**Introduction**

A number of clinical applications require detection limits below that of many ICP-MS instruments, especially those that require isotope ratios. Although the total level of U in Urine is ~1-5 ppt, the $^{235}$U concentration level is ~5-30 ppq. Biological matrices such as urine often require time consuming sample preparation / pre-concentration procedures to be carried out. A much more favorable procedure is the "dilute and shoot" method, whereby minimal sample preparation is carried out prior to introduction to the ICP-MS.

**Instrumentation and Sample Introduction**

- Thermo Element2 HR-ICP-MS
- PFA-100 MicroFlow Nebulizer
- Apex Q

- 100 µL Urine diluted 1:10
- Final Solution: 15% H$_2$O$_2$, 1% HNO$_3$
- 0.1% Surfactant

**APEX Q**

The Apex is a fully-integrated inlet system that connects directly to the torch injector and incorporates ESI's PFA MicroFlow nebulizer technology. Liquid samples are nebulized into a heated cyclonic spray chamber and peltier cooled desolvation system where the sample aerosol is conditioned to produce uniform aerosol that is transported to the ICP.

**Procedure**

Digestion of the sample occurs when the urine/peroxide/acid mixture is aspirated into the heated spray chamber of the Apex. This prevents many of the problems caused by injector and cone clogging when directly aspirating clinical samples with both organic and high TDS. The addition of 0.1% surfactant prevents the self aspiration flow from stopping due to bubbles in the nebulizer capillary.

**Performance**

The Apex Q not only performs online digestion of the sample, but also increases the aerosol transport efficiency, increasing sensitivity. This permits accurate $^{235}$U:$^{238}$U ratios to be calculated as low as 5 ppt compared to concentrations over 100 ppt with conventional sample introduction systems (Fig 1). Although the sensitivity of the Apex Q in combination with the Element2 was sensitive enough to measure lower concentrations of U, the isotope ratio was incorrect. Further investigation using a medium resolution scan of the m/z 235 showed a small interference peak, possibly $^{12}$C$^{40}$Ar$_4$H$^{14}$N$^{16}$O$_3$ (Fig 2). By modifying the method with a mass offset of 0.15 it was possible to measure the $^{235}$U peak without including the interference improving accuracy (Table 1).

**Fig 1:** Ratio of $^{235}$U:$^{238}$U.

**Fig 2:** Measurement of $^{12}$C$^{40}$Ar$_4$H$^{14}$N$^{16}$O$_3$ interference peak

<table>
<thead>
<tr>
<th>$^{235}$U:$^{238}$U Method Offset</th>
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<tbody>
<tr>
<td>0.008061</td>
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<tr>
<td>0.007409</td>
</tr>
<tr>
<td>0.007295±0.000064</td>
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