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Determination of priority pollutants in surface water using passive sampling

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Contents

Summary of pages

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Foreword

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Introduction

Priority pollutants have been defined by the EU and are listed in Council Decision 2455/2001/EC [1]. They include:

organohalogen compounds and substances that may form such compounds in the aquatic environment;

organophosphorus compounds;

organotin compounds;

substances and preparations, or the breakdown products of such, which have been proved to possess carcinogenic or mutagenic properties or properties which may affect steroidogenic, thyroid, reproduction or other endocrine-related functions in or via the aquatic environment;

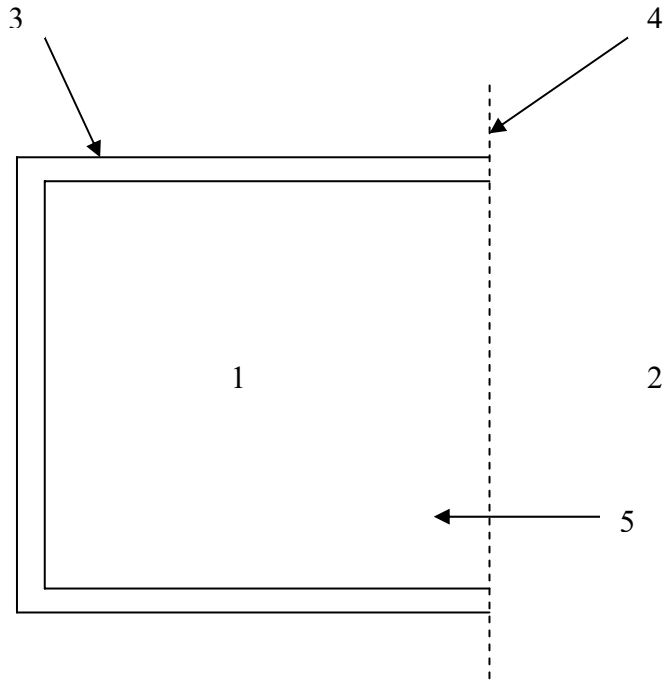
- persistent and bioaccumable and toxic (PBT) and very Persistent and very Bioaccumulating substances (vPvB);
- cyanides;
- metals and their compounds;
- arsenic and its compounds;
- biocides and plant protection products;
- materials in suspension;
- substances that contribute to eutrophication (in particular, nitrates and phosphates);
- substances that have an unfavourable influence on the oxygen balance (and can be measured using parameters such as BOD (biochemical oxygen demand), COD (chemical oxygen demand), etc.

Pollutant levels in surface water have traditionally been monitored by spot sampling (also known as bottle or grab sampling). Such sampling gives a snapshot of pollutant levels at a particular time. But pollutant levels in surface water have a tendency to fluctuate and so it is desirable to monitor pollutant levels over time. This may be achieved by repeated spot sampling, continuous monitoring, biomonitoring or passive sampling.

Passive sampling involves the deployment of a calibrated device that uses a diffusion gradient to collect pollutants over a period of days to weeks, followed by extraction and analysis of the pollutants in a laboratory. This provides a measure of time-weighted average concentrations of pollutants to which the sampling device was exposed.

Passive sampling devices used in surface water typically consist of a receiving phase (typically a solvent or sorbent) that acts as a sink for compounds of interest, which may be held behind or surrounded by a membrane through which the target substances can permeate. A schematic representation of such a sampling device is shown in Figure 1. In its simplest form a passive sampling device is comprised solely of a membrane, or fibre, or bulk sorbent which acts as a receiving phase.

Figure 1 **Schematic representation of a passive sampling device**



Key

1 Receiving phase

2 Water

3 Housing

4 Membrane

5 Pollutants

NOTE In some sampling device designs, the housing is replaced by a membrane that completely encloses the receiving phase. For more information on individual types of passive sampling devices, refer to the Bibliography.

1 Scope

This PAS describes a method for the determination of time-weighted average concentrations of priority pollutants in surface water by passive sampling, followed by analysis.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

BS 6068-1.2, ISO 6107-2, *Water quality – Glossary – Part 2: Additional terms relating to types of water, and treatment and storage of water and waste water, and terms used in sampling and analysis of water*

BS 6068-6.4, ISO 5667-4, *Water quality – Sampling – Part 4: Guidance on sampling from lakes, natural and man made*

BS 6068-6.14, ISO 5667-14, *Water quality – Sampling – Part 14: Guidance on quality assurance of environmental water-sampling and handling*

BS EN 25667-1, BS 6068-6.1, ISO 5667-1, *Water quality – Sampling – Part 1: Guidance on the design of sampling programmes*

BS EN ISO 5667-3:2003, BS 6068-6.3:2003, *Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples*

BS ISO 5667-6, *Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams*

3 Terms and definitions

For the purposes of this PAS, the terms and definitions given in BS 6068-1.2 (ISO 6107-2) and the following apply.

3.1 analytical recovery standard
compound added to sampling device receiving phase prior to analysis and whose recovery levels during analysis are used to provide information about recovery efficiency

3.2 fabrication control
quality control sampling device to record contamination from the manufacturing process, sampling device components, laboratory storage, processing and analytical procedures

3.3 field control
quality control sampling device to record any chemical accumulated in sampling devices during transportation, deployment and retrieval

3.4 passive sampling
collection of chemical compounds without provision of energy from an external source

3.5 priority pollutant
substance which is a potential source of water pollution

NOTE A list of priority pollutants is given in the EU Water Framework Directive [2].

