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Manganese speciation in seawater: reaching the (sub)nanomolar scale

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Our previous work from the Chesapeake Bay and the Saint Lawrence Estuary showed that Mn(III) concentration varies considerably and may account for up to 100 % of dissolved manganese. As the concentration for total dissolved manganese in open ocean is very low (0.3 - 30 nM), there is no information about manganese speciation and the cycling between the three oxidation states of Mn in seawater (II, III, IV) is unknown. Here we present the optimization of a competitive ligand addition UV-Vis spectrophotometric method using a 100 cm pathlength quartz cell without any sample dilution to measure soluble Mn speciation. We achieve a sample detection limit below one nanomolar in seawater samples and have measured water column samples from the open Atlantic and Pacific oceans. Moreover, because we do not need sample pre-concentration, this method is easy to use especially at sea.