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-13

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

Appendix 3

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PART B GENERAL GUIDELINES ON QUALITY ASSURANCE FOR MONITORING IN THE BALTIC SEA

ANNEX B-13 TECHNICAL NOTE ON THE DETERMINATION OF HEAVY METALS AND PERSISTENT ORGANIC COMPOUNDS IN MARINE SEDIMENTS

ANNEX B-13 APPENDIX 3. : TECHNICAL NOTE ON THE DETERMINATION OF HEAVY METALS AND PERSISTENT ORGANIC COMPOUNDS IN MARINE SEDIMENT

1. SAMPLING AND SAMPLE HANDLING

The major criterion for successful sediment sampling is to guarantee a fairly undisturbed sample stratification. Of particular interest is the undamaged surface of the sample. Reasonable results are obtained by the application of box corer devices or a multiple corer.

Trend monitoring in sediments requires information about the current trace substance burden in the uppermost sediment layer (e.g., 2 cm). This first centimetres accumulate the deposits of the recent few years and thus are the object of the routine sediment analysis. Only if long-term time series (decades/centuries) of the trace substance burden of the deposit (or background concentration studies) are part of the investigations, is the analysis of deeper sediment layers required.

Immediately after sampling, the first 2 cm of the core is removed and stored. If the entire core is the object of the investigation, it is recommended to dissect the first 10 cm into five 2 cm layers. The deeper part should only be analysed in distinct sections, which cover the ranges: 15–17 cm, 22–24 cm, and 29–31 cm (Perttilä and Brügmann, 1992). Pieces of glass or colourless polyethylene tools are recommended for the sectioning of the core. After each layer has been cut off, the tools should be changed and cleaned. The selected sediment layers (samples) should be placed in separate and clean glass or polyethylene (polypropylene/polystyrene) containers carefully labelled and pre-weighted. The label should contain at least the sample identification number, and the date and location of sampling.

The following procedure is recommended for cleaning the tools and containers for sediment sample handling prior to the sampling campaign. Wash by soaking for 2–3 days in diluted (10%) HNO_3, then rinse with high purity water. During the sampling campaign, the reused tools, the table, and corer components should be carefully cleaned by rinsing with seawater.

The tools and containers must be stored dust-free when not in use. A comprehensive description of cleaning procedures for plastic and glass laboratoryware can be found in Annex B-12, Appendix 1 "Technical notes on the determination of trace metals (Cd, Pb, Cu, Co, Zn, Ni, Fe) including mercury in seawater" of these "Guidelines".

The samples should be deep frozen as soon as possible after packing. Take note that freezing of a large bulk of containers should be avoided; the samples in the centre would take longer to cool and this may result in some loss of mercury. Once frozen, the samples can be stored at temperatures of –20ºC or below.

2. SAMPLE PRETREATMENT; CONTAMINATION CONTROL

Because trace metals are mostly associated with the fine sediment fraction, it is often recommended that a defined grain size fraction of the sediment be considered (<63 µm; <20 µm). Therefore, the sediment samples have pass through a sieving procedure (Smedes et al., 2000; Loring, 1991; Limpenny and Rowlatt, 1994).

Sieving should preferably be carried out on wet sediment using water from the sampling location (Smedes et al., 2000).

Prior to the instrumental detection, sediment samples must be digested. The removal of water from the frozen samples is recommended, preferably by freeze-drying. The freeze-drying can be performed directly on the frozen sediments and without change of the container; the loss of mercury is also thus avoided. The freeze-dried sediments can be then stored almost indefinitely.

During freeze-drying, samples can (and should) be protected from cross-contamination (particles and vapours) by applying a lid with a small hole covered with filter-paper over the sample container.

After drying, the sediments should be carefully homogenized, e.g., using a ball mill.

For the complete digestion of marine sediments, a pressure wet ashing is recommended (Loring and Rantala, 1991; UNICAM, 1991). Since the rate of digestion and efficiency of acid decomposition increase substantially with elevated temperatures and pressure, the closed vessel techniques, using conventional heating or microwave energy, are applied preferably to open systems. The most widely applied technique for sediment mineralization is at present microwave digestion with concentrated acids, mostly nitric and hydrofluoric acids(Loring and Rantala, 1990; McCarthy and Ellis, 1991). Hydrofluoric acid is added to the sediment to remove silica (SiO_2). Al, Li, and Fe are commonly used for normalization of the results of analyses. The normalization procedure gives best results if Al values from partially digested samples are used. More information about the application of normalization procedures can be found in Annex B16 and Smedes et al. (2000).

Further requirements to avoid losses of the determinand or to solve contamination problems are described by, e.g., Boutron (1990) and Schmidt and Gerwinski (1994). The availability of high purity reagents is a prerequisite for reliable determination of heavy metal concentrations. And the first order of priority is a sufficient supply of high purity water. For contamination control, a procedural blank (recommended in triplicate) has to be carried out throughout all the operational steps parallel to the samples.

3. CALIBRATION

For calibration purposes, single standard stock solutions at a concentration of 1000 mg dm^{-3}, purchased from a qualified manufacturer, can be used. Fresh standard stock solutions should be compared with the older standard solutions. Single or mixed working element standard solutions are prepared by dilution of the stock solution using dilute acid, as required, though a mixed standard solution is more convenient in use. The concentrations of particular elements in a mixed standard stock solution can be matched in such a way as to produce a single series of working standard solutions for all elements analysed (with the exception of Al and Fe whose concentrations fall in a different range). All standard solutions have to be stored in polyethylene, borosilicate or quartz volumetric flasks. Standard solutions with lower concentrations, if prepared correctly and controlled in a QA system (checking of old versus new, and checking with standards from a different source), can be kept for a period no longer than one month.

It must be mentioned that plastic materials used for the production of laboratoryware exhibit certain adsorptive or exchange properties. Hence, boundary-surface interactions can be very important when very dilute analytical solutions are handled. It is thus imperative that volumetric flasks, reagent vessels, pipette tips, etc., for handling sample solutions and low level reference or analyte solutions must never be used for transferring or processing stock solutions of analyte or concentrated reagents.

The calibration procedure has to meet some basic criteria in order to give the best estimate of the true element concentration of the sample analysed:

- the concentrations of standards for the preparation of the calibration curve (function) should cover the range of concentrations as related to practical conditions; the mean of the range should be roughly equal to the expected analyte concentration in the sample;
- the required analytical precision should be known and achievable throughout the entire range of concentrations;
- the measured value (instrument signal) at the lower end of the range has to be significantly different from the procedural analytical blank;
- the chemical and physical properties of the calibration standards must closely resemble those of the sample under investigation, i.e., the difference in density between the standard and environmental sample should be minimized (this is of particular importance in flame atomic absorption determinations);

- as a general rule, the analysis of each batch of environmental samples should be accompanied by analysis of a certified reference material (CRM) or at least a laboratory reference material (LRM).

4. INSTRUMENTAL DETERMINATION

Heavy metals appear in marine sediments in low concentrations, ranging from mg kg−1 to µg kg−1 (Szefer, 2002). Stoeppler (1991) provided a comprehensive review of the most frequently used techniques for quantitative analysis of metallic trace elements.

Instrumental determination of heavy metals in the acidic solution obtained is carried out depending on the instrument and manufacturer’s specifications. In most cases, i.e., in most marine sediments, Cd and Pb can be determined by GFAAS (Graphite Furnace Atomic Absorption), while Cu, Zn, Cr, Ni, Mn, Al, and Fe can also be determined by the less sensitive flame atomization.

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