Manual for Marine Monitoring in the

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Programme of HELCOM

Part B

General guidelines on quality assurance for monitoring in the Baltic Sea

Annex B-17

Technical note on the determination of organic carbon in seawater

ANNEX B-17 TECHNICAL NOTE ON THE DETERMINATION OF ORGANIC CARBON IN SEAWATER

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PARTICULATE MATTER

The particle size of the organically bound carbon of particles (POC) generally ranges between 0.45 µm and 300 µm. This includes both living organisms, such as phytoplankton, yeasts, bacteria, and microzooplankton, and detrital particles and aggregates. The production and decomposition of biogenic particles as well as their fractional removal to the deep sea control the distribution of most trace elements in the oceans. Microbial decomposition, desorption, and dissolution of suspended or sinking marine particles can release elements associated with labile (e.g., organic) fractions back to the sea water. On the other hand, particles can scavenge trace elements from the dissolved phase and thereby transport them to sediments. Analysis of the composition and distribution of the particulate fractions in the oceans is therefore required to understand the behaviour and geochemical cycling of, e.g., trace elements.

DISSOLVED MATTER

Among the different carbon reservoirs, dissolved organic matter (DOM) has the greatest mass, representing about 1000 ´ 10^{15} g of carbon, and not least because of its importance for the global climate there is a need to obtain accurate and comparable data on dissolved organic carbon (DOC) concentrations. Methods for the determination of DOC developed at a rather slow pace due to difficulties related to the composition of sea water. While DOC concentrations are around 1 mg dm^{-3}, sea water usually contains more than 35 g dm^{-3} of salts and more than 25 mg dm^{-3} of inorganic carbon as CO_2, HCO_3^-, and CO_3^{2-}.

1. SAMPLE HANDLING

The sample should be handled and transferred between containers as little as possible to avoid contamination during the steps between sampling and analysis.

It is important to obtain a representative sample, which during certain circumstances, e.g., during heavy algal blooms, can be achieved by shaking the water sampler immediately before taking the sub-sample. The homogeneity of the sample may be verified, for example, by separately analysing sub-samples from the upper and lower layers of the bottle.

For POC determinations, suspended particles are collected on filters. Since organic carbon is to be measured, filters must be made of inorganic material, e.g., glass fibre or metal foil (precombusted for 4 hours at 450 °C). Whatman GF/F glass fibre filters are recommended.

The determination of DOC implies that the samples are filtered. The limit between dissolved and particulate organic carbon is determined by the filter porosity (generally 0.45 µm).

If the water samples are not filtered, the organic carbon content analysed would represent TOC, i.e., the sum of organically bound carbon present in water, bonded to dissolved or suspended matter.

2. STORAGE OF SAMPLES

Filters containing particulate matter collected for POC analysis should be dried under vacuum for at least one day and stored dry in a desiccator with silica gel or, alternatively, temporarily stored in a freezer and later dried in a drying oven at 60 °C for 30 min.

A major potential problem for DOC analysis of samples of sea water is contamination. A particular problem for DOC samples is contamination by volatile water-soluble compounds such as ketones and alcohols. Exposure of the sample to the laboratory atmosphere should be limited and this type of work should have dedicated areas away from potential contamination sources.

The water sample should be stored in a refrigerator (2–5 °C), and analysed within one week. If a longer storage time is needed, the water sample could be stored frozen (–15 °C to –20 °C) for several weeks. One way to prevent contamination during storage is to store the water samples in sealed glass ampoules.

3. SAMPLE PRETREATMENT

If only DOC is to be determined, the sample should be filtered through a suitable filter, with a nominal pore size of 0.45 µm.

4. APPROPRIATE CHEMICAL ANALYTICAL METHODS

For POC analysis, a variety of similar instruments currently appear on the market. In particular, Carlo Erba and Hewlett-Packard CHN analysers have been frequently used. The main components of the analysers are basically the same, with an autosampler, a combustion column reactor, a reduction column, a gas chromatographic separation system, the detector unit, and an output device for the analytical results. Helium is used as the carrier gas. In the combustion reactor, oxygen gas and other oxidizing and catalysing reagents support the completeness of high- temperature combustion of organic carbon and nitrogen compounds to carbon dioxide, elemental nitrogen, and N-oxides. Elemental copper in the reduction column reduces nitrogen oxides to N_2 and binds excess oxygen. Water and the combustion products CO_2 and N_2 are separated by gas chromatography, and N_2 and CO_2 are detected and quantified by thermal conductivity detectors (TCD).

The analytical strategy for determinations of DOC in sea water typically comprises three stages: (1) initial removal of inorganic carbon species, (2) oxidation of the organic material into carbon dioxide, and (3) quantification of the carbon dioxide produced. The most difficult and controversial step in DOC determinations has been the oxidation. The oxidation method has to quantitatively transform the carbon bound in very complex mixtures of organic molecules into carbon dioxide, without formation of artefacts. Organic carbon is oxidized to carbon dioxide by combustion, by the addition of an appropriate oxidant, by UV radiation or any other high-energy radiation.

5. CALIBRATION AND THE BLANK

Analysis of POC is most often carried out together with analysis of PON (particulate organic nitrogen). For POC and PON determinations, the instrument is calibrated with high purity acetanilide (analytical-reagent grade). Acetanilide is used because its elemental composition matches the elemental composition of particulate material obtained from sea water, i.e., C:N = 8. At least ten filters should be analysed to determine the procedural blanks and the standard deviations from the mean values. These filters are treated in the same way as the sample filters, but the same water which is used for rinsing the sample filters (filtered sea water or artificial sea water) is filtered through the blank filters.

The DOC and TOC determinations are calibrated by analysing potassium hydrogen phthalate standard solutions of adequate concentrations. As a control of the DOC filtration, the carbon content of the filtrate after washing blank filters with dilution water should be determined and taken into account. The TOC of the water used for dilution and for preparation of the calibration standards should be sufficiently low to be negligible in comparison with the lowest TOC concentration to be determined.

6. INTERNAL QUALITY ASSURANCE AND CONTROL

The internal quality control should be carried out to check the operational performance of the system, by regularly analysing control samples and duplicate samples. If acetanilide is used as a control sample for POC and PON, it should be from another batch and preferably bought from another company than the calibration standard. For DOC and TOC analysis, copper phthalocyanine is suitable as a control sample solution. The control samples should be analysed with each series of samples and duplicate samples should be analysed regularly. These results should be plotted on control charts in order to verify the accuracy of the results, and estimate the measurement uncertainty.

REFERENCES

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