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The Measurement of Soluble (< 10 kDa) Trace Metals in seawater by the Vivaflow[®] 50

Dr. Peter Croot

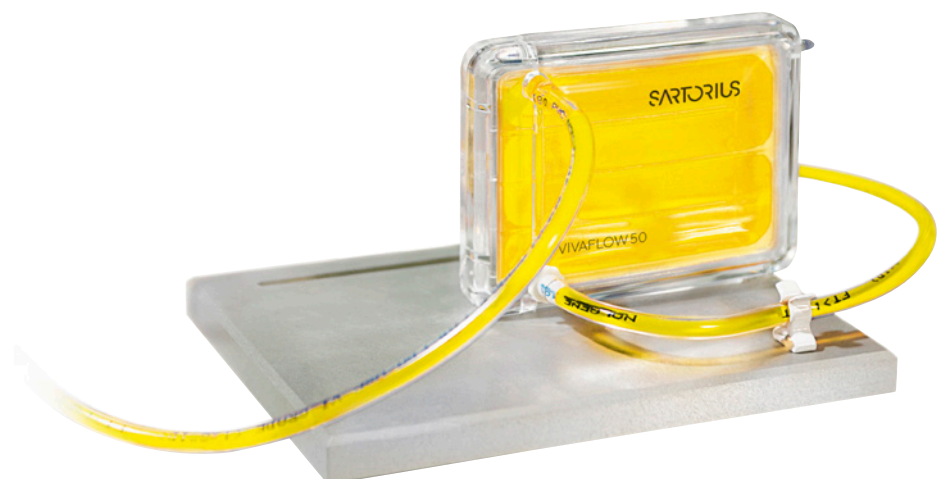
Leibniz Institut für Meereswissenschaften (IFM-GEOMAR)

Düsternbrooker Weg 20

24103 Kiel, Germany

Summary

A procedure for the determination of soluble (< 10 kDa) iron in seawater is described using Ultrafiltration with the Vivaflow[®] 50. The procedure outlines a rigorous cleaning procedure that allows examination of soluble metals at ambient seawater concentrations. It is suggested that this method can also be employed for other trace metals and for metal binding organic complexes in seawater. This preliminary data suggest that the Vivaflow[®] 50 is a fast, convenient and accurate way to separate soluble and colloidal metal species in seawater.



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Introduction

The physical speciation of trace metals in aquatic waters is of great importance in understanding their reactivity, bioavailability and overall residence time within the ocean. Processes such as colloidal formation, scavenging by particles and ligand dissolution of particles create a dynamic equilibrium between soluble, colloidal and particulate forms of metals. In open ocean systems phytoplankton productivity can be controlled by the concentrations of iron; which in oxic seawater is mostly present as insoluble Fe (III) colloids and particles.

However organic complexation of Fe (III) can increase the solubility and it is assumed change the physical size spectra for Fe towards more soluble complexes which may be more bioavailable to phytoplankton. Thus it is of great importance to determine the soluble and colloidal speciation of iron to further understand the biogeochemical cycling of iron in the ocean.

Concentration of Soluble and Colloidal Metals in Seawater

For the laboratory tests described here we use the cleaning procedure as outlined below and for all experiments we used a 10 kDa membrane. Initial tests showed that cleaning the Vivaflow® 50 membrane with dilute HCl was often insufficient to remove contamination from Fe in the system.

Contamination appeared to mostly come from two sources: Iron in the membrane and iron leached from the permeate tubing. To remove this contamination we added an extra rinsing of the system with an EDTA solution (10 mM: NaEDTA in Ultrapure water). The EDTA will bind all the metal contaminants in the system and the free ligand and metal complexes pass through the ultrafilter membrane. In the absence of Ca²⁺ and Mg²⁺ the kinetics of complexation formation should be relatively fast and the EDTA removes the metal contaminants rapidly. Residual EDTA in the system should be removed in the final ultrapure water rinse. Low concentrations of EDTA remaining in the system should not affect seawater measurements, as the trace metals will be out-competed for the EDTA by Ca²⁺ and Mg²⁺ but may interfere for freshwater samples. Use of the EDTA rinse reduced contamination substantially particularly with regard to contamination from the permeate outflow.

For the preliminary tests of the Vivaflow system reported here we used a seawater sample collected from the Southern Ocean to which we added a small amount of Fe (3 nM) to completely titrate out the natural complexing ligands present in the seawater, which had been previously measured as 2.4 nM (by Voltammetry). We used a Vivaflow® 50 with a 10 kDa membrane, cleaned as outlined in the procedure below, and the Fe content was analyzed by flow injection chemiluminescence analysis for Fe(II) after acidification and reduction of the Fe(III) in the sample.

To check for the possibilities of contamination or incomplete recovery, mass balances for the element of interest should always be performed.



The mass balance conditions are;

$$(1) C_i V_i = C_R V_R + C_P V_P$$

where C denotes concentration, V volume and the subscripts, i, r and p are respectively the initial sample, retentate and permeate.

