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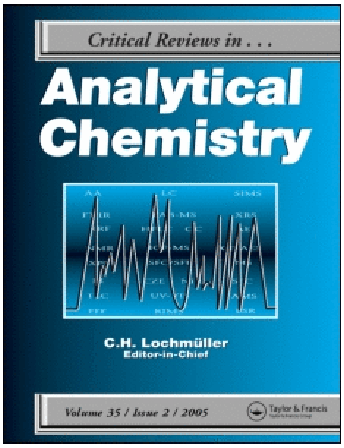

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SAMPLING AND STORAGE OF NATURAL WATER FOR TRACE METALS

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I. INTRODUCTION

This article is not intended to be an instruction manual on water sampling. Rather, it presents current information concerning the sampling, sample handling, and storage procedures for trace metals in fresh, estuarine, and marine waters. "Trace metals" will refer not only to the transition metals but also those elements in groups IV-A, V-A, and VI-A which form covalent hydrides.

Many bodies of water exhibit significant spatial (e.g., thermocline, chemocline) and temporal variations and the collection of a representative sample can become quite complex. Obtaining representative samples and maintaining their integrity are critical to any monitoring or enforcement program. It is axiomatic that the generation of reliable, accurate, and meaningful results cannot occur if the sample or sampling procedure is compromised by significant random errors or if the samples change composition following their removal from the natural environment.

The general aspects of sampling for chemical analysis have been reviewed in recent articles.[1,2] A brief summary of the most important questions that must be addressed in designing a sampling plan has been given by Kratochvil and Taylor.[3] For the purposes of this article, special attention must be given to the following: (1) is the sample considered to be homogeneous or heterogeneous relative to the data requirement? If heterogeneous, is this general, localized, or stratified; (2) is the composition constant or variable with respect to time, temperature, or other physical conditions; (3) what mode of sampling should be used: random, systematic, continuous, intermittent, discrete, composite; (4) will the sample change due to interactions of components, chemical or physical reactions with the container, or because of environmental influences during transit or storage? If stabilization is required, what stabilizers should be used?

General guidelines which address these questions as well as present standard practices for sampling water are available from a number of sources.[4-14] An introduction to statistical considerations, type of sampling, selection of sampling sites, frequency of sampling, samplers, containers, and cleaning procedures, as well as recommended storage practices are discussed in this literature.

There are two distinct types of samples, i.e., the discrete or grab and the composite; either may be obtained manually or automatically. The nature and composition of the system as well as the information required will determine the type of samples to be collected.

Individual or grab samples that are taken at the same time at different points or successively in the same place are useful when the water to be sampled does not flow on a continuous basis (i.e., ocean or lake) or when a composite sample obscures extreme conditions of composition (e.g., periodic waste discharge into an estuary or stratification). Grab samples allow the determination of local spatial or temporal inhomogeneities within the water body, thereby approximating real conditions at the time of sampling.

Composite samples are obtained by combining a large number of samples taken at different intervals (temporal, spatial, or both). An average composition is thereby obtained. Although composite sampling minimizes the number of samples to be analyzed, it has the disadvantage that any compositional variations within the water system become undetectable.

Apart from waste management control, which will not be dealt with here, there is an interest in the global baseline monitoring of trace metals in fresh and marine waters. Additionally, the trace metal loads of these water bodies are of interest to the study of the biogeochemical cycles of metals. Measurement of their distributions in water columns is useful in identifying the sources and sinks of the element. Grab samples are particularly suited to this purpose and will be the sampling technique of choice discussed throughout this article. An excellent treatment of sample compositing is given in the U.S. EPA handbook.[6]

With the advent of the mid-1970s, perceived concentrations of many trace elements steadily declined in lake and ocean waters. Data presented in Tables 1 and 2 illustrate the dramatic change in "baseline" levels over the past few decades. The decreased concentrations do not reflect a real effect but rather reveal an artifact of successive improvements in the reduction and control of contamination. Major advances in analytical instrumentation and separation/concentration techniques coupled with the elimination, or control, of contamination during sampling, storage, and analysis have markedly improved our knowledge of the concentrations and processes controlling the distributions of these metals.[15]

In this regard, it should be noted that contamination of the sample may include both positive contamination, which results from the adventitious addition of analyte to the sample, as well as negative contamination, due to unexpected losses. The latter is generally a more prevalent problem with sample storage. Detection of random and systematic errors during the sampling process is difficult and can only be inferred by after-the-fact comparison of analytical data for consistency with those reported by other contemporary studies undertaken at identical or similar sampling locations and attainment of "oceanographically consistent" and interpretable results. The extent of contamination suffered by samples following prolonged storage or during transport to the laboratory can often be gauged from a comparison of analytical data acquired immediately following collection with that made at subsequent time intervals.[16] Seawater reference materials certified for trace metal content are available (NASS-1 and CASS-1) to characterize both unfiltered deep ocean (1300 m) North Atlantic seawater[16] as well as near-shore North Atlantic seawater.[17] At present, no lake water certified reference material is available. However, a certified riverine water (SLRS-1) is now also available from the National Research Council of Canada in Ottawa (cf. Table 7). Although these materials are invaluable for verifying the accuracy of analytical data generated in the laboratory, they are of no use in the quality control of the actual sampling operation.

The degree of sample contamination may vary from one trace element to another, such contamination being a function of the concentration of the element in the water body and its ubiquitousness in the environment (the "environment" varying anywhere from that associated with an oceanographic research vessel to that of a clean air laboratory).

Table 1
TRACE METAL CONCENTRATIONS IN SEAWATER

	Reference	Element (µg/l) Cd	Cu	Pb	Zn	Ni
A.	Compiled Data					
	Sverdrup et al.[176] (1942)	Present	10	4	5	0.1
	Goldberg[177] (1965)	0.11	3	0.03	10	—
	Brewer[178] (1975)	0.1	0.5	0.03	4.9	1.7
B.	Original Data					
	[a]Chester and Stoner[131] (1974)	0.07	0.8	—	1.4	—
	[a]Bruland et al.[30] (1979)	0.015	0.11	—	0.007	0.31
	[a]Schaule and Patterson[32] (1981)	—		0.013	—	—
	[a]Spencer et al.[31] (1982)	0.004	0.10	0.027	0.01	—
	Boyle and Huested[179] (1983)	0.002	0.06	0.021	—	0.12
	Berman et al.[16] (1983)	0.03	0.10	0.04	0.16	0.26
	[a]Jones and Murray[75] (1984)	0.011	0.19	—	—	0.32

Surface water samples.

Table 2
TRACE METAL CONCENTRATIONS IN LAKE HURON[a]

Year	Element (µg/l) Fe	Cd	Cu	Cr	Pb	Ni	Zn	Mn	Hg
1965	—	<5	<5	<5	<5	<5	<5	—	—
1970	6.3	1.0	3.5	1	1.7	1.4	6.8	1	0.17
1971	3.2	0.71	3.7	0.72	2.3	1.5	7.3	0.31	0.32
1974	2.7	—	2.1	0.30	1.3	2.5	5.1	0.43	0.052
1976	2.0	0.057	0.78	—	1.0	2.3	2.4	—	—
1977	—	—	—	—	0.23	—	1.5	—	—
1978	—	—	0.72	—	0.20	—	2.2	—	—
1980	1.7	0.0038	0.30	0.11	0.019	0.64	0.26	0.27	0.050

Filtered samples collected a 1 m depth.[180]

II. MATERIALS AND CONTAMINATION

The determination of trace elements at extremely low levels can be compromised by the often high and variable contamination introduced under the guise of the analytical blank. During every stage of sampling and sample treatment, there is a danger of the samples becoming contaminated with the elements to be analyzed, and every material with which the sample may come into contact until the time of analysis must be considered a potential source of contamination. The first sources of potential error are associated with the sampling and subsequent storage of the sample prior to analysis. The sample container must be selected to avoid contamination due to the leaching of metals into the sample and also to minimize losses of metal from the solution by adsorption onto the walls of the container (negative contamination). In addition to the intrinsic "purity" of the materials themselves, the cleaning procedure used is of great importance and, if care and forethought are not exercised, the very act of cleaning may only serve to further the contamination (e.g., the use of chromic-sulfuric acid). Patterson and Settle[18] have given a lucid treatment of these problems with respect to the determination of lead in environmental samples. A more generalized introduction to this topic has been given by Tschöpel and Tölg.[19]

Robertson,[20,21] Lamotte and Revel,[22] and Moody and Lindstrom[23] have reviewed the trace metal composition of a large number of laboratory materials and reagents. Table 3 summarizes some of the data available on the trace metal contents of several materials often used in the construction of samplers, sample handling equipment, and storage containers. Materials to be avoided include all metals or plastic-coated metals (as coatings are often porous and subject to abrasion and stress cracking), rubber, and soft glass.

With few exceptions, borosilicate glass should also be avoided. This material, however, has been found useful for the collection and storage of samples for analysis of mercury[24] and the (volatile) organometallic forms of several other elements, i.e., Pb,[25] Bi,[26] and Se.[27,28] The borosilicate surface may be rendered more inert by coating it with an amorphous SiO_2-ZrO_2 film.[29]

Synthetic polymeric plastics have found widespread application in trace metal work. Among these materials, FEP Teflon®, polypropylene, and high-pressure polyethylene are the most desirable. Polyvinylchloride (PVC) contains high levels of Zn, Fe, Sb, Sn, and Cu, while structural nylon is highly contaminated with Co (see References 20 and 21).

High-purity plastics have distinct advantages over glass with respect to weight, cost, durability, and cleanliness. However, considerable variation in both the composition and trace metal content may be present in a particular material depending on the manufacturing process (cf. Table 3, e.g., low- and high-pressure polyethylene). It is widely known that Teflon® TFE products often suffer from Fe, Cr, and Ni contamination due to particulate inclusions in vessel walls as a consequence of the sintering and molding processes used during their manufacture.

The extent of improvement afforded by the use of plastic materials is dependent on how meticulously they are cleaned prior to use.

Although storage containers and sample handling apparatus are usually rigorously cleaned prior to use, sampling bottles (except surface samplers) have generally escaped attention. Often, thorough cleaning of the sampler is impractical because of the presence of metallic or rubber components. Bruland et al.[30] thoroughly cleaned their samplers (300-*l* Go-Flo) with Micro detergent, rinsed with deionized water, filled with 1 *M* HCl for several days and finally rinsed with deionized water. Spencer et al.[31] gave their sampler (30-*l* Go-Flo) an initial cleaning using 10% HCl. During the sampling cruise, the Go-Flo bottle was rinsed with 1% Ultrex HCl, wrapped in plastic, and stored in a clean area until used. Similar cleaning procedures were implemented by Berman et al.[16] when using 12-*l* Go-Flo bottles.

