Sampling and Analytical Methods for the Determination of Trace Metals in Surface Seawater

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SAMPLING AND ANALYTICAL METHODS FOR THE DETERMINATION OF TRACE METALS IN SURFACE SEAWATER

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New recently implemented techniques and sample strategies for the determination of trace metals in seawater are discussed. It is shown that only with the highest precautions to prevent contamination, reliable results can be obtained. These precautions start already with the preparation of the sample bottles and sampling equipment in the laboratory. A rubber boat, Go-Flo samplers and a specially designed teflon-coated winch with Kevlar rope is used to collect the samples. At sea, the prevention of contamination of the samples is the highest priority. This implicates the use of a clean air van or at least a laminary flow bench. Acids have to be subboiling distilled in a quartz still and stored in teflon bottles. Preconcentration of the samples on board or in the home laboratory has to be done in clean rooms. This paper gives an account of current procedures used for sampling and analysing seawater for trace metal determinations.

KEY WORDS: Sea water sampling, trace metals, Atlantic Ocean.

INTRODUCTION

In the last decade, major progress has been made in the sampling and handling of seawater samples for the determination of trace elements (1, 2, 3). This development is not in the last place stimulated by the increasing interest for iron, which is supposed to stimulate primary production like the macronutrients nitrate, phosphate and silicate. It is well known that problems related to sampling and analysis of seawater for trace metals are very difficult to solve, due to the high risk of contamination. Especially the sampling of surface seawater close to the ship gives rise to unrealistic iron data as well as scatter in other trace metal data. Culture experiments with iron depleted seawater to which low iron concentrations (1–2 nM) were added to study growth rates of natural phytoplankton communities, strengthen the need of clean upper water column sampling. To avoid and exclude the contamination problem it has been necessary to give more attention to the sampling and analytical procedures (4). This resulted not only in a more reliable and realistic description of the very low dissolved iron concentration in open seawater, but also in the improvement of the data quality of other trace metals (5–11). With this improved method it is now possible to exclude to a great extent contamination and determine small concentration gradients in seawater, and to study biogeochemical processes in which metals are incorporated.

This paper describes the whole procedure, from sampling to final analysis, for the determination of trace elements in seawater. The described work is based on a large experience gained at the Netherlands Institute for Sea Research and other institutes in the U.S.A and Europe.

EXPERIMENTAL

Cleaning procedures

An important part of the whole procedure for seawater sampling and analysis is the cleaning of sample bottles, sampling equipment, filters and filter holders. If this part of the procedure is ignored or not done in the right way, all following handlings give bad results and lead to wrong conclusions. The best material for sample bottles are, high density polyethylene, polypropylene, teflon or quartz because they have low metal sorption and resorption properties (12–16) and good chemical resistance. In our institute we prefer high density polyethylene sample bottles with a volume of one liter, because they are inexpensive, unbreakable and easy to clean. New bottles have to be treated with a detergent, rinsed with milli–Q water and further soaked in hot 6M HCl for one week, followed by hot 6M HNO_3 for one week. Then the bottles are rinsed with milli–Q water, dried in a laminary flow bench and, after drying, wrapped in double plastic bags. For bottles used beforehand the soaking can be restricted to one day. Sampler bottles are 1.7 liter Go–Flo samplers, which have been shown to be the best device for seawater sampling to determine trace metals (15, 17). They are extensively cleaned with 0.1M HCl, rinsed with milli–Q water and stored in plastic bags. Before use they are filled with sea water, acidified to pH 2, and left to stand overnight. Then they are rinsed with sea water again and sampling can take place.

Filters from polycarbonate or cellulosenitrate or -acetate can be used (18–20); however the polycarbonate filters are preferred, because of their defined poresize and lower weight (18). Filters are soaked in 6M HCl for 24 hours, rinsed with milli–Q water up to pH 7, dried at 60°C, weighed and stored in numbered precleaned polycarbonate petri dishes. Celluloseacetate filters cannot be cleaned by 6M HCl and because of this they cannot be used. The filter holders are all-teflon and directly connected to the Go-Flo samplers. They are rinsed in 6M HCl for several days, rinsed with milli-Q water and packed in plastic bags. During the operations on board they are continuously stored in dilute HCl. All acids used in the analytical procedures are threefold subboiling quartz distilled and stored in teflon bottles. All teflon material used during the whole procedure is cleaned in the same way as the sample bottles.

