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Trace metals in sea water: Sampling and storage methods

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TRACE METALS IN SEA WATER: SAMPLING AND STORAGE METHODS

1 INTRODUCTION

Sampling procedures for dissolved trace metals in sea water have progressed to the extent that it is now possible to describe reliable methods for the collection, preservation, and storage of seawater samples. A review of the sampling methods being used for trace metals in sea water has recently been produced (Berman and Yeats, 1985). The accumulated experience of a number of workers in the field as well as the results from several intercalibration exercises run by ICES, IOC, and others have been used to determine the best sampling procedures. For many metals a single procedure is adequate, however, for some others separate procedures must be used.

2 SAMPLING DEVICES

Surface samples (< 1 m) can be collected in several ways but in all cases it is important to avoid contamination from the sampling vessel. Good procedures include dipping the storage bottle into the water over the bow of a small launch as it is moving slowly ahead (preferably upwind and up-current). Surface sampling from a larger vessel can be done by extending the storage bottle over the side of the slowly moving ship at the end of a long pole (Boyle *et al.*, 1981) or with a peristaltic pump/teflon tubing system in which the tubing is extended over the side of the ship on a boom (Windom and Smith, 1979). Any of these methods would be suitable. Hydrowire sampling of surface waters, however, should be avoided because of the potential for contamination.

For deeper waters, sampling with water samplers deployed either on a hydrowire or a rosette is unavoidable. The best, and increasingly commonly used, water sampler for most trace metals is the General Oceanics (5535 NW 7th Ave, Miami, Florida 33127, USA) teflon-coated Go-Flo sampler modified by replacement of the drain cock with a solid teflon stopcock (e.g., Chemplast Ltd., Chemfluor plug valves, 150 Deys Road, Wayne, NJ 07470, USA) and the internal o-rings and seals with ones of silicone rubber (available from General Oceanics). This type of sampler has been successfully used by a number of investigators for a whole range of metals, including Ag, Cd, Co, Cu, Fe, Mn, Ni, and Zn (Bruland *et al.*, 1979; Yeats and Campbell, 1983; Landing and Bruland, 1980; Martin and Knauer, 1980; Gordon *et al.*, 1982; Knauer *et al.*, 1982; Murozumi, 1981; Martin *et al.*, 1983; Danielsson and Westerlund, 1983). The IOC sampler/hydrowire intercalibration (Bewers and Windom, 1982) also identified these modified Go-Flos as the best samplers.

For lead, a more complicated piston sampler (Schaule and Patterson, 1981; Mart *et al.*, 1983) is the best but an experiment conducted by

Magnusson and Rasmussen (1982) indicates that, at least at coastal levels, suitably modified and cleaned Go-Flos should also give good results.

For most metals, a traditional Niskin bottle with the internal spring replaced by surgical rubber, silicone rubber or a teflon-coated stainless steel spring would appear to be adequate (Bewers and Windom, 1982; Boyle *et al.*, 1976, 1977; Bender and Gagner, 1976). Niskin bottles, however, are probably not suitable for lead or zinc. A recently developed Hydrobios close-open-close sampler may also be useful but has not been used extensively enough for evaluation.

Another type of sampler ("MERCOS") has been used for ultra-trace metal analysis in surface water to a maximum depth of 100 m (Freimann *et al.*, 1983). To prevent contamination, exchangeable 500-ml teflon bottles are used for sampling, and also as storage vessels. The sampler passes the contaminated surface layer of the sea in a closed configuration and is released at the desired depth by a conventional PTFE messenger. The water samples are stabilized *in situ* by pre-acidifying the sampling bottles with 10 ml ultra-pure HNO_3 for Hg, and by immediately acidifying with ultra-pure HCl for the other metals.

Precleaning of water samplers is very important. In general, cleaning procedures for the samplers will be rather similar to those used for storage bottles and other labware. A good procedure, essentially following that of Bruland *et al.* (1979), consists of an initial washing of the sampler with detergent, rinsing with high-purity water, leaching with 1 to 2 mol/l high-purity HCl, and final rinsing several times with high-purity water.

3 DEPLOYMENT OF SAMPLERS

Three different types of hydrowire were tested for Cd, Cu, Fe, Mn, Ni, and Zn in the IOC intercalibration (Bewers and Windom, 1982) and plastic-coated steel wire was found to be the best, but stainless steel and Kevlar were not greatly inferior. Based on these results, plastic-coated wire would be recommended but the work of Bruland and others with Kevlar adequately demonstrates that Kevlar is acceptable. Similarly, stainless steel wire has been shown to be adequate (Magnusson and Westerlund, 1983; Moore, 1983; Yeats and Campbell, 1983). The viability of a stainless steel hydrowire, however, may depend on its age as it will tend to become somewhat corroded with use. Whatever hydrowire is used, it is important to use weighted plastic messengers with no exposed metallic parts. One good type of messenger is the teflon button messenger made by Seargear Corp. (9605 NW 79th Ave, Hisaleah Gardens, Florida 33016, USA).

