Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Uncertainty Propagation

For the interference correction, the equations are as follows:

$$\begin{cases} {}^{187}Os_{cor-sam} = b_{(\mathrm{IC2-IC0})} \times {}^{187}Total_{mea-sam} - {}^{187}Re_{sam} \\ {}^{187}Re_{sam} = c_{(\mathrm{IC3-IC0})} \times {}^{185}Re_{mea-sam} \times \dfrac{{}^{187}Re/{}^{185}Re_{ref}}{(M_{187}/M_{185})^{\beta_{Re-sam}}} \\ \beta_{Re-std} = ln\left(\dfrac{{}^{187}Re/{}^{185}Re_{ref}}{{}^{187}Re/{}^{185}Re_{mea-std} \times (b_{(\mathrm{IC2-IC0})}/c_{(\mathrm{IC3-IC0})})}\right) \Big/ ln(M_{187}/M_{185}) \\ \beta_{Re-sam} = linear\ \ interpolation\ \ (\beta_{Re-std}) \end{cases}$$

Because the SSB method is adopted for calibration, we can get the equation as follows:

$${}^{187}Re/{}^{185}Re_{Re-std} = \frac{{}^{187}Re/{}^{185}Re_{ref}}{(M_{187}/M_{185})^{\beta_{Re-std}}} = \frac{{}^{187}Re/{}^{185}Re_{ref}}{(M_{187}/M_{185})^{\beta_{Re-sam}}}$$

Then, the equation about ${}^{187}Os_{cor-sam}$ can be rewritten as follows:

$${}^{187}Os_{cor-sam} = b_{(\mathrm{IC2-IC0})} \times {}^{187}Total_{mea-sam} - c_{(\mathrm{IC3-IC0})} \times {}^{185}Re_{mea-sam} \times {}^{187}Re/{}^{185}Re_{Re-std} = f$$

If we assume that ${}^{187}Total_{mea-sam} = \mathrm{a}_1$, ${}^{185}Re_{mea-sam} = \mathrm{a}_2$, ${}^{187}Re/{}^{185}Re_{Re-std} = \mathrm{a}_3$, the following equation can be reduced as follows:

$$\begin{cases} \dfrac{\partial f}{\partial a_1} = b_{(\mathrm{IC2-IC0})} \\ \dfrac{\partial f}{\partial a_2} = c_{(\mathrm{IC3-IC0})} \times {}^{187}Re/{}^{185}Re_{Re-std} \\ \dfrac{\partial f}{\partial a_3} = c_{(\mathrm{IC3-IC0})} \times {}^{185}Re_{mea-sam} \end{cases}$$

The uncertainty of ${}^{187}Os_{cor-sam}$ can be calculated as the following equation:

$$U(^{187}Os_{cor-sam})^2 = \left(\frac{\partial f}{\partial a_1}\right)^2 \times U(^{187}Total_{mea-sam})^2 + \left(\frac{\partial f}{\partial a_2}\right)^2 \times U(^{185}Re_{mea-sam})^2 + \left(\frac{\partial f}{\partial a_3}\right)^2 \times U\left(^{187}Re/^{185}Re_{Re-std}\right)^2$$

And the equations of mass fractionation correction are listed as follows:

$$\begin{cases} ^{187}Os/^{188}Os_{sam} = \dfrac{^{187}Os_{cor-sam}\big/(a_{(\mathrm{IC1-IC0})} \times {}^{188}Os_{sam})}{(M_{187}/M_{188})^{\beta_{Os-sam}}} \\ \beta_{Os-std} = ln\left(\dfrac{^{187}Os/^{188}Os_{ref}}{^{187}Os/^{188}Os_{mea-std} \times (b_{(\mathrm{IC2-IC0})}/a_{(\mathrm{IC1-IC0})})}\right)\Big/ ln(M_{187}/M_{188}) \\ \beta_{Os-sam} = linear\ \ interpolation\ \ (\beta_{Os-std}) \end{cases}$$

