Sampling and Sample-handling Protocols for GEOTRACES–related IPY Cruises, 2007-2008

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I. Introduction

The GEOTRACES Standards and Intercalibration (S&I) Committee is charged with ensuring that the data generated during GEOTRACES are as accurate as possible, which includes all the steps from sampling to analysis. Thus, sampling methods for dissolved and particulate constituents must take a representative (of the water depth/water mass) and uncontaminated sample, the samples must be stored (or immediately analyzed) in a fashion that preserves the concentrations (activities) and chemical speciation, and the analyses of these samples must yield accurate data (concentration, activity, isotopic composition, chemical speciation). The first tasks, sampling and sample storage, are being addressed via the GEOTRACES Sampling and Intercalibration grant (G. Cutter, K. Bruland, and R. Sherrell, co-PIs; 2007-2009) that is funded by the US National Science Foundation, and sampling and sample handling manuals will be created near it's completion. The S&I Committee will interface directly with this Intercalibration

program. However, International Polar Year (IPY) cruises will take place well before, or during this Intercalibration study, and some draft or interim protocols that can be used for IPY cruises are needed. This document includes protocols that the Committee feels represent the state-of-the-art at this time. However, they must be viewed as preliminary and the IPY researchers are encouraged to seek out the best methods that meet their needs while still maintaining the best overall accuracy. The protocols here are divided into 3 major groups: Hydrography and Ancillary Parameters, Radioactive Isotopes, and Trace Elements.

II. General Considerations

The following items should be included as a part of a standard intercalibration effort during all GEOTRACES IPY cruises:

A. Because there will be no GEOTRACES Baseline Stations to occupy during the IPY cruises, we strongly recommend that an intercalibration be conducted via replicate sampling during each cruise. In particular, a minimum of 3 depths (e.g., near surface, mid-water, and deep) at 2 stations should be sampled in duplicate, and samples from these replicates sent to different labs for the determination of trace elements and isotopes. The results from this effort can be examined later for data integrity and coherence.

B. Unless there is compelling evidence to the contrary, trace elements should be sampled from a "trace metal-clean" rosette or specialized samplers such as GO-Flo bottles deployed on Kevlar cable and tripped with plastic messengers, trace metal-clean sampling fish/pump systems, or MITESS vane samples (Bell, J., J. Betts, and E. Boyle. 2002. MITESS: A moored in-situ trace element serial sampler for deep-sea moorings, Deep-Sea Res. I, 49: 2103-2118). In contrast, radioactive isotope samples can be acquired using a more conventional CTD/rosette sampling system.

C. Nutrient and salinity samples should be taken along with all trace element samples in order to verify proper bottle and rosette operation and sampling depths (i.e., compare to the hydrography established with the conventional CTD/rosette).

D. While we will not recommend specific analytical methods for most variables (except for the ancillary parameters and two methods suggested in the Trace element section), during analyses (at sea or in a shore-based lab) appropriate certified reference materials (See VII. Glossary of terms), or SAFe samples as described in the Trace Element section, should be analyzed to assess accuracy.

III. Hydrography and Ancillary Parameters

Although GEOTRACES is focused on trace elements and their isotopes (TEIs), to achieve the overarching goal of understanding the biogeochemical processes controlling them, the suite of TEIs must be examined in the context of the oceans' hydrography, including nutrient (C, N, P, Si) cycling. Therefore, the same care in sampling and sample processing of ancillary parameters must be included in GEOTRACES protocols to ensure the best possible precision and accuracy. In addition to the basic water column hydrographic parameters of salinity, temperature, and depth, as well as in situ measurements of fluorescence, transmissometry, and oxygen concentrations, Table 1 lists GEOTRACES ancillary parameters (and suggested methods of determination) for discrete samples.

Table 1. Ancillary Parameters and Recommended Methods for GEOTRACES-IPY Cruises

Parameter	Method	Detection Limit	Reference
Salinity	Conductivity	NA (not applicable)	JGOFS Report 19
Oxygen	Manual or automated Winkler	1 μmol l^{-1}	JGOFS Report 19
Ammonium	Automated colorimetric	0.1 μmol l^{-1}	Parsons et al., 1984
Nitrite	Automated colorimetric	0.1 μmol l^{-1}	JGOFS Report 19
Nitrate	Automated colorimetric	0.1 μmol l^{-1}	JGOFS Report 19
Phosphate	Automated colorimetric	0.03 μmol l^{-1}	JGOFS Report 19
Silicate	Automated colorimetric	0.4 μmol l^{-1}	Parsons et al., 1984
Pigments	Fluorometry and HPLC	NA	JGOFS Report 19
DOC/DON	Oxidative Combustion	NA	PICES Report 34
POC/PON	Oxidative Combustion	NA	JGOFS Report 19

Parsons, T.R., Y. Maita, and C.M. Lalli. 1984. *A Manual of Chemical and Biological Methods for Seawater Analysis*. Pergamon, Oxford, 173 pp.

JGOFS Report 19, amended to cover the GEOTRACES-relevant parameters, and the PICES Report 34, DOC/DON section, are included at the end of this document. Modified Report 19, Report 34, and the publication by Parsons et al. (1984) cover all recommended procedures for sampling, sample processing/storage, and analyses for hydrography and ancillary data for 2007-2008 IPY cruises.

IV. Radioactive Isotopes

A. Protocols for ^{230}Th and ^{231}Pa

There is not a unique sampling and analytical procedure that can be recommended, but samples should be 0.4 – 0.8 μm filtered to measure separately dissolved and particulate ^{230}Th and ^{231}Pa.

Analytical instrument

The most widely used instruments for seawater analysis are sector-field ICP-MS (multi or single collector; Choi et al., Mar. Chem. 76, 99, 2001; Shen et al., Chem. Geol., 185, 165, 2002) and TIMS (Shen et al., 2003). ICP-MS is increasingly the instrument of choice because of higher sample throughput.

Volume required

The volume required for analysis of dissolved ^{230}Th and ^{231}Pa range from a few liters (Shen et al., 2002) to 15-20 liters (Choi et al., 2001). As a rule of thumb, the volume required to analyze suspended particles is 5 x larger for ^{230}Th (10-100L) and 20 x larger for ^{231}Pa (40-400L). The volume required for analysis bears significantly on sampling methods (for particles) and sample processing (for dissolved).

There are several options at each step of the procedure. This provides flexibility but will necessitate careful intercalibrations.

Sampling

Dissolved: If the volume required is 10-20 L, dedicated hydrocasts may be necessary.

Particles: All seawater samples must be filtered as soon and as fast as possible to avoid loss of dissolved Th and Pa by absorption on bottle walls (gravity filtration may be too slow to avoid loss by absorption on filters). These filters could be analyzed for ^{230}Th and ^{231}Pa using the most sensitive analytical techniques (Shen et al., 2002; 2003), but less sensitive methods (Choi et al., 2001) will require collecting larger samples by in-situ pumping. In the latter case, particles collected by hydrocast can be used for ancillary analysis (C_{org}, opal, carbonate, etc...).

Filtered seawater samples must be stored in acid-cleaned high or low density polyethylene (HDPE or LDPE) containers.

Sample volume or weight: A variety of approaches have been used to record sample weight or volume, and the literature should be consulted for the best one to use in a particular cruise (e.g., open water vs. in the ice).

Question to be addressed during GEOTRACES Intercalibration cruises, but to be kept in mind during the IPY cruises:

- Contamination during sampling: Can we safely use regular Niskin bottles with black rubber internal springs? Do we need to use Niskin bottles with epoxy-coated stainless steel springs? Do we need to use TM-clean rosettes? The latter does not seem necessary but this has never been clearly established
- Filtration of particles: The most widely used filter types are Versapor 800 (0.8 μm) and Nuclepore (0.4 μm). We will have to compare gravity, pressure and in-situ filtration and the use of peristaltic pumps with the two different filter types.

