P-29

Poster Session Day 2

Isotope analysis of nano-mole perchlorate using ESI-Orbitrap-MS

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Perchlorate is found in both terrestrial and extraterrestrial environments, with its formation mechanisms remaining enigmatic. While stable isotopes can reveal formation mechanisms at the molecular level, conventional method using isotope-ratio mass spectrometry (IRMS) requires a large sample size, usually at micro-mole levels. Recent ESI-Orbitrap-MS based methods have achieved precisions better than 1‰ for $\delta^{18}O$, $\delta^{34}S$, or $\delta^{15}N$ for water soluble oxyanions such as sulfate, nitrate, and phosphate [1-3]. The feasibility of ESI-Orbitrap-MS for hours perchlorate injection method [4] has been reported, but the precisions of nanomole-sized perchlorate ESI-Orbitrap-MS versus IRMS calibration is still unknown. We have tested ESI-Orbitrap-MS measurement for perchlorate and discovered that ESI-stability and precisions are both poorer than those of the other oxyanions. Furthermore, we found the accuracy and long-term precision for isotope measurements are affected by sample matrix [2], spray settings [5] and instrument reset [4]. In this study, we highlight that the key of the problem is how to apply identical treatment (IT) principle [5] in both sample preparation and data processing during sample/standard comparison. For sample preparation, we applied a multi-stock solution method to ensure all perchlorate samples and reference to conform to the IT principle, achieving precisions of approximately 1‰ for $\delta^{37}Cl$, $\delta^{17}O$, and $\delta^{18}O$ for nanomole-sized perchlorate. As for data processing, we identified a significant correlation between the Total Ion Current*Injection Time and the ratio measured in ESI-Orbitrap-MS. By controlling data with the correlation and IT principle, we could improve the precision of perchlorate isotope to 0.5‰ level, closer to the statistical theoretical limit (i.e. shot noise limit). The approach we developed is not only applicable to nanomole-sized perchlorate but also to other substances analyzed using ESI-Orbitrap-MS.

References

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