Because the SSB method is adopted for calibration, we can get the equation:

$$^{187}Os/^{188}Os_{Os-std} = \frac{^{187}Os/^{185}Os_{ref}}{(M_{187}/M_{188})^{\beta_{Os-std}}} = \frac{^{187}Os/^{188}Os_{ref}}{(M_{187}/M_{188})^{\beta_{Os-sam}}}$$

Then the equation about $^{187}Os/^{188}Os_{sam}$ can be rewritten as follows:

$$^{187}Os/^{188}Os_{sam} = \frac{^{187}Os_{cor-sam}\big/(a_{(\mathrm{IC1-IC0})} \times {}^{188}Os_{sam})}{^{187}Os/^{188}Os_{ref}} \times {}^{187}Os/^{188}Os_{Os-std} = g$$

If we assume that $^{187}Os_{cor-sam} = \mathrm{b}_1$, $^{188}Os_{sam} = \mathrm{b}_2$, $^{187}Os/^{188}Os_{Os-std} = \mathrm{b}_3$, the following equations can be reduced:

$$\begin{cases} \dfrac{\partial g}{\partial b_1} = \dfrac{^{187}Os/^{188}Os_{Os-std}}{(a_{(\mathrm{IC1-IC0})} \times {}^{188}Os_{sam}) \times {}^{187}Os/^{188}Os_{ref}} \\ \dfrac{\partial g}{\partial b_2} = \dfrac{^{187}Os_{cor-sam} \times {}^{187}Os/^{188}Os_{Os-std}}{a_{(\mathrm{IC1-IC0})} \times {}^{187}Os/^{188}Os_{ref}} \times \dfrac{1}{^{188}{Os_{sam}}^2} \\ \dfrac{\partial g}{\partial b_3} = \dfrac{^{187}Os_{cor-sam}}{(a_{(\mathrm{IC1-IC0})} \times {}^{188}Os_{sam}) \times {}^{187}Os/^{188}Os_{ref}} \end{cases}$$

Above all, we can reduce the formula about the uncertainty of ${}^{187}Os/{}^{188}Os_{sam}$ as follows:

$$U({}^{187}Os/{}^{188}Os_{sam})^2$$

$$= \left(\frac{\partial g}{\partial b_1}\right)^2 \times U({}^{187}Os_{cor-sam})^2 + \left(\frac{\partial g}{\partial b_2}\right)^2 \times U({}^{188}Os_{sam})^2 + \left(\frac{\partial g}{\partial a_3}\right)^2 \times U\left({}^{187}Os/{}^{188}Os_{Os-std}\right)^2$$

$$= \left(\frac{\partial g}{\partial b_1}\right)^2 \left[\left(\frac{\partial f}{\partial a_1}\right)^2 \times U({}^{187}Total_{mea-sam})^2 + \left(\frac{\partial f}{\partial a_2}\right)^2 \times U({}^{185}Re_{mea-sam})^2 + \left(\frac{\partial f}{\partial a_3}\right)^2 \times U\left({}^{187}Re/{}^{185}Re_{Re-std}\right)^2\right] + \left(\frac{\partial g}{\partial b_2}\right)^2 \times U({}^{188}Os_{sam})^2 + \left(\frac{\partial g}{\partial a_3}\right)^2 \times U\left({}^{187}Os/{}^{188}Os_{Os-std}\right)^2$$