Acidification, spiking and pre-concentration

In previous studies (see below), filtered seawater samples have either been acidified, spiked and pre-concentrated at sea or acidified, and shipped to the home laboratory for spiking and pre-concentration. For larger volumes, "at sea" processing is often the method of choice. Smaller samples can more easily be shipped to home institutions. The advantages of "at sea" processing are: (1) lower risk of ^{230}Th and ^{231}Pa loss by absorption on the walls of the storage container (2) avoids shipping of large quantity of seawater. The advantages of "on land" processing are: (1) avoids shipping and handling of radioisotopes at sea (2) requires less space and personnel on-board.

Acidification: Add 1 mL concentrated HCl (ultraclean) or HNO_3 (suprapur) per L of seawater (pH 2).

Spiking: Measurements are done by isotope dilution using ^{229}Th for ^{230}Th and ^{233}Pa for ^{231}Pa.

^{233}Pa spike preparation: There are two ways for producing ^{233}Pa: (1) by milking ^{237}Np (2) by neutron activation of ^{232}Th.

- ^{237}Np milking: the ^{233}Pa spike must be checked for ^{237}Np bleeding (2nd cleaning step may be needed).
  Advantages: No ^{231}Pa blank; No ^{232}Th contamination
- ^{232}Th irradiation: Advantages: Large quantities (1mCi) can be easily produced
  Disadvantages: ^{232}Th contamination precludes its measurement in the same sample. ^{231}Pa is produced by neutron activation of ^{230}Th traces in the ^{232}Th target. ^{231}Pa contamination can be kept low by preparing a new spike before the cruise to minimize the ^{231}Pa/^{233}Pa in the spike. It can also be precisely quantified by measuring ^{231}Pa/^{233}U in the spike after ^{233}Pa decay. Typically, ^{231}Pa blanks range from ~10% in surface water to ~1% in deep water

Pre-concentration: Pre-concentration of ^{230}Th and ^{231}Pa is done by adsorption on a precipitate formed in seawater (scavenging), which is then recovered by decantation and centrifugation and returned to the home laboratory for ^{230}Th and ^{231}Pa purification by ion-

exchange. Several scavenging methods have been used: (1) on Fe hydroxide (2) on Mg hydroxide (3) on MnO_2.

- Fe hydroxide: 0.05 ml $FeCl_3$ (50mg Fe/ml; cleaned by extraction in isopropyl ether) is added per liter of acidified seawater with the ^{229}Th and ^{233}Pa spikes. The spiked seawater is left to equilibrate for at least 24 hours. Thereafter, ~20ml conc. Ammonium Hydroxide (ultraclean) is added to bring the pH to 8.5-9 and precipitate $Fe(OH)_3$. After 12-24 hours of settling, most of the supernatant is removed and the precipitate is centrifuged.
- Mg hydroxide: Seawater is acidified, spiked and left to equilibrate for 24 hours. Thereafter, concentrated NH_4OH (ultraclean) is added to precipitate $Mg(OH)_2$. The precipitate is decanted and transferred into 250ml polyethylene bottles. 7N HNO3 is then slowly added to reduce the volume of precipitate.
- Mn dioxide: Seawater is spiked and left to equilibrate for 12 hours. Thereafter, a few drops of ultraclean concentrated ammonia are added, with 0.75mg/L $KMnO_4$ and 2mg/L $MnCl_2$ (Rutgers van der Loeff and Moore, 1999). After 24 hours, the MnO_2 is filtered on 1µm polycarbonate filter.

Question to be addressed during GEOTRACES Intercalibration cruises, but to be kept in mind during the IPY cruises:

- Can we store filtered acidified samples for subsequent spiking, pre-concentration and analysis without losing ^{230}Th or ^{231}Pa on the walls of the containers? For how long can we store the samples?
- Compare the different scavenging methods ($Fe(OH)_3$ vs. $Mg(OH)_2$ vs. MnO_2)

Spike calibrations

GEOTRACES should agree on a primary Th standard (e.g. NIST SRM 3159) to calibrate the ^{229}Th spikes used by different laboratories. In the meantime, ^{229}Th spikes used in GEOTRACES cruises should be archived for future inter-calibrations.

Calibration of ^{233}Pa is best done by measuring the ingrowth of ^{233}U by isotope dilution with a ^{236}U standard. GEOTRACES should agree on a primary U standard (e.g. NIST CRM-145) to calibrate the ^{236}U standards used by different laboratories. In the meantime, the ^{236}U standards used to calibrate ^{233}Pa spikes for GEOTRACES cruises should be archived for future inter-calibrations.

Evaluation of precision of measurements

Precision of measurements conducted on each cruise would be best documented by analyzing a set of replicate seawater samples (3 to 6) in the mid-concentration range during each cruise (see IIA. above).

References

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B. Protocols for ^{234}Th

The method of choice for sampling and analysis of ^{234}Th will depend on the environment and on the questions to be answered. We refer to the recent review of (Rutgers van der Loeff et al., 2003) and the methodological papers on which this is based (Buesseler et al., 2001; Buesseler et al., 1992; Cai et al., 2006; Pike et al., 2005; Rutgers van der Loeff and Moore, 1999). For direction in choosing the appropriate ^{234}Th procedure, a decision flow chart was developed by Rutgers van der Loeff et al. (2006).We include here some recommendations from that paper for the measurement of dissolved, particulate, and total ^{234}Th:

1. First and foremost, the validity of the U–Salinity relationship is only appropriate for estimating dissolved ^{238}U in the open ocean, where waters are well oxygenated and removed from freshwater input. In other regimes, i.e. continental shelves, estuaries, marginal or semi-closed seas, and suboxic/anoxic basins, the U concentration must be measured.

2. In the collection and measurement of ^{234}Th, Mn cartridges and the "cartridge formula" should be used with care. There are persistent problems related to variations in the extraction efficiency of MnO_2-coated cartridges. The assumption of a constant extraction efficiency determined by the ratio of two cartridges in series may cause both random and systematic errors in calculated ^{234}Th activity that are highest when the extraction efficiency is lowest, i.e. under conditions of high flow rate and in the presence of high concentrations of humic substances. The factors that cause the observed variations on the relative and absolute extraction efficiencies may be addressed in the future with laboratory experiments and field studies using multiple cartridges and ultrafiltration. As long as these variations cannot be quantified or prevented, the method using the "cartridge formula" should be discouraged if high precision and accuracy are required.

3. The MnO_2 co-precipitation technique should only be applied to unfiltered samples if the self-absorption of beta radiation by the particulate fraction on the filter can be neglected or quantified. Yield tracers should be used for the small volume technique unless reproducibility can be maintained e.g. through automation. If no yield tracer is used routinely, it should be checked whether the precipitation efficiency of the sample and of the standard is comparable. This may be an issue when calibrating coastal samples with water from the open ocean.

4. When samples are filtered to separate the particulate fraction, the effect of sorption of dissolved ^{234}Th onto the filter should be considered, especially in open ocean studies where particulate ^{234}Th activities are low.

5. Beta counting of filters can be well calibrated only if a) the loading is small enough that self-absorption of ^{234m}Pa is absent or b) the loading is constant and can be reproduced with a standard or c) the filter can be prepared to form a homogeneous source of radiation (as in the case of a multiply folded filter) which allows the correction technique described in Section 3.2 of Rutgers van der Loeff (2006). In other cases there is no way to correct for self-absorption of the sample and non-destructive beta counting is not a viable option.

6. We recommend that an intercalibration study be conducted of the methods measuring ^{234}Th on particles collected in bottles, in situ pumps, continuous centrifuge, surface sediment and sediment traps.

7. Calibration of detectors for various sample types remains a complex issue. In order to standardize the use of "home-made" standards (such as the examples described in section 3.5 of the paper), it would be extremely useful to provide the scientific community with a standard operational procedure. A relatively easy method that can be followed by any lab is to process a natural sample of aged acidified filtered (sea)water in which ^{234}Th and ^{238}U have reached secular equilibrium and ^{238}U activity has been determined (by alpha spectrometry or ICP-MS). Alternatively, one of the best standards for the inter-calibration of ^{234}Th techniques is to use filtered aged deep-ocean water where the activity of ^{238}U is precisely known and the colloidal ^{234}Th significantly lower than that found in surface waters. Care must be taken in storing that water, e.g. by acidifying it immediately after collection, to prevent Th absorption onto container walls. Aliquots of this water would then be neutralized to seawater pH prior to use. Although this method is quite useful for standardizing procedures that use small volumes (less than 20 L), large-volume filtration techniques will require the storage of large volumes of deep water. This generates predictable logistical problems. For larger volumes, a standard can be prepared on board by adding a known amount of ^{238}U (which is in secular equilibrium with ^{234}Th) to a known volume of ^{234}Th-free filtered water or to a carefully prepared ^{234}Th-free synthetic seawater.

