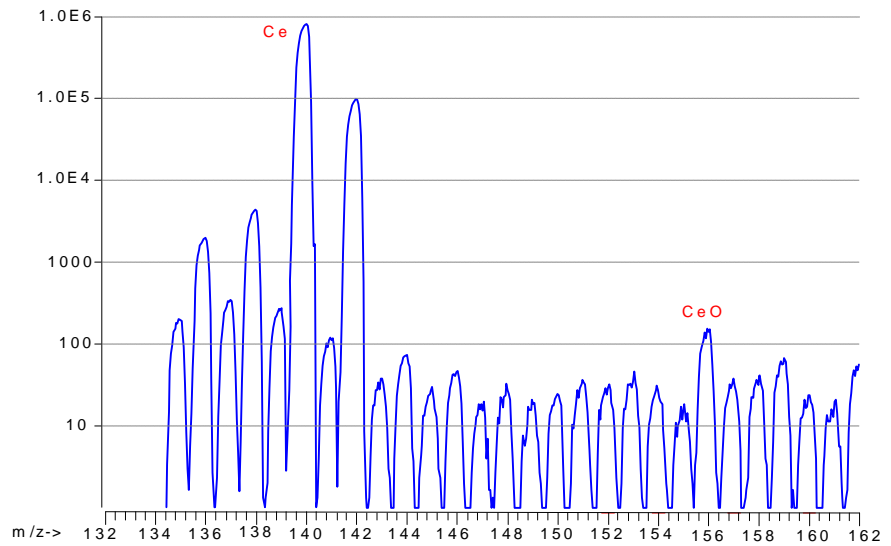


Figure 2. Spectrum of 10 ppb Ce in 0.1% Nitric Acid using Membrane Desolvation.

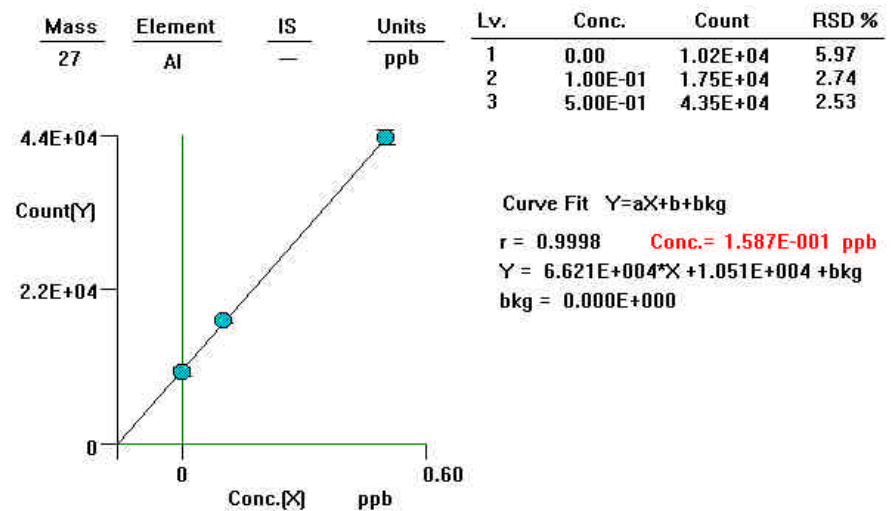


Figure 3. ^{27}Al Standard Addition Curve in 1% Boric Acid Showing 0.16 ppb aluminum in the blank boric acid solution.

to analyze samples containing high concentrations of boron allows trace level boron measurements to be performed on the same ICP-MS by simply installing a standard nebulizer and spray chamber. Since the boron matrix does not reach the ICP-MS, sub-ppb boron

determinations can be made only minutes after the analysis of impurities in 1% boric acid. This is of great benefit in the nuclear industry, where the measurement of trace boron fuel in materials and cladding is a key requirement.

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