Accurate and precise $^{235}$U quantification by combining isotopic dilution method and ICP/AES measurements

O. Vigneau, N. Arnal

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Introduction

Isotopic dilution method is currently applied to ICP/MS measurements (IDMS). Nevertheless, an ICP/AES owning a high resolving power is able to measure the isotopic shift in emission atomic lines for heavy elements such as uranium. Uranium isotopes, such as $^{235}$U and $^{238}$U, are therefore clearly separated and identified. Using this phenomenon, the accurate and precise quantification of uranium or its isotopes is possible. Indeed, the transposition of IDMS method to our ICP/AES instrument allows to quantify, with trueness and precision, the amount content of $^{235}$U of an uranyl nitrate solution. The method is named IDAES for “Isotopic Dilution Atomic Emission Spectrometry”. In this study, the accuracy and precision of the $^{235}$U quantification by IDAES are compared to those obtained by IDMS using a MC-ICP/MS instrument.

Instruments

<table>
<thead>
<tr>
<th>Plasma parameters</th>
<th>ICP/AES</th>
<th>MC ICP/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio frequency</td>
<td>40 kHz</td>
<td>27 kHz</td>
</tr>
<tr>
<td>Forward power</td>
<td>1000 W</td>
<td>1200 W</td>
</tr>
<tr>
<td>Argon gas flow rate</td>
<td>12 L.min$^{-1}$</td>
<td>15 L.min$^{-1}$</td>
</tr>
<tr>
<td>Nebuliser gas</td>
<td>0.9 L.min$^{-1}$</td>
<td>0.945 L.min$^{-1}$</td>
</tr>
<tr>
<td>Auxiliary gas</td>
<td>0.15 L.min$^{-1}$</td>
<td>0.70 L.min$^{-1}$</td>
</tr>
</tbody>
</table>

Acquisition parameters

| Spray chamber     | Quartz cylindrical (combination of a cyclonic and a Scott-type spray chamber) |
| Nebuliser         | Concentric nebuliser (self-aspirating PFA concentric nebuliser) |
| Sample uptake     | 1 mL.min$^{-1}$ (peristaltic pump) |
| Integration time  | 10 s |
| Number of replicates | 30 |
| Collection mode   | Not applicable |

ICP/AES ACTIVA M

• spectral windows up to 8 nm
• simultaneous measurement of multiple lines and backgrounds
• resolution equal to 10 pm in the range of 120-430 nm

Optimum wavelengths for ICP/AES measurements

Isotopic dilution principle

The sample is a highly enriched uranium solution of the certified reference material SRM U-930 ($^{235}$U-238U powder) in which the amount of $^{235}$U is between 100 and 50 µg.g$^{-1}$. The spike (named IRMM-053) is an isotopic reference material certified for $^{235}$U amount content (JRC IRMM, Geel, Belgium). The blend is prepared by mixing perfectly known weights of spike and sample.

Isotopic dilution formula applied to determine amount content of $^{235}$U ($c_{235}^{\text{U}}$) in the sample using a $^{238}$U enriched CRM $R_{S}=n_{(238}\text{U})/n_{(235}\text{U})$ in the unknown sample, $R_{B}=n_{(238}\text{U})/n_{(235}\text{U})$ in the spike material, $R_{S} = m_{S}/m_{S}$ weight of the unknown sample used to prepare the blend, $m_{U}$ = weight of the spike solution used to prepare the blend, $c_{235}^{\text{U}}= m_{S} R_{B}/R_{S}$ is amount content of $^{235}$U per kilogram of spike solution.

Idaes and Idms

15-fold dilution

$[U] \sim 5 \text{ mg.L}^{-1}$

20-fold dilution

$[U] \sim 250 \mu\text{g.L}^{-1}$

Ratios of the blend are determined using the “Sample Standard Bracketing” method in order to correct instrumental bias (for ICPAES and MC ICP/MS). The SSB method is based on an external correction. An isotopic reference material (SRM U-500) measured before and after the blend is used and the relative bias between the true and the experimental value is assumed to be valid for the blend as well. The ratio B is then equal to $R_{B} = R_{\text{sample}}^{\text{true}} \times R_{\text{sample}}^{\text{true}} / R_{\text{sample}}^{\text{meas}}$.

Conclusions

ICP-AES technique combined with isotopic dilution method (leading to IDAES) is fully appropriate for the determination of $^{235}$U and/or $^{238}$U concentrations, in terms of accuracy (trueness of the results) and precision. Indeed, results obtained thanks to this technique are quite similar to those given by MC ICP/MS (IDMS method) which is the preferred choice. This result is particularly remarkable because the physical principles of measurements of both instruments are different.

The highest precision of the IDMS method compared to the IDAES one is the result of the very high precision of measurement of the MC ICP/MS. Nevertheless, this instrument is ten times more expensive than the ICP/AES one. The IDAES method is usable for physical follow-up and nuclear materials account.