Reactivity of S- or Se- containing model peptides with environmental relevant Hg ions: LC-MS/MS study

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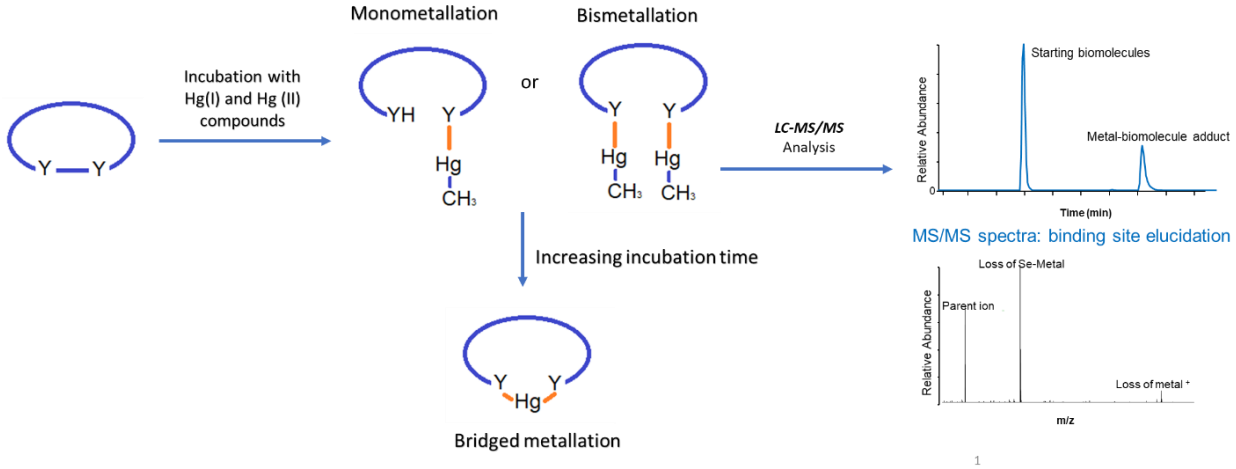
Selenium (Se) is an essential element being present in the form of the naturally occurring amino acid selenocysteine (Sec), 25 human proteins involved in different cellular pathways contain Sec[1]. As the most potent intracellular soft Lewis base, selenocysteine (SeCys) is able to bind electron poor soft acids as heavy metals, of awareness for environmental and human toxicology, Hg ions bind Se by means of higher equilibrium constants than sulfur (ca. 10^6 times), therefore these values compensate the lower cellular abundance (10^5 times) of selenols compared to thiols[2]. In this communication we present a comparative reactivity study of Hg(I) and Hg(II) compounds with model peptides: vasopressin (AVP) hormone with antidiuretic and vasopressor actions and its Sec containing analogs. These peptides were synthesized either by standard solid phase peptide Fmoc or Boc protocols. The metal ion interaction with these peptides was investigated by RP- LC coupled with electrospray MS/MS detection (LC-MS/MS).



We observed mono, bis and bridged peptide metallations as detailed in the Scheme. Taking into consideration the stability of Se-Hg bonds, our results support the hypothesis of a binding preference of Hg to Sec residues in selenoproteins.

References

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2.Kryukov, G. V. Castellano, S. Novoselov, S. V. Lobanov, A. V. Zehtab, O. Guigo, R. Gladyshev, V. N. *Science* **2003**, *300*, 1439-1443.

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