

Manual for Marine Monitoring in the

COMBINE

Programme of HELCOM

Part B

General guidelines on **quality assurance** for monitoring in the Baltic Sea

Annex B-11

Technical note on the determination of heavy metals and persistent organic compounds in seawater

Appendix 1

Technical note on the determination of tracemetals (Cd, Pb, Cu, Co, Zn, Ni, Fe), including mercury, in seawater



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ANNEX B-11 TECHNICAL NOTE ON THE DETERMINATION OF HEAVY METALS AND PERSISTENT ORGANIC COMPOUNDS IN SEAWATER

ANNEX B-11, APPENDIX 1. TECHNICAL NOTE ON THE DETERMINATION OF TRACEMETALS (CD, PB, CU, CO, ZN, NI, FE), INCLUDING MERCURY, IN SEAWATER

Introduction	Error! Bookmark not defined.
1. Clean Laboratory; Clean Benches.....	Error! Bookmark not defined.
2. Preparations	Error! Bookmark not defined.
3. Sampling and Sample Handling	Error! Bookmark not defined.
4. Filtration Procedure	Error! Bookmark not defined.
5. Storage of Samples.....	Error! Bookmark not defined.
6. Sample Pretreatment.....	Error! Bookmark not defined.
7. Instrumentation	Error! Bookmark not defined.
8. Quality Control	Error! Bookmark not defined.
References.....	Error! Bookmark not defined.

INTRODUCTION

General techniques which address the questions of water sampling, storage, filtration procedures and determination of trace metals in natural sea water are described by Sturgeon and Berman (1987) and Gill and Fitzgerald (1985, 1987).

For the determination of mercury in sea water, the chemical species of this element are of importance. Therefore, a differentiation between the several Hg species, including ionic, volatile, dissolved (organic) complexes or particulate adsorbed Hg, has to be considered during sample preparation.

Several definitions of mercury compounds are common (Cossa et al., 1996, 1997), for example:

Reactive mercury (HgR): A methodologically defined fraction consisting mostly of inorganic Hg(II).

Total mercury (HgT): Mercury content of an unfiltered sample, after digestion with an oxidizing compound (e.g., K MnO₄).

Total dissolved mercury: Mercury content of a filtered sample, after digestion with an oxidizing compound (e.g., K MnO₄).

Dissolved gaseous mercury (DGM): This includes elemental mercury (Hg), monomethylmercury (MM-Hg) and dimethylmercury (DM-Hg).

1. CLEAN LABORATORY; CLEAN BENCHES

Particles are everywhere, including dust in the air or on clothes, hair or skin. Owing to the clothes, the person who is working with the samples for trace metal analysis is the main source of contamination because this person is a particle producer. One of the most important things during sample pretreatment for trace metal analysis is to eliminate particles that can contaminate the samples or the sample containers from the laboratory environment.

The best way to eliminate most of this contamination is to work under a laminar flow box with a laminar horizontal flow (sample protection). Recommended conditions for a 'clean bench' or a 'clean lab' are class 100 (US Norm) which means that there are still about one hundred particles present per cubic foot or class 3 (DIN-Norm), which equals 3000 particles per m³ (corresponding to class 100 US Norm).

2. PREPARATIONS

Chemicals

High purity water (e.g., 'Milli-Q water', 18 M cm⁻¹) freshly prepared, is termed 'water' in the following text.

A sub-boiling quartz still is recommended for the distillation of highly purified acids and solvents. A teflon still is recommended for the distillation of HF.

Amalgamation (filtration of oversaturated solutions with goldnet) and volatilization (bubbling with ultrapure argon) are effective methods to purify (clean) chemicals and solutions for mercury analysis.

In order to avoid contamination problems, all plastic ware, bottles and containers must be treated with acids (HCl or HNO₃) for several weeks and then rinsed with water and covered in plastic bags until use.

The following procedures (Patterson and Settle, 1976) are suggested:

Laboratory ware

Store in 2M HCl (high purity) for one week, rinse with water, store in water for one week and dry under dust-free conditions (clean bench).

