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Suspended particulate matter: Collection methods for
gravimetric and trace metal analysis

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SUSPENDED PARTICULATE MATTER: COLLECTION METHODS FOR GRAVIMETRIC AND TRACE METAL ANALYSIS

1 INTRODUCTION

Filtration is the most commonly used method for separating the dissolved and particulate fractions of seawater samples. A wide variety of filter types with different pore sizes has been used for this purpose. Filtration of water samples for trace metal analysis has generally been done using either Millipore 0.45 μm cellulose acetate/nitrate filter membranes, Nuclepore 0.4 μm polycarbonate filter membranes, or similar filter membranes produced by other companies.

Several studies have shown that the concentrations of suspended particulate matter (SPM) measured using different types of filters can vary significantly. For example, Tambiev and Demina (1982) have shown, using samples from the Baltic Sea, that 0.7 μm cellulose nitrate filters can give a suspended particulate matter concentration that is five times that found with 0.4 μm Nuclepore polycarbonate or 0.5 μm Dubna polyethylene-terephthalate membranes. The metal blanks were also higher for the cellulose nitrate membranes. Likewise, Brzezinska-Paudyn *et al.* (1985) observed that 0.45 μm cellulose acetate and 0.45 μm glass fibre filters gave significantly higher particulate matter concentrations than did 0.4 μm Nuclepore filters. Danielsson (1982) found that 0.45 μm Millipore membrane filters introduce large errors due to changing pore size during filtration. He also showed that the iron concentrations in the filtrates decreased with time and became nearly zero when the filters clogged.

Most experienced laboratories have chosen to use Nuclepore filter membranes whenever gravimetric determination of the suspended particulate matter has been desired. One advantage of these membranes is the well-defined pore sizes that give a relatively precise cut-off in the size of particles retained by the filter. Other filter types tend to collect particles finer than the nominal pore size of the filters to a much greater extent. Another advantage is that polycarbonate is a very suitable material from the point of view of trace metal blanks. The metal contents of the filters are considerably lower than those of Millipore filters (Dulka and Risby, 1976) and can be lowered further by leaching with high-purity acids. In addition, they are hydrophobic and do not tend to adsorb water. This makes it easy to tare the filters and dry them for reweighing after sample collection. Finally, the filters are much less brittle than Millipore filters and can be handled without undue risk of damaging the membranes. The major disadvantage of Nuclepore filters is that they clog at relatively low loadings. This can seriously limit the amount of material (1 to 2 milligrams for 47 mm diameter filters) that can be collected on a filter.

The collection of suspended particulate matter samples by filtration will always follow a basic three-step procedure, but the details will vary depending on a number of factors. The basic three steps are: (1) preparation of the filters, including washing, drying, and pre-weighing as necessary; (2) collection of the particulate matter samples; and (3) washing of the filter to remove salt, drying, and reweighing. The basic collection technique usually consists of pressure filtration of the water through Nuclepore filters in clean plastic filter holders. Polycarbonate filter holders for 47 mm diameter filters (Millipore 'Swinnex', Nuclepore, Sartorius model SM16541B with plastic fittings and air vents, or similar) or Millipore Teflon filter holders for 150 mm diameter filters are all suitable.

2 COLLECTION OF SUSPENDED PARTICULATE MATTER FOR GRAVIMETRIC ANALYSIS

If the samples are being collected solely for the determination of suspended particulate matter concentrations, the pre-cleaning of filters and filter holders and other preparations for sampling are quite straightforward. The filters can be weighed, without pre-washing, on any microbalance capable of weighing an ~20 mg filter to ± 0.01 mg. All handling of the filter should be done with Teflon, polyethylene or polycarbonate tweezers. Washing of filters, if desired, should not affect their weights. After weighing, the filters have to be stored in individual, numbered containers that have been cleaned to remove any solid particles. Plastic Petri dishes (50 mm diameter), small (5-10 ml) vials, or parchment envelopes can all be used. The filters have to be stored without folding because they will have to be loaded flat onto the filter holders. They can be rolled up for storage in vials. All this preparation should be done in as dust-free an environment as possible because the filters tend to build up static charge and thus attract particles from the air. A clean room would be the best environment for handling filters, but a laminar-flow clean bench should suffice. Because of static charge build-up, it is important to have an anti-static device in the balance when weighing or some other means of removing any static charge immediately before weighing.