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C. Protocols for ^{226}Ra and ^{228}Ra by Ba(Ra)SO_4 precipitation

The precipitation of radium as Ba(Ra)SO_4 is a quantitative method for the determination of ^{226}Ra and ^{228}Ra by gamma-spectrometry. Prerequisite to this is the slow and complete precipitation of radium in the presence of a barium carrier solution from a known volume of water, thereby making use of the natural sulfate content. $BaCl_2$ solutions are prepared prior to a cruise/campaign as pre-weighed 100ml aliquots, following the method described by Rutgers van der Loeff and Moore (1999). This method takes advantage of the low solubility product of $BaSO_4$ and the chemical similarity of barium and radium. Efficiency is determined gravimetrically through $BaSO_4$ recovery.

Sampling procedure

- Use a pre-weighed container, note empty weight in logsheet to work out sample volume
- Rinse container twice with sample water
- Fill 20-40 L of sea water in container
- Weigh the container, note total weight in logsheet
- Place a magnetic stirring bar (about 5 cm in length) on the bottom of the container and put container on magnetic stirrer
- Place a syringe or small column, equipped with a tip at the end, over the container, fill with deionised water and check dripping velocity; adjust by

squeezing tip more or less; 100ml should roughly take 20 min to percolate through

- Fill one pre-weighed $BaCl_2$ aliquot in syringe and let drip into sample
- Rinse bottle of aliquot, including lid, several times and add to syringe
- Rinse syringe several times after aliquot has passed through
- Let the sample on the stirrer for another 60-90 min; white clouds of $BaSO_4$ should start forming after 15 min
- Stop magnetic stirrer, remove and rinse magnetic stirring bar
- Close container and set aside for 2-3 days to allow $BaSO_4$ crystals to settle; knock on container walls after about a day to remove air bubbles
- Concentrate crystals by repeated decantation and transfer to smaller containers (20 L -> 5 L, maybe 1 L), allow time for crystals to settle in-between, remove air bubbles from container walls; finally concentrate crystals in falcon tube by centrifugation
- Clean containers, syringe and magnetic stirring bar mechanically with sponge or paper; take especially care of corners and taps, give rinse with diluted HCl and deionised water
- Store syringe in plastic bag between precipitations
- To be done in the home lab:
    - Wash precipitate with deionised water and centrifuge; repeat this step 3-5 times until all interfering ions are washed out
    - Dry crystals in glass beakers
    - Weigh crystals into vials or plastic tubs suitable for gamma spectrometry; samples should be sealed with e.g. Parafilm.

Additional remarks

- The use of clear containers (polycarbonate) facilitates recovery of the white crystals and subsequent cleaning.
- Empty weight of the containers should be known and marked on lid before the cruise.
- Weighing on a moving ship can introduce an error; yet even under rough conditions it hardly exceeds 100 g for 20 L when carefully carried out.
- Surface water should be prefiltered before precipitation as the particulate matter will alter the recovery which is determined gravimetrically.
- Sampling can be done either on station or on a sailing ship. In the latter case, it is recommended to split the sampling in 3 x 7 L, evenly distributed over the sampling transect. Note sample points in logsheet.
- Addition of extra SO_4^{2-} ions might become necessary for samples of lower salinity (Baltic Sea, estuaries). Use e.g. diluted sulphuric acid.
- Water profiles: 3 Niskin bottles are necessary for one depth. If station time is restricted, less water can be used (which must be compensated by longer gamma-counting times). Add extra SO_4^{2-} ions when using only 12 L of water.
- If samples cannot be precipitated straight after sampling, acidify sample with 6 HCl.

- When filling the dried precipitates into counting tubes, care should be taken to apply the same pressure for all samples. Similarity in density and geometry is one prerequisite for the successful calibration of the samples.
- Sealing of the dried $BaSO_4$ precipitates is more important to prevent the loss of sample material than the escape of Radon. Radium is tightly bound in the crystal lattice of $BaSO_4$. If any, only a small fraction of ^{222}Rn will be able to leave the sample within its short half-life (<2%; Michel et al. 1981).
- Care should be applied to the preparation of a calibration source with a certified ^{226}Ra and ^{228}Ra activity. This is best done by precipitation of a spike solution of known activity with a $BaCl_2$ aliquot. This will result in a calibration source of same matrix, geometry and density as the samples (Reyss et al. 1995). Ideally, three to five sources are prepared and the samples calibrated against the mean of them.

An alternative approach to this method is the use of MnO_2-coated fibre. With a low flowrate (< 1 L/min), the activity is transferred quantitatively onto the fibre. This method is identical to the sampling for short-lived radium isotopes (see corresponding protocol). Subsequent rinsing and ashing gives a sufficiently small amount of ash to be counted in a bore-hole gamma detector. Ashing is done at 820° C for 16 hours in a covered 250 mL ceramic crucible. Thirty grams (dry wt) fiber is reduced to ~3-4 g of ash. The ash is then homogenized with a spatula, placed in a counting vial, and sealed with epoxy for >3 weeks prior to counting to allow for ingrowth of the ^{214}Pb daughter (M. Charette, pers. com.).

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D. Protocols for short-lived radium isotopes: ^{223}Ra, ^{224}Ra

The method of choice for the analysis of ^{223}Ra and ^{224}Ra is the delayed coincidence technique of Moore and Arnold (1996). Radium is extracted from seawater onto a column of MnO_2-coated acrylic fibre (Moore, 1976; Moore and Reid, 1973).

Samples are collected in 100-1000 liter tanks. In turbid waters samples are filtered (e.g., 1-μm Hytrex II cartridge). The filtrate is then passed through a column of MnO_2-coated

acrylic fiber ("Mn-fiber") at <1 l/min to quantitatively remove radium (Moore, submitted; Moore et al., 1985). The amount of fiber needed should be adapted to the volume of water sampled, but should be at least 15 g dry MnO_2-coated fiber (Moore, 1976; Sun and Torgersen, 1998). It is advised to use occasionally two fiber packages (A and B) in series to check the adsorption efficiency of each fiber package. Preparation of the fiber is described in Rutgers van der Loeff and Moore (1999).

Each Mn-fiber sample containing adsorbed Ra is partially dried by passing compressed air through a vertical tube containing the fiber for 2-7 min, which should then have a water-to-fiber weight ratio of 0.7 to 2.5 (Sun and Torgersen, 1998). The damp fiber is fluffed and placed in a tube connected to the closed loop circulation system described by Moore and Arnold (1996).

Further details of the procedure by Dulaiova and Burnett (2004) and recommendations made by W.S. Moore follow.