No experiments have conclusively demonstrated that lead samples can be collected with a traditional hydrowire deployment. The only indisputably clean lead samples have been collected from samplers mounted at the end of a cable and tripped while the cable is being lowered. Rosette samplers have been used for some trace metal sampling (Boyle

et al., 1976, 1977; Sclater et al., 1976; Yeats and Campbell, 1983), but not yet for all metals. Mart et al. (1983) collected samples for lead with a rosette by tripping the samplers as the rosette was being lowered. Samples for other trace metals could presumably be collected in the same way.

4 SAMPLE HANDLING AND STORAGE

Once the samplers have been retrieved, subsamples for subsequent trace metal analysis must be withdrawn from the samplers. Ideally, all subsampling and other processing should be done in a portable laboratory or other area fitted out as a clean room (Bruland et al., 1979; Danielsson and Westerlund, 1983). If a clean room is not available, it should be possible to obtain reasonable results using portable clean benches and trying to ensure that samples are exposed to the ship's atmosphere as little as possible. Nevertheless, use of a clean room is the only sure way to avoid ship-borne contamination.

Filtration of samples is probably required when working in coastal waters and may even be required in open-ocean surface waters for some metals. Filtration can be accomplished in two ways, either directly from the sampler or in a separate filtration step in the clean room or clean bench. Direct filtration is accomplished by attaching a filter to the drain spigot and forcing the sample through the filter with nitrogen pressure applied through the sampler's air vent. If an unfiltered subsample is initially collected for subsequent filtration, it is important to minimize the time between sample collection and filtration as interactions between the dissolved and particulate phases may occur in the temporary storage bottles.

Several filtration apparatuses and direct filtration were compared in an ICES intercalibration exercise (Bewers et al., 1985). This experiment showed that any one of a rather wide variety of pressure filtration devices gave very similar results. Direct filtration from the sampler is probably preferable because it minimizes manipulation of the sample, but it is evident from the ICES experiment that a carefully designed and operated filtration apparatus can also give good results. The most commonly used filters are Nuclepore 0.4 μm pore size polycarbonate filters (Nuclepore Corp., 7035 Commerce Circle, Pleasanton, California 94566, USA). Filters can be cleaned by soaking in dilute (1-4 mol/l) HCl, followed by rinsing with dilute high-purity HCl and high-purity water. Filter holders should be washed with the same procedures used for storage bottles and other plastic labware.

Trace metal samples are generally stored in either teflon or conventional polyethylene bottles (Bruland et al., 1979; Yeats and Campbell, 1983; Danielsson and Westerlund, 1983). Other materials, such as quartz, have also been used (e.g., Kremling, 1983) but would seem to offer no advantages over the inexpensive, rugged, and readily available conventional polyethylene.

Samples have generally been preserved for storage in one of two ways, either acidified or frozen. Acidification would be the preferred

method. It is now being used almost exclusively by the more experienced laboratories and the results of the ICES Fourth Round Inter-calibration on Trace Metals in Sea Water would suggest that freezing results in losses of some metals (Bewers *et al.*, 1981). Either 1 to 2 ml of nitric acid per litre of sample (Danielsson and Westerlund, 1983; Kremling, 1983) or 2 to 4 ml of hydrochloric acid per litre (Bruland *et al.*, 1979; Yeats and Campbell, 1983) are suitable. In either case, very high-quality acid (preferably quartz sub-boiling distilled) must be used. Quartz sub-boiling distilled acid can be prepared in the laboratory (Kuehner *et al.*, 1972) or purchased. In Canada, it is available from Sea Star Chemicals (2045 Mills Road, Sidney, British Columbia, V8L 3S1 Canada) and in the United States from the National Bureau of Standards or from GFS Chemicals (P.O. Box 23214, Columbus, Ohio 43223, USA). Shelf lives of at least one year would be expected for samples preserved in this way.

In some cases, such as speciation studies by ASV, acidification must be avoided. Freezing or refrigeration of the samples will be the only alternatives to acidification, but in these cases storage time should be minimized. Storage bottles must be acid cleaned before use. Most procedures include initial washing with detergent followed by soaking with concentrated HCl, dilute HCl, and high-purity water (Moody and Lindström, 1977; Bruland *et al.*, 1979; Mart *et al.*, 1983; Magnusson and Westerlund, 1983; etc.). Bottles are then stored, either empty or filled with pure water, wrapped in polyethylene bags.

Storage of samples for mercury is a special case. The generally accepted procedure of Hg is to store samples in glass bottles acidified with 5 to 10 ml/l of concentrated nitric acid (Olafsson, 1983; Dalziel and Yeats, 1985). Glass bottles for Hg samples can be cleaned by soaking with concentrated nitric acid followed by rinsing with a 10:1 HCl:HF solution and high-purity water.

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