

LC-IRMS Persulfate Oxidation: A Case Study of Neonicotinoid-Related Structures

Felix Niemann^{1*}, Annika Gruhlke¹, Marcel Plonowski¹, Maik A. Jochmann¹, & Torsten C. Schmidt¹

¹ Instrumental Analytical Chemistry, University of Duisburg-Essen

*Presenting Author Email: felix.niemann@uni-due.de

There is a gap in compound-specific isotope analysis (CSIA) methods for polar thermally labile substances. Many authors resort to derivatization and gas chromatography isotope ratio mass spectrometry (GC-IRMS). ESI-Orbitrap MS may become a growing contributor with new challenges and prospects for complex samples. Another commercially available technique for $\delta^{13}\text{C}$ measurements is liquid chromatography isotope ratio mass spectrometry (LC-IRMS). It involves aqueous chromatographic separation, wet-persulfate-based oxidation of analytes to CO_2 , a gas separator membrane, and finally analysis of the formed CO_2 by IRMS. Inefficient mineralization at the oxidation interface can be a major challenge for method developers as it can introduce isotopic bias and site-specific discrimination. Halogenated compounds and those with conjugated $\text{C}=\text{N}$ bonds are particularly challenging. Neonicotinoids, the most widely used class of insecticides, contain these structures, are thermally labile and polar. We used them as proxies to systematically investigate wet persulfate oxidation in the LC-IRMS interface. The influence of reaction time, reactor temperature, oxidant, acid and AgNO_3 concentration was evaluated for 12 model compounds in μ -EA mode. These compounds include nitroguanidine neonicotinoids such as imidacloprid and clothianidin, as well as structural subunits such as nitroguanidine, guanidine and 6-chloronicotinic acid. Peak areas and $\delta^{13}\text{C}$ values were compared to an inorganic carbon standard of known concentration and isotopic composition. Increasing reaction time, temperature, and oxidant concentration resulted in predictable improvements, whereas H_3PO_4 and AgNO_3 additions are highly compound dependent. Quantitative mineralization under conditions applicable to situations involving LC separation could not be achieved for most proxies, highlighting the need for new reactor designs or alternative reagents.