

Identification of volatile metal(loid) compounds formed by intestinal microorganisms by use of simultaneous EI-MS and ICP-MS detection after gas chromatographic separation

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For investigation of biotransformation processes of heteroelements in the environment, both molecular and element-sensitive detection systems are used in hyphenation to chromatographic separation. In this work, we studied the potential of our recently developed gas chromatographic system with parallel electron impact mass spectrometry and inductively coupled plasma mass spectrometry (GC/EI-MS/ICP-MS) for non-target screening and subsequent identification of volatile arsenic compounds formed by intestinal microorganisms. Therefore, either fresh fecal slurries or continuous culture sampled from the Simulator of the Human Intestinal Ecosystem (SHIME), an *in vitro* gastrointestinal model, was amended with inorganic metal(oid) salts (Ge, As, Sn, Sb, Te, Hg, Pb and Bi) as well as the nonmetal selenium.

While for Sb, Te and Bi only permethylated species were detected, a broad range of complex volatile As and Se species was observed. By combined use of molecular and elemental detection after gas chromatographic separation (GC-EI-MS/ICP-MS) as well as synthesis experiments, these compounds were identified as methylthio species (dimethyl-methylthio-arsine, $(\text{CH}_3)_2\text{AsSCH}_3$, methyl-di(methylthio)-arsine, $\text{CH}_3\text{As}(\text{SCH}_3)_2$, methyl-methylthio-selenide, $\text{CH}_3\text{SeSCH}_3$, di(methylthio)-selenide $(\text{CH}_3\text{S})_2\text{Se}$), methyl-dithio species, (dimethyl-methyl-dithio-arsine, $(\text{CH}_3)_2\text{AsSSCH}_3$, methyl-methyl-dithio-selenide $\text{CH}_3\text{SeSSCH}_3$) as well as methyl-methylthio-ethylthio-arsine, $\text{CH}_3\text{As}(\text{SCH}_3)(\text{SC}_2\text{H}_5)$, dimethylthioarsinous acid, $(\text{CH}_3)_2\text{AsSH}$ and thio-bis(dimethylarsine), $((\text{CH}_3)_2\text{As})_2\text{S}$. Furthermore, one mixed arsenic/selenium compound, dimethyl-methylseleno-arsine, $(\text{CH}_3)_2\text{AsSeCH}_3$ was identified.

Five of these species, namely methyl-di(methylthio)-arsine, dimethyl-methyl-dithio-arsine, thio-bis(dimethylarsine), methyl-methylthio-ethylthio-arsine and dimethyl-methylseleno-arsine have not been described in environmental or human matrices before. Finally, the advantages of elemental and molecular detection after gas chromatographic separation are discussed.