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Accurate determination of natural and enriched Cl isotopic ratios in diverse sample matrices with tandem mass spectrometry using an O_2 reaction gas

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Chlorine isotopic ratio measurements are useful for stable isotope tracers, isotopic abundance measurements in nuclear chemistry, and accurate determination of concentrations using isotope dilution methods. Accurate and precise determination of Cl isotopic ratios using inductively coupled plasma mass spectrometry (ICPMS) methods is challenging due to major polyatomic interferences of $^{16}O^{18}O^{1}H$ and $^{36}Ar^{1}H$ on ^{35}Cl and ^{37}Cl, respectively. Previous work has demonstrated that using tandem mass spectrometry (ICP-MS/MS) with either H_2 or O_2 gas in the collision/reaction cell can significantly improve the precision, but not necessarily accuracy, of chlorine isotopic measurements over single-quad techniques[1]. In this work we further investigate ICP-MS/MS, using O_2 as a reaction gas, as a technique for accurate determination of Cl isotopic ratios. We expand on previous work by targeting both natural and enriched Cl isotopic ratios within diverse sample matrices.

Using an Agilent 8900 QQQ ICPMS in MS/MS mode with O2 as the reaction gas, we measured natural and enriched Cl isotopic ratios in various sample matrices. In detail, we measured natural Cl isotopic ratios ($^{37}Cl/^{35}Cl$=0.3199) within a simple HCl matrix as well as in a variety of buffer solutions. The measured $^{37}Cl/^{35}Cl$ (*n=7*) in HCl was 0.317±0.001 (0.46%), while the buffers ranged from 0.312 – 0.316. These results indicate that it is possible to accurately determine natural Cl isotopic ratios within diverse sample matrices using this approach.

We also tested this approach for measuring enriched Cl isotopic ratios. We made HCl and Mg-acetate solutions with calculated $^{37}Cl/^{35}Cl$ of 0.92 and 0.98, respectively, by spiking in a known amount of enriched Cl reference material (ERM®-AE642, $^{37}Cl/^{35}Cl$ = 55.24). Measured $^{37}Cl/^{35}Cl$ of these enriched solutions are within ~1.5% of the calculated $^{37}Cl/^{35}Cl$. Furthermore, we generated a calibration curve for Mg-acetate solutions with $^{37}Cl/^{35}Cl$ ranging from 0.320-2.003. The resulting calibration curve yields an R^2 = 0.998. In summary, we demonstrate the ability to accurately measure natural and enriched Cl isotopic ratios within both simple (HCl) and more complicated matrices using ICP-MS/MS with O_2 as a reaction gas.

[1] M. Ohata, Y. Zhu, and N. Nonose, *Analytical Sciences,* **2017**, *33*, 375.