By far, the most rigorous cleaning procedures reported for samplers pertains to work published by Patterson and colleagues[18,32] using the California Institute of Technology (CIT) device. All FEP Teflon® parts were treated for 3 days in hot (70°C) concentrated nitric acid, rinsed with the purest water, and further treated in a 70°C bath of 0.05% high-purity nitric acid for 24 hr. Following a rinse with the purest water, a clean 0.05% nitric acid leach was repeated for an additional 5 days at 70°C at the end of which the acid was again discarded, a water rinse performed, and the Teflon® stored in 0.5% high-purity nitric acid until required for use. Polyethylene bags used with this sampler were cleaned by partially filling with cold, concentrated analytical reagent-grade nitric acid, folding the top shut, shaking, and finally rinsing 3 or 4 times with

AND STORAGE[a]

	Metals (ng/g)										
Materials	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ag	Sb	Pb	Hg
Polystyrene	<6	3.8	<1000	2.0	—	6.1	50	—	<0.2	—	<3
Polypropylene	—	20	—	40	—	—	—	—	600	—	—
Polycarbonate	—	—	—	6	—	—	—	—	—	—	—
Polyvinylchloride											
Structural	2	—	2.7×10^5	45	—	630	7100	<5	2700	—	—
Tygon	6000	2000	5×10^4	—	2×10^5	1×10^4	5000	600	—	2×10^5	—
Polyethylene											
High pressure	15—300	<10	600—2100	5	—	4	90	20	<5	200	—
Low pressure	180—1500	—	—	10—370	—	—	300	<10	<10	—	—
Plexiglass	<10	—	<140	<0.05	—	<10	<10	<0.03	<0.01	—	—
Nylon (structural)	—	—	—	1.4×10^6	—	—	—	—	—	—	—
Teflon®	20	—	35	1	—	22	8	<0.3	0.4	—	—
Surgical (rubber) tubing	4.2×10^5	—	<100	7500	—	—	4.1×10^7	<700	360	—	—
Neoprene rubber	—	—	—	2300	—	—	1.8×10^7	<1000	290	—	—
Quartz tubing	6.5	—	395	0.44	—	2.0	1.5	0.05	0.05	—	—
Vitreous silica	30	<20	<200	0.1	—	<1000	<100	—	100	—	<100
Borosilicate glass	—	1×10^6	3×10^6	81	—	—	730	<0.001	2900	—	—
Millipore (HA) filters	1.8×10^4	—	330	13	—	—	2400	<0.5	39	—	<0.015
Nuclepore filters	2000	130	2.8×10^4	25	—	1800	2300	—	<20	—	—

[a] Compiled from References 20 to 23, 181, and 182.

the purest water. The bags could then be dried by hanging them from a plastic line. All operations were performed under clean room conditions.

In general, samplers are not cleaned between casts during cruises.

Plastic storage containers and sample handling apparatus are usually more amenable to cleaning operations. Many methods have been suggested and the several which have been shown to be sufficient for the purpose are all similar in that they employ acid leaches and distilled-deionized water rinses.[16,23,30,32-36] Surface metal impurities are readily leached with dilute acids. However, as pointed out by Karin et al.,[33] many plastic materials exhibit inhomogeneous metal contamination, i.e., that within the polymer matrix, a portion adsorbed onto the surface, and a fraction found just below the surface.

Following a comprehensive study of the acid leaching of heavy metal impurities from a dozen different plastics commonly used for manufacture of storage and sample-handling containers, Moody and Lindstrom[23] recommended the following multistep acid leach: (1) fill with 1 + 1 HCl (AR grade); (2) allow to stand 1 week at room temperature (80°C for Teflon®); (3) empty and rinse with distilled water; (4) fill with 1 + 1 HNO_3 (AR grade); (5) allow to stand 1 week at room temperature (80°C for Teflon®); (6) empty and rinse with distilled water; (7) fill with the purest available deionized water; (8) allow to stand several weeks or until needed, changing water periodically to ensure continued cleaning; (9) rinse with the purest water and allow to dry in a particle- and fume-free environment. With the exception of the latter step, and an additional chloroform rinse to degrease Teflon® surfaces prior to undertaking this procedure,[32] this "recipe" has been followed by the majority of workers. Hydrochloric and nitric acids appear to leach various elements with different efficiencies,[23] thus, use of both acids in sequence is recommended. Although very time consuming, such procedures are a necessary precaution if reliable data are to be obtained for elements in the extreme trace range of concentration.

The rigorous cleaning procedures outlined above may simply be consuming an undue amount of the analyst's time as well as tying up a large number of containers "under preparation" if the elements of interest in the sample are expected to be comparatively high, as for example Fe, Mn, Cu, and Zn in rivers, tributaries, and estuaries.[37-39] In this connection, Laxen and Harrison[40] recommended that a simple 48-hr leach with 10% nitric acid be used for both the preliminary cleaning of new polyethylene bottles and for routine cleaning. This protocol was found suitable for analysis of Zn, Cd, Pb, and Cu in stored river water samples.

Following cleaning operations, the present authors recommend room temperature storage of vessels filled with dilute ultrapure nitric acid (0.2%) and encased in sealed, clean polyethylene bags until used. Provided such acid blanks are low, rinsing the vessel with sample prior to collection is not recommended.

Modified cleaning procedures may be required for some materials. Nylon and plexiglass are both attacked by concentrated acids, and PVC is thermally unstable above 80°C. Pyrex® glass containers used for the collection and storage of samples for mercury are usually cleaned using an oxidizing procedure similar to that described by Bothner and Robertson,[41] Erickson,[42] or Bloom and Crecelius.[43] Bottles are filled with a solution of 0.1% $KMnO_4$, 0.1% $K_2S_2O_8$, and 2.5% HNO_3 and heated for 2 hr at 80°C. After cooling, 2 mℓ 12% hydroxylamine hydrochloride (NH_2OHCl) are added to reduce dissolved Cl_2 and particulate MnO_2. Any Hg present is then reduced by adding 10 mℓ 10% $SnCl_2$ and the solution sparged by bubbling N_2 through the samples. The bottles are then rinsed three times with distilled water. Wong et al.[35] simplified this treatment by rinsing the bottles after the first cleaning step at 80°C and subsequently stored them filled with 2% HNO_3 containing 0.01% $K_2Cr_2O_7$ until ready for use.

Olafsson[24] precleaned Pyrex® bottles with both HNO_3 and a solution of HNO_3 and HF(10:1) and subsequently stored them up to the time of sampling holding a small volume of HNO_3.

III. TYPES OF SAMPLERS

Where suitable instruments are available, there are obvious advantages in measuring the quality of water *in situ* utilizing appropriate sensors or probes which can be lowered from the surface to give a profile of the water column.[43a] Although this can be accomplished for a few parameters (pH, temperature, salinity, P_{O_2}, P_{CO_2}), determination of trace elements is far from feasible. Characterization is thus dependent on the collection of a water sample. An ideal field sampling device should satisfy a number of criteria: (1) the sampler must quantitatively recover trace metals at the nanogram-per-liter and microgram-per-liter levels typical of marine and fresh water, respectively. In this regard, the sampler must not introduce analyte (metallic) contamination or remove constitutents from the water by adsorption or other processes; (2) the sampler should traverse the water surface as well as the contaminated water surrounding the research vessel in a closed configuration and must have a reliable method for opening at a predetermined depth; (3) the sampler must flush rapidly and not impede the exchange between the surrounding water and that within the sampler so that as it is lowered through the water it does not drag water from shallower depths with it; (4) sample bottle closure must be reliable with positive sealing to ensure no exchange of water from the sampling depth with the surroundings as it is brought back to the surface; (5) it should be light and easy to manipulate but rugged enough so as not to require elaborate preparation or handling in the field as well as give an adequate sample volume; (6) it should be capable of accurate positioning in the field to enable reproducible profiling of the water column.

There is no single type of water sampler which is suitable for all applications, especially considering that various sampling techniques (discussed in Section IV) are required for collection of water from the surface microlayer, surface, and deepwater fractions of the water column. By far, the greatest amount of work devoted to the study of samplers and sampling techniques has been in the marine field and most of the ensuing discussion will, of necessity, draw heavily from this area. All considerations apply equally well to the sampling of fresh waters.

A. Surface Microlayer Samplers

The chemical composition of the aqueous film at the atmosphere-hydrosphere boundary is significantly different from that of the underlying surface waters.[44] In particular, the trace metal content of the sea surface microlayer is enriched relative to that of subsurface water only a few centimeters below[45-49] and is associated with chloroform-extractable organic material and/or small particles.[49]

Because of its properties, specialized techniques are required for sampling the surface microlayer. The most commonly used film collection method is the screen technique devised by Garrett[50] and used by other investigators, in modified forms, to collect the upper 100 to 540 μm of the surface microlayer. Screen materials have included Monel,[50] stainless steel,[51] and polyethylene or nylon.[48,52,53] The screen is first rinsed by immersion several times and samples obtained by withdrawing it horizontally through the water surface. The layer adhering to the screen is allowed to drain into a collection bottle. By repeating the operation 200 to 250 times, it is possible to collect about 20 *l* of water, corresponding to a collection of approximately 100 m² of surface water (100 to 150 μm thick). Polyethylene gloves are worn throughout the collection and care is taken to ensure that the sample is not contaminated by the collection boat or personnel. Between stations, the screen should be stored in dilute HCl contained in a polypropylene bath.[53]

The screen technique suffers from potential inactivation due to irreversible adsorption of some microlayer material as well as the time-consuming nature of the operation.

Additional surface film samplers include a rotating ceramic drum[54,55] from which the adhering surface layer (60 to 100 μm) is removed by a wiper and drained into a collection vessel; a glass plate[49,56] immersed and withdrawn vertically from the surface and scraped clean with a Teflon® blade; germanium prisms;[57] a hydrophobic Teflon® plate perforated with conical holes to sample 50- to 100-μm layers;[58,59] a liquid N_2-cooled freezing probe;[60] and a floating PVC boom.[61]

A comparison of these and several other such microlayer sampling techniques was made by Van Vleet and Williams[62] and by Carlson.[63] Van Vleet and Williams[62] concluded that widely differing results for the chemical nature of surface films can be obtained, depending on the collection device and sampling material used. For simplicity, screens remain the most attractive collection technique, yet they collect less film relative to bulk water than the rotating drum or glass plate.[64] Van Vleet and Williams[62] suggest that glass fiber filters and Teflon® plates and screens would not be efficient in sampling the microlayer due to strong preferential adsorption of lipid material, which can only be removed by rinsing with solvents.

A significantly thinner layer of surface film can be sampled using "bubble microtome" procedures developed by McIntyre.[65] Rising gas bubbles are efficient collectors of surface material and when they break at the surface jet droplets of surface material are ejected into the air where they may be collected. Fasching et al.[66] developed a surface sampler based on this principle, and Duce et al.[67] subsequently applied this bubble interfacial microlayer sampler (BIMS) to a study of the enrichment of Cu, Zn, and Fe in the sea surface microlayer at the mouth of Narragansett Bay. The BIMS was subsequently used by Fitzgerald et al.[68] to collect volatile Hg species from open ocean surface waters and by Wallace[69] to collect Cu, Hg, and Pb.

A large bubble adsorptive device which produces and collects bubbles of known size and can be operated at sea has recently been reported by Gershey.[70] It was estimated that the top 1 μm of water is sampled with this technique.

Apart from the BIMS and prism dip techniques (which sample 10^{-2} μm depth) most other samplers described above collect the top 100 ± 50 μm of water. Enrichment of trace metals is generally observed only in the organic fraction of the surface layer material and there are no reports of the inorganic forms of trace metals being enriched. Since the real surface microlayer and static boundary layer containing the metal enrichment is probably 50 μm in thickness,[49] the enrichment factors obtained with most collection techniques are probably minimum values and may presently be severely underestimated.

With the exception of the device described by Gershey,[70] all surface microlayer collection techniques are restricted to calm water body conditions.

B. Surface Samplers

It is evident from the foregoing that the collection of representative samples of bulk surface water should avoid contamination from the surface microlayer. Properly designed samplers for surface and deep fractions must therefore be capable of being lowered through the surface in a protected state and opened or uncovered at depth.

Collection of samples from surface waters is simpler, faster, and less expensive than deep water collection because of the proximity of the sampling vessel to the source.

There are two basic methods of sampling currently in use: the volume of water to be sampled can either be pumped into a collection vessel at the surface or a discrete volume may be trapped at depth using a sampling bottle or bag. Pumping techniques will be described in Section III.D. Surface samples have been collected using deepwater sampling bottles deployed on hydrowires (see Section III.D), with plastic buckets dropped over the side of the ship,[71-73] and by hand from either the main vessel or from a small boat at some distance from the main ship. The majority of surface sampling is undertaken by hand with 500 to 1000 mℓ precleaned LPE or CPE bottles,[30,32,75-80] 1000 mℓ Teflon® FEP bottles,[31,81] or glass bottles.[82] The latter were used in an effort to preserve the P_{O_2} of the sample in order to maintain the identity of oxidation state of Se (IV) and Se (VI) in the sample. Glass containers are also often used for the collection of samples intended for Hg analysis. It is usually recommended that only plastic surfaces contact the sample.

