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Designing valid and optimised standard addition calibrations: Application to the determination of anions in seawater

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Abstract

A strategy for designing valid standard addition calibrations and for optimising their uncertainty is presented. The design of calibrations involves the development of models of the sensitivity and precision of the instrumental signal, in a wide range of analyte concentration (or any other studied quantity), and the definition of sample dilution and standard addition procedures that allow fulfilling the assumptions of the linear unweighted regression model in, typically, a smaller range of standard addition calibrations. Calibrators are prepared by diluting the sample and adding analyte with negligible uncertainty to fit in a concentration range where signals are homoscedastic. The minimisation of the uncertainty is supported on detailed measurement uncertainty models function of calibrators preparation procedure and of analytical instrumentation performance. The number of collected signals replicates is defined by balancing their impact on the estimated expanded uncertainty, the resources needed and the target (maximum) uncertainty for the intended use of measurements.

The calibration design strategy was successfully applied to the determination of the mass concentration (mg L^{-1}) of Cl^- , Br^- , NO_3^- and SO_4^{2-} in seawater by ion chromatography. A target

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