Because the filter holders are usually reused, they have to be thoroughly cleaned after use, especially when sampling in turbid waters. Cleaning in an ultrasonic bath is helpful for removing particles that may become attached to the filter holders. The cleaning procedure would be to clean the filter holders in an ultrasonic bath with laboratory detergent and rinse several times with de-ionized water. The filter holders are then air dried in a clean-air bench and loaded with the pre-weighed filters using plastic tweezers.

3 COLLECTION OF SUSPENDED PARTICULATE MATTER FOR TRACE METAL ANALYSIS

If the samples are being collected for trace metal analysis of the suspended particulate matter or if the filtrate is being used for dissolved trace metal analysis, more extensive cleaning is required.

This includes additional acid washing of all parts of the apparatus. In general, the procedures for washing filters consist of soaking the filters in dilute acid, followed by several rinses with high-purity water and drying, with all steps being conducted in a clean room or on a clean bench. The detailed procedures will vary from laboratory to laboratory, but should retain basically the same steps. At the Institute of Marine Research, Rostock-Warnemünde (IMR), 0.4 μm 47 mm diameter Nuclepore filters are leached for several weeks in 2N HCl (suprapure quality), rinsed and soaked with several aliquots of Milli-Q water, dried in a laminar-flow hood, stored over a desiccant, pre-weighed on an electronic microbalance and wrapped in pre-numbered parchment envelopes. At the Bedford Institute of Oceanography (BIO), the Nuclepore filters are soaked for 24 hrs in 2N HNO₃ (Merck, for analysis) and rinsed several times with Milli-Q water. The filters are stored in pre-cleaned (rinsed with Milli-Q water, then soaked in 6N HCl and rinsed again) Petri dishes and dried in a microwave oven. When the filters have returned to room temperature, they are weighed on a microbalance (Mettler AE163).

4 SAMPLING PROCEDURE

Sample collection on board ship will generally follow one of two basic routes: direct on-line filtration from the Go-flo, Niskin bottle or other sampler, or initial collection of an unfiltered water sample followed by filtration of this sample in a separate filtration apparatus. The choice of preferred sampling method depends mostly on the suspended matter level of the sample.

For highly turbid waters, filtration directly from the water sampler will result in underestimation of the true suspended particulate matter concentration because of settling of particles in the sampler. This problem is particularly acute in estuarine waters where the density and, therefore, settling rate of the predominantly inorganic particles are quite high. For this type of sample, it is better to withdraw quickly a suitable aliquot of unfiltered water from the sampler and subsequently filter this sub-sample in a filtration apparatus, such as one of those described by Bewers *et al.* (1985). It is important to use a representative aliquot of the total sample in this off-line filtration procedure. Therefore, immediately before withdrawing the water from the sampler, the suspended matter should be resuspended by agitating the sample. Inverting the sampler and returning it to upright should serve this purpose. The sub-sample that is obtained should then be filtered completely. At the Institute of Marine Research, 0.5 to 2 litre sub-samples are filtered in a Sartorius model SM16511 pressure filtration device in a laminar-flow hood. The size of the sub-sample will depend on the anticipated suspended matter concentration. The Bedford Institute of Oceanography off-line filtration apparatus consists of a 500 ml polyethylene separatory funnel with screw top that has been adapted for pressure filtration by welding a fitting for a pressure line into the lid. The filter in a Sartorius model SM16541B filter holder is attached to the bottom of the separatory funnel with a short piece of silicone tubing, an aliquot of un-

filtered water is poured into the funnel, the top is screwed on, and pressure is applied. An air filter is placed in the nitrogen gas line that supplies the pressure to prevent introduction of particulate contamination through the gas line.

For waters with much less than 0.5 mg/l of suspended particulate matter, insufficient suspended particulate matter is collected in this procedure unless very large water samples are filtered. Off-line processing of these large samples becomes laborious. Thus, for these lower concentration samples, direct filtration from a Go-flo, Niskin bottle or other sampler with sufficient volume (10-30 l) is preferable. In this technique, the filter in its filter holder is attached to the drain spigot of the sampler with a piece of clean plastic tubing and nitrogen pressure (maximum of ~0.8 atm) is applied by attaching the pressure line using an adapter designed to hold the nitrogen line and screw into the sampler's air vent. As before, an air filter is used in the gas line to prevent contamination. The suspended matter is collected by filtering all the water in the sampler and the water volume is measured. The filtrate can also be saved for dissolved measurements by filtering the water into appropriate sample bottles.