C. Deepwater Samplers

Requirements of an ideal water sampler for trace metals have been noted earlier in this section. There are a variety of methods and apparatus designed to collect water which meet these requirements with varying degrees of success.

Most early samplers (Nansen, Ekman, and Knudsen bottles) were mechanically reliable but were made of brass or nickel-plated copper alloy, rendering them equally unsuitable for both trace metal as well as other chemical sampling.[8] Furthermore, they suffered from poor flushing characteristics and imperfect closures. The introduction of the predominantly plastic sampler by Van Dorn in 1956 heralded a significant improvement for trace metal water sample collection. The Van Dorn sampler consisted of a plexiglass cylinder with the ends sealed by rubber plungers and joined by rubber tubing such that the end plugs could be drawn open but would pull together on release. This sampler was of simple design, reliable in operation, and cheap to build. With subsequent refinements, the Van Dorn sampler has become the most widely used type of bottle for all sampling requirements.

As stated in Section I, the first reasonably uncontaminated trace metal samples were collected in the early 1970s employing Niskin (modified Van Dorn samplers), Hydrobios TPN (improved, transparent plastic Nansen's), and NIO bottles (Institute of Oceanographic Sciences, Wormley, U.K.).

The Niskin sampler is essentially a PVC cylinder with two PVC end plugs joined by a silicone rubber spring passing through the bottle.[83] By contrast, TPN and NIO bottles have external closing mechanisms. The NIO sampler is made of polypropylene with two neoprene rubber end plugs activated by an external rubber spring. The TPN sampler consists of a polycarbonate cylinder with plastic ball valves and Teflon® seals. It has an external stainless steel triggering mechanism. This transparent Nansen-type sampler is constructed of suitable materials, but its small volume (1.7 ℓ) makes it potentially impractical for many trace metal studies if other parameters (biological and chemical) are to be determined.

Van Dorn-type bottles (including Niskin) are susceptible to trace metal contamination because their rubber end caps and/or internal black rubber springs may release significant quantities of metals into the water sample. This is particularly true for deep water sampling where the sampler bottle acts as a temporary storage container for several hours. A number of modifications have been made to these samplers in an effort to overcome this problem, including replacement of the internal rubber spring with a Teflon®-coated stainless steel spring[84] or PTFE-coated rubber shock cord.[85]

NIO samplers have large neoprene rubber end caps that may cause contamination problems. Topping[86] covered the endcaps with low-density polyethylene sheeting in an effort to reduce potential contamination.

A more recent modification of the Niskin sampler was the introduction of the "top-drop" version in the early 1970s by General Oceanics (Miami, Fla.). This PVC sampler had no internal closure spring and PVC end plugs. Both top and bottom plugs were loaded at the top of the bottle before lowering. Following external triggering, the bottom plug fell free to the bottom of the bottle to rest on an "O"-ring, thereby sealing the sampler.

Segar and Berberian[87] compared these bottles to standard Niskins and Niskins equipped with Teflon®-coated stainless steel coil springs. Regular Niskins showed elevated Zn and Fe levels, while the "top-drop" gave slightly lower levels than the modified Niskin. Zn concentrations were also observed to increase with time in the regular and modified Niskin but not in the "top-drop".

This sampler bottle has been superceded by the Go-Flo (General Oceanics) sampler and is no longer produced. It, along with all of the earlier bottle designs described above, suffered from the fact that they passed through the surface in an open configuration and were thus susceptible to widespread and variable contamination from the surface microlayer.

There are two commercial samplers now available which can be deployed in a closed configuration through the surface. General Oceanics markets the Go-Flo sampler, consisting of a PVC cylindrical body, ball valves, Delrin stopcocks and push rod, stainless steel wingnuts for the hydrowire clamp, latex rubber external spring, and Viton "O"-ring seals. The sampler enters the water with the ball valves sealed, opens automatically by hydrostatic pressure at an 8 to 10 m depth, and is finally closed at the sampling depth by a triggering mechanism using a messenger sent down the hydrowire.

A second such "close-open-close" (C-O-C) sampler based on a modification of the TPN bottle was developed by Fischer in 1968 (Hydrobios, Apparatbau GmbH, Kiel, W. Germany). This sampler is a modification of the TPN device and is constructed of polycarbonate with PVC ball valves and Teflon® seals, a tripping mechanism of stainless steel, latex tubing, and plastic spigots. It is lowered through the surface in a closed configuration and opens automatically by hydrostatic pressure at a 7 to 10 m depth. The sampler is subsequently closed at the sampling depth by a messenger-activated trigger.

A trace metal water sampler designed by Seakem Oceanography (Sidney, British Columbia, Canada) operates like a syringe and consists of a TFE Teflon® cylinder and piston. In the cocked position, the piston almost touches the base plate of the interior sample cylinder. A polyethylene bag, sealed at the piston and top plate, prevents surface water from contacting the inside sampler wall. At 15 to 20 m, a small air pocket is sufficiently compressed to expel a disposable Teflon® plug used to prevent surface waters from contaminating the intake. The sample is triggered with a messenger at the desired depth and the piston, attached to a piece of silicone tubing, pulls in water via a one-way valve. No substantial data are yet available to assess the performance of the Seakem or Hydrobios samplers.

The greatest effort at avoiding contamination during sampling has been devoted to studies of lead and resulted in the development of the CIT sampler.[32] The Seakem sampler was modeled after the CIT device, which is itself a syringe-type sampler. The CIT, lowered on a hydrowire, consists only of CPE and Teflon® FEP components and collects water as it moves downward into undisturbed regions, trailing any contamination behind. Inside the stainless steel sampler housing, a piston, under which a CPE bag has been collapsed, is withdrawn for sampling, sucking water through an extended port into the bag. A Teflon® check valve retains water in the filled bag. The sampling port is protected by a cup during deployment and retrieval.

There are several advantages to the operation of the CIT device. The samples are collected in water unaffected by the presence of a hydrowire and its weight. The sample is only in contact with an easily cleaned polyethylene bag which is replaced for each new sample. Additionally, the sampler goes through the surface in a closed configuration. The major disadvantages are the cost and the restriction that only one sample can be collected per cast.

Mart et al.[88] have recently reported on a modified version of the CIT which allows collection of three samples per cast, each being independently electronically triggered at selected depths.

The performance of these various samplers will be discussed in Section IV.

Some plastic-coated or lined large-volume samplers have been designed and used for radionuclide studies[89,90] for which samples varying from 220 *l* to 30 tons in size have been collected.[91] These will not be considered in this article.

Table 4 summarizes the types of sampling bottles which have been used in trace metal studies since the introduction of the Van Dorn sampler. It should be noted that personal modifications to basic designs are frequently made. For example, the Go-Flo is rapidly becoming the most widely used sampler, and modifications to this bottle have included replacement of all "O"-rings and seals by equivalents made of silicone and replacement of delrin draincocks by those made of Teflon®.[92] Furthermore, these bottles have been coated with Teflon® and (for work in cold arctic waters) rubber tubing has been replaced by stainless steel springs.[93]

Van Dorn, Niskin, Nansen, Kammerer, and hand-held bottles, as well as simple bucket samplers, are often used for open lakes, whereas tributaries are sampled with pumps, hand-held bottles, Van Dorn, and Kemmerer samplers.[7]

D. Pumping Techniques

Sampling of a water column utilizing pumping techniques is attractive in that much larger volumes can be collected in a relatively short time and finer column profiling is possible than with sampling bottles. For surface and near-surface samples, the microlayer can easily be penetrated without contamination and the need for hydrowire and subsampling is eliminated.

Although deep water samples (to 3000 m) can be collected by pumping water up to the ship,[94,95] these samples are obtained almost exclusively using bottle casts on a hydrowire. Collapse of the tubing on the winch drum under its own weight presents a considerable problem and for this reason pumping from depths much greater than 100 to 200 m is not frequently practiced.

Preston et al.[71] used a 2.5-cm diameter reinforced PVC hose and an electric pump which, except for a small carbon shaft seal, was constructed entirely of polypropylene and PTFE. Near-surface waters were sampled for Zn, Fe, Mn, Cu, Ni, Pb, Ag, and Cd. No significant differences in results were found with this method compared to bottle samples. Segar and Berberian[87] compared results for samples collected using an Inter-Ocean OSEAS pumping system (which featured a submersible, multistage axial flow pump with all Teflon®-coated metal parts) with those collected in PVC Niskin samplers for Cu, Mn, Ni, and Fe. For Cu, and to a lesser extent for Ni and Fe, the pump system contaminated the sample, indicating the unreliability of using coated metal components.

Bruland et al.[96] successfully used a system consisting of 100 m of 1.9-cm I.D. tygon tubing connected to 1.3-cm I.D. polyethylene pump tubing and an all Teflon® diaphragm pump to sample coastal water for Cd at a depth of 30 m. Results were in agreement with those obtained from hydrocasts of Go-Flo bottles.

Wong and Stukas[97] utilized a "vacuum intercept pumping system" employing a Jabsco impeller pump connected to CPE tubing (deployed from an aluminum storage reel

Table 4
BOTTLE SAMPLERS USED IN TRACE METAL STUDIES

Sampler	Construction	Operation	Comments	Ref.
Van Dorn	Plexiglass cylinder with rubber end plugs and latex rubber internal band for closure	Cocked open at surface, lowered on hydrowire; closed by tripping release mechanism with brass messenger	Originally 4 and 12 gal capacity; excellent flushing and sealing characteristics	183—185
	Modifications to replace end cups with rubber balls and plastic drain spigots; PVC replaced plexiglass; endcaps replaced by PVC cones with "O"-ring seal		Most popular type of sampler	Hydrobios Products, San Diego, Calif. Kahl Scientific Instruments Corp. San Diego, Calif.
Niskin (modified Van Dorn)	Originally lucite end plugs, now all PVC construction; latex rubber closure mechanism with delrin drain spigot	As above	1.7 to 30 *l* capacity; stainless steel tripping mechanism	General Oceanics, Miami, Fla. Sea Gear Corp., Miami Fla.
Modified Niskin	As above except latex rubber closure replaced with Teflon® coated stainless steel spring or PTFE-coated rubber shock cord	As above	As above	84, 85
Transparent plastic Nansen (TPN)	Polycarbonate cylinder; plastic ball valves with Teflon® seals; plastic drain in spigot and air bleed	Similar to Nansen but $^1/_3$ of the weight; cocked open at surface	1.7 *l* capacity; improved flushing and sealing characteristics w/r/t regular Nansen	Hydrobios Apparataebau, Kiel-Holtenau, W. Germany
NIO	Polypropylene cylinder with plastic drain spigots and neoprene rubber end plugs; Plastic trigger with stainless steel spring external closure	Cocked open at surface; messenger triggered	1.3—9 *l* capacity; excellent flushing characteristics; reliable	86, 186 Institute of Oceanographic Sciences, Wormley, U.K.
Close-Open-Close (modified TPN)	Polycarbonate cylinder with PVC ball valves, Teflon® seals, plastic endcaps, and spigots	Lowered closed through surface; hydrostatic pressure (7—10 m)-activated opening; messenger-activated closure	Relatively new sampler	35, 121, 187 Hydrobios, Kiel, W. Germany

Table 4 (continued)
BOTTLE SAMPLERS USED IN TRACE METAL STUDIES

Sampler	Construction	Operation	Comments	Ref.
Top Drop Niskin	PVC cylinder and endcaps; delrin stopcock and push-rod; latex rubber external closure	Bottle lowered open; messenger triggered; on triggering, bottom plate falls from top of cylinder to rest on bottom "O"-ring	No internal closing mechanism; excellent flushing 5—30 *l* capacity (no longer produced)	General Oceanics, Miami, Fla.
		Top plate secured by external latex bands		87
Go-Flo	PVC cylinder and ball valves; delrin stopcocks and push rod, latex external spring; Viton "O"-ring seals	Lowered closed through surface; hydrostatic pressure (8—10 m)-activated opening; messenger-triggered closure	1.7—60 *l* capacity; available with Teflon® coating	General Oceanics, Miami, Fla.
CIT sampler	Stainless steel sampler housing; sampler all CPE and Teflon® FEP construction; sample collected in CPE bag	Syringe operation draws water through protected port; triggered at depth; 10 *l* volume	Goes through surface in closed position; expensive, only 1—3 samples per cast	32, 88
Seakem sampler	Main body TFE Teflon®, nylon and delrin triggering mechanism; surgical tubing enclosed in silicone tube for spring mechanism	Syringe operation; intake protected from surface contamination with disposable plug; hydrostatic triggering	2.5 *l* capacity; expensive; passes through surface in closed configuration	Seakem Oceanography, Sidney, British Columbia, Can. 35

on ship deck) to sample water down to 300 m. Samples were collected in 2-*l* bottles placed within a partially evacuated chamber situated in a laminar flow clean hood upstream from the pump. A T-valve assembly on the sampler port permitted sample collection by intercepting a portion of the pumped sample from the incoming line. Flow rates of 15 *l*/min were achieved.

