Introduction

Tetramethylammonium hydroxide (TMAH) is widely used as a basic solvent in the development of acidic photoresist in the semiconductor photolithography process and in liquid crystal display (LCD) manufacturing. Its wide usage in these demanding applications has made the analysis of impurities in TMAH more and more critical. SEMI Standard C46-03061 specifies limits for 25% TMAH with contamination limits to less than 10 ppb for each element. TMAH, however, is not commonly used in its concentrated form; in fact, most applications would have the concentration between 1 and 3%.

With its ability to determine analytes rapidly at the ultra trace (ng/L or parts-per-trillion) level in various process chemicals, inductively coupled plasma mass spectrometry (ICP-MS) has become an indispensable analytical tool for quality control. It is, however, extremely important to address the significant matrix-derived polyatomic interferences, as well as matrix suppression effects, due to carbon content. These issues are especially prominent when analyzing organic solvents directly. Although cool plasma has been shown to be effective in reducing argon-based interferences, it is even more prone to matrix suppression than hot plasma. Additionally, the low plasma energy may result in preferential formation of other polyatomic interferences which are not seen under hot plasma conditions. Collision cells using multipoles and nonreactive gases have proven useful in reducing polyatomic interferences. However, kinetic energy discrimination results in the loss of sensitivity, which
is an issue when analyzing ng/L levels. Reaction mode is another technique which uses a reactive gas, such as NH₃, to selectively react with the polyatomic interference and a quadrupole mass filter to create dynamic bandpass to prevent undesirable by-product ions formation, thereby removing the polyatomic interference effectively without suppressing the analytes’ signal.

This application note demonstrates the ability of PerkinElmer’s NexION® 300S ICP-MS to remove interferences so that trace levels of impurities in TMAH can be easily measured using hot plasma conditions for all analytes in a single analysis.

**Experimental conditions**
The concentration of TMAH (Tamapure-AA, Tama Chemicals, Tokyo, Japan) is about 25%, and sample preparation consisted of a five-fold dilution with pure water, resulting in a 5% (W/W) solution. Standard solutions were made from a 10 mg/L multi-element standard (PerkinElmer Pure, PerkinElmer, Shelton, CT USA). The instrument used for this experiment was a NexION 300S ICP-MS (PerkinElmer, Shelton, CT USA). Instrumental parameters and sample introduction components are shown in Table 1.

**Results**
25% TMAH was quantitatively analyzed using the method of additions with a five-fold dilution; the calibration curves in 5% TMAH for Mg, Al and Cr are shown in Figures 1–3 and demonstrate good linearity, which is possible with all the carbon-related polyatomic interferences removed by the reactive NH₃ gas in combination with the bandpass.

| Spray Chamber: | Quartz Cyclonic | Nebulizer: | Meinhard® Concentric Quartz |
| Torch: | Standard Quartz | Plasma Gas: | 18 L/min |
| Torch Injector: | 2-mm Quartz | Auxiliary Gas: | 1.1 L/min |
| Sampler Cone: | Platinum | RF Power: | 1500 W |
| Skimmer Cone: | Platinum | Integration Time: | 1 sec/mass |

**Table 1. Instrumental parameters and sample introduction components for the NexION 300S ICP-MS.**

**Figure 1.** Mg calibration, with NH₃ cell gas flow of 0.3 mL/min.

**Figure 2.** Al calibration, with NH₃ cell gas flow of 0.6 mL/min.
The detection limits (DLs) and background equivalent concentrations (BECs) were both determined in 5% TMAH, while accounting for the sensitivities in 5% TMAH. DLs were calculated by multiplying the standard deviation by three, and BECs were determined by measuring the signal intensities. Recoveries were determined from 20 ng/L spikes. The results are summarized in Table 2.

TMAH is known to cause spiky signals in ICP-MS due to its capability to wash out particles and contaminants along the sample introduction pathway and interface of the ICP-MS. To demonstrate the superior configuration of the NexION 300S ICP-MS to handle TMAH, a cyclic analysis between 5% TMAH spiked with 500 ng/L and 1% HNO₃ was carried out. Figure 4 clearly shows a good, stable signal of 500 ng/L spiked TMAH when switching to and from 1% HNO₃.