This sampling equipment is brought into a clean air laboratory van, which is placed on the research ship.

Sampling

When the desired sampling position is reached, the protected sample bottles and Go-Flo samplers are brought in a rubber boat. This boat is equipped with a small teflon-coated winch with 200 meter Kevlar wire (6 mm), a counter weight of watertight PVC pipe filled with 10 kg lead and a meter wheel to determine sampling depth. The boat is then lowered to the water surface and sails more than 500 meter from the ship, taking into account the ship's position and wind direction. All these precautions are done to avoid iron and other trace metal contamination from the ship, especially for the upper water column where biological precesses take place. First, the upper surface is sampled by directly submerging a sample bottle from the bow of the slowly moving boat by hand (hands covered with plastic gloves). The full bottle is then again packed in its plastic bag and stored in a plastic crate, which is protected by a plastic bag too. Next, the Go-Flo bottles are taken out of the plastic bags and attached to the Kevlar wire. In this way 5 Go-Flo samplers at intervals of

10–20 meter are deployed, with a teflon messenger on each bottle. Upon recovery the Go-Flo samplers are directly wrapped in their plastic bags again.

Water samples collected from greater depths than 100 meter, are taken from the ship with 12 liter Go-Flo's attached to a Kevlar cable (9 mm).

Back to the ship the samples and Go-Flo samplers are directly brought into the clean air van. The filter holder, with a pre-weighed filter (47 mm, 0.4 µm), are connected to the Go-Flo samplers with teflon tubing and pressurized with nitrogen gas at 1.5 bar for filtration. The sample bottle is rinsed twice with the filtered seawater and subsequently filled with the sample. In a laminary flow bench the samples are acidified with 1 ml threefold subboiled quartz distilled HNO_3 to pH 2 and stored. Finally, the filters are rinsed with milli-Q water and stored in the petri dishes.

Trace metal analysis

Our present analytical procedure is a hybrid of methods published by Bruland *et al.*[1] and Danielsson *et al.*[2] All analytical handling is performed in a Class 100 clean room.

500 mL of the sample is transfered to a clean teflon separatory funnel and brought to pH 4.5 with ~ 1 mL of an ammoniumacetate buffer. The pH is checked with pH paper. This buffer is made by purging high purity ammonia gas, (which is essential to obtain a low blank), through three times quartz distilled acetic acid in an all-teflon set up. The 10 mL of quartz distilled chloroform is added. Next step is the addition of 2 mL of a 1% APDC/DDDC solution previously precleaned by a four time extraction with chloroform. The solution is shaken for two minutes and the phases are left to separate for 5 minutes. The chloroform is collected in a 30 mL teflon vial. Another 5 mL chloroform is added to the sample and extracted as mentioned before. After phase separation the chloroform is collected in the same teflon vial.

The vials with the chloroform extract are placed on a corrosion protected hot plate in a laminary flow cabinet. In the cabinet, filtered air is led over the sample vials and the samples are dried overnight at a low temperature. Next morning 100 µL three times quartz distilled HNO_3 is added to the samples, to oxidize matrix components, and the solution is dried again. This procedure is repeated one time, and the sample is finally redissolved in 3 mL 1M HNO_3. In this way a concentration factor of 167 is obtained. For storage the samples are transfered into clean 4 mL high density polyethelene bottles.

Blanks are performed in the same way as the samples, by extraction of previously three times cleaned sea water samples. Extraction efficiency is checked by the method of standard addition.

The metals are determined by graphite furnace atomic absorption spectrometry and Zeeman background correction (Perkin Elmer Z 5100 PC). Calibrants have the same matrix as the samples. Again all precautions are taken to avoid contamination. Plastic gloves are used during the whole procedure and sample handling. The sample tray is prepared in a laminary flow bench using precleaned sample cups.

RESULTS AND DISCUSSION

Results of blanks obtained over a two year period are shown in Table 1. It is obvious from this Table that in this period the blanks became lower and reproducibility improved remarkably. This is mostly due to the fact that we now use a cleaner buffer solution and no back extraction, but evaporation of the chloroform extract. Also the change from

freon to chloroform can contribute to the improvement of the results. The blanks are now so low and constant, that they have no influence on the trace metal determinations. Compared to metal concentrations found in most sea water samples, these blank concentrations are negligible. This implies that small concentration gradients observed in a sampling program can be used to identify water masses, and processes which take place in the watercolumn can be studied. It also shows that contamination problems, especially extremely difficult in the determination of iron and lead, are now under control.