As the normalization factors of IC1, IC2 and IC3 to IC0, the value of $a_{(IC1\text{-}IC0)}$, $b_{(IC2\text{-}IC0)}$ and $c_{(IC3\text{-}IC0)}$ are close to 1. If we assume the value of $a_{(IC1\text{-}IC0)}$, $b_{(IC2\text{-}IC0)}$ and $c_{(IC3\text{-}IC0)}$ are all equal to 1, the partial differential equations can be calculated as follows:

$$\begin{cases} \dfrac{\partial f}{\partial a_1} = b_{(\mathrm{IC2-IC0})} = 1 \\ \dfrac{\partial f}{\partial a_2} = c_{(\mathrm{IC3-IC0})} \times {}^{187}Re/{}^{185}Re_{Re-std} = {}^{187}Re/{}^{185}Re_{Re-std} \\ \dfrac{\partial f}{\partial a_3} = c_{(\mathrm{IC3-IC0})} \times {}^{185}Re_{mea-sam} = {}^{185}Re_{mea-sam} \end{cases}$$

$$\begin{cases} \dfrac{\partial g}{\partial b_1} = \dfrac{{}^{187}Os/{}^{188}Os_{Os-std}}{(a_{(\mathrm{IC1-IC0})} \times {}^{188}Os_{sam}) \times {}^{187}Os/{}^{188}Os_{ref}} = \dfrac{{}^{187}Os/{}^{188}Os_{Os-std}}{{}^{188}Os_{sam} \times {}^{187}Os/{}^{188}Os_{ref}} \\ \dfrac{\partial g}{\partial b_2} = \dfrac{{}^{187}Os_{cor-sam} \times {}^{187}Os/{}^{188}Os_{Os-std}}{a_{(\mathrm{IC1-IC0})} \times {}^{187}Os/{}^{188}Os_{ref}} \times \dfrac{1}{{}^{188}Os_{sam}{}^2} = \dfrac{{}^{187}Os_{cor-sam} \times {}^{187}Os/{}^{188}Os_{Os-std}}{{}^{187}Os/{}^{188}Os_{ref} \times {}^{188}Os_{sam}{}^2} \\ \dfrac{\partial g}{\partial b_3} = \dfrac{{}^{187}Os_{cor-sam}}{(a_{(\mathrm{IC1-IC0})} \times {}^{188}Os_{sam}) \times {}^{187}Os/{}^{188}Os_{ref}} = \dfrac{{}^{187}Os_{cor-sam}}{{}^{188}Os_{sam} \times {}^{187}Os/{}^{188}Os_{ref}} \end{cases}$$

Hence, the formula about the uncertainty of ${}^{187}Os/{}^{188}Os_{sam}$ can be reduced as follows:

$$U({}^{187}Os/{}^{188}Os_{sam})^2 =$$

$$= \left(\frac{{}^{187}Os/{}^{188}Os_{Os-std}}{{}^{188}Os_{sam} \times {}^{187}Os/{}^{188}Os_{ref}}\right)^2 \left[U({}^{187}Total_{mea-sam})^2 + \left({}^{187}Re/{}^{185}Re_{Re-std}\right)^2 \times U({}^{185}Re_{mea-sam})^2 + ({}^{185}Re_{mea-sam})^2 \times U\left({}^{187}Re/{}^{185}Re_{Re-std}\right)^2\right] + \left(\frac{{}^{187}Os_{cor-sam} \times {}^{187}Os/{}^{188}Os_{Os-std}}{{}^{187}Os/{}^{188}Os_{ref} \times {}^{188}Os_{sam}{}^2}\right)^2 \times U({}^{188}Os_{sam})^2 + \left(\frac{{}^{187}Os_{cor-sam}}{{}^{188}Os_{sam} \times {}^{187}Os/{}^{188}Os_{ref}}\right)^2 \times U\left({}^{187}Os/{}^{188}Os_{Os-std}\right)^2$$

According to the Os and Re isotopic ratio of the reference materials and synthetic sulfides

$$\begin{cases} {}^{187}Os/{}^{188}Os_{ref} = 0.10700 \\ {}^{187}Os/{}^{188}Os_{Os-std} = 0.10700 \\ {}^{187}Os_{cor-sam}/{}^{188}Os_{sam} = 0.10700 \\ {}^{187}Re/{}^{185}Re_{Re-std} = 1.6739 \end{cases}$$

