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Performance and limits of liquid chromatography isotope ratio mass spectrometry system for halogenated compounds

Tetyana Gilevska, Matthias Gehre, and Hans Richnow

Helmholtz-Centre for Environmental Research – UFZ, Department for Isotope Biogeochemistry, Permoserstrasse 15, 04318 Leipzig, Germany (tetyana.gilevska@ufz.de)

Compound Specific Isotope Analysis (CSIA) has been an important step for the assessment of the origin and fate of compounds in environmental science.[1] Biologically or pharmaceutically important compounds often are not amenable for gas chromatographic separation because of high polarity and lacking volatility, thermostability.

In 2004 liquid chromatography isotope ratio mass spectrometry (LC-IRMS) became commercially available. LC-IRMS system intent a quantitative conversion of analytes separation into CO_2 via wet oxidation with sodium persulfate in the presence of phosphoric acid while analytes are still dissolved in the aqueous liquid phase.[2]

The aim of this study is to analyze the oxidation capacity of the interface of the LC-IRMS system and determine which parameters could improve oxidation of compounds which are resistant to persulfate oxidation. Oxidation capacity of the liquid chromatography isotope ratio mass spectrometry system was tested with halogenated acetic acid and a set of aromatic compounds with different substitutes. Acetic acid (AA) was taken as a model compound for complete oxidation and compared to the oxidation of other analytes on a molar basis. Correct values were obtained for di- and mono chlorinated and fluorinated and also for tribrominated acetic acid and for all studied aromatic compounds. Incomplete oxidation for trichloroacetic (TCAA) and trifluoroacetic (TFAA) acid was revealed with lower recovery compared to acetic acid and isotope fractionation leading to depleted carbon isotope composition compared to values obtained with an elementary analyzer connected to an isotope mass spectrometer Several optimization steps were tried in order to improve the oxidation of TCAA and TFAA: (i) increasing the concentration of the oxidizing agent, (ii) variation of flow rate of the oxidizing and acid solution, (iii) variation of flow rate of liquid chromatography pump (iv) addition of a catalyzer. These modifications lead to longer reaction time in the coil and increase in the concentration of radical but complete combustion of highly chlorinated or fluorinated compounds was not achieved. Due to these findings the limit for a LC-IRMS system for similar structure compounds can be predicted.

1. Elsner, M., et al., Current challenges in compound-specific stable isotope analysis of environmental organic contaminants. Analytical and Bioanalytical Chemistry, 2012. 403(9): p. 2471-2491.
2. Krummen, M., et al., A new concept for isotope ratio monitoring liquid chromatography/mass spectrometry. Rapid Communications in Mass Spectrometry, 2004. 18(19): p. 2260-2266.