The colloidal concentration can then be calculated as follows:

$$(2) [\text{Colloid}] = \frac{[\text{retentate}] - [\text{permeate}]}{CF}$$

where CF denotes the concentration factor [$CF = (\text{total volume}) / (\text{total volume} - \text{permeate volume})$]

The results of these experiments are shown in Figure 1. As expected the permeate concentration was lower than the initial concentration of the sample indicating rejection of colloidal iron, correspondingly there was an increase in the retentate. Calculated mass balances (shown in figure 2) for these recovery experiments were $107 \pm 9\%$ at the first time point and $101 \pm 7\%$ at the second time point indicating a good mass balance for the Vivaflow® 50 under the conditions of this experiment. For shipboard experiments we have used higher CF ratios of 2–5 at ambient iron concentrations ($30\text{--}300 \text{ pmol L}^{-1}$) and still observed good mass balances (ElFeX cruise: Jan–Mar 2004).

Estimates of the colloidal concentration for these samples is then $0.81 \pm 0.29 \text{ nM}$ and $0.71 \pm 0.14 \text{ nM}$ for the 1st and 2nd time points respectively. Indicating that the solubility, iron < 10 kDa, of the iron in this sample was controlled by the presence of the 2.4 nM colloidal ligand which was presumably mostly in the soluble size range.

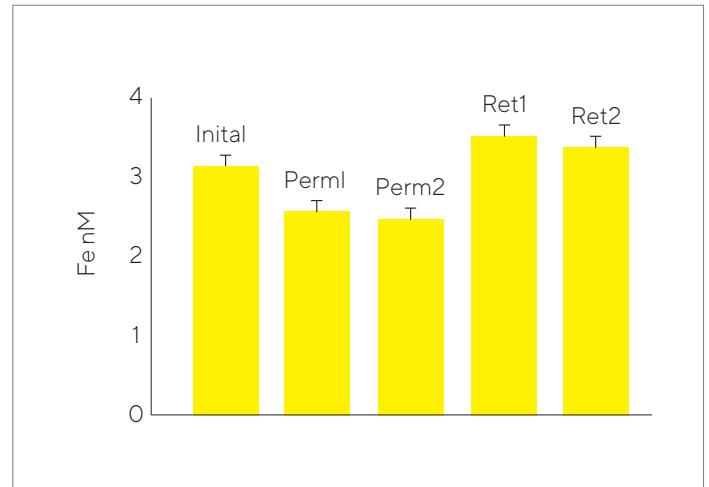


Figure 1: Concentrations of the initial 0.2 μm filtered seawater sample, permeate and retentate from the Vivaflow® 50 during recovery experiments.

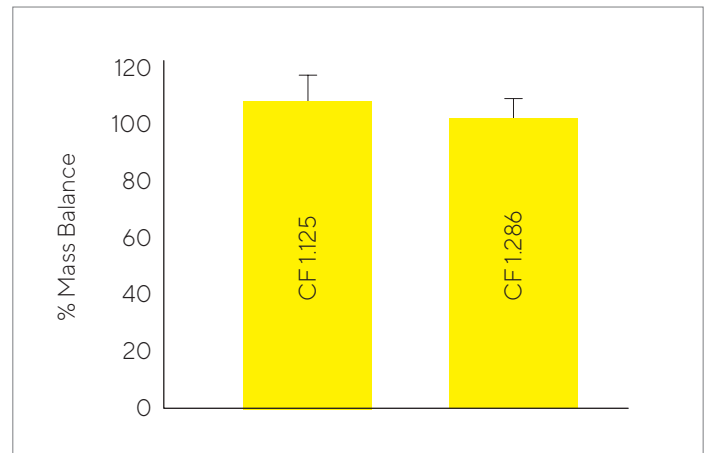


Figure 2: Mass balance for recovery of sample from experiments shown in figure 1.

Suggested Procedure

Seawater samples are collected cleanly using established techniques; this includes GO-FLO samplers for samples from the water column and the use of PTFE diaphragm pumps for near surface samples.

All handling and manipulation of the samples should take place in a Class 100 laminar flow bench and trace metal clean procedures should be used throughout. Seawater samples should be initially pre-filtered through 0.2-1 µm filters to remove particulates and the filtered sample should be processed as quickly as possible afterwards through the Vivaflow® 50.

The Vivaflow® 50 should be pre-cleaned by sequential rinsing with Ultrapure water, 1% HCl, the EDTA wash solution and then finally a last rinse with Ultrapure water to remove trace metal contamination.

The filtered seawater sample (200 mL) should then be concentrated using the Vivaflow® 50 to a concentration factor of between 2 and 5 for best results. Metal concentrations should be measured in both the retentate and permeate to ensure mass balance conditions are met.

For total metal analysis it may be necessary to UV irradiate all samples to remove interference from organic complexing agents.

Conclusions

The procedure described here for using the Vivaflow® 50 for ultrafiltration of seawater samples for trace metal analysis could be applied to other trace metals such as Co, Cu, Cd, Mn and Pb. The procedure can also be used in laboratory studies, with or without radiotracers. The procedure is fast, simple to use and can be used on low volume (100–400 mL) samples.

Sales and Service Contacts

For further contacts, visit
sartorius.com

Germany

Sartorius Lab Instruments
GmbH & Co. KG
Otto-Brenner-Strasse 20
37079 Goettingen
Phone +49 551 308 0

USA

Sartorius Corporation
565 Johnson Avenue
Bohemia, NY 11716
Phone +1 631 254 4249
Toll-Free +1 800 635 2906