

## GEOTRACES Intercalibration Document

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Element(s): Dissolved vanadium (V); dissolved copper (Cu); dissolved nickel (Ni); dissolved manganese (Mn); all reported in nmol/kg-sw.

Cruise(s): GP16 (US East Pacific Zonal Section; EPZT); also known as TN303.

### Analytical Methodology:

Water column samples were taken from the GEOTRACES carousel and filtered through pre-cleaned, 0.2  $\mu\text{m}$  Pall Acropak Supor filter capsules as described elsewhere (e.g., Cutter et al., 2012; Hatta et al., 2015). Near surface water samples were collected using an underway towed-fish pumped seawater system (Bruland et al., 2005) with samples filtered through sequential 0.45  $\mu\text{m}$  Osmonics and 0.2  $\mu\text{m}$  Polycarbonate (PCTE) cartridge filters. Filtered water was collected in 125 mL HDPE bottles (Nalgene) that had been pre-cleaned by soaking in hot 1.2 M HCl (reagent grade) for at least 8 h with subsequent thorough rinsing with ultrapure distilled deionized water (Barnstead E-pure). Samples were acidified in a laminar flow bench aboard ship using 0.5 mL of ultrapure HCl per 125 mL sample.

For analysis of dissolved V, Ni, Cu, and Mn, 14 mL of sample was spiked with a mixture of isotopically-enriched Ni-62, Cu-65, and V-50 (Oak Ridge Nat'l. Labs). Each spike was >90% enriched in the listed isotopes, except for V-50 (0.25% natural abundance) which was 44.3% enriched. The sample/spike ratio was chosen so as to have the analytical isotope ratios approximately the geometric mean of the natural and enriched spike isotope ratios. Samples were then extracted/pre-concentrated using a SeaFAST system (Elemental Scientific, Inc.) operated in offline mode. A 10-mL sample loop was employed and the elution volume was 750  $\mu\text{L}$ . A similar online SeaFAST extraction procedure is described by Hawthorn et al. (2012) for rare earth elements. The extracted samples were subsequently analyzed using a Thermo-Fisher high resolution ICP-MS with an Apex-FAST high efficiency sample introduction system with Spiro desolvator (Elemental Scientific, Inc.). All elements were determined in medium resolution. For Mn-55 the V, Ni, and Cu spikes served as internal standards. Calibration was checked by analysis of a large-volume composite North Atlantic surface seawater sample. Spiked (with a natural isotopic abundance elemental spike) and unspiked aliquots of this sample were analyzed twice in each analytical run. Ti-47 and Cr-52 were monitored to correct for any Ti-50 or Cr-50 isobaric interference on V-50; the correction was generally <1%.

The reproducibility error of this method was estimated by comparing samples collected at the same depths on different casts at the same station. For 32 pairs of these replicate samples, the average absolute deviation was 0.8 nmol/kg or typically 2%. Repeated runs of runs of US GEOTRACES intercalibration samples and in-house reference solutions suggest a precision of

$\pm 1.5\%$ ; the limit of detection for vanadium was  $\sim 0.5$  nmol/kg. Recovery of the method, as determined by repeated analysis of a spiked and unspiked seawater sample was  $99.5 \pm 2.8\%$ .

Intercalibration:

Table 1, below, shows information on recovery (based on spiked samples), precision, and analysis of GEOTRACES reference waters. Dissolved Mn data were compared with results from the Bruland, Wu, and Resing labs. Dissolved Cu data were compared with results from the Bruland and Wu labs. Dissolved Ni data were compared with results from the Bruland lab. In general, excellent agreement (generally within 5%) was observed among these various datasets.

We have been unable to find any GEOTRACES reference water determinations of dissolved V in seawater, though there are reports of analyses of the NASS series (e.g., Poehle et al., 2015) which we have not analyzed. In general, other reports find dissolved vanadium in deep ocean water to be  $\sim 35$  nmol/kg with about a slight reduction in concentration in the upper water column (e.g., Collier, 1984; Sherrell & Boyle, 1988; Middelburg et al., 1988). There is one report suggesting deep Pacific concentrations might be 10-15 nmol/kg higher than this (Jeandel et al., 1987), though their intercalibration effort showed somewhat variable results and Middelburg et al. (1988) show only a few nmol/kg inter-basin increase. Our results are in general agreement with the concept of  $\sim 35$  nmol/kg deep ocean V concentrations. Specifically, the average of our deep ( $>1000$  m) V data is 34.5 nmol/kg with a relative standard deviation of 7%. We provide here our analysis of GEOTRACES reference waters GS and GD which yield the following results (n = 16): GS =  $34.6 \pm 0.5$  nmol/kg; GD =  $32.9 \pm 0.5$  nmol/kg.

Our conclusion is that data from the literature indicates that our V results are within 5% of the consensus for the deep Pacific Ocean.

**Table 1**

	nmol/kg				
	Ni	Cu	Mn	V	
<b>Recovery</b>	100.1%	108.5%	98.9%	100.1%	n=14
<b>Stdev</b>	1.5%	5.7%	7.5%	2.0%	
<b>Detn Limit</b>	0.06	0.2	0.06	1	
<b>GS-16</b>	2.23	1.00	1.60	34.5	n=13
<b>Stdev</b>	0.02	0.04	0.04	0.4	
<b>GD-192</b>	4.22	1.75	0.28	32.9	n=13
<b>Stdev</b>	0.06	0.09	0.02	0.4	

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