



Guideline for the determination of heavy metals in sediment

1. Introduction

This Technical note provides advice on the analysis of heavy metals in total marine and coastal sediments and sieved fractions, including sampling and sample handling. The analysis of heavy metals in sediments basically includes digestion and detection by Graphite Furnace Atomic Absorption (GFAAS), flame atomization, ICP-ES or ICP-MS.

All steps of the procedure are susceptible to insufficient recovery and contamination. Quality control measures are recommended in order to regularly monitor the performance of the method. These guidelines are intended to encourage and assist analytical chemists to critically review their methods and to improve their procedures and quality assurance measures, if necessary.

These guidelines are not intended as complete laboratory manual. If necessary, guidance should be sought from specialized laboratories. Laboratories should demonstrate validity of each methodological step. Moreover, use of an alternative method, carried out concurrently to the routine procedure, is recommended for validation. The analyses should be carried out by experienced staff.

Contracting parties should follow the HELCOM monitoring guideline but minor deviations from this are acceptable if the method achieves comparable results. Validation of the adopted method needs to be performed on the relevant matrix and concentration range e.g. by taking part in intercomparison studies or proficiency testing schemes.

2. 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., 0-1 cm). This first centimeter accumulates the deposits of the recent few years and thus is the object of the routine sediment analysis. In practice, apart from this kind of specialised environment where bioturbation and physical disturbance of sediment are negligible and undisturbed surface sediments can be sampled, it is recommended to sample the top layer of the sediment, from 1 to 5 cm depth, depending on the deposition rate (EU, 2010)

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, the analysis of deeper sediment layers is required.

Immediately after sampling, the first 0-1 cm of the core is removed and stored. If the water content is very high it is usually required to get replicates of the sample in order to obtain enough dry weight material for an analyses of a large number of metals. 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 Brüggmann, 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 or nylon bags 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%) HNO₃, 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 laboratory ware 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. At least immediate cooling in a fridge after sampling is recommended. 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 –20°C or below.

3. Sample pretreatment; contamination control

Because trace metals are mostly associated with the fine sediment fraction, it is recommended to focus sampling on muddy sediments, consisting of a predominantly fine grain fraction of less than 63 µm. In case of uncertain grain composition of the sample or sandy sediments, it is recommended to pass the samples through a sieving procedure (OSPAR 2015), to separate a well defined <63µm fraction for further analysis. Be aware that sieving sampled sediments come with a risk of contamination due to the extra working step before analyzing the sample. A quantification of the fine grain fraction (<63µm) of the sediment sample by sieving or measurement with a particle laser provides valuable information to determine the sediment type. Furthermore, this information could be used as a normalization parameter.

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, it needs to be secured that the sample is thoroughly homogenized before subsampling for metals analysis. To ensure proper homogenization the sediments could be carefully homogenized if needed, e.g., using a ball mill.

For the complete digestion of marine sediments, a pressure wet ashing is recommended (e.g. Loring and Rantala, 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. Open systems should be checked thoroughly for loss of Hg. The most widely applied technique for sediment mineralization is at present microwave digestion with concentrated acids. Dependent on the matrix optimized compositions of nitric, perchloric and hydrofluoric acid are widely applied. An omission of hydrofluoric acid results in a partial digestion, which leaves the crystalline (SiO₂) matrix of the sediment sample untouched. A full digestion method, which is based on the application of a mixture of nitric and hydrofluoric acid, is described in Loring and Rantala (1990) or McCarthy and Ellis (1991). Al, Li, Fe and TOC are commonly used for normalization of the results of analyses. More information about the application of normalization procedures can be found in Annex B16, OSPAR (2015) 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.

4. Calibration

For calibration purposes, single standard stock solutions, purchased from a qualified manufacturer or a multielement standard, can be used. Fresh standard stock solutions should be compared with the older standard solutions. Single or multielement standard solutions are prepared by dilution of the stock solution using dilute acid, as required. 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).

5. Instrumental determination

Heavy metals appear in marine sediments in low concentrations, ranging from $\mu\text{g kg}^{-1}$ to mg 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.

Multielement methods with plasma atomization have become the standard for analysis of metals in later years (Larsen et al, 2011), as ICP-OES and ICP-MS have the ability to determine all elements in one go.

ICP-OES is very robust and generally sensitive enough to cover the metal concentrations expected in sediments, perhaps except Cd, over a large concentration range. As the method is based on emission spectra for ionized metals, possible spectral overlap needs to be corrected, and it is recommended to measure at more than one wavelength if sensitivity allows for it. Both radial and axial view ICP-OES are now available, and have extended the linear range of the calibration to avoid dilution. Detection limits are usually between those of flame and graphite furnace AAS, but new developments are pushing the detection limits closer to the GFAAS limits.

ICP-MS is currently state-of-the-art instrumentation for metal analysis, with the possibility to determine almost the entire periodic table at sub ng/l concentrations. Most routine instruments utilize a quadrupole mass spectrometer, so mass resolution is not high enough to avoid overlap of double charged elements or multi-element ions (mainly hydrides, oxides and hydroxides) formed in the plasma. The main concern is for the Ar interferences as the plasma is usually an argon plasma, overlapping with $^{75}\text{As}^+$ as $^{37}\text{Cl}^{40}\text{Ar}^+$, and of the Se masses. For As no alternative mass is available but for most other elements, measurement of two or more isotopes can be used for quantification. It is recommended to use a cell with a small gas flow (collision cell or dynamic reaction cell) of H_2 , He, NH_3 or CH_4 to remove the polyatomic interference by collision or reaction with the gas in the cell, in combination with mass overlap correction formulas (e.g. de Boer (2000), USEPA 6020 or ISO 17294-2). To correct for changes in the nebulizer and cone system used to transport the ion beam from atmospheric pressure to vacuum in the MS detector, it is recommended to use internal standards of e.g. Ir, Rh, Ge or In. Some elements are prone to memory effects (particularly Hg) and needs extra precautions to avoid carry over effects (e.g. addition of HCl or Au to digest or rinse solution). For both ICP-OES and ICP-MS, modern instruments software includes all the tuning and correction formulas needed and described above to perform the analysis.

High resolution ICP-MS can be used to avoid mass overlap corrections, but instruments are more expensive and often difficult to tune and maintain for routine laboratories.

6. Quality Assurance

A number of measures should be taken to ensure sufficient quality of the analysis. Six main areas can be identified:

digestion efficiency;

calibrant and calibration;

system performance;

long-term stability;

internal standards; and

frequent participation in interlaboratory proficiency testing schemes (e.g. QUASIMEME two times a year, www.quasimeme.org).

7. References

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