

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

SAFe S = 0.79 ± 0.06 nmol/kg

SAFe D2 = 0.35 ± 0.05 nmol/kg

These are the current consensus values for the SAFe S and D2 reference samples as of May 2013. There is no significant difference between UV-oxidized and non-UV treated samples for dissolved Mn. SAFe D1 appears similar to SAFe D2, however not enough data has been submitted to report a value.

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 μ l of low Mn seawater instead of 1.6ml.

Jeff Mendez (CIT, U.S.):

Concentrated off-line with the $Mg(OH)_2$ 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 (Biller and Bruland, 2012).

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.

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).

Maria Lagerstrom and Rob Sherrell (Rutgers University, US)

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

References:

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