Pumping of surface waters with simple peristaltic pump configurations has also been used for 1 to 22 m depth profiling lake waters for Mn[98] and at 25 m depth sampling of the St. Lawrence estuary for Hg.[99]

Wong et al.[35] intercompared peristaltic pumping of seawater from a 9 m depth in a controlled ecosystem pollution experiment (CEPEX) enclosure with sampling by several different water bottles. No significant differences were found for Pb, Cu, Cd, Ni, and Zn in all samples.

Windom and Smith[100] sampled surface waters for Cu using a perstaltic pump fitted with Teflon® tubing secured to a 10 m boom over the edge of a ship. The tube was kept at a 2 to 4 m depth using a Teflon®-coated weight and the water pumped into Teflon® bottles as the ship steamed slowly ahead. Essentially the same method was used in 1985 by the National Research Council of Canada to collect the water for the certified riverine reference material SLRS-1. Bev-A-Line IV tubing (Cole Parmer) was used in place of Telfon®.

Carpenter et al.[38] used a nylon pump and polyethylene hose for the collection of 100-*l* samples for heavy metal analysis from the Chesapeake Bay and the Susquehanna River. The water was pumped into covered polyethylene tanks.

Estuarine water from the Amazon River was collected by Boyle et al.[101] by sampling through polyethylene tubing (from a towed bathythermograph shell) streaming 5 m off the side of the vessel. The samples were collected in acid-cleaned polyethylene bags held in a rigid container connected to a vacuum pump.

It is good practice to store dilute acid (1 *N* HCl) in the pump system between sampling stations[96] and ensure adequate flushing of the line prior to sampling. In general, high speed pumps increase turbulence during flow, maintaining a sharply defined boundary within the tube, thereby permitting accurate depth profiling with decreased possibility of cross contamination of samples.

IV. SAMPLING TECHNIQUES AND THEIR ASSESSMENT

With the exception of small lakes, rivers, sheltered embayments and channels, and near-shore coastal water, sampling at sea or on the great lakes requires a seagoing vessel sufficiently large enough to accommodate the personnel and deploy equipment to gather water from great depth. Vessels meeting these requirements present numerous sources of possible contamination and, as stated by Erickson,[42] "the trace metal chemist is faced with the dilemma of how to sample a very clean environment from a very dirty platform." Sampling techniques must therefore take into account the numerous contamination risks entailed with field work.

Techniques for sampling the surface microlayer have already been addressed in Section III.A. Surface and subsurface samples are generally grab samples but the techniques utilized are different, depending on sampling depth.

A. Surface Sampling

Collection of samples from surface waters is technically much simpler than subsurface collection. However, the presence of the sampling vessel in this surface environment creates a rapidly expanding cloud of trace metal polluted water. Mart[102] has discussed the problems of choosing the sampling area under such conditions, indicating that several factors must be taken into consideration: (1) waters which have been crossed by the ship before its stop must be avoided as they are severely polluted; (2) a ship drifting with the wind, when its engines are stopped, will also produce a contaminated zone; (3) airborne contamination from smoke stacks, corrosion products, and dust particles from the ship will further contaminate a large surface zone, depending on the wind direction and strength. The only unaltered area not affected by the ship is upcurrent and upwind some distance from the ship route.

In relatively calm waters, sampling at or near the surface is usually done by hand, preferably from a small boat and some distance upwind from the mothership, as discussed above.[30,32,68,77,79,93,96,103-106] Frequently, a rubber raft is dispatched 200 to 500 m upwind in a water mass through which the research vessel did not pass. Plastic sampling bottles (500 to 1000 m*l* polyetheylene, Teflon®, or polypropylene) transported in clean polyethylene bags are emptied of storage water (typically diluted HCl) just prior to being used. Sample collection should be undertaken at arm's length from the bow of the boat as it is slowly rowed upwind into virgin waters. Shoulder-length plastic gloves should be worn and the bottle should only be uncapped below the surface

(∿0.5 m) and recapped while submerged so as to avoid contamination from the surface microlayer. Samples should then be wrapped in clean polyethylene bags for transport. As an example, Spencer et al.[31] used swimmers wearing nylon attire to open Teflon® bottles underwater, upstream from a Boston whaler. After rinsing three times, the bottle was filled with sample and immediately placed in a clean polyethylene bag on return to the whaler.

As an alternative to hand sampling from small craft, the water surface can be reached using a sampling bottle placed within a holder at the end of a telescopic pole.[36,88,102] Mart et al.[88] described sampling at the 0.5 to 1 m depth using a nylon-coated stainless steel telescopic bar at the end of which was a holder for 0.5-*l* polyethylene bottles. The bottle was quickly immersed through the water at sampling depth. After rinsing twice, the bottle was filled. Each immersion took place at a different location, thereby avoiding the contamination left by the bar itself.

Mills and Quinn[81] described the collection of surface samples (1 m depth) using 1-*l* Teflon® bottles and a custom made PVC sampling pole which allowed the bottles to be opened and closed underwater, thereby completely eliminating possible contamination by the surface microlayer.

"Surface" samples (down to 30 m) have also been collected utilizing sampler bottles and techniques normally associated with deepwater studies.[31,35,93,107] Thus, Spencer et al.[31] used a 30-*l* Teflon®-coated Go-Flo bottle to collect water from a 3 m depth. The bottle was handled by two swimmers from a Boston whaler, 0.8 km upstream of a research vessel. The Go-Flo was floated a further 30 m upstream from the whaler, opened and submerged to about 15 m depth, retrieved by a Kevlar line, and tripped by hand at a depth of 3 m.

Danielsson and Westerlund[93] also collected surface samples taken by hand using a Go-Flo bottle hung on a polyester line and weighted with lead encased in plexiglass. The sampler was tripped with a Teflon®-coated messenger. Mart et al.[88] collected samples to depths of 60 m using hand-deployed Go-Flos on a hydroline. The samplers were triggered during continuous lowering, thereby sampling dynamically at the end of the hydrowire, similar to the CIT device.[32] The sampling depth was easily read from the hydroline. A similar procedure was used by Brügmann et al.[108] for the collection of seawater samples from shallow depths.

Wong et al.[35] sampled water from a CEPEX enclosure at a depth of 9 m using hand deployment of Go-Flo, Niskin, C-O-C, and the Seakem piston sampler on vinyl-coated stainless steel wire. The samplers were closed by triggering with a Teflon® messenger. All personnel wore polyethylene gloves to avoid contamination.

Sampling by hand is only practical in relatively calm water and the high cost of oceanographic ship time usually precludes waiting for settled conditions. Surface samples must frequently be taken from the research vessel in such circumstances and are preferably acquired from the bow as the ship is slowly steaming. Thus, Boyle et al.[74] undertook surface sampling from the bow of a ship while it was steaming at 2 kn using a 15- to 20-foot pole. At the end of the pole, a plexiglass holder was fitted to which the bottles were attached by tygon straps. The bottles were immersed upside down, turned over, and allowed to fill. They were then emptied, rerinsed using the same procedure, filled, and immediately capped. Polyethylene gloves were worn throughout the operation.

Usually a plastic bucket and line[71-73] or a pumping system are used. Typically, the bucket is simply tossed over the side or bow, retrieved, and the water sample poured into a storage container. This method of sampling suffers from the enhanced prospect of contamination, not only from the surface microlayer and the fouled water from the vessel, but also from airborne particulates.

Pumping systems are advantageous in that they are sealed from the atmosphere of the ship, can easily penetrate the microlayer, and permit collection of large volumes of water. Bruland et al.[96] used both tygon and polyethylene tubing weighted with a polypropylene cube filled with lead shot to pump water from surface and intermediate depths (20 to 30 m) for Cd determinations. No significant difference in the levels of Cd were obtained when this method of sample collection was compared with sampling by hand from a raft or using Go-Flo bottles.

Kremling[109] collected samples for trace metal analysis from a depth of 6 m by pumping water through polyethylene tubing attached to a stainless steel shell suspended underneath the hull of the ship. The water was delivered directly to acid-cleaned 0.5-*l* quartz bottles kept on clean air benches.

Windom and Smith[100] collected surface samples for Cu analysis using a peristaltic pump connected to Teflon® tubing in which the tubing was extended out from the ship on a 10-m long fiberglass boom. Sample depth was 2 to 4 m, maintained with the aid of a Teflon®-coated weight. Water was pumped into precleaned Teflon® bottles as the ship steamed slowly ahead.

Trefry and Presley[110] described a similar closed-system pumping arrangement in which acid-washed polyethylene tubing, tied to a nylon rope and lowered from a boom extended about 10 m abeam of the ship, was used to collect samples from the Mississippi River.

The enhanced potential for contamination of surface samples collected from a stationary vessel has prompted several comparative studies in an effort to evaluate the magnitude of this problem. Bender and Gagner[111] and Bender et al.[112] compared samples collected by hydrocast (acid-washed 30-*l* PVC Niskin bottles fitted with surgical rubber tubing closures and hung on stainless steel wire and 12-*l* PVC metal-free Niskin bottles hung on polyethylene rope) with those collected in the same samplers deployed from a small rubber raft. Samples taken by hydrocast from the ship contained almost twice as much Cu, but no differences were found for Cd, Mn, and Ni. Magnusson and Rasmussen[107] found no difference between surface samples collected with Go-Flo hydrocasts and those taken from a small boat away from the ship for Cd, Cu, Ni, Zn, and Pb. Bruland et al.[96] obtained consistent results for Cd sampled from 20 and 30 m depths when comparing hydrocasts of Go-Flo bottles on Kevlar line with samples obtained using an all Teflon® diaphragm pump and polyethylene tubing. Similar conclusions were drawn by Spencer et al.[31] for Cd and Cu when comparing a ship-cast and swimmer-deployed Go-Flo with hand sampling in 1-*l* Teflon® bottles, whereas elevated concentrations (with respect to hand collected 1-*l* samples) of Zn and Pb were obtained with the Go-Flo bottle, irrespective of its method of deployment. This suggested that the contamination was an artifact of the particular Go-Flo bottle used.

Despite such efforts at intercomparison, collection of surface waters against the side of a stationary ship will always lead to questions about sample contamination.[113]

B. Subsurface Sampling

Procedures required for subsurface sampling are more complex and time consuming than those for surface samples. Simply lowering and retrieving a sampler at a 4000 m depth can require several hours. The traditional method of deploying bottle samplers has been to employ a winch and weighted wire rope to which the samplers are attached and lowered to depth. Both open-close (Van Dorn, Niskin, Nansen, NIO, top-drop Niskin) and C-O-C (Go-Flo, TPN, COC, and CIT) samplers are closed by sending a messenger (small metal or plastic-coated metal weight) down the wire to trigger the mechanisms that close the samplers.