Once the suspended matter sample has been collected, it has to be washed to remove salt, dried, and then returned to the shore laboratory for reweighing and subsequent chemical analysis. At the Institute of Marine Research, the filters from the on-line filtration are transferred dust-protected into a 50 ml plastic (Millipore) syringe connected to a filter holder. The filters are washed twice with 10 ml aliquots of Milli-Q water, folded twice using Teflon tweezers, with the loaded surface inside, returned to their parchment envelopes, and stored in a deep-freezer. At the Bedford Institute, the filters are washed while still in their filter holders with two 50 ml aliquots of Milli-Q water. The apparatus used for off-line filtration is used for this procedure. The washed filters are then returned to their Petri dishes, dried in a microwave oven, and stored at room temperature. All filter handling on board ship is done in a portable clean bench.

A number of filtration systems, both off-line and on-line systems, were tested in the ICES Fifth Round Intercalibration on Trace Metals in Sea Water (Bewers *et al.*, 1985, 1986). This experiment was designed to test the effect of filtration on dissolved metal results and was not a test of procedures for gravimetric analysis of suspended particulate matter. In addition, some modifications were made to established procedures to adapt the systems to this particular experiment. Nevertheless, the filtration systems described in these papers should be a good guide to the types of filtration systems being used in marine laboratories. The description of the filtration systems taken from Bewers *et al.* (1986) is reproduced in the annex.

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ANNEX

FILTRATION SYSTEMS USED IN THE ICES FIFTH ROUND INTERCALIBRATION ON TRACE METALS IN SEA WATER

Systems 1 to 6 are off-line filtration systems and systems 7 and 8 are on-line systems.

Systems 1 and 2: These filtration systems consisted of large TFE-Teflon cylinders screwed directly onto the top of Teflon filter supports. Water was poured into the top of the cylinder, a pressure adapter was screwed onto the top and the sample was filtered by applying nitrogen pressure from a filtered high pressure cylinder. Three parallel systems were used to process the replicate samples. System 1 was equipped with 0.4 μm 47 mm diameter Nuclepore polycarbonate filters and System 2 was equipped with 0.45 μm 47 mm diameter Millipore filters.

System 3: This system comprised one-litre Teflon separatory funnels attached by silicone tubing to 50 mm Millipore 'Swinnex' polycarbonate filter holders containing 0.4 μm 47 mm diameter Nuclepore filters. The entire system, including filters, was pre-washed with dilute hydrochloric acid and Super-Q water prior to use. The system was pressurized with filtered nitrogen and three parallel funnels were used to process the replicates. Water was transferred to the separatory funnels in a pre-cleaned polyethylene bottle.

System 4: This system used direct pressure filtration from Go-flo samplers. Samples from the polyethylene reservoir were transferred through silicone tubing into a 2.5 litre Go-flo sampler. An 0.4 μm 47 mm diameter Nuclepore filter in a Sartorius polycarbonate filter holder was attached to the drain spigot by a Teflon connector and nitrogen pressure was applied via the sampler air vent. The first 50 ml of sample was used to rinse the filter assembly. The Go-flo sampler was refilled and the filtration process repeated for the collection of replicates. A new pre-cleaned filter was used for each sample.

System 5: This system consisted of a 250 ml volume Sartorius pressure filtration unit equipped with 0.4 μm 47 mm diameter Nuclepore filters. The filters were pre-washed for 24 hours in 20% Suprapure nitric acid, rinsed four times with Nanopure water and dried in a clean bench. Samples for this system were transferred directly from the main reservoir through silicone tubing and a single unit was used to process all samples. This system was operated entirely in a clean bench.

System 6: This system comprised a 1-litre TFE-Teflon reservoir connected with Teflon tubing to a 50 mm Nuclepore filter holder containing an 0.4 μm 47 mm diameter Nuclepore filter. The system was pressurized with filtered nitrogen. All Teflon parts were pre-cleaned with concentrated nitric acid and the filter holder and filter with dilute hydrochloric acid. Samples were transferred from the main

reservoir with Teflon tubing and one filtration unit was used for the processing of all samples.

System 7: This system consisted of three 0.4 μm 47 mm diameter Nuclepore filters mounted in Millipore 'Swinnex' holders attached with silicone tubing directly to spigots on the polyethylene reservoir. The reservoir was pressurized with filtered nitrogen to force water through the filters.

System 8: This system comprised 0.4 μm 47 mm diameter Nuclepore filters mounted in Sartorius filter holders. Three such assemblies were connected to the main polyethylene reservoir in the same manner as for the on-line system 7.