If contamination problems during sampling and treatment of the samples on board are also under control, then reliable trace metal data can be produced.

Table I Mean analytical blanks with standard deviation for iron, copper, nickel, cadmium, lead, zinc, silver and cobalt obtained in a one year period. Total number of analysis is 116.

Date	Replicate	Fe (nM)	Cu (pM)	Ni (pM)	Cd (pM)	Pb (pM)	Zn (pM)	Ag (pM)	Co (pM)
February 92	Mean	0.38	55	430	3	3	230	–	26
	S.D.	0.18	26	220	2	1	140	–	27
	n	9	9	17	22	19	15	–	16
	D.L. (3xS.D.)	0.54	78	630	6	3	420	–	81
June 92	Mean	0.28	190	300	2	10	70	–	36
	S.D.	0.08	150	100	1	7	20	–	16
	n	8	8	8	8	8	8	–	8
	D.L. (3xS.D.)	0.24	450	300	3	21	60	–	48
March 93	Mean	0.12	24	85	0.5	5	53	–	8
	S.D.	0.04	11	24	0.5	5	20	–	4
	n	6	6	8	6	6	6	–	6
	D.L. (3xS.D.)	0.12	33	72	1.5	15	60	–	12
May 93	Mean	0.22	19	45	0.5	3	20	5	–
	S.D.	0.06	7	44	0.4	2	6	4	–
	n	9	12	12	12	12	5	12	–
	D.L. (3xS.D.)	0.18	21	132	1.2	6	18	12	–
June 93	Mean	0.12	17	30	0.8	1.9	30	3.3	11
	S.D.	0.04	14	24	0.7	1.8	16	1.3	5
	n	24	26	13	28	15	7	7	6
	D.L. (3xS.D.)	0.12	42	72	2.1	5.4	48	3.9	15
July 93	Mean	0.18	13	20	0.5	–	40	1.5	–
	S.D.	0.06	7	20	0.3	–	3	3.6	–
	n	8	7	6	7	–	3	5	–
	D.L. (3xS.D.)	0.18	21	60	0.9	–	9	10.8	–
Oct. 93	Mean	0.09	29	39	0.9	–	–	–	–
	S.D.	0.06	25	10	0.5	–	–	–	–
	n	12	12	6	11	–	–	–	–
	D.L. (3xS.D.)	0.18	75	30	1.5	–	–	–	–
Nov. 93	Mean	0.16	–	–	–	–	–	–	–
	S.D.	0.04	–	–	–	–	–	–	–
	n	13	–	–	–	–	–	–	–
	D.L. (3xS.D.)	0.12	–	–	–	–	–	–	–
De. 93	Mean	0.11	35	–	–	–	–	–	–
	S.D.	0.03	18	–	–	–	–	–	–
	n	27	16	–	–	–	–	–	–
	D.L. (3xS.D.)	0.09	54	–	–	–	–	–	–

As examples some recent data and profiles, from the upper surface layer of NIOZ expeditions in the North Sea and the Antarctic Ocean are presented.

