

Contribution of multidimensional liquid chromatography with Inductively Coupled Plasma Mass Spectrometry and Ion Mobility Mass Spectrometry detection in speciation analyses of selenium containing from selenium-rich yeasts

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Selenium (Se) is an essential trace element. Several reports like the NPC [1] clinical trial support that high dietary intake of organic Se has beneficial effects, notably protective effects against various cancers. Nonetheless the average selenium dietary intake is lower than the recommended intake value. For example the average selenium intake of Belgium people is ranged from 28 to 61 $\mu\text{g}\cdot\text{day}^{-1}$ per person although the recommended intake value is 70 $\mu\text{g}\cdot\text{day}^{-1}$ per person according to the Belgium scientific committee [2].

Selenium-rich yeast is one of the most popular and cheap commercial Se supplements because of its ability to accumulate high content of organic Se, considered as safe and non toxic. Se is actually incorporated into metabolites by selenium – sulfur non-specific substitution. Selenium in Se-rich yeast is included in almost all bio-molecules usually containing sulfur but mainly as L-selenomethionine. Interestingly, the SELECT [3] clinical trial has demonstrated that L-selenomethionine was not the Se protective form of Se for cancer prevention.

The selenium speciation in Se-rich yeast is still in progress in order to understand the potential of molecular mechanisms of the protective effects. Some reports achieved to characterize several selenium containing oligopeptides in Se-rich yeast water extract using multidimensional liquid chromatography with elemental mass spectrometry (ICP MS) and molecular detection electrospray tandem MS [4,5]. Based on the MS/MS spectra, these reports supported that isomer forms of some selenium containing compounds were coeluted during liquid chromatography. The isomer forms may have potentially different efficiency in biological mechanisms of cancer prevention and have to be characterized.

Ion Mobility Mass Spectrometry (IM-MS) is an emerging field of mass spectrometry. The general principles is to separate ions using an acceleration potential into a slightly pressurizer flying tube. The velocity of ion will be affected according to their respective cross section. IM-MS is theoretically able to discriminate between the isomer forms because of the expected different cross section. The mass of parent and fragment ions can be obtained by hyphenation

of IM cell and tandem quadrupole - Time of Flight (ToF) Mass Spectrometer for example (it is the case for Waters© HR Synapt G2, IM ToF MS).

This work demonstrates the potentiality of the multidimensional liquid chromatography strategy for the purification of the selenium containing oligopeptides. The IM ToF MS is used to discriminate and identify the isomer forms on the basis of mobility time and tandem mass spectra. The amount of each isomer form (ratio) can be at least estimated. This analytical advance allows now the characterization of selenium containing compound to be obtained, including the isomer determination.

- [1] NPC, Nutritional Prevention of Cancer clinical trial, Clark *et al.*, JAMA (1996), **276**, 1957-1963.
- [2] Rayman, M.P., British Journal of Nutrition (2004), **92**, 557-573.
- [3] SELECT, the SELEnium and vitamine E Cancer prevention Trial, Lippmann *et al.*, JAMA (2009) **301**, 39-51.
- [4] Dernovics *et al.*, Metallomics (2009), **1**, 317-329.
- [5] Far *et al.*, ACA (2010), **657**, 175-190.