A second, more recent method of deploying bottles[83] has been to use a multiple bottle array (rosette system — General Oceanics) to which a group of samplers is attached to a metal framework (which can be plastic coated) equipped with electronic triggering devices, permitting triggering from the surface. The array is lowered with a neoprene-sheathed electrical cable, eliminating the hydrowire bottom weight and messenger. Samples can be collected as the unit is lowered and, since the bottoms of these samplers are near the bottom of the package, contamination should always be trailing behind, as with the CIT device. This sampling method (using 30-*l* PVC Niskin bottles) has proved reliable in a number of studies. Oceanographically consistent results obtained during the Geochemical Ocean Section Study (GEOSECS) program have been reported for Cu,[114] Cd,[115] Ni,[78] Mn,[116] Ba,[117] and Se[82] using this sampling system. However, this technique did not permit uncontaminated samples to be collected for such elements as Zn, Fe, and Pb.[15]

The most commonly used sampling procedures involve the traditional hydrographic cast with the deployment of Go-Flo, Niskin, and Hydrobios bottles (modified TPN) on Kevlar, nylon, and stainless steel hydrowires.[118] This relatively simple procedure permits large volumes of water to be collected even in fairly severe weather conditions. However, many potential sources of contamination are present.

A major source of contamination is the hydrowire and its weight. A steel wire can become contaminated with oil and grease from the ship, or corroded and metal messengers can slough off particulate iron as they slide down the line.[119] Furthermore, the bottom weight on the line is usually made of steel and may also be corroded. Since it precedes the sampling bottles through the water column, it also presents a source of contamination. Plastic-encased concrete[31] or plastic-enclosed lead weights[30] have been used in attempts to avoid this situation. Stainless steel line, more expensive than regular steel, is a considerable improvement, although it will still corrode with extensive use.

Ideally, plastic or plastic-coated lines should be used. Nylon may be used at shallow depths but it is too elastic to be practical for very deep sampling.[42] The performance of various hydrowires was evaluated as part of a recent International Oceanographic Commission (IOC)-sponsored sampling device intercomparison.[120] It was concluded from this study that plastic-coated steel hydrowire was superior to both type 302 unlubricated stainless steel and Kevlar lines in that bottles cast on this line consistently permitted collection of water samples with lower trace metal levels (and thus, presumably, less contamination) than did the other lines. Kevlar and stainless steel appeared equally useful, except for apparently elevated Fe in samples taken with the stainless steel line.

Another source of potential contamination is the messenger which, in sliding down the hydrowire, is subject to abrasion, thus releasing particulate metal into the water column. These were traditionally made of brass- or chrome-plated weights, but plastic-coated and solid plastic messengers are becoming more popular.[30,31,93] Since the samplers close as soon as the messengers arrive, they are probably closed before any such particles can enter the bottles.[113]

Contamination from the sampling bottle itself is a subject that requires further study. Several laboratories have undertaken limited tests in this area[30,31,87,96,106,111,121,122] and two major interlaboratory intercalibration excercises have recently attempted to address this question.[35,92] Consistency of results among various samplers implies that the samples collected are, in fact, uncontaminated and meaningful in terms of understanding the hydrogeochemistry of the elements.

Early experiments compared samples collected using hydrocasts of Niskin bottles with those collected by hand from a small boat.[112] Mn concentrations were found to be unaffected by collection in 30-*l* PVC Niskins with surgical rubber tubing closures, 12-*l* PVC Niskins completely free of metal fittings, and Niskins with Teflon®- or epoxy-coated steel springs. Cd showed no significant differences in samples taken by a pumping technique, Go-Flo bottle, CIT sampler, or polyethylene bottle.[121]

Bruland et al.[96] compared concentrations of Cu, Cd, Zn, and Ni in seawater samples collected in modified Teflon®-coated Go-Flo bottles with those from the CIT sampler. No significant differences were noted for any of these elements.

Spencer et al.[31] conducted a similar experiment comparing a standard Teflon®-coated 30-*l* Go-Flo sampler with hand-collected samples. The latter were taken with both a Go-Flo bottle and 1-*l* Teflon® bottles. Whereas Cu and Cd data were consistent for all methods of sample collection, significant contamination was noted for Pb and Zn. Concentrations of these metals were elevated by about 0.2 and 0.8 to 2 nmol kg^{-1}, respectively, in the Go-Flo bottle, irrespective of whether they were collected by normal hydrocast (Kevlar line and Teflon® messengers) or by hand away from the ship. Magnusson and Rasmussen[107] collected samples of coastal seawater for determination of Cd, Cu, Ni, Pb, and Zn using a 2.5-*l* Teflon®-coated Go-Flo (equipped with Teflon® spigots), a 3-*l* Danish delrin sampler, Rtn 3 (Oceanographic, Niva, Den.), and a 1.8-*l* Hydrobios TPN bottle. Samples were hydrocast on a PVC-coated wire and were also acquired by hand in a polypropylene bottle from a small boat. Good agreement was obtained for Cd and Cu for all sampling regimes, slightly higher values for Ni in TPN and Rtn 3 samplers, and significant contamination of Pb and Zn was reported for TPN and Rtn 3 samplers. Go-Flo results compared well with those from hand-collected samples. The different results were probably due to the fact that while the Go-Flo bottle enters the surface water in a closed position the other two samplers are open and likely to be contaminated by the microlayer. Freimann et al.[121] compared coastal seawater samples collected in a C-O-C TPN Hydrobios bottle with those from a custom-built 500-m*l* Teflon® bottle sampler (Mercos sampler-Deutsches Hydrographisches Institut, Hamburg, W. Germany). The C-O-C samples showed elevated levels of Mn and Ni and, to a lesser extent, Fe and Cu. No difference was observed for Cd.

Bewers and Windom[92] have reported on the results of the IOC sampling device intercomparison exercise for trace metals in open-ocean seawater (1200 to 1300 m depth). There were four different types of samplers deployed into a homogeneous water mass and the samples analyzed by up to 15 different laboratories for Cd, Cu, Fe, Mn, Ni, and Zn. Unmodified 10-*l* Teflon®-coated Go-Flos; modified 12-*l* Teflon®-coated Go-Flos in which the "O"-rings had been replaced by silicone equivalents and the drain cocks replaced by ones made of Teflon®; modified Niskin bottles with internal springs of silicone tubing; and unmodified Hydrobios TPN bottles were used. A comparison of the results showed that TPN samplers gave high results for Cu, Ni, Fe, and Zn and possibly Cd; unmodified Go-Flos gave high results for Cu, Fe, and Zn and possibly Cd; and the Niskin bottles produced high Zn results. No definitive conclusions could be drawn with respect to the Mn data, although one "high-precision" participant reported no significant differences among the four samplers. It was concluded that both modified Go-Flo and modified Niskin samplers were suitable for most trace element studies with the proviso that their application to the reliable collection of samples from metal-depleted open-ocean surface waters (where contamination levels may be more significant compared with ambient metal concentrations) may not necessarily follow.

A second, more recent NATO-sponsored intercomparison of sampling devices was conducted using seawater at 9 m depth contained in a 65-m^3 CEPEX enclosure.[35] Sampling methods included peristaltic pumping with Teflon® tubing, a 5-*l* Niskin PVC sampler with Teflon®-coated stainless steel spring closure mechanism, a standard Go-Flo, a Hydrobios C-O-C sampler, and a 2.5-*l* Seakem Teflon® piston sampler. A vinyl-coated hydrowire with a polyethylene-covered stainless steel weight and Teflon®

messenger were used to deploy the samplers. Samples were all analyzed in the same clean room facility for Hg, Pb, Cu, Ni, Cd, Fe, Zn, Co, and Mn and, with the exception of Hg and Pb, were found to be at concentrations reasonably representative of coastal seawater. All samplers gave comparable results for Pb, Cu, Ni, Zn, and Cd. The Seakem piston device gave higher results for Hg, the Hydrobios gave high results for Fe, and the Niskin and Go-Flo gave high results for Mn. Only the peristaltic pump produced low values for all of the elements.

In conclusion, the authors stated that "it is not desirable or possible to endorse or to condemn the performance of a certain type of sampler . . . based on the results of one set of tests . . . ", in particular since cleaning procedures are important factors in successful sampler intercomparisons.[35]

Table 5 summarizes the suitability of various sampling bottles for water collection. Although the information presented is primarily drawn from marine studies, the conclusions apply equally well to the sampling of lake, estuarine, and river waters.[6,7] Specific modifications made to some sampling bottles (e.g., Niskin-metal free types, silicone rubber closures, Teflon®- or epoxy-coated stainless steel spring closures) are indicated in the appropriate reference and are not delineated in the table. Bottles which, through some form of intercomparison study, have yielded contaminated samples for a particular element, are indicated with a solid circle; acceptable performance is designated with an open circle. Experience with many samplers is limited and unassigned positions in the table indicate either no data available or conflicting data reported. In some cases, unacceptable performance of a sampler was not apparent in an original paper dealing with the device but was revealed by subsequent sampling with a different bottle type, possibly by a different researcher.

The most extensive and rigorous program to develop contamination-free samplers and collection procedures is that of Patterson and co-workers,[18,32] who pursued the study of Pb. Indeed, Patterson has shown that, apart from the CIT sampler, no other sampler bottle can collect samples of seawater below 1 m depth without some probability of serious Pb contamination. Surface samples collected by hand dipping bottles, as described in Section IV.A, are the only type that can provide noncontaminated seawater samples. Samples obtained down to 100 m by means of cleaned and flushed plastic hoses and pumps taken at a distant from the research vessel have not yet been correlated with CIT results, but indications are that this may be a suitable collection technique for analysis of Pb. Table 6 illustrates the degree of Pb contamination contributed by samplers in common use today. Only the Caltech CIT sampler may provide samples uncontaminated with artifact Pb.[123]

There is no doubt that the elaborate, expensive, and time-consuming methodologies proposed by Patterson yield high quality results, but the extent to which such precautions are needed in all trace metal studies is open to question. A major conclusion of the IOC sampler intercomparison experiment[92] was that the use of different samplers and hydrowires only accounts for a small portion of the differences between trace metal results from different laboratories and that the major contribution to such differences is, in fact, analytical inconsistency.[124] Today, this conclusion is debatable. Significant improvements in analytical methodologies over the last few years have led to enhancements in interlaboratory comparabilities for experienced laboratories. The major sources of error may again be sampling and storage containers.