During the Bloom Expedition in the northern North Sea with the Dutch R. V. Pelagia (29–6/14–7–1993) water samples for trace metal analyses were collected in and outside a plankton bloom. Sampling was done in the way described above. At least 6 depths were sampled in the upper 70 m water layer. Samples were treated and processed as described above.
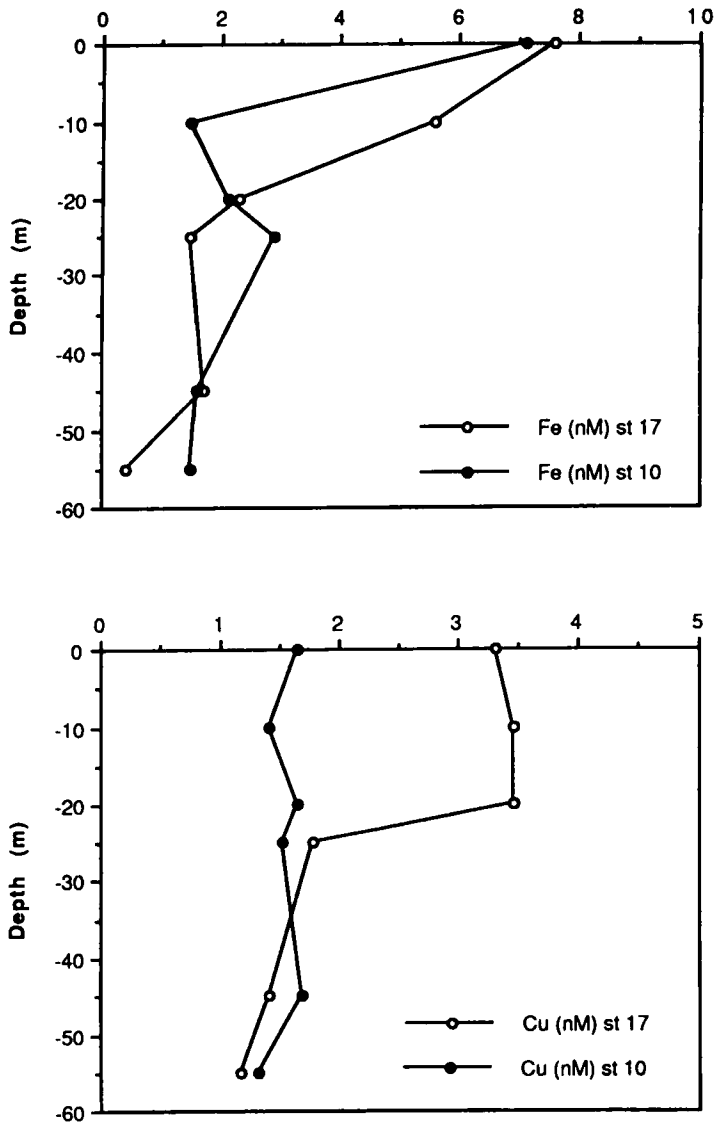
Figure 1   Concentration profiles of dissolved iron and copper at two stations in the northern North Sea. Position and explanation is given in the text.

Some iron profiles are described in Figure 1. One profile is from a station in the Atlantic part of the North Sea (61° 42.8′ N 1° 10.3′W) and the other in the Norwegian Trench (61° 00.4′ N 2° 59.3 E). At the Atlantic station the surface iron concentration was rather high, may be due to atmospheric input and the small oily film always present on the water surface. Below the surface the iron concentration was almost constant in the first 60 meters. The profile in the Norwegian Trench was different. At this station the water body was characterized by a low saline surface water layer of 20 meter, due to fresh water inputs, and below this layer by high saline Atlantic water. The shape of the iron profile could be explained by the results from the first profile. In the first 20 meter the influence of the fresh water input was reflected by high iron concentrations whereas below this layer the iron concentrations were dictated by the Atlantic waters. This was supported by the copper profiles observed at the same stations (Figure 1) which showed the same trend as for iron. All other elements showed the same picture but are not given here. This example illustrates that trace metal data can serve to discriminate between two different water bodies.

Another example is given by some profiles from an expedition with the German R. V. Polarstern in the Antarctic Ocean (29–9/29–11–1992) (Figure 2). For copper and iron three depth profiles are given from three different transects. For cadmium and nickel three depth profiles are given from two transects and for zinc two depth profiles from one transect. This selection is done because at this moment not all elements are analysed. Cadmium and nickel (Figure 2) showed the same pattern, a change in concentration when different water masses are sampled. Cadmium and nickel concentrations decreased in western and northern direction. This change in concentration can be used to identify different water masses. If we look at the positions of the stations, it shows indeed that station 901 is situated in the Polar Front Zone and stations 865 and 887 in the Antarctic Circumpolar Current, thus representing different water sources. The three profiles of copper and iron (Figure 2) do not show these strong concentration gradients, which can be explained by the fact that these stations are situated at the same latitude and the concentrations are more or less dictated by local processes like algal blooms. It is clear, however, that small concentration gradients are detectable and biological processes in which trace metals are involved can be studied. An example, for the reliability of the data is given by the zinc profiles (Figure 2). Samples collected in the same water mass (Polar Front Zone), but at different days, showed almost identical profiles with the same concentration range, which indicates that sampling and processing of the samples were not influenced by contamination problems.

CONCLUSIONS

It is shown that with the extreme precautions taken to avoid contamination during sampling and analysing sea water samples, reliable and accurate trace metal data can be obtained. Consequently, sources of water masses can be detected and the interpretation and description of processes which take place in the water column can now be quantified. One has to keep in mind that the described method presents the results from many years of experience and is recommended if very accurate and precise trace metal data have to be obtained at the nano- and picomolar level.

