A study of *in vivo* HgSe particle formation with multi-element single particle ICP-TOFMS

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MeHg is toxic to humans and the mechanism of its detoxification is still not entirely understood. Selenium is believed to play the role of defender in the detoxification scheme, converting MeHg to less toxic species such as HgSe. Formation of HgSe, on the other hand, is believed to deplete the Se pool in the body, misbalancing the normal biological cycle and suppressing antioxidant activity of Se-proteins.

The mechanism of *in vivo* HgSe formation was recently studied in liver and brain specimens of stranded pilot whales, which can incorporate relatively high levels of Hg[1]. HgSe clusters with size up to 5 µm and Hg/Se molar ratio close to 1 were found in adult animals using synchrotron µ-XRF imaging with 800 nm lateral resolution. Smaller aggregates surrounding large clusters had Hg/Se molar ratio <1, which suggests the growing of HgSe nanoparticles on Se-rich core center structures. Single particle quadrupole inductively coupled plasma mass spectrometry (ICP-MS) analysis revealed increases in particle size and concentration with increasing animal age.

To shed more light on the mechanism of HgSe formation we characterized Hg/Se molar ratios in individual particles extracted from whale liver using multi-element single particle analysis with the TOFWERK icpTOF.

HgSe particles from the liver extract had sizes in the range of 40-100 nm and a mean Hg/Se molar ratio of 0.7. A slight increase of Hg/Se with increase in particle size was observed, which is in agreement with the results of the synchrotron µ-XRF. In addition to Hg and Se, the icpTOF also detected Cd and Fe at significant levels, with molar ratios of Hg/Cd=1.1 and Hg/Fe=0.02.

Though it is still unclear whether the Cd and Fe observations can provide further insight into HgSe crystal formation and growth, this finding demonstrates the potential of multi-element single particle icpTOF analysis for complex biological samples.

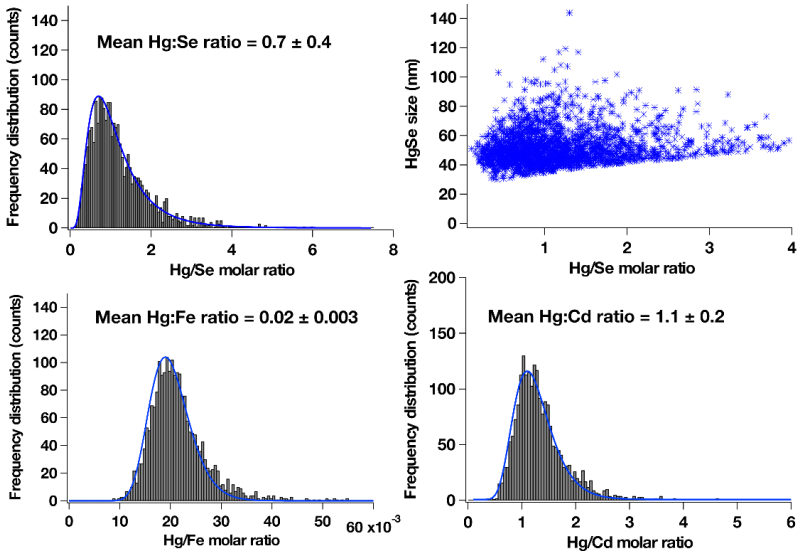

Figure 1. Frequency distribution histograms of Hg/Se, Hg/Fe, and Hg/Cd molar ratios in individual particles extracted from a whale liver and a correlation plot of HgSe particle sizes vs Hg/Se molar ratios acquired with an icpTOF in multi-element single particle mode. The collision-reaction cell was pressurized with 3 ml/min hydrogen to suppress Ar_2+ interference on ^{80}Se+. For details on sample preparation and sample characterization refer to[1]. An isotope-specific threshold was applied to discriminate nanoparticle signals from the ionic background. Element molar masses per particle and particle sizes were determined using Au 8013 NIST CRM nanoparticles, Au solutions, Hg, Se, Cd, Fe-containing calibration solutions and the method proposed by Pace et al. based on known size of 8013 Au particle standard[2]. Sample specific size detection limits for HgSe particles were estimated to be 40 nm assuming the density of 13.5 g/cm^3 that corresponds to 110 ag of Hg and 300 ag of Se. Fe is most likely bound to the particle in a form of metalloprotein. Co-accumulation of Cd with Hg has been already observed in the previous work[3].

References

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