V. *IN SITU* PRECONCENTRATION

It is evident from the foregoing that one of the major factors influencing the precision and accuracy of trace metal determinations in natural waters is the sampling pro-

Table 5
SUITABILITY OF SAMPLING BOTTLES FOR WATER COLLECTION

Element	Niskin	Modified Niskin	Go-Flo	Modified Go-Flo	C-O-C	Rtn3	Seakem Piston	TPN	NIO	CIT
Cd	○ Burton et al.[106] ○ Wong et al.[35]	○ Boyle et al.[110] ○ Bewers and Windom[92]	○ Spencer et al.[31] ○ Bewers and Windom[92]	○ Martin and Knauer[109] ○ Bruland et al.[30] ○ Yeats and Campbell[100] ○ Danielsson and Westerlund[93] ○ Magnusson and Rasmussen[107] ○ Bewers and Windom[92] ○ Berman et al.[16] ○ Bruland[103]	○ Wong et al.[35]	○ Magnusson and Rasmussen[107]	○ Wong et al.[35]	○ Olafsson[34] ○ Magnuson and Rasmussen[107] ○ Bewers and Windom[92]	○ Burton et al.[108]	○ Bruland et al.[30] ○ Mart et al.[36] ○ Nürnberg et al.[105]
Cu	○ Wong et al.[35] ○ Bender and Gagner[111]	○ Boyle et al.[114]	●Bewers and Windom[92] ○ Magnusson and Rasmussen[107] ○ Spencer et al.[31] ○ Wong et al.[35] ○ Paulson and Feely[101]	○ Bruland et al.[30] ○ Yeats and Campbell[100] ○ Berman et al.[16] ○ Bruland[103]		○ Magnusson and Rasmussen[107]	○ Wong et al.[35]	● Bewers and Windom[92] ● Nürnberg et al.[105]		○ Bruland et al.[30] ○ Nürnberg et al.[105] ○ Bruland and Franks[104]
Ni	○ Wong et al.[35] ○ Bender and Gagner[111] ○ Sclater et al.[78]	○ Bewers and Windom[92]	○ Wong et al.[35]	○ Bruland et al.[30] ○ Berman et al.[16] ○ Bruland[103]	○ Wong et al.[35]	○ Magnusson and Rasmussen[107]	○ Wong et al.[35]	● Magnusson and Rasmussen[107] ● Bewers and Windom[92]		○ Bruland et al.[30] ○ Bruland and Franks[104]
Zn	○ Wong et al.[35] ● Segar and Berberian[87]	● Bewers and Windom[92]	○ Wong et al.[35] ● Spencer et al.[31] ● Bewers and Windom[92]	○ Bruland et al.[30] ○ Berman et al.[16] ○ Bruland[103]	○ Wong et al.[35]	● Magnusson and Rasmussen[107]	○ Wong et al.[35]	● Magnusson and Rasmussen[107] ● Bewers and Windom[92]		
Mn	○ Segar and Berberian[87] ○ Jones and Murray[102]	○ Burton et al.[106] ○ Bewers and Windom[92] ○ Bender et al.[112]	● Wong et al.[35] ○ Landing and Bruland[76]	○ Bewers and Windom[92] ○ Berman et al.[16] ○ Martin and Knauer[114]	○ Wong et al.[35]		○ Wong et al.[35]	○ Bewers and Windom[92]	○ Burton et al.[108]	○ Bruland and Franks[104] ○ Landing and Bruland[76]

Fe	• Segar and Bergerian[97]	O Klinkhammer and Bender[114] • Wong et al.[28] • Landing and Bruland[76] O Segar and Bergerian[97]	O *Moore*[171] O Hong and Kester[188] • Bewers and Windom[92]	O *Gordon et al.*[193] O Berman et al.[16]	• Wong et al.[35]		• Wong et al.[28]	• Bewers and Windom[92]	
Pb	• Schaule and Patterson[123]	• Schaule and Patterson[123]	• Spencer et al.[31] • Schaule and Patterson[123] O Paulson and Feely[191]	OMart et al.[88] O Magnusson and Rasmussen[107] • Schaule and Patterson[123]		• Magnusson and Rasmussen[107]			O Nürnberg et al.[105] O Schaule and Patterson[33] O Schaule and Patterson[129]
Co			• Wong et al.[35]	O Bruland et al.[30]	O Wong et al.[35]			O Danielsson et al.[194]	
Hg		O Fitzgerald and Lyons[122]	O Bloom and Crecelius[43]	O Berman et al.[16]				O Olafsson[34]	
Cr	O Cranston and Murray[195]	O Cranston[196]	O Jeandel and Minster[197]	O Campbell and Yeats[198] O Berman et al.[16]					
As	O Kremling et al.[182]		O Kremling et al.[182]	O Berman et al.[16]	O Kremling et al.[182]			O Kremling et al.[182]	
Sb	O Kremling et al.[182]		O Kremling et al.[182]		O Kremling et al.[182]			O Kremling et al.[182]	
Se			O Andreae et al.[199]	O *Cutter and Bruland*[200]					

Note: Acceptable performance = O; contaminated sample = •.

Table 6
LEAD CONTAMINATION FROM DEEPWATER SAMPLERS[a]

Sampler	Volume (*l*)	Features	Measured Pb (ng/kg)	True Pb Conc. in CIT (ng/kg)
Niskin	30	PVC, internal rubber band	3000—5000	1—15 (est.)
Modified Niskin	100	All stainless external closures	30—200	1—15 (est.)
Swedish lucite	5	All plexiglass	20	4
Top Drop	30	PVC, Teflon®-coated	10	1.7
Go-Flo	30	PVC, Teflon®-coated on plastic wire	40	4
Modified Go-Flo	30	Teflon® drain plugs	5.7	2.9
Caltech CIT	10	CPE, FEP Teflon® stainless housing	1.0	1.0

[a] Data from Reference 123.

cedure. An alternative to the difficulties involved in collecting, preserving, and transporting large volumes of water samples to a laboratory for analysis is on-site or *in situ* preconcentration, wherein the trace metals in the sample are converted to a nonlabile species through some method of preconcentration.[125] Mĕranger et al.[126] have recently reviewed this aspect of sampling of natural waters. The advantages of this approach can be significant and include (1) transportation and storage of large volumes of water are not required; (2) *in situ* preconcentration is a composite sampling method, enabling a large, fairly respresentative sample to be concentrated to a smaller volume; and (3) a concentrated sample in a controlled chemical form will be more stable.

Similar to grab-sampling samplers discussed in Section III, an ideal *in situ* field sampler should meet the following criteria: (1) it must recover trace metals quantitatively; (2) it should be rugged and not require excessive set-up procedures in the field.

As with grab samplers, no field device has yet been designed to meet all of these requirements, particularly with respect to criterion (2) above. In this regard, it is of interest to note that, while most field applicable concentration techniques detect labile complexes, the above limitation is probably close to one presently imposed by the majority of techniques used for the determination of trace metals in grab samples.[126] A majority of on-site trace metal concentration devices (discussed below) are based on the use of chelating functionalities (imminodiacetate, dithiocarbamato, 1,2,-diamino, 8-hydroxyquinoline, dithizone, etc.) immobilized onto various substrates (filter membranes, open pore polyurethane foam, silica gel, polystyrene divinylbenzene); hydrophobic supports for ionic trace metals (XAD-2) and organometallic complexes (C_{18}-octadecyl silica gel) have also been utilized.

Leyden et al.[127] silylated silica gel substrates and produced dithiocarbamato and 1,2-diamino chelating groups used for the quantitative recoveries of Co, Cu, Fe, Mn, Ni, Pb, and Zn from lake waters by pumping the sample through columns of coated glass beads at 50 m*l*/min. The columns were then taken back to the laboratory for extraction of the metal ions.

Open pore polyurethane foam impregnated with dithizone has been used for the collection of Hg(II) and CH_3Hg^+ species from lake water.[128] This support has also been used in combination with a variety of other reagents.[128a]

Davey and Soper[129] described an apparatus for *in situ* concentration of dissolved trace metals using Chelex-100 resin. Polyethylene bottles were suspended below the surface on a styrene float and vented to the surface. The depth of the bottles provided the hydrostatic pressure to force the water through an in-line filter to the resin column connected to the bottles. The device is restricted to shallow depth applications ($\leq$100 m). The sampler can be used to concentrate trace metals from almost any volume of water by adjusting the size of the container bottle and thus can be designed to integrate the water collected over a period of 1 to 7 days. Cd, Cr, Cu, Mn, Ni, Pb, and Zn were determined in Naragansett Bay.

Shuman and Dempsey[130] utilized anion (AG-1X50) and cation (AG-50WX8) exchange columns in series for field concentration of dissolved Cd, Cr, Cu, Pb, and Zn from North Carolina river waters. Field samples of 10-*l* volumes could be processed in 15 to 20 min (by peristaltic pumping at flow rates of 600 m*l*/min) followed by batch elution of the columns in the laboratory with 3 *N*HCl. Anionic species of Cr, Zn, and Cu were reported.

Chester and Stoner[131] sampled near-shore and open-ocean surface waters by pumping the water on deck with plastic tubing from a position in the bows (to minimize ship contamination), filtered it through a 0.45-μm membrane filter, and collected 10-*l* volumes in clean plastic flasks. These samples were then preconcentrated by passage through a glass column containing Chelex-100 resin. The columns were then sealed and stored for return to the laboratory where they were subsequently eluted for the determination of Zn, Ni, Cu, Cd, Mn, and Fe.

Kremling et al.[132] described an *in situ* field preconcentration technique for the isolation of Cu organic substances in seawater. Samples pumped from an 8 to 10 m depth were pH adjusted and the dissolved organic material, containing Cu, sequestered by passage through columns of Amberlite® XAD-2 resin and porous glass CPG 10 containing immobilized octadecyl groups (C_{18}). Seawater volumes up to 400 *l* from a single 5-day anchor station, as well as an integrated volume of 300 to 400 *l*, were collected during a cruise. Similarly, Miyake and Suzuki[73] concentrated dissolved organic Hg from 2- to 10-*l* volumes of surface water by passing the filtered sample through a column of XAD-2 resin at natural pH aboard ship. Columns were subsequently eluted and the concentrate analyzed on shore.

Pahlavanpour et al.[133] preconcentrated 500 m*l* field samples of freshwater by coprecipitating trace metals with rubeanic acid and collecting them on a membrane filter. The precipitate was redissolved from the filter, by acid digestion, back in the laboratory. The method should be equally suitable for saline waters. The fate of nonionic or nonlabile metal species was uncertain.

Organometallic complexes of Cu, Zn, Fe, Mg, Ni, Cr, Mn, and Cd were field concentrated from 6-*l* volumes of estuarine water by passage through a 0.45-μm membrane filter and SEP-PAK (C_{18} Waters Scientific) cartridge at 1 *l*/hr using a peristaltic pump.[134]

Recently, Seastar Instruments Ltd. (Sidney, British Columbia, Canada) initiated marketing of an *in situ* water sampler consisting of a submersible (300 m) battery-powered pumping unit which can be fitted with a prefilter unit and a variety of types of extraction columns. A microprocessor controls the pump rate, measures the water volume processed, and allows the sampler to be operated over a period of several days in a moored position with a float and anchor or attached to a hydrowire and activated with a messenger. The extraction column, prepared in the laboratory under clean room conditions, is a Teflon® tube containing an adsorbent material mounted externally and upstream from the pump. This configuration permits a variety of column materials to be used for preconcentration of organic materials and metal ions from soluble labile complexes including polyurethane foam for PAHs and PCBs, as well as dithizone-impregnated polyurethane foam (for Hg and CH_3Hg^+) and 8-hydroxyquinoline immobilized on polystyrene-divinylbenzene[135] for Cd, Zn, Cu, Al, Pb, Ni, Co, Fe, and Mn. The system should also be capable of utilizing macroreticular acrylic ester resins[136] for trace metal uptake. Once sampling is completed, the unit is retrieved and the column is removed, capped, and sealed in a bag until analyzed.

Batley and Gardner[137] cautioned against use of such *in situ* devices by pointing out that exchange columns, such as Chelex-100 resin, may not remove all of the dissolved metal fraction from the sampled water.[138] In unpolluted seawater samples, the resin-removable fractions for Cd, Pb, and Cu lie in the range 30 to 70% of the total metal concentrations. In polluted water, this fraction is higher since metal pollutants usually consist of ionic species. The nonretained metal is present primarily as metal adsorbed on organic and inorganic colloidal particles which pass through 0.45-μm filters.

This potential problem can be partially overcome through use of immobilized ligands which form complexes possessing high stability constants with the metals of interest, thereby sequestering them from such "dissolved", bound species.[139]

VI. SAMPLE HANDLING

Once the samplers are retrieved from the hydroline or hand-collection station, a number of handling operations must be completed, depending on the type of sample, analytes of interest, and nature of the study. In general, these include possible filtration, subsampling, on-board preconcentration and analysis, transfer of sample to storage containers, and preservation. These procedures must be initiated immediately after sampling and given rigorous care and attention to prevent subsequent contamination from the sampling vessel. Although it would be preferable to eliminate all shipboard handling by taking advantage of *in situ* preconcentration procedures (Section V), techniques for this have not yet been satisfactorily developed.