Table 2. Detection limits (DLs), background equivalent concentrations (BECs), and 20 ng/L spike recoveries for all analytes in 5% TMAH (units in ng/L).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Cell Gas Flow* (mL/min)</th>
<th>DL (ppt)</th>
<th>BEC (ppt)</th>
<th>20 ppt Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>7</td>
<td>0.25</td>
<td>0.06 ND</td>
<td>98%</td>
</tr>
<tr>
<td>Be</td>
<td>9</td>
<td>0.25</td>
<td>0.08 ND</td>
<td>97%</td>
</tr>
<tr>
<td>B</td>
<td>11</td>
<td>0.25</td>
<td>0.8 5.9</td>
<td>99%</td>
</tr>
<tr>
<td>Na</td>
<td>23</td>
<td>0.25</td>
<td>0.9 7.0</td>
<td>104%</td>
</tr>
<tr>
<td>Mg</td>
<td>24</td>
<td>0.3</td>
<td>0.5 3.0</td>
<td>111%</td>
</tr>
<tr>
<td>Al</td>
<td>27</td>
<td>0.6</td>
<td>0.5 2.10</td>
<td>94%</td>
</tr>
<tr>
<td>K</td>
<td>39</td>
<td>0.6</td>
<td>0.5 1.17</td>
<td>105%</td>
</tr>
<tr>
<td>Ca</td>
<td>40</td>
<td>1</td>
<td>0.5 19.4</td>
<td>98%</td>
</tr>
<tr>
<td>Ti</td>
<td>48</td>
<td>0.3</td>
<td>0.5 1.6</td>
<td>90%</td>
</tr>
<tr>
<td>V</td>
<td>51</td>
<td>0.6</td>
<td>0.5 0.07 ND</td>
<td>102%</td>
</tr>
<tr>
<td>Cr</td>
<td>52</td>
<td>0.6</td>
<td>0.5 5.1</td>
<td>95%</td>
</tr>
<tr>
<td>Mn</td>
<td>55</td>
<td>0.6</td>
<td>0.7 1.0</td>
<td>102%</td>
</tr>
<tr>
<td>Fe</td>
<td>56</td>
<td>0.6</td>
<td>0.5 1.33</td>
<td>99%</td>
</tr>
<tr>
<td>Co</td>
<td>59</td>
<td>0.3</td>
<td>0.5 0.34</td>
<td>115%</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
<td>0.3</td>
<td>0.7 2.4</td>
<td>108%</td>
</tr>
<tr>
<td>Cu</td>
<td>63</td>
<td>0</td>
<td>0.25 1.5</td>
<td>93%</td>
</tr>
<tr>
<td>Zn</td>
<td>64</td>
<td>0.3</td>
<td>0.65 27.3</td>
<td>106%</td>
</tr>
<tr>
<td>Ga</td>
<td>69</td>
<td>0.6</td>
<td>0.5 0.1</td>
<td>97%</td>
</tr>
<tr>
<td>Ge</td>
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<td>0.65 1.0</td>
<td>102%</td>
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<tr>
<td>As</td>
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<td>0</td>
<td>0.25 0.7</td>
<td>ND 99%</td>
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<tr>
<td>Sr</td>
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<td>0.6</td>
<td>0.5 0.09</td>
<td>104%</td>
</tr>
<tr>
<td>Zr</td>
<td>90</td>
<td>0</td>
<td>0.25 0.09</td>
<td>0.16 99%</td>
</tr>
<tr>
<td>Nb</td>
<td>93</td>
<td>0</td>
<td>0.25 0.1</td>
<td>ND 99%</td>
</tr>
<tr>
<td>Mo</td>
<td>98</td>
<td>0</td>
<td>0.25 0.2</td>
<td>ND 104%</td>
</tr>
<tr>
<td>Ru</td>
<td>102</td>
<td>0</td>
<td>0.25 0.09</td>
<td>ND 103%</td>
</tr>
<tr>
<td>Rh</td>
<td>103</td>
<td>0</td>
<td>0.25 0.1</td>
<td>0.2 99%</td>
</tr>
<tr>
<td>Pd</td>
<td>106</td>
<td>0</td>
<td>0.25 0.1</td>
<td>0.2 103%</td>
</tr>
<tr>
<td>Ag</td>
<td>107</td>
<td>0</td>
<td>0.25 0.3</td>
<td>0.5 90%</td>
</tr>
<tr>
<td>Cd</td>
<td>114</td>
<td>0</td>
<td>0.25 0.2</td>
<td>1.1 100%</td>
</tr>
<tr>
<td>In</td>
<td>115</td>
<td>0</td>
<td>0.25 0.03</td>
<td>0.08 101%</td>
</tr>
<tr>
<td>Sn</td>
<td>120</td>
<td>0</td>
<td>0.25 0.6</td>
<td>7.4 104%</td>
</tr>
<tr>
<td>Sb</td>
<td>121</td>
<td>0</td>
<td>0.25 0.08</td>
<td>0.11 94%</td>
</tr>
<tr>
<td>Ba</td>
<td>138</td>
<td>0</td>
<td>0.25 0.3</td>
<td>0.6 100%</td>
</tr>
<tr>
<td>Ta</td>
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<td>0</td>
<td>0.25 0.07</td>
<td>ND 99%</td>
</tr>
<tr>
<td>W</td>
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<td>0</td>
<td>0.25 0.3</td>
<td>1.0 98%</td>
</tr>
<tr>
<td>Pt</td>
<td>195</td>
<td>0</td>
<td>0.25 0.9</td>
<td>1.4 101%</td>
</tr>
<tr>
<td>Au</td>
<td>197</td>
<td>0</td>
<td>0.25 0.3</td>
<td>ND 105%</td>
</tr>
<tr>
<td>Tl</td>
<td>205</td>
<td>0</td>
<td>0.25 0.02</td>
<td>ND 103%</td>
</tr>
<tr>
<td>Pb</td>
<td>208</td>
<td>0</td>
<td>0.25 0.2</td>
<td>0.6 98%</td>
</tr>
<tr>
<td>Bi</td>
<td>209</td>
<td>0</td>
<td>0.25 0.2</td>
<td>0.3 100%</td>
</tr>
<tr>
<td>U</td>
<td>238</td>
<td>0</td>
<td>0.25 0.02</td>
<td>ND 99%</td>
</tr>
</tbody>
</table>

*Cell gas used is NH₃.

Figure 3. Cr calibration, with NH₃ cell gas flow of 0.6 mL/min.

Figure 4. Continuous analysis of 5% TMAH spiked with 500 ng/L standards and 1% HNO₃.
Conclusion

The NexION® 300S ICP-MS is shown to be robust and suitable for the routine quantification of ultratrace impurities at the ng/L level in TMAH. It has also been shown that by using the Reaction mode in the Universal Cell, the argon- and carbon-based polyatomic spectral interferences can be eliminated, allowing for the determination of many of the traditionally problematic elements with good spike recovery and precision. By means of computer controlled switching between Standard and Reaction modes, interference-free analysis using hot plasma conditions for all analytes is possible during a single sample run.

References