

**Dissolved Manganese – values in nmol/kg  
Consensus values ( $\pm$  1 std. dev.) for North Atlantic GEOTRACES  
Reference Samples as of May 2013**

**GEOTRACES GS = 1.50  $\pm$  0.11 nmol/kg**

**GEOTRACES GD = 0.21  $\pm$  0.03 nmol/kg**

These are the current consensus values for the GEOTRACES reference samples as of May 2013.

**Labs participating in the analysis of the North Atlantic GEOTRACES  
reference samples to determine consensus values for dissolved Mn:**

**Maeve Lohan (U of Plymouth, U.K.):**

Flow injection method using an IDA Toyopearl AF-Chelate resin with catalytically enhanced UV/Vis detection based upon the method of Aguilar-Islas et al. (2006).

**Yoshiki Sohrin (U of Kyoto, Japan):**

Off line concentration using an EDTriA-type chelating resin with subsequent analyses by ICP-MS using the method of Sohrin et al. (2008)

**Ana Aguilar-Islas/Jingfeng Wu (UAF, U.S.):**

Concentrated off-line with the Mg(OH)<sub>2</sub> coprecipitation and analyzed by ICP-MS. Manganese was analyzed by two methods.

Method 1: The ratio between the natural abundance of <sup>55</sup>Mn and an added <sup>57</sup>Fe spike was used. 1.6ml of sample and spike were added and allowed to equilibrate for several minutes. A single co-precipitation step was carried out followed by dilution of the precipitate with 4% HNO<sub>3</sub>. A standard curve was created using Mn/Fe ratios vs. added Mn. Corrections were applied for the difference in co-precipitation efficiency between Mn and Fe, and for the amount of <sup>57</sup>Fe found in the sample (monitoring <sup>56</sup>Fe counts).

Method 2: Standard additions. 1ppb Co added to the nitric acid for tracking instrument fluctuations. The consistency of the precipitate was maintained by keeping the co-precipitation timing and solution pH identical for all additions.

For both methods blanks were quantified using 50  $\mu$ l of low Mn seawater instead of 1.6ml.

**Dondra Biller/Ken Bruland (UCSC, U.S.):**

Off-line concentration using a Nobias PA-1 chelating resin with subsequent analyses by ICP-MS (Biller and Bruland, submitted) based upon the method of Sohrin et al. (2008). The method entails an eight column manifold enabling eight separate  $\sim$  40 mL samples to be processed simultaneously (Biller and Bruland, 2012).

**Rob Middag/Hein de Baar (NIOZ, Netherlands):**

Analyses was based upon a flow injection method developed by Doi et al. (2004) with some slight modifications in the preparation and brands of the chemicals used. Furthermore, samples were buffered in-line with an ammonium borate sample buffer. Dissolved Mn in the buffered

sample was pre-concentrated on a Toyopearl AF-Chelate 650M (TesoHaas, Germany) column (Aguilar-Islas et al. 2006).

**Angie Milne/Bill Landing (FSU, U.S.):**

Off-line extraction using IDA Toyopearl AF-Chelate resin followed by analysis using ICP-MS (Milne et al. 2010). Prior to extraction the samples (12 mL) were UV oxidized and buffered to pH ~6.2. The method of standard additions was used for quantification and to account for any column extraction inefficiencies.

**Maria Lagerstrom and Rob Sherrell (Rutgers University, US)**

On-line flow injection with a modified seaFAST system, the Nobias PA-1 resin, isotope dilution and ICP-MS detection.

**Christian Schlosser and Eric Achterberg (Plymouth, UK)**

Off-line extraction using a WAKO chelating resin (Kagaya, 2009) followed by analysis on an Element XR ICP-MS. Samples were UV digested for 3 hours.

**Rob Middag and Ken Bruland (UCSC, US)**

Off-line extraction with Nobias PA-1 chelating resin and analysis on an Element XR ICP-MS (Middag et al., submitted).

**References:**

1. Aguilar-Islas, A.M., J. Reising, and K.W. Bruland. Catalytically enhanced spectrophotometric determination of manganese in seawater by flow-injection analysis with a commercially available resin for on-line preconcentration. *Limnology & Oceanography: Methods*, **4**: 105-113 (2006).
2. Doi, T., H. Obata, M. Maruo. Shipboard analysis of picomolar levels of manganese in seawater by chelating resin concentration and chemiluminescence detection. *Anal. Bioanal. Chem.* **378**: 1288-1293 (2004).
3. Sohrin, Y., S. Urushihara, S. Nakatsuka, T. Kono, E. Higo, T. Minami, K. Norisuye, and S. Umetani. Multielemental determination of GEOTRACES key trace metals in seawater by ICP-MS after preconcentration using an ethylenediaminetriacetic acid chelating resin. *Analytical Chemistry*, **80**: 6267-6273 (2008).
4. Milne, A., W. Landing, M. Bizimis and P. Morton. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Analytica Chimica Acta*, **665**: 200-207 (2010).
5. Biller, D.V. and K.W. Bruland. Analysis of eight trace metals in seawater using the Nobias-chelate PA-1 resin and magnetic sector inductively coupled plasma mass spectrometry. *Marine Chemistry*, **130/131**: 12-20 (2012).
6. Kagaya et al. A solid phased extraction using a chelate resin immobilizing ..., *Talanta*, **79**: 146-152 (2009).
7. Middag, R., K.W. Bruland and H.J.W. de Baar. GEOTRACES intercomparison of dissolved trace metals at the Bermuda Atlantic Time Series station. Submitted to *Limnology and Oceanography: Methods*.