Samplers and bottles

Sampling devices: Fill with 1% HNO₃ (high purity), store at room temperature for three weeks, and rinse with water .

Teflon/quartz bottles: Store in warm (40 C ±5 C) 1:1 diluted HCl for one week. Then rinse with water and store with 1M HNO₃ (high purity) until the final use (a minimum of three weeks).

Modified cleaning procedures are required for mercury. Glass containers (borosilicate, quartz) used for the collection and storage of samples for the determination of mercury are usually cleaned using an oxidizing procedure described by Sturgeon and Berman (1987). Bottles are filled with a solution of 0.1 % KMnO₄, 0.1% K₂S₂O₈ and 2.5 % HNO₃ and heated for 2 hours at 80 C. The bottles are then rinsed with water and stored with 2 % HNO₃ containing 0.01 % K₂Cr₂O₇ or KMnO₄ until ready for use.

Filters

Polycarbonate filters (e.g., Nuclepore) (0.4 m, 47 mm diameter) are recommended for trace metals except mercury. Store the filters in 2M HCl (high purity) for a minimum of three weeks. After rinsing with water, store for one more week in water.

For the determination of mercury, glass microfibre filters (GF/F grade, Millipore type) and teflon filters are recommended for the filtration of natural water samples. Cleaning of these filters is comparable to the procedure used for polycarbonate filters. For GF/F filters, an additional drying step has to be considered (450 C for 12-24 hr) to volatilize gaseous mercury. This procedure is described in detail by Queremais & Cossa (1997).

If trace metals in suspended particulate matter (SPM) are to be determined, filters have to be placed in precleaned plastic dishes, dried in a clean bench for two days, and stored in a desiccator until they are weighed using an electronic microbalance with antistatic properties. Each filter has to be weighed daily for several days until the weight is constant. The same procedure for drying and weighing should be applied to the filters loaded with SPM (Pohl, 1997).

3. SAMPLING AND SAMPLE HANDLING

The basis for the reliable measurement of extremely low concentrations of trace metals in sea water is a well-performed sampling to avoid contamination risk from the ship. Careful handling is recommended because copper and tin are still the main substances used in antifouling paints on ships and there is also a risk of contamination by zinc (anodes of the ship), iron or lead.

In coastal and continental shelf waters, samples are collected using 30 l teflon-coated GO-FLO (General Oceanics, close-open-close system) bottles with teflon O-rings deployed on Kevlar or on a Hostalen coated wire. Niskin bottles deployed on rosettes using standard stainless steel hydrowire are also acceptable. For surface waters, an all-teflon MERCOS-Sampler (Hydrobios) could be chosen.

PVC gloves should be worn during subsampling into the precleaned quartz or teflon bottles (teflon has an extra low content of trace metals). Subsampling should be carried out in a clean lab or a clean-lab container, if available.

Pumping of samples using peristaltic or teflon piston pumps must be carried out using precleaned silicon- or teflon-lined tubes.

In the absence of clean-lab conditions, sampling and sample handling must be carried out in a closed system, or contamination cannot be avoided.

For mercury analysis, it should be noted that the integrity during sampling and storage may be jeopardized by the addition of mercury to the sample as well as by unexpected losses owing to volatilization.

4. FILTRATION PROCEDURE

In the environmental and geochemical scientific community concerned with water analysis, it has generally been accepted that the term 'dissolved' refers to that fraction of water and its constituents which have passed through a 0.45 µm membrane filter. This is an operationally defined fraction. Coastal and shelf water samples have to be filtered to eliminate particles from the water. A number of metal species pass through this filter pore size, including metals bound to colloids or clays or to humic, fulvic, amino, and fatty acids.

To prevent desorption of metal ions from particle surfaces or from biological degradation of SPM, separation between the dissolved phase and the particulate phase has to be done immediately after sampling by filtering the water through a 0.45 µm polycarbonate filter. This procedure should be carried out under clean conditions (clean benches are recommended on board the ship).