Details of the procedure and recommendations by H. Dulaiova (2004)

Approximately 150 cm^3 (~25 g dry weight) of fiber is packed into a cylindrical cartridge. The water is either slowly (1 to 2 L min-l) passed through the fiber without collection at a controlled flow-rate, or it is collected in containers and processed at a more convenient time. The flow-rate of water passing through the fiber has to be below 2 L min^{-1} to achieve quantitative radium adsorption (Moore, 1976; Moore et al., 1995). Kim et al. (2001) have checked for complete radium uptake by pumping 500 L of groundwater through two columns connected in series. No detectable radium was found on the downstream column, while significant radium was on the initial column, confirming quantitative adsorption. In certain cases groundwater can be reducing, containing hydrogen sulfide or other reducing agents. In such cases the water can reduce and thus dissolve the manganese on the fiber, causing less than quantitative radium recoveries. In such cases we pump the water into an open container, and the sample is degassed and oxidized before processing. In a different approach, one could pass water samples through Mn fiber using a high flow-rate to yield only the ratios of ^{223}Ra, ^{224}Ra, and ^{228}Ra to ^{226}Ra, and then the ^{223}Ra, ^{224}Ra, and ^{228}Ra are quantified by a separate measurement of ^{226}Ra using standard radon-emanation or some other convenient method. This later approach is preferred if the sampling time needs to be as short as possible. In a similar manner, if one desires to measure just the activity ratios of radium isotopes, the fiber could be either immersed in situ in the water to passively collect radium or towed through the water for times depending on the expected activities. After exposing natural waters to the Mn fiber by whatever means, the fiber is flushed with Ra-free deionized water. This rinse is important to wash out any particulates and sea salts that can interfere with radon emanation during the measurement (Moore, 2000; Sun and Torgersen, 1998)

After radium is extracted and Mn fiber is rinsed, the moisture of the fiber is adjusted to have a water-to-fiber weight ratio in a range from 0.7 to 2.5 (Kim et al., 2001; Sun and Torgersen, 1998). This adjustment is easily performed by either hand squeezing or drying via compressed air. The short-lived isotopes ^{223}Ra ($T_{1/2}$ = 11 d) and ^{224}Ra ($T_{1/2}$ = 3.6 d)

are then measured by a delayed coincidence counter system developed by (Moore and Arnold, 1996). The partially dried fiber is placed in a helium-circulation system in which the short-lived radon daughters of ^{223}Ra and ^{224}Ra (^{219}Rn and ^{220}Rn) are swept into a scintillation detector, and a delayed coincidence circuit discriminates the alpha decays of the different radium daughters by the timing of the alpha-decay events. The system is calibrated using ^{232}Th and ^{227}Ac standards that are known to have their daughters in radioactive equilibrium and are adsorbed onto a MnO_2-coated fiber. Alternatively, one could measure ^{224}Ra on the fiber by a method developed by Kim et al. (2001) that uses a commercially available radon-in-air monitor (RAD-7, Durridge) to count ^{220}Rn released from the fiber.

When the short-lived radium measurements are completed, the fiber is processed for the measurement of long-lived ^{226}Ra and ^{228}Ra by gamma-spectrometry.

Further recommendations by H. Dulaiova

1. Supply of surface seawater supply. When collecting large sample volumes for short-lived radium isotopes the ships' seawater intake may not be appropriate if the pipes have scale containing Mn and Fe precipitates that sorb Th and ^{228}Ra, since all these are usually a source of ^{224}Ra and ^{223}Ra. One should test the water from the pipes before relying on its use. I had bad experience even with a ships clean-water intake, on the other hand a fire-intake worked fine just because it was flushed better and the flow rate was so high that the scale could not deposit.

2. Standards. For the short-lived radium isotope counting via the delayed coincidence counter special care should be taken while preparing the standards from ^{232}Th and ^{227}Ac. Some issues have been described in Burnett et al. (submitted to Monaco special issue of Marine Chemistry). They found that standards prepared from DI water did not have a quantitative Th and Ac uptake and therefore were not good standards.

3. Rinsing. Rinsing the fiber is very important both before and after sample collection. Since we do not have a very efficient way of rinsing the fiber after cooking, it has some residual Mn on it that can be washed out before passing the sample through. I make great care that the fiber is washed especially well before standard preparation.

Recommendations by W.S. Moore (cf. Moore, submitted)

1. Flow rate. We have demonstrated that 97±3% of the Ra is recovered at flow rates of 1 L/min or less. Such flow rates avoid the use of a B column. At this flow rate we have repeatedly extracted 97% of the Ra present in 835 L of sea water. The alternative of using higher flow rates to determine Ra isotope ratios plus a quantitative ^{226}Ra measurement is fine.

   2. Quantity of Mn-fiber. I favor using 25 g dry weight, which in my experience is about 250 ml fluffed fiber. The Mn-fiber should be prewashed to remove unbound MnO_2 particles.

3. Column clogging. The outlet of the Mn-fiber column may become clogged with strings of fiber. This is avoided by putting a small plug of raw acrylic fiber at the base of the Mn-fiber.

4. Reducing waters. This must be approached on an individual basis. We have found that aerating highly sulfidic waters produces a thick cloud of S that fouls everything. I think the best approach here is to use extra Mn-fiber, maybe an A+B+C column and to verify recovery with a quantitative ^{226}Ra precipitation.

5. Drying for RaDeCC. A flow of compressed air for 2-7 minutes will dry the fiber sufficiently for the short-lived measurements. Hand squeezing tends to dislodge particles of MnO_2.

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E. Protocols for ^{210}Po, ^{210}Pb, and ^{7}Be

^{210}Po and ^{210}Pb

The determination of ^{210}Po and ^{210}Pb is routinely conducted in the same sample, first by measuring ^{210}Po (called 'in-situ' ^{210}Po) and then keeping the sample for a period of 6 months to 2 years for the in-growth of ^{210}Po from ^{210}Pb. The second ^{210}Po (called 'parent-supported') measurement provides the data on the concentration of ^{210}Pb. Decay and in-growth corrections are applied in the determination of ^{210}Po and ^{210}Pb activities at the time of sampling.

Analytical instrument:
The most widely used instrument for seawater (both dissolved and particulate) ^{210}Po and ^{210}Pb analysis is alpha spectroscopy (Fleer and Bacon, 1984; Sarin et al., 1992; Radakovitch et al., 1998; Hong et al., 1999; Kim et al., 1999; Rutgers van der Loeff and Moore, 1999; Friedrich and Rutgers van der Loeff, 2002; Masque et al., 2002; Stewart et al., 2007).

Volume required:
The volume required for analysis of dissolved and particulate ^{210}Po and ^{210}Pb range from a few liters (Hong et al., 1999) to 20-30 L (Sarin et al., 1992; Kim et al., 1999; Friedrich and Rutgers van der Loeff, 2002; Masque et al., 2002; Stewart et al., 2007).

Sampling:
Dissolved: Water samples will be collected using 30-L Niskin bottles and filtered through 0.7 μm GFF filter. Filtering 20-30 L water samples through 0.2 or 0.4 μm filter may be a challenge and hence it is recommended that we use 0.7 μm filters.
Particulate: The used 0.7 μm GFF filter will be utilized for the determination of particulate ^{210}Po and ^{210}Pb.
Sample weight or volume: When water sample from the Niskin bottle is collected in a pre-cleaned cubitainer, the total weight can be measured on a balance (precision ± 1 g). In a boat, it may be difficult to obtain ± 1 g, but even ± 10 g error will only result in a error of ± 0.05% on a 20-L sample.

Questions to be addressed during GEOTRACES Intercalibration cruises, but to be kept in mind during the IPY cruises:
Testing the storage artifacts for ^{210}Po and ^{210}Pb in acid cleaned 20-L low density polyethylene cubitainers will be conducted. Documentation of the effects of storage on

time scales comparable to the storage times of samples in the field (1-5 days) will be completed prior to the cruise. The sorption of dissolved 210Po and 210Pb on to GFF filter paper will be evaluated prior to the cruise.

Acidification and spiking:
Immediately after the sample collection, the water sample should be filtered through 0.7 μm filter paper. The filtrate will be acidified using 25 ml high-purity conc. HCl immediately after filtration. To the filtrate 70 mg of Fe (in the form of $FeCl_3$ which is tested for blank levels of ^{210}Po and ^{210}Pb) will be added. The acidified sample will be spiked with NIST-^{209}Po tracer (SRM 4326 - Polonium-209 Solution**;** equivalent to 3 dpm) and 5 mg of Pb (made from old Pb or high-quality AAS standard which is tested for blank ^{210}Pb and ^{210}Po). The activity of ^{210}Po and ^{210}Pb in the Pb carrier should be checked prior to its use.

Pre-concentration and onboard preliminary analysis:
The acidified and spiked sample will be allowed to equilibrate for about 4 hours. After equilibration of spikes/carriers, Pb and Po will be simultaneously co-precipitated with $Fe(OH)_3$. The precipitate and the solution can be separated either by centrifugation or filtration. The precipitate will be dissolved by adding 10 ml of 6M HCl followed by washing of the filter paper with 90 ml of deionized water. To this solution, 200 mg of ascorbic acid will be added and Po isotopes will be separated by spontaneous electroplating onto a silver plate (Flynn, 1968). This solution will be dried completely and the residue will be taken in 5 ml of 9M HCl for the separation of Po and Pb using an anion-exchange column (Sarin et al., 1992). The purified Pb fraction will be spiked with ^{209}Po and stored in a clean plastic bottle for about 6 months – 1 year and ^{210}Pb activity will be measured by the ingrown activity of its granddaughter, ^{210}Po.