, the formula about the uncertainty of ${}^{187}Os/{}^{188}Os_{sam}$ can be simplified as follows:

$$U({}^{187}Os/{}^{188}Os_{sam})^2$$

$$= \left(\frac{1}{{}^{188}Os_{sam}}\right)^2 \times U({}^{187}Total_{mea-sam})^2 + \left(\frac{1.6739}{{}^{188}Os_{sam}}\right)^2 \times U({}^{185}Re_{mea-sam})^2 + \left(\frac{1}{{}^{188}Os_{sam}}\right)^2 \times 0.107^2 \times U({}^{188}Os_{sam})^2 + \left(\frac{{}^{185}Re_{mea-sam}}{{}^{188}Os_{sam}}\right)^2 \times U\left({}^{187}Re/{}^{185}Re_{Re-std}\right)^2 + U\left({}^{187}Os/{}^{188}Os_{Os-std}\right)^2$$

When we simultaneously measure the numerator and the denominator of the ratio, the measurement is accompanied by flicker noise, which is an important noise component in ICP-MS signals of moderate and high intensity irrespective of whether a multi-collector or a single-collector instrument is used. In the case of flicker noise, the intensity of ^{187}Re and intensity of ^{185}Re are correlated (increase or decrease simultaneously) in a time-resolved signal. The parallel collection of the signal by MC-ICP-MS significantly increases this correlation compared to single-collector instruments. Even if the numerator and the denominator oscillate, the ratio remains relatively stable that improves the precision significantly. Because a multi-collector instrument was used for measurement in this work, the covariance term would be already excluded, if we calculated the error according to the uncertainty of isotopic ratio. For the convenience of modelling uncertainty propagation, the formula is expressed in terms of relative standard errors (RSE) of isotopic intensities.

$$U(^{187}Os/^{188}Os_{sam})^2 = \left(\frac{^{187}Total_{mea-sam}}{^{188}Os_{sam}}\right)^2 \times \left(\frac{U(^{187}Total_{mea-sam})}{^{187}Total_{mea-sam}}\right)^2 + \left(\frac{^{187}Re_{mea-sam}}{^{188}Os_{sam}}\right)^2 \times \left(\frac{U(^{185}Re_{mea-sam})}{^{185}Re_{mea-sam}}\right)^2 + 0.107^2 \times \left(\frac{U(^{188}Os_{sam})}{^{188}Os_{sam}}\right)^2 + \left(\frac{^{187}Re_{mea-sam}}{^{188}Os_{sam} \times 1.6739}\right)^2 \times U\left(^{187}Re/^{185}Re_{Re-std}\right)^2 + U\left(^{187}Os/^{188}Os_{Os-std}\right)^2$$

Base on the theory of uncertainty propagation, the compositions of the uncertainty of the $^{187}Re/^{185}Re$ ratio can be expressed by the following equation:

$$U(^{187}Re/^{185}Re)^2 = (\frac{1}{^{185}Re})^2 \times U(^{187}Re)^2 + (\frac{^{187}Re}{^{185}Re^2})^2 \times U(^{185}Re)^2$$

$$\mathrm{RSE}(^{187}Re/^{185}Re)^2 = \frac{U(^{187}Re/^{185}Re)^2}{(^{187}Re/^{185}Re)^2}$$

$$= (\frac{1}{^{187}Re})^2 \times U(^{187}Re)^2 + (\frac{1}{^{185}Re})^2 \times U(^{185}Re)^2$$

$$\mathrm{RSE}(^{185}Re)^2 = (\frac{1}{^{185}Re})^2 \times U(^{185}Re)^2 < \mathrm{RSE}(^{187}Re/^{185}Re)^2$$

it is reasonable to adopt the value of $\mathrm{RSE}(^{187}Re/^{185}Re)$ as a max estimate for $\mathrm{RSE}(^{185}Re)$.