If metals in both the dissolved and particulate phases are to be analysed, pressure filtration with nitrogen is recommended. After filtration the filter should be rinsed with high purity isotonic solution to remove sea salt residues. Only a few millilitres are necessary because a change of pH could cause desorption of metal ions from the particles. In pumping systems, on-line filtration is possible.

5. STORAGE OF SAMPLES

To avoid wall adsorption of metal ions, 1.5 ml HNO₃ or HCl (high purity) should be added per litre of seawater sample immediately after filtration for acidification to pH 1.0-1.6. The sample containers should be stored in plastic bags under controlled environmental conditions. The filters should be stored in plastic dishes at -18 °C or below. Under these conditions, both water samples and SPM on filters can be stored for at least one year.

Special consideration must be given to samples destined for Hg determinations. It is necessary to add either oxidants (Cr₂O₇²⁻) in addition to acidification or complexing agents (cysteine) to neutral or alkaline samples to prevent Hg losses during storage.

6. SAMPLE PRETREATMENT

Water samples

Depending on the expected concentration range (10⁻⁷-10⁻⁹ gkg⁻¹) of trace metals (dissolved) in Baltic Sea water and because of the salt matrix interfering during the measurement process, preconcentration

techniques and/or the elimination of sea salt has to be carried out prior to the analytical measurement. Detailed method information is available in the open literature (e.g., Danielsson et al., 1978; Kremling et al., 1983; and Pohl, 1994).

Filters

Different methods to analyse the material on the filter are described by Hovind and Skei (1992) and Loring and Rantala (1991). Pressure decomposition with an acid mixture (HCl, HNO₃, HF) is recommended. If the silica content is high due to diatoms, the HF concentration should be increased accordingly. If the organic content increases, it is advisable to work with perchloric acid.

Depending on the digestion system used (high pressure autoclave, microwave digestion, wet ashing in an open system, or dry ashing), the completeness of the digestion is a function of temperature, time, digestion material and pressure, and has to be tested and validated in pilot studies with (certified) reference materials (see the detailed remarks in Annex B-7, Section 4.3).

Digestion of samples for mercury analysis must always be carried out in a closed system to prevent losses by evaporation.

7. INSTRUMENTATION

For the analytical measurements, several analytical techniques can be used, such as GFAAS (graphite furnace atomic absorption spectrometry), electrochemical methods, ICP-MS (inductively coupled plasma-mass spectrometry), ICP-AES (inductively coupled plasma-atomic emission spectrometry), or total-reflection X-ray fluorescence (TXRF).

Because of the very low mercury concentrations in sea water, the most widely used technique for mercury is the cold vapour technique (reduction of mercury with SnCl₂ to elemental Hg) and preconcentration of mercury by amalgamation on a gold trap. This is followed by atomic absorption spectrometry or by atomic fluorescence spectrometry, with detection limits adequate for the purpose. In the case of anoxic (sulfur-containing waters), see Annex B-11.

8. QUALITY CONTROL

The internal quality control is described in Chapter B.5 of the Manual.

Blank

Particularly in the case of trace metal analysis, with high contamination risks at each step of the analytical work, a satisfactory blank control is necessary. Therefore, it is important to control the blank daily, for reproducibility and constancy over a longer time. The blank should include all analytical pretreatment procedures, including the addition of the same quantities of chemical substances as for the sample.

Calibration

For calibration purposes, single element standard stock solutions at a concentration of 1000 mg dm⁻³, purchased from a qualified manufacturer, should be available. Preparation date and concentration should be marked on the bottle. From this stock solution, a multi-element working standard solution can be prepared using dilute HCl or HNO₃ as required (normally 1M acid is used).

Traceability can be ensured by the use of CRMs or participation in intercomparison exercises.

The working standard should be prepared from the stock standard solution for every batch of samples and kept no longer than two weeks. Precleaned teflon containers are preferable for storage.

To evaluate effects from the matrix, the method of standard addition can be used, particularly in connection with the analytical method of voltammetric stripping. For other techniques, the method of standard addition should generally be used with care (Cardone, 1986a, 1986b).

Reference materials

Owing to problems in defining the blank, the use of a low-concentration CRM is important. Regular participation in intercomparison exercises should be considered mandatory.

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