A detailed description of the extraction procedure and cleaning processes can be obtained from the authors.
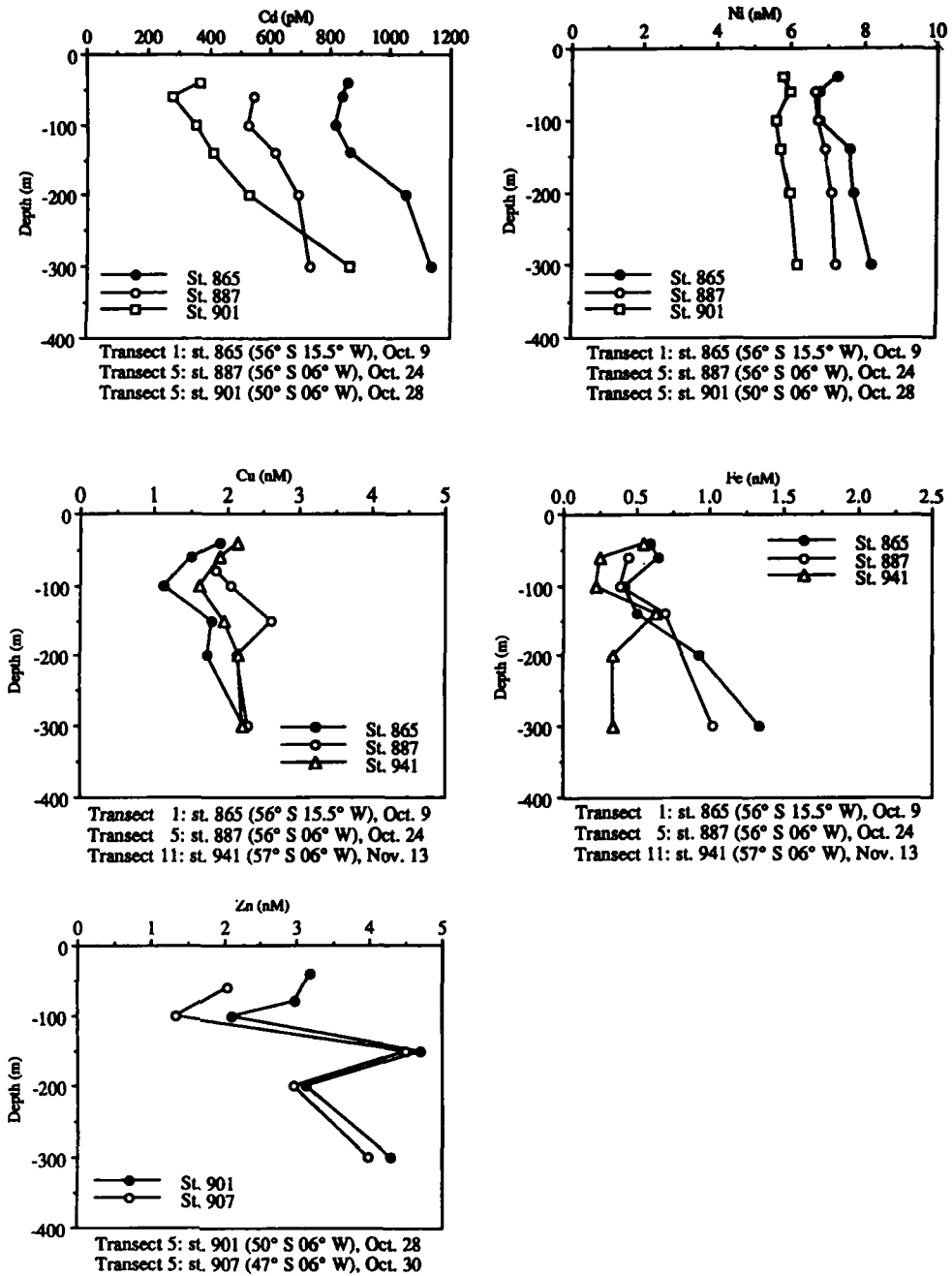
Figure 2 Concentration profiles of dissolved cadmium, nickel, copper, iron and zinc from some stations in the southern Atlantic Ocean.

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