

**Dissolved Manganese – values in nmol/kg
Consensus values (\pm 1 std. dev.) for SAFe Reference Samples as of
November 2011**

SAFe S = 0.79 ± 0.06 nmol/kg

SAFe D2 = 0.35 ± 0.06 nmol/kg

These are the current consensus values for the SAFe S and D2 reference samples as of November 2011. It is surprising to see such a wide range of concentrations for a trace metal where all the various methods have excellent detection limits, blanks and contamination is not a major factor. In general, methods based upon ICP-MS yield higher concentrations and methods based upon catalytic-enhanced flow injection yield lower concentrations – particularly for the SAFe D2 sample. Hopefully, this discrepancy will be resolved.

One subset of analysts yield the following data:

SAFe S = 0.74 ± 0.05 nmol/kg, and SAFe D2 = 0.29 ± 0.01 nmol/kg

Versus another subset of analysts that yield:

SAFe S = 0.82 ± 0.05 nmol/kg, and SAFe D2 = 0.39 ± 0.05 nmol/kg

Labs have not noticed a significant difference between UV treatment and non-UV treated samples for dissolved Mn.

Although only a small amount of data is available for SAFe D1, it appears to be the same concentration as SAFe D2.

**Labs participating in the analysis of the SAFe 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 EDTri-A-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 $Mg(OH)_2$ coprecipitation and analyzed by ICP-MS. Manganese was analyzed by two methods.

Method 1: The ratio between the natural abundance of ^{55}Mn and an added ^{57}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_3 . 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 ^{57}Fe found in the sample (monitoring ^{56}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 μl of low Mn seawater instead of 1.6ml.

Jeff Mendez (CIT, U.S.):

Concentrated off-line with the $\text{Mg}(\text{OH})_2$ copptn method and analyzed by ICPMS (Mendez et al., 2008). Using Fe isotope dilution as a yield tracer for Mn recovery.

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 six separate ~ 40 mL samples to be processed simultaneously. The samples were UV oxidized for 1.5 hrs, amended with H_2O_2 (final concentration of $10 \mu\text{M}$), and adjusted to pH 6.5 with ammonium acetate prior to the concentration step. The resin columns were rinsed with a weak ammonium acetate buffer at a pH of 6.5 and eluted with 3 mL of 1 N nitric acid for a concentration factor of ~ 13 , with subsequent analyses by ICP-MS. The Mo interference and correction were greatly reduced with the use of a PC3-SSI Peltier, water-cooled, spray chamber (Elemental Scientific Inc.).

Farah Idrus/Peter Statham (Southampton, U.K.):

Analysis was based upon the flow injection method developed by Doi *et al.* (2004), and subsequently used by Middag/de Baar at the NIOZ laboratory. This method has been modified and improved by incorporating six changes. The three major changes are 1) the use of a commercially available iminodiacetate (IDA) resin (Toyopearl AF-chelate 650M) in place of metal alkoxide glass containing fluoride-iminodiacetate-immobilized (MAF-IDA) for on-line preconcentration of manganese and matrix removal, and 2) the use of an NTA-type chelating resin column to remove interfering iron ions in the carrier solution (eluent), and 3) the use of a 1 meter mixing reaction coil instead of 10 meters to reduce light emission before going through the photomultiplier tube (PMT). Three minor improvements include use of more sodium carbonate in place of potassium carbonate to make up the luminol stock solution, degassing the formic acid eluent solution to prevent generation of air bubbles in the flow system, and the use of longer preconcentration and elution times.

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.

Pete Morton/John Donat/Bill Landing (ODU/FSU, U.S.):

Use of 8-hydroxyquinoline chelating resin off-line with subsequent analysis by ICPMS.

Geoff Smith/Ken Bruland (UCSC, U.S.):

On-line flow injection analysis of 4 ml of sea water using an EDTA-type chelating resin (Sohrin et al., 2008) at pH 6 utilizing purified ammonium acetate buffer and eluting analytes with 1.5M HNO₃ followed by detection with ICPMS.

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. Mendez, J., C. Guieu and J. Adkins. Atmospheric input of manganese and iron to the ocean: Seawater dissolution experiments with Saharan and North American dusts. *Marine Chemistry*, doi:10.1016/j.marchem.2008.08.006 (2008).
4. 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).
5. 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).
6. 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. Submitted to *Marine Chemistry*.