According to raw isotopic intensities of analysis, the RSE of ratios among the intensity of different mass were calculated and listed as follows:

Intensity ratio	187/188	185/188	188/187	187/185	185/187
RSE	0.0010796	0.00108315	0.001065	0.00025018	0.0002502

By a similar method, the RSE value of the isotopic intensities can be assessed as follows:

$$\begin{cases} \frac{U(^{187}Total_{mea-sam})}{^{187}Total_{mea-sam}} = 0.00107 \\ \frac{U(^{185}Re_{mea-sam})}{^{185}Re_{mea-sam}} = 0.00025 \\ \frac{U(^{188}Os_{sam})}{^{188}Os_{sam}} = 0.00108 \\ U(^{187}Re/^{185}Re_{Re-std}) = 0.00025 \times 1.6739 \\ U(^{187}Os/^{188}Os_{Os-std}) = 0.00108 \times 0.10700 \end{cases}$$

Then, we can get a formula was expressed in terms of $^{187}Re/^{188}Os$ as follows:

$$U(^{187}Os/^{188}Os_{sam})^2$$

$$= \left(\frac{^{187}Re_{mea-sam}}{^{188}Os_{sam}} + 0.107\right)^2 \times (0.00107)^2 + \left(\frac{^{187}Re_{mea-sam}}{^{188}Os_{sam}}\right)^2 \times (0.00025)^2 + 0.107^2 \times (0.00108)^2 + \left(\frac{^{187}Re_{mea-sam}}{^{188}Os_{sam}}\right)^2 \times (0.00025)^2 + (0.00108 \times 0.10700)^2$$

According to this formula, we can calculate the Line 1 that displays the relationship between the $^{187}Re/^{188}Os$ ratio and max estimate of RSE. If we assume that the true RSE for intensities of sample and isotopic ratio of external standards is half of the max estimate, the variation of RSE over the $^{187}Re/^{188}Os$ ratio is displayed by Line 2 (Figure S1). In general, the variation uncertainty meets an agreement with the calculated results.

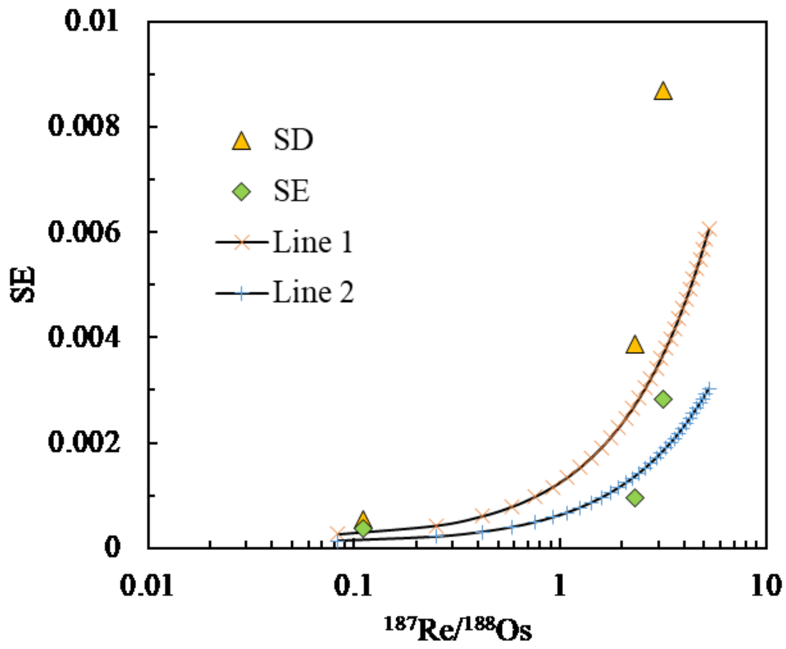

Figure S1. The relationship between the $^{187}Re/^{188}Os$ ratio and the calculated uncertainty.