TiO$_2$ nanomaterials detection in calcium rich matrices by spICPMS.

A matter of resolution and treatment.

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High Ca concentrations in complex matrices such as river waters often hamper detection of titanium nanomaterials (TiO$_2$ NPs) by single particle inductively coupled plasma mass spectrometry (spICPMS), because of isobaric interferences of $^{48}$Ca on the most abundant Ti isotope ($^{48}$Ti). Several approaches were used to reduce this interference while measuring TiO$_2$ in solutions with different Ca concentrations up to 100 mg/L. ICP-MS/MS was used with ammonia as reaction cell gas and high resolution (HR) ICP-MS was used at different resolution settings. These approaches were compared with measuring different Ti isotopes ($^{47}$Ti, $^{49}$Ti). spICPMS data was then treated with a deconvolution method to filter out dissolved signals and identify the best approach to detect the lowest possible corresponding spherical size of TiO$_2$ NP ($D_{\text{min}}$). ICP-MS/MS allowed for an important decrease of $D_{\text{min}}$ compared to standard quadrupole ICP-MS, down to 64 nm in ultrapure water, however sensitivity was reduced by the reaction gas and increasing Ca concentrations also increased the $D_{\text{min}}$. The comparably higher sensitivity of HR-ICP-MS allowed for measuring $D_{\text{min}}$ of 10 nm in ultrapure water. Combined with the deconvolution analysis, the highest resolution mode of the HR-ICP-MS leads to the lowest $D_{\text{min}}$, even though significant broadening of the measured TiO$_2$ mass distributions occurred at Ca concentrations up to 100 mg/L. Thereby, this work shows the feasibility of quantifying TiO$_2$ NPs and consequently Ti-colloids in presence of Ca.