Complementary Use of ESI-MS and ICP-MS Hyphenated with HPLC for Identification of Metalloid Containing Metabolome

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Metalloids, i.e., elements which have in-between or mixture properties of metals and non-metals such as arsenic (As), antimony (Sb), selenium (Se) and tellurium (Te), are utilized in the metabolic pathways of animals and plants to form metalloid-containing compounds having carbon-metalloid covalent bond(s) (organometallic metabolites). Therefore, it is necessary to identify organometallic metabolites to determine the metabolic pathway of metalloids and understand the beneficial or toxicological effects of these compounds. However, these metalloids exist at extremely low concentrations in animals. The difficulty of detecting the metalloids in each organometallic metabolite after separation on the basis of chemical properties (chemical speciation) has been overcome with the emergence of inductively coupled plasma-mass spectrometry (ICP-MS) as the most sensitive and robust element detector available to date. Easily hyphenated with HPLC, HPLC-ICP-MS is the technique of choice for the speciation of metalloids in biological samples. However, there remains a critical disadvantage in the identification of organometallic metabolites by HPLC-ICP-MS. Although ICP-MS is sensitive to target elements and is robust to matrices, it provides little molecular information of organometallic metabolites. Thus, the identification by HPLC-ICP-MS is limited to the situation where certified or authentic metalloid species are available. As an alternative to HPLC-ICP-MS, electro spray ionization (ESI) and atmospheric pressure chemical ionization (APCI)-tandem mass spectrometry (MS-MS) is used to identify unknown organometallic metabolites [1,2]. ESI is a softer technique than ICP, and can provide molecular information. In addition, MS-MS enables structure elucidation. However, ESI-MS-MS has a number of weak points compared with ICP-MS. First, the detection limits of ESI-MS-MS for organometallic metabolites are inferior to that of ICP-MS. Second, ESI is severely affected by the sample matrix. To counter this problem, ESI-MS-MS is coupled with HPLC. Therefore, the complementary use of HPLC-ICP-MS and HPLC-ESI (APCI)-MS-MS is a powerful tool for the speciation and identification of organometallic metabolites. Indeed, unique metalloid-containing metabolites have been reported by the complementary use of inorganic and organic mass spectrometers [3,4].

The evolution of instruments for speciation, particularly for the identification of target organometallic metabolites in trace amounts in complex matrices, has contributed immensely to the exploration of metalloid-containing metabolome. In addition, ICP-tandem MS, i.e., ICP-MS-MS has been recently developed. ICP-MS-MS improves the detections of phosphorus (P) and sulfur (S) compromised in ICP-MS [5]. Hence, the complementary use of ICP-MS-MS and ESI-MS-MS may be applicable to speciation/identification of non-metallic element such as P and S-containing metabolites in near future.

References

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