In many instances, transfer of the water from sampler to storage container aboard ship is the minimum procedure required for subsurface samples. Further sample manipulation may then be completed on shore in clean room laboratories. Ideally, transfer, filtration, acidification, or other on-board processing of samples should be done in a clean room facility. As oceanographic vessels are often used for many applications, it is not usually practical to dedicate a portion of ship lab space to clean room factilities. An alternative is to use portable laboratory modules, complete with positive-pressure filtered air clean room stations that can be fitted onto the deck of the research vessel.[30,31,35,93,96]

Water samples can either be carried into these clean modules[31,93] or secured in a rack on the outside of the lab with the drain spigot connected to clean tubing leading through the wall of the lab to a flow control valve.[30]

Where no clean room facilities are available, samples are processed on deck or in the laboratory of the ship, utilizing procedures which minimize exposure of the sample to the air[16] and by using laminar flow clean benches whenever possible.[74]

A. Filtration

Natural waters contain varying quantities of suspended inorganic and organic material. Concentrations of particulate matter may vary between 0.5 μg/ℓ in deep ocean waters to several milligrams per liter in near-shore and surface waters.[140,141] A large portion of this suspended material is made up of organic compounds, the remainder is composed mostly of alumino silicates, quartz, carbonates, and amorphous silica.

By convention, the dissolved fraction of trace metals is that fraction passing through a filter of a 0.45-μm nominal pore size. A wide variety of membrane filters are commercially available, including those made from cellulose esters, Teflon®, nylon, polycarbonate, PVC, polyamide, and silver foil. Glass fiber filters are also popularly used for samples intended for Hg determinations. Polycarbonate (Nuclepore) and cellulose ester (Millipore) filters are most commonly used for trace metal analyses with preference generally being given to Nuclepore because of its superior retention power for submicron-sized particles, small salt retention, lower intrinsic trace metal impurities (cf. Table 3), and relative ease of obtaining reproducible filter weights.

In practice, the separation of truly dissolved and particulate fractions of metals in natural waters is inadequate, especially for colloid-laden samples and for elements such as Fe and Al.[142-144] Furthermore, the effective pore size may be influenced by the mass of particles on the filter,[145] finer particles being retained with greater efficiency as the effective pore size decreases with loading. The median retention size of Nuclepore filters, however, remains constant until the filter becomes blocked, making them potentially useful for particle sizing. In general, frequent filter changes and/or large area filters should be used for large volume filtrations.

Suspended material may contaminate samples during prolonged storage through sorption processes[146,147] or bacterial action.[148] However, since the risk of contamination is increased by each additional procedure, removal of particulates may constitute a greater hazard to sample integrity than their presence. For this reason, deep ocean samples are generally not filtered since the only trace metals for which the particulate fraction will constitute an important portion of the total metal concentration are Fe and Al and possibly Mn.[92] Filtration, when required for the purposes of the study or for storage of samples, should be limited to turbid river waters, estuaries, shallow coastal areas, and eutrophic lakes.[35]

Filters and apparatus may introduce both positive and negative contamination. Losses of Cu due to adsorption have been reported by Truitt and Weber[149] when using Nuclepore polycarbonate and Gelman cellulose filters. Substantial losses of Cd and Pb were also reported by Nürnberg et al.[150] when unconditioned filter membranes were used and Millipore filters adsorb Hg.[151]

Positive contamination from filters can be reduced to insignificant levels by their proper conditioning and the cleaning of filter supports prior to use. Glass fiber filters, although unsuitable for the majority of metals, are recommended for Hg and are easily cleaned by ignition at 500°C. Membrane filters are usually cleaned by successive acid leaches. Kremling et al.[152] described a rigorous procedure beginning with a 3-day soaking in 6 *M* HCl followed by rinsing in high purity water and a further 3-day soaking in 1% ultrapure HCl at 55°C. After a final rinse with ultrapure water, the filters were dried at 60°C and stored in cleaned plastic dishes. Once mounted in the filter apparatus, they were again rinsed with pure water prior to use. In contrast to this, Mart[35a] does not recommend drying the clean filter membranes but rather storing them in 1% ultrapure HCl until some days prior to their use, at which time they are conditioned by storage in clean seawater until used. Often the first 0.5 to 1 *l* of sample is used to precondition the cleaned filter system in the field and is then discarded.[137]

The type of filtration apparatus to be used is also an important consideration. Whereas Pyrex® glass units are preferable for Hg samples, Teflon® is the recommended choice for other metals.[153]

Filtration can be performed under partial vacuum or under pressure. With either technique, it is essential that only low pressures are used since rupture of phytoplankton cells occurs at pressures greater than 20 mmHg. This may lead to increases in the heavy metal content in the filtrate because these cells often contain concentrations of Cu, Zn, Cd, and Pb which are several orders of magnitude greater than the aqueous phase.[154]

Field filtration can be accomplished either by pressurizing the sample with nitrogen and using an on-line filter in the tubing between the sampler and the storage bottle or by a separate filtration step subsequent to the initial subsampling of the sample (off-line filtration). Pressure filtration is advantageous in that it permits filtration directly from the sampler bottle under an inert atmosphere, thereby minimizing airborne contamination. Also, pressure filtration can be accomplished as quickly as possible after collection and sample handling is minimized. However, this method delays redeployment of the water samplers until filtration is completed, and additionally, settling of the suspended particulate matter (SPM) occurs within the bottle during filtration, which is detrimental to the collection of representative SPM samples (if desired).

The second approach is to transfer the sample to a holding tank and complete filtration in a separate filtration apparatus. Although samplers are ready for redeployment more rapidly and differential settling problems are minimized with such off-line techniques, additional sample handling is required.

Both techniques have been used in the field, although pressurized on-line filtration is the most popular. Vacuum filtration, inherently an off-line technique, should be performed in a laminar flow clean bench in order to avoid airborne contamination.

A recent ICES experiment[155] undertaken to assess various filtration procedures employed in coastal waters revealed that filtrates from on-line systems did not exhibit marked differences from their off-line counterparts except in the case of Zn, where they gave lower results. Commercial on-line Sartorius pressure filtration units, Nuclepore filter holders, Millipore "Swinnex" holders, and custom Teflon® support units holding 47-mm, 0.4-μm Nuclepore filters were all capable of producing and generally gave contamination-free filtrates for Cu, Ni, Co, Mn, Cd, and Fe at levels normally encountered in uncontaminated coastal waters. Comparable results were obtained for Zn and Pb, although at elevated levels.

B. On-Board Preconcentration

Because of the problems of stabilizing trace heavy metals in natural waters, a desirable method of storing samples is in concentrated form. This can be accomplished in a variety of ways including (1) chelation-solvent extraction, (2) coprecipitation, and (3) ion exchange. The latter technique is best suited for shipboard use as it requires a minimum of sample handling. In any case, such manipulations should be restricted to clean laboratory facilities (portable clean labs) or isolated laminar flow clean air benches. In ideal circumstances, full analyses should be completed on site immediately after the sample is taken,[31,105,108,156-159] but this is seldom possible for both analytical and technical reasons. There is obviously much activity in this area at present, but the lack of published information makes these efforts difficult to describe and assess.

C. Preservation and Storage

The majority of field samples must be returned to the laboratory for subsequent analysis. With this in mind, the transfer of samples from the sampler bottle directly to the intended storage container (with on-line filtration) should be considered. Water samples may undergo changes with regard to their physical, chemical, or biological state at varying rates from their time of sampling. Changes in metal concentration can occur as a result of sorption processes between the metals, container walls, and suspended particles; chemical changes such as precipitation or colloid formation; and by bacterial growth and degradation. Included among the many factors which influence the stability of a specific metal in solution are the type of storage container, element, concentration, pH, temperature, concentrations of other salts, organic compounds, and the particulate material content.

Although there have been a number of studies conducted on the long-term storage of dilute aqueous solutions,[20,160,161] there has been a great deal of controversy over losses of trace metal ions to storage containers.[42,162] A poor consensus has developed as to the proper storage conditions for most metals, emphasizing the need for more definitive studies. Storage experiments generally support the conclusion that Teflon®

or high-density polyethylene or polypropylene are the preferred high-purity materials for storage containers.[137] Borosilicate glass is often used for storage of samples intended for Hg analysis.

While acid leaching of sample containers is essential to ensure cleanliness, this treatment may lead to the activation of adsorption sites capable of removing trace metals from solution.[162] For this reason, after acid treatment, it is essential that the container be conditioned at the same acidity as sample storage. Nürnberg et al.[150] use conditioning salt solutions containing Ca and Mg sulfates for inland water sampling and a mixture of NaCl and Ca and Mg sulfates for seawater. Florence and Batley[162] reuse the same aged containers, rinsing between samples with sample, not acid, to maintain well equilibrated surfaces. Berman et al.[16] store the containers filled with high-purity water acidified to pH 1.6 with ultrapure nitric acid. This is the pH to which their collected samples are acidified for storage.

A major problem in many storage experiments has been the actual measurement of natural levels of heavy metals and for this reason storage integrity has usually been assessed with radiotracers or the addition of a measurable ionic spike. The possibility of an incomplete exchange of added tracer with other chemical species of a given element may cast doubt on the conclusions drawn.[137] Similarly, large ionic metal additions may drastically disturb the solution equilibria in the natural sample and the behavior of metal spikes may be different from that of the natural sample. The most reliable experiments are those which directly measure the metal concentrations as a function of storage time.

A universally applicable method of preserving water samples has yet to be found since the individual parameters to be investigated are influenced in different ways by the various preservation techniques. Complete stability for every sample constituent can never be achieved. At best, preservation techniques can only retard chemical and biological changes that take place in a sample once it is removed from the parent source. Both physical (refrigeration) and chemical (addition of chemicals) methods of preservation are currently practiced.

When delineation of the speciation of an element is of interest, rather than the total metal concentration, additional care must be taken to ensure that the method of preservation does not alter the numerous equilibria within the sample.[138,163] Some metals can be effectively stored at natural pH. Robertson[20] reported negligible adsorption of Zn, Cs, Sr, and Sb on Pyrex® and polyethylene surfaces at the natural pH of seawater. Spencer and Brewer[164] stored filtered seawater in polyethylene containers for up to 3 months without loss of Cu, Fe, Co, Zn, and Ni. However, the metal concentrations studied by these workers were probably too high to supply meaningful conclusions for actual natural waters.

Fukai and Huynh-Ngoc[165] successfully stored Cu, Cd, and Zn in unacidified seawater for several months in polyethylene containers. Slowey and Hood[166] also stored unfiltered seawater for up to 2 years in Pyrex® glass without the loss of Cu, Mn, or Zn. Florence[163] reported no detectable change in Cu, Pb, Cd, and Zn in freshwater samples (pH 6.1) stored for 4 weeks in polyethylene containers, and Batley and Gardner[137] effectively stored Cu, Cd, and Pb in filtered seawater for up to 90 days in polyethylene bottles. Subramanian et al.,[167] however, observed significant losses of metals from river water samples (pH 6.8) during their first 10 days of storage in polyethylene containers, and Laxen and Harrison[40] reported both gains and losses of Zn, Pb, and Cu in river water (pH 7.7) stored for 28 days in polyethylene bottles. Similarly, Robertson[20] found that Co and Fe were lost when samples of filtered seawater were stored in polyethylene and O'Connor and Kester[168] observed a significant loss of Cu from seawater stored in polyethylene containers.

Laxen and Harrison[40] have suggested that such contradictory results may arise because of the different cleaning methods used to prepare the sample container. However, other factors, such as sample volume per container surface area, filtration, and analytical technique may also affect conclusions. Changes in the bacterial content of samples may occur during storage as may formation of particles on aggregations of bacteria.[169] Both processes may lead to the physical loss of metals independent of the nature of the storage vessel. For most metals, insufficient data are available with which to make definitive judgments.

