

# Critical Assessment of Dopants Used for Precise Cu Isotope Measurement by Multicollector ICP MS

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Variation of stable isotope ratios is a powerful tool for tracing the fate of copper in contaminated environments. The isotope variations encountered, however, are in ‰ units, and high precision measurements of isotopic variations at the sub per mil level are paramount. One key obstacle to this is instrumental mass bias, which refers to the preferential passage of heavier isotopes from the introduction to the arrival at the detector. External doping is widely used for mass bias correction, and Zn, Ni, and Ga have been assessed for copper with typical precisions of 0.08 (2s- direct standard-sample bracketing (enSSB)), 0.05 (2s- enSSB), and 0.04 (U- combined standard-sample-standard bracketing- internal normalization (CSSBIN)), respectively. The review of Sullivan et al. [1] suggested that Ga is the best dopant for copper due to absence of spectral interferences. However, comparison of precision was not under consistent conditions i.e., instrument operation mode, mass bias correction, and uncertainty calculation. Additionally, common parameters in literature that control dopant performance are mass similarity and ionization potential. However, mass similarity would make Ni and Zn outperform Ga, and similar ionization potential would suggest Ni outperformance. This study aimed to identify the optimal dopant for best precision of Cu isotope measurements under consistent conditions. To this end, we first optimized conditions for each Cu-dopant system, then determined precision and accuracy for each system and parameters controlling dopants' performance i.e., mass similarity, ion potential, and published dopant systems. Experiments were conducted using NuPlasma HR MC-ICP-MS. To test accuracy, three in-house standards were measured in external labs. We achieved optimization for Ni with 1 cycle using <sup>61/62</sup>Ni, while Ga included 2 cycles. The optimized comparison using U-CCSBIN showed outperformance of Ni, suggesting ionization potential and direct neighboring as substantial factors. Our findings agree with Malinovsky et al [2] where C was the best dopant among Mg and Li for due to mass similarity. Accuracy tests matched external labs well.

[1] Sullivan, Kaj V. et al. (2022), The Science of the total environment 838.Pt 2, 156084–156084.

[2] Malinovsky, D., Dunn, P. J. H., & Goenaga-Infante, H. (2020), Journal of Analytical Atomic Spectrometry 35(11), 2723–2731.