^{210}Pb determination:
An aliquot of the stored solution (5%, 5 ml out of 100 ml) will be taken in a 25 ml pre-cleaned polyethylene bottle and stored for stable Pb determination (either AAS/ICP-MS, or any other suitable instrument) to obtain the chemical recovery of Pb. The remaining solution will be utilized for the electroplating of Po. The final activity of ^{210}Pb calculation will involve the in-growth factor for ^{210}Po, decay of ^{210}Pb from collection to the second ^{210}Po plating, chemical recovery of Pb, among other factors.

Model calculations:
A set of model calculations will be posted online which will show step-by-step calculation, with details on decay/in-growth corrections, blank/background subtractions and error propagation.

Some issues that need to be considered:

1) Separation of ^{210}Po and ^{210}Pb immediately after first plating (in-situ ^{210}Po) is critical, as incomplete plating of ^{210}Po will result in residual ^{209}Po and ^{210}Po remaining in the solution. While about 84% of the residual ^{210}Po would decay away after 1 year of storage time, only ~0.7% of the residual ^{209}Po will decay away. Adding secondary silver plates to remove Po does not guarantee the

complete removal of Po and hence, it is very important that the Po and Pb are separated immediately after the first plating.

2) The corrections for the in-growth (of the grand-daughter, ^{210}Po) and decay of ^{210}Po and ^{210}Pb during the time elapsed between: i) collection – first plating – 9M HCl ion-exchange column separation – second plating – counting of the Ag plates needs to be applied. Using standard Bateman's equations, explicit correction terms need to be established for routine procedure.

<u>^{7}Be</u>

The determination of ^{7}Be is routinely conducted using large-volume samples.

Analytical instrument:
The most widely used instrument for seawater (both dissolved and particulate) ^{7}Be determination is gamma-ray spectroscopy (e.g., Baskaran et al., 1997; Baskaran and Swarzenski, 2007).

Volume required:
Large volume water sample (>500 L) is required for the determination of particulate ^{7}Be. For dissolved ^{7}Be, ~200 L is needed.

Sampling:
Dissolved and particulate: Large-volume water samples (>500 L) will be filtered through cartridge filters to retain suspended particulate matter for the particulate ^{7}Be measurements. Submersible pumping system is a suitable method to collect large volume water samples and will be filtered through filter cartridges. The filtrate (~200 L) will be collected in large-volume containers and will be pre-concentrated using standard $Fe(OH)_3$ co-precipitation method after the addition of stable Be as a yield monitor (Baskaran et al., 1997; Baskaran and Swarzenski, 2007).
Sample weight or volume: Standard flow meter gauges will be utilized to monitor the volume of water filtered through the prefilter.

Questions to be addressed during GEOTRACES Intercalibration cruises, but to be kept in mind during the IPY cruises:
How much of the dissolved ^{7}Be will be sorbed (if any) onto the prefilter needs to be evaluated prior to the cruise.

Acidification and spiking:
The filtrate will be acidified using 250 ml high-purity conc. HCl immediately after filtration. To the filtrate 5 mg of Be (AAS standard) and 500 mg of Fe (in the form of $FeCl_3$) will be added.

Pre-concentration and onboard preliminary analysis:
The acidified and spiked sample will be allowed to equilibrate for about 4 hours. After equilibration of spikes/carriers, Be will be simultaneously co-precipitated with $Fe(OH)_3$. The precipitate and solution will be separated by filtering through Whatman 42 filter

paper. The filter paper will be taken to the shore-based laboratory for further analysis (Baskaran et al., 1997).

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V. Radiogenic Isotopes

Protocols for Nd isotopes $^{143}Nd/^{144}Nd$ ($\varepsilon_{Nd(0)}$)

Samples for Nd isotopes and REE should be collected using GO-Flo bottles (General Oceanics) or Niskin bottles suitable for trace elements. The samples should be 0.2µm filtered to measure dissolved Nd.

Analytical instrument

The most widely used instrument for analysis of dissolved $^{143}Nd/^{144}Nd$ in seawater analysis is Thermal Ionisation Mass Spectrometry, TIMS (Dahlqvist et al. 2005; Lacan and Jeandel, 2005; Shimizu et al., 1994; Piepgras and Wasserburg, 1987), but Multiple Collector Inductively Coupled Mass Spectrometry, MC-ICPMS, is also likely to become an important method (e.g., Vance et al., 2004).

Volume required

The volume of water required for analysis of dissolved $^{143}Nd/^{144}Nd$ depends on the sensitivity of the used TIMS or MC-ICPMS instrument and method. The amount of required Nd ranges from 1 to 30 ng with the lower range requiring requiring either analyses of Nd on TIMS using NdO^+ beam by TIMS or analyses with very sensitive MC-ICP-MS machines, while the higher range allows analyses of Nd as metal by TIMS or analyses of Nd by less sensitive MC-ICP-MS machines. The concentration of Nd in most open ocean water generally ranges from 10 to 40 pmol/kg (Nozaki, 2001) and thus a 10L sample will yield between 15 to 60 ng of total Nd.

Analysis of particulate Nd is likely to require filtration of larger volumes of water in most parts of the oceans. For example, Nd concentrations of particles in the Sargasso Sea vary between 2.9 to 12 µg/g, dependent on particle size (Jeandel et al., 1995). Assuming a minimum particle concentration in the subthermocline water column of about 10 µg/l, filtration of 100 liters would provide between 3 and 12 ng of Nd, which is sufficient to obtain a Nd isotopic composition by TIMS instruments (analyzing NdO^+) and some very sensitive MC-ICP-MS instruments.

Sampling

10 l (up to 20 l in the surface waters of the oligotrophic gyres) are recommended. All seawater samples should be filtered as soon as possible. Filtered seawater samples must be stored in acid-cleaned high or low density polyethylene (HDPE or LDPE) containers.

Acidification, spiking and pre-concentration

Samples can be: i) spiked and pre-concentrated on the ship after sampling and filtration (reduces the volumes of water that needs to be shipped to land based laboratories) ii) acidified onboard and shipped to the laboratory where spiking, precipitation, separation chemistry and analysis take place.

Given the amount of water necessary to perform all suggested analysis within the GEOTRACES program it will probably be necessary to precipitate and analyze several isotope systems on the same samples (e.g., Be, Nd, Pa, Th and even ^{226}Ra, depending on the reagent used to preconcentrate).

Acidification: Add 1 mL concentrated HCl (ultraclean) per L of filtered seawater (pH 2).

Spiking: If the Nd concentration are measured on the same sample a ^{150}Nd spike can be used for determination of the Nd concentration in the filtered water. The spike addition is optimized to achieve a ^{150}Nd/^{144}Nd ratio in the spike sample mixture that introduces the smallest error (i.e. ~ 0.7 to 1). The spiked seawater is left to equilibrate for at least 48 hours. Some users would prefer to collect an aliquot of ca 500 ml or 1 l to measure all the REE including Nd on the same sample: in such case, the aliquot only will be spiked, for ICP/MS concentration determination.

Pre-concentration: Pre-concentration of Nd and REE could be done by adsorption on a Fe hydroxide precipitate (and/or Mn oxides or C18 cartridges preconditioned with HDEHP/H2MEHP, see below) formed in seawater (scavenging), which is then recovered by decantation and centrifugation.

Fe hydroxide: 0.1 ml of ultra-pure $FeCl_3$ (20mg Fe/ml) is added per liter of acidified and spiked seawater and stirred by a magnetic stirrer for 2h for complete mixing. Thereafter, ~2-5 mL conc. Ammonium Hydroxide (ultraclean) is added per L sample to bring the pH to 8.5-9 and precipitate $Fe(OH)_3$. The sample is stirred by a magnetic stirrer during ammonium addition. After 12-24 hours of settling, most of the supernatant is removed and the precipitate is centrifuged (or filtered).

