Comparison of different numerical approaches for multiple spiking species-specific isotope dilution analysis exemplified by the determination of butyltin species in sediments

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The application of isotope dilution analysis (IDA) in elemental speciation has allowed in the past years the development of highly accurate and precise quantification approaches for the determination of a wide range of elemental species even when analysing complicated matrices. Those applications have been always performed under two different spiking modes: species-specific and species-unspecific spiking. Nevertheless, only the first can be regarded as a reference or highly qualified primary method for speciation analysis as the unspecific mode is exclusively limited to the correction of errors derived from the detection step.

The main disadvantage of the species-specific spiking is the need of spike solutions containing the species to be analysed in an isotopically labelled form (previously synthesised or acquired if they are commercially available). However, once a complete mixing between the added enriched and the endogenous species is achieved, all the traditional advantages of isotope dilution analysis can be fully exploited. Furthermore, when several species of the same element need to be analysed, each compound can be enriched in a different isotope of the element, opening up a unique capability of quantification: Multiple Spiking Species-Specific-IDA. This form of isotopic labelling is able to quantify the concentration of species even when opposite or simultaneous degradation processes occur. Therefore, the multiple spiking is normally used for two main purposes: first, to study the extent or rate of transformation processes of elemental species in natural ecosystems or living organisms and second, to correct for the transformation reactions that the analyte species may suffer during the chemical analysis.

Depending on the availability of the isotopically enriched species and the complexity of the interconversion model (number of species to be analysed and their possible degradation/formation pathways), a more or less sophisticated and specific mathematical approach must be developed to quantify the extent of those processes and finally, the species corrected concentrations. An examination and comparison of all the mathematical approaches for multiple spiking species-specific isotope dilution analysis published so far in the literature is presented in this work with the determination of TBT and DBT in sediments. The basis of four different numerical approaches -"Calculation of Stable Isotope Concentrations", "Speciated Isotope Dilution Analysis", "Species-Specific Isotope Dilution Analysis" and "Isotope Pattern Deconvolution") are explained and compared in terms of complexity and analytical figures of merit. The capability of extending the methodologies to a higher number of analytes by the use of additional enriched species as well as the specific advantages of the different methods will be discussed.