



Iron Speciation in the Subtropical Waters East of New Zealand using Multi Detection Window CLE-AdCSV Titrations.

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Iron plays a significant role in the ocean productivity as a micro nutrient that facilitates the growth of marine phytoplankton and microbes. The bioavailability of iron in the ocean depends on its speciation. Iron is bio available in its dissolved form and about 99.9% of dissolved iron in seawater is organically complexed with natural ligands. The competitive ligand equilibration - adsorptive cathodic stripping voltammetry (CLE-AdCSV) is the widely used technique to examine Fe speciation. The method has its own limitations. The analytical window employed in this technique has a distinct impact on Fe speciation results (Buck, Moffett et al. 2012). Recently, (Pizeta, Sander et al. in preparation) have shown that the accuracy of complexometric titrations improve if multiple analytical windows (MAW) are solved as a united dataset. Several programs are now available that enable this approach with the KMS (Kineteql.xls , Hudson 2014), which is based on an Excel application based on speciation calculation (Hudson, Rue et al. 2003, Sander, Hunter et al. 2011), being one of them.

In the present work, the unified MAW data analysis method is applied to determine iron speciation by CLE-AdCSV with salicyl aldoxime (SA) (Abualhaija and van den Berg 2014) in real seawater samples from the Spring bloom FeCycle III voyage, which took place in an anticyclonic eddy in subtropical waters east of New Zealand in spring 2012. Two different analytical windows (5 and 15 μ M SA) were applied to samples from depth profiles taken during this cruise. The data obtained was analysed using the program KMS (Kineteql.xls). Most samples only returned one Fe-binding ligands class. Higher ligand concentrations were observed in the upper water column and the stability constants were above 22 (e.g. 22.25 \pm 0.21 for station 63). Our results will be discussed in the context of microbial community distribution as well as other biogeochemical parameters.

Abualhaija, M. M. and C. M. G. van den Berg (2014). "Chemical speciation of iron in seawater using catalytic cathodic stripping voltammetry with ligand competition against salicylaldehyde." *Marine Chemistry* 164(0): 60-74.

Buck, K. N., J. Moffett, K. A. Barbeau, R. M. Bundy, Y. Kondo and J. Wu (2012). "The organic complexation of iron and copper: an intercomparison of competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-AdCSV) techniques " *Limnology and Oceanography: Methods* 10: 496-515.

Hudson, R. J. M., E. L. Rue and K. W. Bruland (2003). "Modeling Complexometric Titrations of Natural Water Samples." *Environ. Sci. Tech.* 37: 1553-1562.

Pizeta, I., S. G. Sander, O. Baars, K. Buck, R. Bundy, G. Carrasco, P. Croot, C. Garnier, L. Gerringa, M. Gledhill, K. Hirose, D. R. Hudson, Y. Kondo-Jacquot, L. Laglera, D. Omanovic, M. Rijkenberg, B. Twining and M. Wells (in preparation). "Intercomparison of estimating metal binding ligand parameters from simulated titration data using different fitting approaches." for *Limnology and Oceanography: Methods*.

Sander, S. G., K. A. Hunter, H. Harms and M. Wells (2011). "Numerical approach to speciation and estimation of parameters used in modeling trace metal bioavailability." *Environmental Science and Technology* 45(15): 6388-6395.