While spiking and preconcentration can be done aboard, the following dissolution of the recovered precipitate and subsequent separation of Nd by ion exchange column chemistry is always carried out in the home laboratory.

Nd is sometimes preconcentrated by adsorption onto C18 SepPak cartridges, which are loaded with a mixture of the strong REE complexants di(2-ethyl)hydrogen-phosphate and 2-ethylhexyldihydrogen-phosphate (HDEHP/H2MEHP) based on a method described by Shabani et al. (1992). This method has been applied extensively by Jeandel and co-workers (e.g., Jeandel et al., 1998; Lacan and Jeandel, 2005).

Other works suggest to co-precipitate using Mn oxides: 375 µl of 60g/L $KMnO_4$ and 150 µl of 400g/L $MnCl_2$, are successively added to the acidified/spiked sample and then pH is

raised to 8 by addition of NH_4OH (Rutgers van der Loeff and Moore, 1999). Then, samples are shaken and let at least 24h for equilibration. The co-precipitated samples are then centrifuged or filtered. Using MnOx allows to coprecipitate tracers like Ra together with Nd.

Spike calibrations and blanks

Any spike used should be calibrated using a gravimetric Nd standard. Measuring different amounts of a calibrated standard solution mixed with the spike solution, and verifying the accuracy and reproducibility of the determined isotopic composition is also a good way to assess the quality and value of the spike. Laboratories participating in $^{143}Nd/^{144}Nd$ measurements in seawater should strive towards inter-calibrations of their used spikes.

Blanks should be determine by isotope dilution and recorded for all batches of reagents and resins used in Nd chemistry. The total chemical procedure should be monitored for blank levels on a frequent basis.

Evaluation of analytical uncertainties

The reproducibility and precision of the mass spectrometric methods, TIMS or MC-ICPMS, should regularly be determined by analyzing international Nd standards e.g. La Jolla Nd, Caltech nNdβ, JNdi-1. The amount of standard used for the reproducibility runs should be comparable to the sea water sample size.

Precision of measurements and inter-laboratory comparison for Nd concentration and $^{143}Nd/^{144}Nd$ ratio should be determined during the GEOTRACES inter-calibration cruises taking place in 2008 and 2009. For the IPY cruises in 2007 and 2008 a set of replicate seawater samples (2-3) should be collected and analysed.

Samples for a first preliminary inter-comparison of $^{143}Nd/^{144}Nd$ between some of the participating labs were collected during Polarstern cruise ANT XXIII/1 in 2005.

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VI. Trace Elements

Acknowledgements

This set of protocols has benefited greatly from the generosity of the trace metal community to willingly share their experiences and information on oceanographic trace metal sampling.

1. Precruise Preparations

1.1 Sampling bottles

GO-Flo bottles (General Oceanics) are the generally-accepted device for collecting trace element depth profiles. Their interior surfaces should be Teflon-coated, the top air-bleed valve replaced with a Swagelok fitting to allow pressurizing with nitrogen or air, and the sample valve replaced with a Teflon plug valve. In addition, all the o-rings should be replaced with silicone (red) or Viton ones. In addition to GO-Flo bottles, Niskin-X (External spring water sampler) bottles have been also been used successfully for water sampling, and should be modified in the same manner as the GO-Flos (e.g., Teflon-coated).

1.2 Sampling bottle cleaning procedure

(Note: There is some disagreement about whether cleaning these bottles is needed or desirable, but if GO-Flo bottles are cleaned; no acid should contact the outside of the bottle, the nylon components in particular.)

1. Fill bottles with 3% of alkaline detergent for one day.
2. Rinse 7x with deionized water (DIW) thoroughly until there is no trace of detergent
3. Rinse 3x with ultra high purity water (UHPW such as Milli-Q)
4. Fill bottles with 0.1M HCl (analytical grade) for one day.
5. Rinse 5x with UHPW
6. Fill bottles with UHPW for more than one day before use
7. After discarding UHPW from bottles, deploy and trigger the bottles in open ocean water.
8. After discarding seawater from Teflon spigot, use bottles for sampling

1.3 Sample Bottle Types

For both total dissolvable and total dissolved trace metal analysis it is recommended that Low Density Polyethylene (LDPE) bottles are used. High Density Polyethylene (HPDE) bottles contain organometallic trialkyl aluminium compounds and are unsuitable for dissolved Al analysis.

For speciation samples it is recommend that either fluorinated polyethylene (FPE), Teflon FEP, or Teflon FPA bottles be used. These bottles are suitable for freezing samples.

1.4 Sample Bottle Cleaning

1.4.1 For LDPE bottles:

1. Rinse bottles in reverse osmosis (ROW) or DIW
2. Soak bottles for one week in an alkaline detergent such as Decon. This process can be sped up by soaking at 60°C for one day
3. Rinse 4x with ROW/DIW
4. Rinse 3x with UHPW
5. Fill bottles with 6M HCl (reagent grade) and submerge in a 2M HCl (reagent grade) bath for one month. Again this can be sped up by heating for one week.
6. Rinse 4x with UHPW inside an ISO Class-5 (see Tables below) laminar flow hood
7. Fill bottles with 0.7 M HNO_3 (trace metal grade) or 1 M HCl (trace metal grade) for at least one month (i.e., transport on cruise filled with this). Should be stored doubled bagged.

1.4.2 For FEP Teflon or FPE bottles:

1. Rinse bottles in ROW
2. Soak bottles for one week in an alkaline detergent. This process can be sped up by soaking at 60°C for one day
3. Rinse 4x with ROW
4. Rinse 3x with UHPW
5. Fill bottles with 6M HCl (reagent grade) and submerge in a 2M HCl (reagent grade) bath for one month. Again this can be sped up by heating for one week.
6. Rinse 4x with UHPW inside an ISO Class-5 laminar flow hood
7. Polish bottles with ~ 100 ml 6M HCl (trace metal grade) for one month shaking very week.
8. Rinse 6x with UHPW
9. Store with UHPW for at least one month. Should be stored doubled bagged.

1.4.3 For PFA Teflon bottles:

1. Soak bottles for one day in an alkaline detergent
2. Rinse 7x with DIW thoroughly until there is no trace of detergent
3. Rinse 3x with UHPW
4. Soak in 6 M reagent grade HCl bath for 1 day
5. Rinse 5x with UHPW
6. Fill bottles with a mixture of 1M (each) nitric acid, sulfuric acid and perchloric acid (analytical grade) and keep them at 100°C for 5 hours in a fume hood
7. Rinse 5x with UHPW water inside an ISO Class-5 laminar flow hood
8. Fill bottles with UHPW water and keep them at 80^{o}C for 5 hours
9. Rinse 5x with UHPW water inside an ISO Class-5 laminar flow hood. Should be stored doubled bagged

2. Sample Collection

2.1 Surface Sampling

It is recommended that a clean surface pump sipper/tow fish system which consists of:

a. All PTFE Teflon diaphragm pump (e.g. Almatec A-15TTT or Osmonics Bruiser; an oil-free compressor is also required to drive these pumps) or large peristaltic pump with silicone pump tubing (e.g., Vink et al. Deep-Sea Res. I, 47: 1141-1156, 2000)
b. PFA Teflon sample tubing; Bev-a-Line IV or Tygon 2275 may also be used, although Hg contamination may be an issue.
c. PVC depressor vane 1 m above a 20 kg weight enclosed in a PVC fish
d. Polyester or Dacron braided line connecting the fish to the depressor and then to the ship; the Teflon sampling tubing is run along this line
e. PFA Teflon tubing is used on the other side of the pump to deliver seawater directly into a clean area for sampling.

For underway surface sampling at speeds from 1 to 7 knots, the sipper system is deployed off the side of the ship using the ship's crane to suspend the fish outside of the bow wake with the intake at approximately 2-m deep. Faster speeds are possible with this sipper design if there is little or no swell and the sipper remains outside of any breaking bow waves (Note: slight design changes to the fish and towing at 4-5 m allow sampling up to 15 knots). The sipper design also allows near-stationary sampling (moving forward into clean water at 0.5 to 1 knots) in order to collect large volumes of trace metal–clean seawater at depths up to 25 m. A YSI Sonde (or equivalent) can also be attached to the bottom of the vane that allows accurate depth samples to be collected as well as providing T and S data. This system pumps water at ca. 10 L min^{-1} and is excellent for large volume collection.

