

Setting up and assessing a trace element sampling system – lessons learned

Thoughts of Greg Cutter (Dept. of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, Norfolk Virginia USA; gcutter@odu.edu) based on 11 years of GEOTRACES experience

Sampling Systems – Overall.

There are essentially two full-featured systems being used for most GEOTRACES cruises, the TITAN system designed and built by The Royal Netherlands Institute for Sea Research (NIOZ; DeBaar et al., 2008; Rijkenberg et al., 2015), and the GEOTRACES sampling carousel designed jointly by Greg Cutter and Sea-Bird Scientific (Cutter and Bruland, 2012) that is commercially available. Were the correct things ordered? Seabird has made a few changes to the pylon that eliminate multiple bottle tripping with the original pylon. Similarly, the termination on the Cortland conducting cable seems to be a problem. To duplicate the GEOTRACES system, there should be NO termination, but a Vectran stopper used. The type of termination was a major issue with Xiamen University's winch and cable when they were supplied with a stainless steel termination that would contaminate samples. Additionally, some sensors, depending on manufacturer, have zinc anodes that cannot be used. Thus, care should be taken to verify the construction of all parts in a sampling system.

The other systems used for GEOTRACES cruises include custom rosettes similar to the Sea-Bird GEOTRACES version with various conducting cables, and Sea-Bird GEOTRACES carousels with non-conducting cables made of Kevlar, Vectran, or Amsteel but with auto-fire modules that trigger sampling bottles at preset depths. A complete list of existing sampling systems and their features are found in 2019 GEOTRACES Sampling Systems Inventory.

Sampling Systems – The research vessel.

Ship's over-boarding system can be a problem. In particular, use of the Vectran stopper that will be 1-1.5 m long and cannot be passed through the sheave (pulley) under load makes the entire "package" taller than conventional CTD/rosette systems. Depending on the height of the ship's rails/bulwarks, they can be an obstruction if the carousel cannot be lifted high enough, so clearance must be checked. Also, the leads of the Vectran conducting cable from winch to the carousel via sheaves ("fairleads" that should be constructed from composites or even nylon, not metal) need to be routed so that no chafing is possible. In spite of Vectran's exceptional in-line strength, it cannot tolerate chafe from rubbing against anything, but especially metal structures on the ship. In this respect, changes in angles as the A-frame or hydraulic boom moves in or out, must also be considered. This issue should be considered in the set up and design of the system at the initial stages; it is difficult to retrofit. Finally, the location of where the carousel is deployed is critical because of the possibility of cable chafe against the ship. Midship is ideal due to minimum motion, but the location of the clean lab needs to be considered as well since the sampling bottles need to be transported into it. To minimize potential breakage if dropped, the carousel to clean lab distance should be minimized.

Sampling Systems – Sampling Bottles.

Use of OTE GO-FLO clone bottles vs. GO-FLOs vs Niskin X bottles need to be fully considered before purchase. GO-FLOs are expensive and have generally poor QC during manufacture, but they are a known quantity and fully covered in the Dr. GO FLO video. I've been recommending the OTE version of GO-FLOs because of better manufacturing and lower cost, but there are some issues with internal stainless steel springs (see photo) and poor closing. I am working on recommended alterations and hope to have a Dr. OTE video on the modifications to make them more reliable than GO FLOs by 2020. If the investigators are not doing particle sampling (but, they must to be GEOTRACES compliant), then Niskin/OTE X bottles are the best choice. However, they are a lot of trouble if they want to do membrane filtration – clamps or specialized racks in the clean lab are needed and these increase the processing time.



OTE sampling bottle with ball assembly removed to show the stainless steel springs that push up on the floating seal ring (not shown) to seal it against the rotating ball (i.e., the ball in a ball valve).

Sampling Systems – Overboard handling.

The GEOTRACES carousel needs to use “tag lines” to prevent damage and injuries during deployment and recovery, but conventional ship’s equipment (e.g., snap hooks onto the frame, dirty lines with metal particles) can damage it. Therefore, the clean sampling system needs to have recovery/tag lines and hooks dedicated to it and it must be kept clean. The best hooks I have found are the Wichard Mooring Hooks (part #92328) that are stainless and when put on a fiberglass pole stay open until the hook contacts the carousel or its tag lines is pulled off the pole (see photo). These considerations apply to the TITAN system as well.



Telescoping fiberglass pole with Wichard mooring hook and line for attaching tag lines to the carousel during recovery.

Sampling Systems - Clean lab design.

Unless the ship has a dedicated clean lab for sampling the carousel bottles, portable clean labs built within a shipping container frame are the conventional solution. The question then is whether the entire carousel should be put inside the clean lab or the bottles removed and brought in for sampling. On deck sampling like on a conventional rosette is not an option due to contamination problems. Because the bottles on the TITAN system are an integral component, it must be placed in the clean lab. My experience is that the logistics and lab space limitations require removing the bottles into the clean lab. With this in mind, the considerations for clean lab design are ease of bottle transfers in and out, optimizing the sampling operations to minimize time, and the number of workers doing the sampling, while still maintaining clean conditions. Another is how to secure the bottles while sampling in any sea state. While it seems logical to use pins like on the carousel to hold the bottles, they are problematic to fit the bottle onto in a seaway (they are heavy and require precise alignment) and don't allow the user to rotate the bottle for inspection and repairs. Thus, putting the bottles on shelves with straps is preferable – see photos in Cutter and Bruland (2012). In designing the clean lab (van), efficiency to save time is an important and frequently overlooked factor. Things like sliding doors from an anteroom to the clean sampling area instead of strips of vinyl curtain really make things slow and awkward as an example.

Training.

All the scientists and crew need to be fully trained on deployment, recovery, and sampling procedures BEFORE the cruise no matter whether TITAN or GEOTRACES system. It is recommended that once the deployment to sampling routines are perfected for a given ship, a user's manual be written and videos of all the operations be recorded for new users to learn.

Shipboard analyses.

For the first test cruise (for training and evaluation), and subsequent cruises, there are shipboard analyses that are absolutely needed: salinity, nutrients, and zinc (Fe and Al are good too). Bottle salinities and comparisons with sensor salinities, and nutrients compared to those from a conventional rosette system allow complete evaluation of bottle leaks and misfires (see Cutter and Bruland, 2012), while zinc determinations (FIA is quickest and easiest) show contamination issues with individual bottles and/or the system. For test/evaluation stations or cruises, I recommend that all the bottle be fired at the same, shallow (low Zn) depth, say 100 m, offshore to examine contamination on a bottle to bottle basis.

A complete list of existing sampling systems and their features are found in GEOTRACES Sampling Systems Inventory available at:

http://www.geotraces.org/images/GEOTRACES_Sampling_Systems.pdf

References

Cutter, G.A. and K. W. Bruland. 2012. Rapid and non-contaminating sampling system for trace elements in global ocean surveys. *Limnol. Oceanogr. Methods*, 10: 425-436.

H.J.W. De Baar, K.R. Timmermans, P. Laan, H.H. De Porto, S. Ober, J.J. Blom, M.C. Bakker, J. Schilling, G. Sarthou, M.G. Smit, and M. Klunder. 2008. Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program. *Mar. Chem.* 111: 4-21.

M.J.A. Rijkenberg, H.J.W. de Baar, K. Bakker, L.J.A. Gerringa, , M. Laan, P. Laan, R. Middag, S. Ober, J. Ooijen, S. Ossebaar, E.M. van Weerlee, and M.G. Smit. 2015. "PRISTINE", a new high volume sampler for ultraclean sampling of trace metals and isotopes. *Mar. Chem.* 177: 501-509.