

Quality assurance aspects



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About...

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- Quality in sampling and handling of samples
- Analysis and quality



Sampling - standards

Matrix	Standards
Surface water	<ul style="list-style-type: none">•ISO 5667-1:2006 Water quality -- Sampling -- Part 1: Guidance on the design of sampling programmes and sampling techniques•ISO 5667-2:2001 Water quality. Sampling. Part 2: Guidance on sampling•ISO 5667-3:2003 Water quality -- Sampling -- Part 3: Guidance on the preservation and handling of water samples•ISO 5667-4:1987 Water quality -- Sampling -- Part 4: Guidance on sampling from lakes, natural and man-made•ISO 5667-6:2005 Water quality -- Sampling -- Part 6: Guidance on sampling of rivers and streams



Sampling - standards

Matrix	Standards
Bottom sediments	<ul style="list-style-type: none">•ISO 5667-12:1995 Water quality -- Sampling -- Part 12: Guidance on sampling of bottom sediments•ISO 5667-15:1999 Water quality -- Sampling -- Part 15: Guidance on preservation and handling of sludge and sediment samples•ISO 5667-19:2004 Water quality -- Sampling -- Part 19: Guidance on sampling of marine sediments



Sampling - standards

Matrix	Standards
Waste water	<ul style="list-style-type: none">•ISO 5667-1:2006 Water quality -- Sampling -- Part 1: Guidance on the design of sampling programmes and sampling techniques•ISO 5667-2:2001 Water quality. Sampling. Part 2: Guidance on sampling•ISO 5667-3:2003 Water quality -- Sampling -- Part 3: Guidance on the preservation and handling of water samples•ISO 5667-10:1992 Water quality. Guidance on sampling of wastewater samples



Sampling - standards

Matrix	Standards
Sludge	<ul style="list-style-type: none">•ISO 5667-1:2006 Water quality -- Sampling -- Part 1: Guidance on the design of sampling programmes and sampling techniques•ISO 5667-13:2000 Water quality -- Sampling -- Part 13: Guidance on sampling of sludge from sewage and water treatment works•ISO 5667-15:1999 Water quality -- Sampling -- Part 15: Guidance on preservation and handling of sludge and sediment samples

If not possible to follow listed standards, make your Standard Activity Procedure!



Preferably samples to be taken by the same institution/person, if not possible, ensure they follow the same procedure!

Do not forget duplicates!



Sampling – other guidelines

- The guidelines of the OSPAR Convention for the Joint Assessment and Monitoring Programme (JAMP) www.ospar.org
 - detailed advice on sample preparation, analytical methods etc for some contaminants in sediment
 - metals, chlorobiphenyls, PAHs, mono-, di- and tributyltin, PBDEs, HBCD
- HELCOM COMBINE manual for marine monitoring http://www.helcom.fi/groups/monas/CombineManual/en_GB/main/



Sampling – some remarks

Advise: use monitoring points

Example:

- Sediments:
 - Deposition areas
 - Erosion sites to be avoided
 - Coastal waters – no strong currents, sedimentation areas
 - Rivers (estuaries) where flow is lower (not in the middle of river)



Handling of samples - dishes

- Discuss with chosen laboratory
- Make list of the HS to be analysed for each site and check with laboratory first on volumes of sample required and type of the bottle → save costs for dishes and transportation costs
- Take precautionary measures:
 - plastic materials except polytetrafluoroethylene (PTFE) must not be used for the samples to be analysed for hydrophobic organic contaminants (e.g., PCBs, PAHs)
 - samples for organic contaminants must be stored in glass, PTFE or stainless steel containers
 - metals → can be stored in closed plastic or glass containers
 - mercury → in acid-washed borosilicate glass or quartz containers as mercury can move through the walls of plastic containers
 - organotins → preferably stored in glass containers
 - phthalates – no plastic cover or isolated with folia



Handling of samples – transportation and storage

- Check with chosen laboratory
- General requirements – mobile freezing box and fridge of $\sim 4^{\circ}\text{C}$
- Ask laboratory if any pre-treatment of sample is needed before sending to them



Keep in mind upcoming directive requirements...

- Draft “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status”
 - all methods of analysis, including laboratory, field and on-line methods, used for the purposes of chemical monitoring programmes carried out under Directive 2000/60/EC are validated and documented in accordance with EN ISO/IEC-17025 standard or other equivalent standards accepted at international level
 - standard analytical methods adopted by ISO or CEN are recommended



Keep in mind upcoming directive requirements...

Minimum performance criteria for methods of analysis

- based on
 - **uncertainty of measurement of 50% or below** ($k = 2$) estimated at the level of relevant environmental quality standards
 - **limit of quantification** equal or below a value of 30% of the relevant environmental quality standards.
- in the absence of EQS or method of analysis meeting the minimum performance criteria → use best available techniques not entailing excessive costs



Keep in mind upcoming directive requirements...

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Quality assurance and control

- laboratories or parties contracted by laboratories apply quality management system practices in accordance with EN ISO/IEC-17025 or other equivalent standards accepted at international level



To remember...

- Accredited
- CEN/ISO
- Ask for method description and check LOD (limit of detection) and MU (measurement uncertainty)
- Check if random double checks, blank samples or reference material checks are included in the offer to ensure the quality of the results → no further costs for quality assurance measures



Groups of substances

Priority Substance	Recommended Components	Comments
Chlorpyrifos	Chlorpyrifos ethyl	
Endosulfan	α -Endosulfan and β -Endosulfan	Total concentration to be reported.
Pentabromodiphenyl Ether	BDE congener numbers 28, 47, 99, 100, 153, 154	These congeners constitute approximately 85 % of technical Penta – BDE formulations; Total concentration to be reported.
Hexachlorocyclohexane	α , β , γ , and δ -isomer*	Total concentration to be reported.
C10-13 Chloroalkanes	All C ₁₀ to C ₁₃ chlorinated paraffins (49 % to 70 % Chlorine)	Total of all isomers to be reported. Measurement will usually be done against a technical mixture.
Nonylphenol	All 4-nonylphenol isomers present**	Total concentration of all para isomers to be reported.
Octylphenol	para-tert-Octylphenol***	Total concentration to be reported. Benzo[j]fluoranthene interferes with the determination of either Benzo [b]fluoranthene or Benzo[k]fluoranthene
PAH	Benzo[b]fluoranthene/ Benzo[k]fluoranthene	
Trichlorobenzenes (all isomers)	1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene	Total concentration to be reported.
DDT total	<i>p,p'</i> -DDT, <i>o,p'</i> -DDT, <i>p,p'</i> -DDE, <i>p,p'</i> -DDD	Total concentration and concentration of <i>p,p'</i> -DDT to be reported.

* The CAS number 608-73-1 refers to technical HCH, hence, all relevant isomers have to be analysed for

** Technical nonylphenol consists mainly (~ 90 %) of para-substituted nonylphenols and comprises theoretically 211 isomers; only 4-nonylphenols are of toxicological relevance

*** Octylphenol (CAS No 140-66-9) is a single isomeric compound: 4-(1,1',3,3'-tetramethylbutyl)-phenol (4-tert-octylphenol)



Good info

- **Guidance on surface water chemical monitoring under WFD, guidance document No. 19 (CIRCA website)**
- **Substance Guidance Sheets** - to assist in selecting appropriate methods
 - physico-chemical properties of each substance and preliminary EQS expressed as AA-EQS or MAC-EQS for inland and other surface waters
 - available EN or ISO standard methods for the analysis in water, and where appropriate, in sediment or biota
 - information on sampling, storage and pre-treatment
 - other analytical methods