Cautionary Note on the analysis of seawater for Aluminum

Dissolved aluminum is a key GEOTRACES trace element primarily due to its use as a tracer of atmospheric dust input to the world oceans. Sample storage for dissolved Al analyses has proven to be a critical component of the sampling, storage, and analysis process for this priority GEOTRACES trace element. Brown and Bruland (2008) argued that samples for dissolved Al analysis should be stored in low-density polyethylene (LDPE) bottles with LDPE caps. They observed Al contamination when storing acidified seawater samples in high density polyethylene (HDPE) bottles and fluorinated HDPE bottles (FPE). This is most likely a consequence of the common but not consistent use of an aluminum co-catalyst amongst other metal based co-catalysts (Ti, Hf, and Zr) in the synthesis of particular polyolefins that make up certain types of bottle plastics. In contrast to HDPE, low density polyethylene is synthesized using a peroxide based catalyst with no trace-metals required in the polymerization process.

Unfortunately it is not easy to obtain information from manufacturers or distributors about which co-catalysts were used in any particular batch of plastics in their bottles. While other plastics are suitable for many other trace metals, 100% LDPE bottles should be used for storing acidified seawater samples for dissolved Al analyses (many analysts prefer this same material for a suite of other trace metals including Fe, Mn, Zn, Cu, Co, Cd, Pb, etc.). However, the following should be noted. It is common for some bottle manufacturers to supply LDPE bottles with polypropylene (PP) caps and not LDPE caps due to the fact that PP is a much harder plastic providing a better seal on the sample bottle. The batch of 0.5-L LDPE Nalgene bottles with PP caps used to store the SAFe S, D1 and D2 reference samples since October 2004 were rigorously acid cleaned by following the procedure developed by the Bruland lab and used to prepare their sample bottles for over two decades. Luckily, even though the SAFe sample bottles had PP caps, the SAFe samples appear to be free of Al contamination even after long-term storage at pH 1.7-1.8.

However, with subsequent batches of smaller LDPE Nalgene bottles with wide mouth PP caps cleaned in the same manner as the SAFe sample bottles, Al contamination from the PP caps occurred on a storage time of a few days even after further rigorous acid cleaning of the PP caps separately from the LDPE bottles. A laboratory experiment was undertaken whereby five 125ml LDPE bottles with PP caps were cleaned with two different acids and acid strengths and then filled with ~ 50 ml of low Al (~ 1.3 nM) seawater and stored for one week. One set of bottles was placed upright for one week without the sample ever coming in contact with the PP cap. Duplicate sets of five acid-cleaned LDPE bottles with PP caps, either separately acid cleaned using a select acid treatment or not, were filled with the same low Al seawater sample and placed upside down for one week ensuring sample contact with the PP cap. A marked increase in dissolved Al was observed in nearly all of the upside down samples in contact with the PP cap.

It is interesting to note that although the 125 ml LDPE bottles with PP caps discussed above showed definitive Al contamination resulting from the PP caps, in contrast, the 0.5 L SAFe bottles (LDPE with PP caps) were tested using a similar up/down procedure as described above and no Al contamination was observed from those PP caps. This could be evidence that there is significant batch-to-batch variability in the use of Al as a co-catalyst in the synthesis of PP used for the caps. Therefore, until bottle manufacturers can guarantee the use of no Al co-catalysts in their PP and HDPE

products, a 100% LDPE bottle that has been checked for Al contamination is recommended for dissolved Al samples if long term acidified sample storage is necessary.

Unfortunately that is easier said than done! Since it is harder to make a perfect seal with the softer LDPE than the hard PP many manufacturers (like Nalgene) don't make bottles with 100% LDPE caps and caps with LDPE liners have their own problems making them unsuitable. We knew of two sources of 100% LDPE bottles but recently that dropped to only one. Because of low demand, Dynalab Corp. decided to discontinue supplying the 100% LDPE buttress cap bottles (HUB) which the Bruland lab group (UC Santa Cruz) has used successfully over the last few decades for multiple contamination prone trace-metals for both at-sea analysis and for return to the shore laboratory for analysis and long-term storage in our sample archive. We are looking for other suppliers of the HUB bottles who don't require a minimum order of thousands of bottles.
The only other manufacturer of 100% LDPE bottles that we know of at this time is BelArt who makes buttress and wide mouth versions (also available from Fisher Sci.). At this time we only have experience with and recommend the 100mL wide mouth version (#109060100) but other sizes are available. However we don't recommend the 1L or larger wide mouth bottles since the caps are cumbersome during sampling and they tend to grind bits of plastic from the bottle mouth which end up in the sample. The 0.5L and 1L LDPE buttress bottles with LDPE caps from BelArt need extra care and force tightening of their caps to ensure a perfect seal but the caps are easier to handle during sampling than wide mouth caps. A final note should be made for analysts performing near real-time analyses at sea. While our lab group does not have the experimental data to support this, a number of bottle plastics could likely be used if samples are acidified and analyzed in a relatively short amount of time (< 2 hours). Chris Measures' lab group (U. of Hawaii) has used polymethylpentene bottles with PP caps with success for at-sea determinations of Al and Fe on the CLIVAR repeat hydrography cruises. The Bruland lab group (UC Santa Cruz) has successfully used 100% LDPE bottles for at-sea analysis as well. It is likely that a number of bottle types, even with PP caps, might be used provided that the acidified sample storage time in the bottle is minimal and the contact time of a sample with a PP cap (if any) is kept at a minimum. The safest bet is to check your bottles/caps for Al contamination beforehand, no matter which bottle type is used, particularly if you are planning on long-term storage for low-level dissolved Al seawater samples.

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