2.2 Depth Profiles

Individual GO-Flo bottles (12-30 L) attached to a Kevlar cable and triggered with plastic messengers (Bruland et al., Anal. Chim. Acta, 105: 233-245, 1979) can always be used for trace metal depth profiles. However, an epoxy powder-coated, aluminum rosette (Seabird) that holds twelve 12 L GO-Flo bottles (or Niskin-X) and deployed on a Kevlar

conducting cable allow rapid and contamination-free sampling. The bottles are sent down open, but when on-deck the open bottles are covered with plastic shower caps and the spigots are covered using plastic gloves. These are removed at the last minute before deployment and minimise contamination while on the deck. Sample bottles are triggered using Seabird software on the ascending cast (at 1-3 m min^{-1}). Once onboard the bottles are transported to a clean van for sampling handling. A variant of this system using a titanium rack holding the GO-Flos and pneumatic triggering has also been shown to collect uncontaminated trace element samples.

3. Sample Handling

All sample handling should take place in a clean area preferably an ISO Class-5 area (See attached Tables). To minimize contamination, it is best to use two people for sampling handling. One person will open up the outside sample bottle bag and the other person can then open the inside bag and remove the previously labelled bottle and rinse/fill the bottle in the clean area.

3.1 Total Dissolvable (unfiltered) Samples

Sample bottles (LDPE) are emptied of the weak acid solution and rinsed three times with unfiltered samples from the GO-Flo bottles. Ensure that the caps are also rinsed by placing sample water in the bottle, screwing the lid back on, shaking, and then pouring the sample out over the lid. The sample should be filled to the bottle's shoulder. It is important that all bottles are filled to the same amount so that acidification of samples is equal (i.e., same pH in all bottles). Samples should then be acidified to pH 1.8 using Sea Star hydrochloric acid or 6N sub-boiled distilled trace metal grade HCl (2 mL per L sample), capped tightly, and resealed in the bags.

3.2 Total Dissolved (filtered) Samples

3.2.1 No particle collection

The first consideration is whether only the dissolved sample is being taken (no particle collection), or particle samples are being collected along with the dissolved sample (i.e., the filter and the filtrate will be analyzed). If only the filtered water sample is needed, then: The GO-Flo is pressurized with 0.2 µm-filtered nitrogen or compressed air (5-8 psi maximum) by connecting the polyethylene gas line to the Swagelok fitting on the GO-Flo. A cartridge filter (See below) is connected to the GO-Flo's Teflon plug valve with Teflon PFA tubing and the sample bottles are filled as above with the effluent from this filter (the filter should be rinsed with ca. 0.5 L of sample water prior to collection).

3.2.2 Particle collection

The same method as above is used, but a 47 or 142 mm polycarbonate or TFE Teflon filter holder and filter are used in place of the filter cartridge (filters discussed below). The dissolved sample is collected as above, but the total volume of water passing through the filter must be recorded (e.g., (5) 2 L bottles filled + rinses = 12 L, etc.). After the filtration is complete, a 0.2 µm filtered nitrogen or air line should be connected to the top

of the filter and water forced from the filter (to minimize salt content on the filter), the filter folded in quarters (so that all particles are in the inside), placed in an acid-cleaned polyethylene vial, and immediately frozen.

3.2.3 Filter types and cleaning

There is considerable variation in the types (materials, pore size, diameter) used for trace element sampling. The recommendations here are not definitive and investigators will have to decide on the best type for their applications until after the GEOTRACES Intercalibration Cruises have fully evaluated the best types.

3.2.3.1 Cartridge filters

For cartridge-type filters where only the filtered water is sought, one popular one (SAFe and CLIVAR programs) is the Pall Acropak Supor capsule filter (0.8 or 0.2 μm). PFA Teflon or equivalent tubing should be used to connect the filter cartridge to the pump outlet. The filters are not acid cleaned, but instead they are rinsed for 5 min with surface sipper/tow fish water (in the open ocean), and then stored in freezer until use. One can be used for a single depth profile, working from surface to deep. As noted above the filters are rinsed with ca. 0.5 L of sample water before collecting. These filters were shown to be excellent for the following trace metals, Fe, Zn, Co, Cd, Mn, Pb, Cu and Ni (from both SAFe and Southern Ocean cruises). Other cartridge-type units used previously are the Sartorius Sartobran-PH cartridge (0.4 or 0.2 μm), the 0.22 μm Millipack-100 (Millipore Corp.) polycarbonate capsule filter, and a Teflon-membrane polypropylene capsule filter (Calyx, Osmonics).

Cleaning method for capsule-type polycarbonate filter:

1. Fill capsules with 0.1M HCl (trace metal grade) and keep them heated at about 70°C for one day (Higher than 80°C acid will damage the filters).
2. Rinse capsules with UHPW thoroughly (more than 5x) until there is no residual acid
3. Fill capsules with UHPW and heat at about 70°C for one day
4. Rinse capsules 5x with UHPW
5. Fill and store capsules with UHPW

Cleaning method for capsule type Teflon-membrane polypropylene filter:

1. Connect 8 filters using Bev-a-line polyethylene tubing and polypropylene fittings
2. Using a peristaltic pump, rinse with methanol to wet the Teflon membrane
3. Rinse with UHPW
4. Fill with 4M HNO_3 for one week
5. Rinse with UHPW until there is no residual acid (check pH)
6. Fill with 4M HCl for one week
7. Rinse with UHPW until there is no residual acid (check pH)
8. Store filled with UHPW

3.2.3.2 Membrane filters

When the particles themselves are being collected, the most commonly used filter type is the Plastics-Irradiated-Etched polycarbonate membrane (e.g., Nuclepore, Poretics, etc), typically with a 0.4 μm pore size, although 0.2 μm have been used by many investigators

who didn't require larger volumes (where a larger pore size has faster flow rates). There are other materials such as polysulfone that appear to be non-contaminating for some trace elements. The cleaning procedure for the polycarbonate membranes is the same as that for the polycarbonate cartridges, except the membranes should be dried in a ISO Class-5 laminar flow air bench, and stored unfolded in acid-cleaned polyethylene bags.

3.3 Speciation samples:

Filtered samples should be collected in either FEP or PFA Teflon, or FPE, bottles, and then refrigerated immediately. If samples are not analyzed within 24 hours, they should be frozen.

4. Suggested shipboard analysis techniques for dissolved or total dissolvable Fe and Mn

4.1 FIA for Fe
4.1.1 Luminol/H_2O_2
Sample solution should be lowered at < pH 1.8 for more than 12 hours before measurements. Sample solution pH must be readjusted to around 3 for preconcentration with 8-quinolinol-immobilized chelating resin. If only hydrochloric acid is used for pH adjustment, hydrogen peroxide should be added to prevent reduction of Fe (III). When formic acid – ammonium formate buffer solution is used for pH adjustment, such reduction of Fe has not been observed.

Analysts should record details on their methods. Precision, blank values, and number of measurement should be reported.

4.1.2 DPD
To acidified samples (pH 1.8), add hydrogen peroxide (50 μL of 12 mM H_2O_2 solution added to a 60 mL sample for a final concentration of 10 μM H_2O_2). This solution can then be preconcentrated on the NTA superflow resin. NOTE: if using this method on samples which have only been acidified for 2 days, then the addition of hydrogen peroxide is not necessary.

The NTA Superflow chelating resin is first conditioned with a 1.5 M ammonium acetate/acetic acid solution at pH 3.5 for 15 s. The seawater sample is then loaded onto the resin for 2 to 10 min, depending on the concentration of total dissolved iron in the sample. After a 15 s rinse with 1.5 M ammonium acetate/acetic acid (pH 3.5), the resin is then eluted for 3 min with 1.5 M HCl in the opposite direction to the flow of the sample during the load phase.

Manifold blanks are determined by loading acidified UHPW to which hydrogen peroxide has been added.

