Doubly charged argide ion interferences in the ICPMS

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Doubly charged polyatomic ions consisting of argon and alkaline earth metals were found to occur as spectral interference in ICPMS spectra. The relative abundances of $(MAr)^{2+}/M^{+}$ were even found to occur at higher levels than the corresponding $(MAr)^{+}/M^{+}$ reaching levels of 10^{-4} on a NU Plasma HR MC- ICPMS used in this study. For conventional nebulization, abundance ratios were found to be lower by about an order of magnitude. The $(MAr)^{2+}$ abundances depend on the ICP operating conditions, generally following those of the doubly charged alkaline earth metal ions (M^{2+}). Quantum mechanical calculations indicate that these species can be formed via association of an M^{2+} to a neutral argon atom and their bond energy can reach values of 0.4 ev (Ba) to 1.3 eV (Mg), while the singly charged species are exhibit much smaller bond energies (0.07–0.19 eV).

Even though the $(MAr)^{2+}$ ions occur only at moderate abundances in the ICPMS, their contribution to ion signals measured for analyte ions may be substantial, especially in isotope ratio measurements. The low abundance of $(MgAr)^{2+}$ renderings this species least problematic. The bias determined for $^{33}S^{+}/^{32}S^{+}$ isotope ratios was about 10^{-7} for samples with equimolar Mg and S concentrations. $(CaAr)^{2+}$ only interferes with Ca isotopes but was found to cause a bias of -0.3 per mil on $^{43}Ca^{+}/^{42}Ca^{+}$ and $^{44}Ca^{+}/^{42}Ca^{+}$ intensity ratios. (SrAr)2+ on the other hand was found to cause detectable spectral interferences on $^{63}Cu^{+}/^{65}Cu^{+}$ and $^{64}Zn^{+}/^{66}Zn^{+}$ intensity ratios (-0.02 and -0.3 per mil respectively for equimolar Cu, Zn and Sr), while Sr isotope ratio measurements are significantly affected by $(BaAr)^{2+}$ (0.05 and 0.013 per mil for 87Sr+/86Sr+ and $^{88}Sr^{+}/^{86}Sr^{+}$, equimolar). The latter can explain matrix effects [1] [2] recently observed in Sr isotope ratio analyses in presence of trace Ba concentrations. It is expected that other elements with similarly low second ionization energies like rare earth elements will also lead to spectral interferences of similar magnitude and may affect isotope ratio analyses in particular.

[1] Souza G.F. et al., *Geochim. Cosmochim. Acta*, **74**, 2010, 2596-2614 [2] Scher H.D.et al., *Geochem., Geophys., Geosyst.*, **15**, 2014, 499-508