

# Determination of vanadium redox species V(IV) and V(V) in the South-East Atlantic Ocean using chelating resin and Inductively-Coupled Plasma Mass Spectrometry

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Vanadium exists in three oxidation states and is used as a tracer for biogeochemical processes in Earth surface environment. Its speciation is a complex function of pH, redox conditions, concentration and also biological activities. The pentavalent form V(V) is the dominant redox species in oxidized seawater, while V(IV) occurs under moderately reducing and acidic conditions, and it is also found in coastal seawater. V(III), thermodynamically stable in anoxic environment, is relatively rare in surface and near-surface waters. V(V) is also known as an essential nutrient for phytoplankton in the photic zone, and V(IV) and V(III) are generated via biotic and abiotic reduction of V(V). It is still unclear how V speciation is affected by water column properties, such as redox changes, biological activity and the concentration of other trace metals. In order to examine the distribution of V redox species in seawater and the mutual relationship with other biogeochemical parameters, we have conducted determination of V redox species of seawater taken from the South-East Atlantic Ocean (GEOTRACES research cruise G08, M121), which covered various regional characteristics including open ocean, upwelling seawater, freshwater discharge by river, and atmospheric input from desert.

For the separation of the two dominant V redox species, V(IV) and V(V), we applied a solid phase extraction method adapted after [1]. We then evaluated, modified and refined several methodological parameters e.g. column types, loading flow rate, elution volume, and elution acid to achieve the best separation results. The obtained eluates were analyzed with ICP-MS.

To evaluate the quality of the established separation procedure, we applied the method to a reference seawater NASS-7 (25.4±1.6 nM) and obtained an excellent agreement of total vanadium concentration (recovery rate 98%), with 15.2±3.8 nM for V(V) and 9.4±2.0 nM for V(IV). The preliminary results of 2 coastal seawater samples from a single sampling station show similar total V concentration (32.8 nM) and slightly higher V(V)/V(IV) at shallow depth (depth 60 m, V(V)/V(IV)=18.2) compared to the deeper one (depth 160 m, V(V)/V(IV)=10.8), suggesting a possible positive relationship of V(V)/V(IV) with increasing dissolved oxygen in seawater.

[1] Wang and Sañudo-Wilhelmy, *Marine Chemistry* 112, 72-80, 2008.