4.2 FIA for Mn

Acidified samples (pH 1.8) are buffered in-line using ammonium borate (0.5 M, pH 9.3) and preconcentrated using Toyopearl resin. The Toyopearl resin is first conditioned with a 0.05 M ammonium borate rinse solution for 15 s. The seawater sample is then loaded onto the resin for 2 to 10 min, depending on the concentration of manganese in the sample. After a 15 s rinse with 0.05 M ammonium borate rinse solution, the resin is then eluted for 3 min with 0.9 M HCl in the opposite direction to the flow of the sample during the load phase.

It is crucial that the method in which the blanks are determined is reported as well as the number of measurements. This was highlighted on the SAFe cruise where many labs used different methods; for example, zero load time (can be very difficult if insufficient time is allowed for loading onto a preconcentration column).

5. Chemicals and Reagents

All chemicals and reagents used in sample analyses should obviously be of the highest quality possible. Researchers are encouraged to exchange information on their findings on the quality of the same chemical from different suppliers or different batches from the same supplier. Information on the shelf life and storage of analytical chemicals is also of use.

When primary standards are prepared from solids, the preparation method should be well described. Where possible, primary standards for TEIs should be exchanged between researchers to ensure analytical intercalibration.

6. Analytical Considerations: Precision and Accuracy

The precision and accuracy of each analytical procedure should always be reported. Accuracy is a measure of how close an analysed value is to the true value. In general, the accuracy of an analytical method is determined by the use of calibrated, traceable reference standards. However, it is important to bear in mind that the assessment of accuracy based upon primary standards can be misleading if the standards are not prepared in seawater because of matrix (i.e., salt) effects. In addition, it must be recognized that for many of the TEIs there are no readily available reference materials.

Precision is a measure of the variability of individual measurements (i.e., the analytical reproducibility) and for GEOTRACES two categories of replicates should be measured; field and analytical replicates. Analytical replication is the repeated analysis of a single sample and is a measure of the greatest precision possible for a particular analysis. Field replication is the analysis of two or more samples taken from a single sampling bottle and has an added component of variance due to sub-sampling, storage, and natural within sample variability. The variance of field and analytical replicates should be equal when sampling and storage have no effect on the analysis (assuming the analyte is

homogenously distributed within the sampling bottle). Therefore, the difference between field and analytical replicates provides a first order evaluation of the field sampling procedure.

It should easily be apparent from these definitions that precision and accuracy are not necessarily coupled. An analysis may be precise yet inaccurate, whereas the mean of a variable result may be quite accurate. Therefore, precision and accuracy must be evaluated independently.

It is recommended that the SAFe samples should be used as a Reference Material (RM) to test of the accuracy of the methods used. Currently there is some consensus that the SAFe samples are valid RMs for the following elements: Fe, Zn, Cd, Cu, Mn, Co, and Pb. Presently there is also tentative agreement for Al, pending further analyses. SAFe samples can be obtained by e-mailing: requestsafestandard@ucsc.edu and providing a shipping FED-Ex number. These samples are in LDPE bottles and have an individual sample number. Two types of samples are available; a surface sample and a deep water sample.

7. Data Evaluation and Reporting

Data evaluation and reporting are the final steps in any quality control process and comprise an essential part of the quality assurance program. Data should be reviewed in the context of the entire sample collection, storage and analytical process. Discrepancies or anomalous results should be carefully noted at various stages of the analytical process and the final data evaluated for correctness of analysis by plotting the analyte profile vs. depth and density and investigating those points that are outside the 'anticipated' data envelope (alternatively this may be described as checking for 'oceanographic consistency'). Data outside the 'anticipated' data envelope are not automatically flagged as "bad," but rather investigated for the source of the problem through the sample documentation. If the problem can not be identified the data are flagged "questionable" if the values are outside the 95% confidence interval (greater than 2 standard deviations from the historical mean), and "good" if within this error envelope. If a source for the discrepancy is discovered the data are flagged "bad." At this point all data inside the historic envelope are flagged "good" and together with the "questionable" data added to the historic data set. Finally, all the data should be summarized and included in a short report to the GEOTRACES community, or peer-reviewed publication, along with the appropriate quality flags.

VII. Glossary of Terms

Terminology relevant to GEOTRACES Standards and Intercalibration Activities (not in alphabetical order, but by category)

Accuracy – The degree of agreement of a measured value with the true or expected value of the quantity of concern (Taylor, J.K. 1987. *Quality Assurance of Chemical*

Measurements. Lewis Publishers, Michigan, 328 pp.). Accuracy therefore includes random and systematic errors.

Precision – The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the closeness of results (Taylor, 1987). Precision therefore is a measure of random errors in a method or procedure.

Standard (also, measurement standard or étalon) – Material measure, measuring instrument, reference material or measuring system intended to define, realize, conserve or reproduce a unit or one or more values of a quantity to serve as a reference (ISO. 1993. *International Vocabulary of Basic and General Terms in Metrology, Second Edition*. International Organization of Standardization, Switzerland, 59 pp.). See Primary Standard for a definition more relevant to GEOTRACES.

Primary Standard – Standard that is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to others standards of the same quantity (ISO, 1993).

Reference Material – Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials (ISO, 1993).

Certified Reference Material – Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence (ISO, 1993).

Standard Reference Material – Reference material which by community agreement can be used as an intercomparison sample for stated TEIs. Validation of the SRM is carried out by repeated analysis during an intercalibration exercise.

Intercalibration – The process, procedures, and activities used to ensure that the several laboratories engaged in a monitoring program can produce compatible data. When compatible data outputs are achieved and this situation is maintained, the laboratories can be said to be intercalibrated (Taylor, 1987). Intercalibration therefore is an active process between laboratories that includes all steps from sampling to analyses, with the goal of achieving the same accurate results regardless of the method or lab.

Intercomparison – This is not well defined in the literature, but by implication is the comparison of results between laboratories, but is not the active process of ensuring that the same results are achieved as in an Intercalibration. It also may not include all steps, for example, sampling, sample handling, and analyses.

New Clean Room Standards

OLD

Federal Standard 209E Airborne Particulate Cleanliness Classes											
		Class Limits									
Class Name		0.1μm Volume units		0.2μm Volume units		0.3μm Volume units		0.5μm Volume units		5μm Volume units	
SI	English	m^3	ft^3	m^3	ft^3	m^3	ft^3	m^3	ft^3	m^3	ft^3
M1		350	9.91	75.7	2.14	30.9	0.875	10.0	0.283	—	—
M1.5	1	1,240	35.0	265	7.50	106	3.00	35.3	1.00	—	—
M2		3,500	99.1	757	21.4	309	8.75	100	2.83	—	—
M2.5	10	12,400	350	2,650	75.0	1,060	30.0	353	10.0	—	—
M3		35,000	991	7,570	214	3,090	87.5	1,000	28.3	—	—
M3.5	100	—	—	26,500	750	10,600	300	3,530	100	—	—
M4		—	—	75,500	2,140	30,900	875	10,000	283	—	—
M4.5	1,000	—	—	—	—	—	—	35,300	1,000	247	7.00
M5		—	—	—	—	—	—	100,000	2,830	618	17.5
M5.5	10,000	—	—	—	—	—	—	353,000	10,000	2,470	70.0
M6		—	—	—	—	—	—	1,000,000	28,300	6,180	175
M6.5	100,000	—	—	—	—	—	—	3,530,000	100,000	24,700	700
M7		—	—	—	—	—	—	10,000,000	283,000	61,800	1,750

NEW

ISO/TC209 14644-1 Airborne Particulate Cleanliness Classes						
	Concentration Limits (particles/m^3)					
	0.1μm	**0.2μm**	**0.3μm**	**0.5μm**	**1μm**	**5μm**
ISO Class 1	10	2				
ISO Class 2	100	24	10	4		
ISO Class 3	1,000	237	102	35	8	
ISO Class 4	10,000	2,370	1,020	352	83	
ISO Class 5	100,000	23,700	10,200	3,520	832	29
ISO Class 6	1,000,000	237,000	102,000	35,200	8,320	293
ISO Class 7				352,000	83,200	2,930
ISO Class 8				3,520,000	832,000	29,300
ISO Class 9				35,200,000	8,320,000	293,000