Bacterial activity can be reduced by storage at 4°C and several authors have suggested refrigeration as a preservation technique (e.g., see Reference 170). Deep freezing (to −20°C) after filtration (to avoid contamination through rupture of phytoplankton cell membranes) appears to be a more suitable method.[35a,71,171-173] While potentially useful for total metal preservation, there are reports that speciation of the elements may be irreversibly altered.[35a,137] An additional drawback to the deep freezing of samples is that precipitation frequently occurs. This can often be reversed in the thawed samples by the addition of acid, but rehomogenization must be undertaken before aliquots are removed from the parent sample for analysis.[71] Additionally, low temperature preservation of bulk samples is not practicable for most laboratories and becomes a real problem when samples have to be transported.

Grasshoff[8] suggests chemical preservation (by acidification to pH 1.5) if samples cannot be frozen within 2 hr. Addition of acid can inhibit or prevent the metabolic processes of microorganisms which cause changes in the sample. Furthermore, acidification prevents flocculation and precipitation or hydrolysis of metals and reduces adsorption onto container surfaces. Chemical preservation, however, prohibits subsequent speciation studies, and acidification before filtration will release metals from particulate matter and is not recommended. Kremling et al.[152] suggest that the safest storage procedure for elements such as Zn, Cd, Cu, Co, Ni, Fe, and Mn is to filter the samples (with the exception of open-ocean water), acidify them to pH 1.5 to 2 with high-purity HCl or HNO_3, and store them at about 4°C in suitable containers (Teflon®, polypropylene, polyethylene, and borosilicate glass or Teflon® for Hg).

Corrections must be made for acid blanks, which are often measured by the addition of identical volumes of acid to high-purity water. Boyle et al.[74] utilize a number of deionized water blanks of known volumes so that blank contributions from the deionized water and the acid can be resolved. The availability of subboiling distilled high-purity acids[174] has permitted acid preservation techniques to gain widespread acceptance. Acidification should be performed in clean room facilities or in a laminar flow clean bench when available.[74] Conversely, acidification may be accomplished in-line during the transfer of sample from sampler bottles to storage or transport containers,[16] minimizing the possibility of airborne contamination.

Although acidification of samples has been practiced for many years, only two recent studies[16,175] have documented the long-term storage characteristics of a number of elements preserved in this manner. In both cases, the concentrations of the natural levels of the elements of interest were followed as a function of time. The long-term stability of the three certified natural water reference materials, NASS-1, CASS-1, and SLRS-1, are in themselves documented successful storage experiments. NASS-1 was immediately acidified to pH 1.6 on collection. CASS-1 and SLRS-1 were immediately filtered and acidified.

Table 7 summarizes some of the specific parameters used for the successful short- and long-term storage of a number of trace heavy metals in natural waters. In most cases, the product sample is suitable only for total metal analysis, all vestiges of speciation having been lost in the preservation process.

Table 7
SUCCESSFUL STORAGE METHODS FOR SOME TRACE METALS IN NATURAL WATERS

Element	Sample	Container bottle	Preservative	Storage period	Ref.
Zn	Lake and stream samples	Glass vials, polyethylene caps	pH 1.5, 23°C	1 Year	201
	River water	Polyethylene	(Natural) pH 6.1, frozen at −20°C or 25°C	30 Days	163
	Unfiltered river water	Polyethylene	Natural pH	16 Days	202
	Filtered river water	Polyethylene	pH 1.5 (HNO_3)	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Lake water	Glass vials	pH 1.5, 23°C	1 Year	6
	Lake water	Polyethylene	pH 1.5 (HNO_3)	6 Months	203
	Seawater	Polyethylene	pH 1.8 (HNO_3)	2 Months	108
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Unfiltered seawater	Polyethylene	Natural pH	30 Days at 4°C	165
	Estuarine water	Polyethylene	Natural pH, 4°C	75 Days	204
	Estuarine water	Teflon®	Natural pH, 4°C	35 Days	38
	Coastal filtered seawater	Polyethylene	pH 1.6, 23°C	1.5 Years	175
Cd	Seawater	Polyethylene	Natural pH, 4°C	30 Days	165
	Filtered coastal seawater	Polyethylene	pH 1.6, 23°C	1.5 Years	175
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Unfiltered seawater	Polyethylene	pH 1.8	Several years	101
	Seawater	Polyethylene	pH 1.8	2 Months	108
	River and lake water	Polyethylene	pH 1.5	6 Months	203
	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Lake water	Polyethylene	pH 1	184 Days at −15°C	6
	River water	Polyethylene	Natural pH (6.1); 25°C or frozen at −20°C	30 Days	163
	Filtered seawater	Polyethylene	pH 2	4 Months	35
Pb	Unfiltered seawater	Polyethylene	pH 1.8	Several years	101
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Filtered coastal seawater	Polyethylene	pH 1.6, 23°C	1.5 Years	175
	Unfiltered seawater	Teflon® and polyethylene	pH 1.8	5 Weeks	205
	River water	Polyethylene	Natural pH (6.1), 25°C or frozen at −20°C	30 Days	163
	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Lake water	Polyethylene	pH 1.5	6 Months	203
	Filtered seawater	Polyethylene	pH 2	4 Months	35
	Seawater	Polyethylene	pH 1.8	2 Months	108
Cu	Unfiltered seawater	Polyethylene	Natural pH, 4°C	30 Days	165
	Lake and stream	Glass vials, polyethylene caps	pH 1.5, 23°C	1 Year	201
	Filtered seawater	Polyethylene	Natural pH	3 Months	164
	River water	Polyethylene	Natural pH (6.1), 25°C or frozen at −20°C	30 Days	163
	Filtered coastal seawater	Polyethylene	pH 1.6, 23°C	1.5 Years	175

Table 7 (continued)
SUCCESSFUL STORAGE METHODS FOR SOME TRACE METALS IN NATURAL WATERS

Element	Sample	Container bottle	Preservative	Storage period	Ref.
	Unfiltered seawater	Polyethylene or Teflon®	pH 1.8	5 Weeks	205
	Unfiltered seawater	Polyethylene	pH 1.8	Several years	101
	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Lake water	Glass vials	pH 1.5	1 Year	6
	Lake and river water	Polyethylene	pH 1.5	6 Months	203
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Seawater	Polyethylene	pH 1.8	2 Months	108
Ni	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Lake water	Polyethylene	pH 1.5	6 Months	203
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Unfiltered seawater	Polyethylene	pH 1.8	Several years	101
	Unfiltered seawater	Teflon® and polyethylene	pH 1.8	5 Weeks	205
	Filtered coastal seawater	Polyethylene	pH 1.6, 23°C	1.5 Years	175
	Filtered seawater	Polyethylene	Natural pH	3 Months	164
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Filtered estuarine	Polyethylene	pH 1.5, frozen	3 Weeks	156
	Seawater	Polyethylene	pH 1.8	2 Months	108
Fe	Unfiltered seawater	Teflon® and polyethylene	pH 1.8	5 Weeks	205
	Filtered coastal seawater	Polyethylene	pH 1.6, 23°C	1.5 Years	175
	Filtered seawater	Polyethylene	Natural pH	3 Weeks	164
	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Lake and river water	Polyethylene	pH 1.5	6 Months	203
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Filtered estuarine water	Polyethylene	pH 1.5, frozen	3 Weeks	156
	Unfiltered seawater	Polyethylene	pH 1.5	2 Months	206
Mn	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Lake water	Polyethylene	pH 1.0	184 Days	6
	Lake and river water	Polyethylene	pH 1.5	6 Months	203
	Unfiltered seawater	Polyethylene	pH 1.8	Several years	101
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
Hg	Seawater	Teflon®	pH 1.6—2.2	8 Weeks	122
	Filtered seawater	Pyrex® glass coated with silicone oil, baked	pH 1.0 (H_2SO_4)	6 Weeks	207
	Freshwater	Pyrex®	pH 0.1 (HNO_3) 0.01% $K_2Cr_2O_7$	5 Months	208
	Seawater	Pyrex®	pH 1.5	50 Days	41
	River and lake water	Teflon® or pyrex	pH 0.7 (H_2SO_4) 0.005% $K_2Cr_2O_7$)	1 Month	203
	Seawater	Pyrex	pH 1.0	107 Days	24
	Lake water	Polyethylene	Natural pH, 10 mg/ℓ cysteine	30 Days	209
Cr	Seawater	Pyrex	Natural pH	2 Months	210
	Lake water	Polyethylene	Natural pH (7)	15 Days (for Cr[VI])	211
	Lake and river water	Polyethylene	pH 1.5	6 Months	203

Table 7 (continued)
SUCCESSFUL STORAGE METHODS FOR SOME TRACE METALS IN NATURAL WATERS

Element	*Sample*	*Container bottle*	*Preservative*	*Storage period*	*Ref.*
	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
Al	Fresh water	Polyethylene	pH 1.3, 23°C	4 Weeks	6
	Fresh water	Polyethylene	pH 1.5	6 Months	203
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Unfiltered seawater	Polyethylene	Natural pH	8 Months	212
Co	Unfiltered seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Unfiltered seawater	Polyethylene	pH 1.5	80 Days	206
	Fresh water	Polyethylene	pH 1.5	6 Months	203
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
Se	Fresh water	Polyethylene	pH 1.5	6 Months	203
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 Years	218
	Seawater, estuarine, lake	Pyrex® (Al foil-lined caps)	Natural pH	2 Weeks (for Se IV)	28
	Seawater	Polyethylene or pyrex	pH 2 (HCl)	4.5 Months	27
	Lake, river, estuarine	Polyethylene	pH 2	Several weeks	213
	Freshwater	Polyethylene	pH 1.5	125 Days	214
As	Filtered river water	Polyethylene	pH 1.5	Several months	110
	Filtered river water	Polyethylene	pH 1.6, 5°C	>1.5 years	218
	Freshwater	Polyethylene	4°C	6 Months	203
	Seawater	Polyethylene	pH 1.6, 23°C	>4 Years	16
	Coastal seawater	Polyethylene	pH 1	2 Months	215
	Seawater	Polyethylene	pH 1.3	Several months	152
Sb	Seawater	Polyethylene	pH 1.6, 23°C	>3 Years	16
	Freshwater	Polyethylene	pH 1.5	6 Months	203
	Coastal seawater	Polyethylene	pH 1.0	2 Months	215
	Seawater	Polyethylene	pH 1.3	Several months	152
Sn	Seawater	Polycarbonate	−20°C	100 Days	216
	Seawater	Polyethylene	Natural pH	11 Days	217

Special consideration must be given to samples destined for Hg determinations since their storage and preservation requirements are unique. Batley and Gardner[137] and Erickson[42] have summarized the relevant literature in regard to this metal and, as indicated in Table 7, it is necessary to add oxidants ($Cr_2O_7^{2-}$) or complexing agents (cysteine) in addition to acidification to prevent Hg losses during storage. Teflon® or borosilicate glass containers are preferred containers for Hg because of the permeability of other plastic materials to Hg vapor (producing both negative and positive contamination).[41]

VII. CONCLUSIONS

Well-defined techniques are now available for the collection of natural water samples which potentially avoid heavy metal contamination. Indeed, with respect to marine samples, recent studies[120] indicate that in the hands of competent personnel from experienced laboratories differences resulting from the use of differing sampling procedures may be relatively small in the cases of the most commonly analyzed metals. This suggests that, except for Pb,[123] the problems may now be primarily associated with the analytical stage of the operation. Results of interlaboratory calibration exercises attest to this.[124] On the other hand, the more recent improvements in analytical competence in experienced laboratories[15,218] demonstrate that the analytical measurement stage is, in many instances, under control and that sampling and storage are again the weak links in the overall process for the estimation of trace metals in natural waters.

Obviously, great care must be taken at every stage in order to produce valid data.

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