3.6 performance reference compound (PRC)
compound that has moderate to high fugacity from the sampling device, which does not interfere with the sampling and analytical processes and which is added to the device receiving phase prior to deployment

NOTE 1 The off-loading (elimination) rates of the PRCs are used to provide information about in situ uptake kinetics.

NOTE 2 Currently there are no PRCs available for metals sampling devices.

3.7 reagent control
retained aliquot of reagent used in preparation and analysis of sampling devices which is analysed with the samples in order to diagnose any contamination from the reagents used

3.8 recovery spike
quality control sampling device, pre-spiked with known mass of compounds of interest, used to determine the recovery levels of target compounds from processed sampling devices to establish control limits for the analytical process

3.9 sampling device class
class of target analytes which a sampling device is designed to accumulate

NOTE Sampling device classes include the following:
- *polar organic compounds;*
- *non-polar organic compounds; and*
- *inorganic compounds, including metals.*

3.10 shipping control (optional)
quality control sampling device to record any contamination or changes during transportation and storage of sampling devices on their way to and from the manufacturer to the user and from the user to the laboratory that performs the preparation of sampling devices for analysis

4 Principle

Target priority pollutants accumulate in the receiving phase of a passive sampling device over a defined time period of exposure to surface water. The pollutants are extracted from the sampling devices in the laboratory and the amount of each pollutant accumulated is determined by chemical analysis. Provided that mass transfer of the pollutant to the sampling device varies linearly with concentration, the time weighted average concentration of pollutants to which the sampling device was exposed over the deployment period can be calculated.

The process is illustrated in a flow chart in Figure 2 in Clause **8**.

5 Handling sampling devices

5.1 General

5.1.1 Ensure safety precautions are in place for handling all chemicals.

5.1.2 Because of the high sensitivity of the method, minimize physical contact with the receiving phase or membrane of the sampling devices. Where handling is necessary, use only new, powder free vinyl or latex gloves. Do not re-use gloves.

5.1.3 For some devices minimize exposure to airborne contaminants during manipulation in order to minimize vapour phase contamination.

NOTE The use of a clean room conforming to BS EN ISO 14644-1, or laminar flow hood is recommended when preparing some sampling devices.

5.1.4 Store sampling devices and extracts away from other chemicals, particularly those of a volatile nature.

5.1.5 Use new suitable pipette tips for the addition of reagents to extracts.

5.2 Organics sampling devices

5.2.1 Minimize contact of organics sampling devices with plastic materials.

5.2.2 Clean all equipment that comes into contact with sampling devices.

5.3 Metals sampling devices

5.3.1 Acid wash all equipment that comes in contact with the sample, other than the passive sampling devices, in accordance with BS EN ISO 5667-3:2003, **3.2.2.4**.

5.3.2 Use suprapure acid for addition to samples or for digestion.

6 Estimation of appropriate field deployment time

Prior to deployment, estimate the exposure time for the class of sampling device on the basis of pollutant uptake rate and capacity of the receiving phase for the analytes of interest.

*NOTE 1 The exposure time should not extend to the non-linear uptake phase (see also Clause **4**).*

NOTE 2 Where available, exposure time advised by the manufacturer should be used.

7 Sampling device preparation and assembly

7.1 Sampling device preparation

Where appropriate, prepare performance reference compounds solutions for each class of sampling device. Use these to spike the receiving phase of selected sampling devices prior to assembly, in the interests of quality assurance. Use fresh materials and state the use by date for the loaded passive sampling devices.

NOTE The receiving phase should be homogeneously spiked. In some cases, spiking can be carried out during manufacture.

7.2 Sampling device assembly

7.2.1 Assemble sampling devices in an environmentally controlled room equipped to remove atmospheric contaminants.

7.2.2 Label each sampling device in accordance with BS EN ISO 5667-3:2003, Clause **5**.

NOTE 1 Use of a clean room conforming to BS EN ISO 14644-1, or a laminar flow hood is recommended when preparing some sampling devices.

NOTE 2 The addition of a suitable label for each sampling device by the manufacturer will aid sampling device identification during deployment and recovery and after recovery.

7.3 Sampling device storage

Store prepared sampling devices in vapour-tight containers at controlled temperatures selected in accordance with manufacturer's instructions.

8 Quality assurance

8.1 General

Implement quality assurance measures throughout the fabrication, sampling and handling processes in accordance with BS 6068-6.14 (ISO 5667-14).

Compare results of analysis of sampling devices deployed together (as specified in **8.2**), and of sampling devices with sampling device controls (as specified in **8.3**), in order to calculate uncertainty of the sampling (see Clause **13**).

NOTE 1 Figure 2 illustrates how the quality assurance steps fit into the passive sampling process.

NOTE 2 Guidance for analytical quality control is given in DD ENV ISO 13530.

8.2 Replicate quality control sampling devices

Prepare multiple sampling devices (e.g. 3 to 5 per sampling site) for each sampling device class: polar organics, non-polar organics and inorganics including metals.

8.3 Sampling device controls

For each sampling device set (group of sampling devices deployed together), prepare sampling device controls in accordance with Table 1. The number and type of controls is determined by the end user and is dependent upon the required level of confidence.

NOTE For monitoring the concentration of chemicals near their limit of detection, more controls may be required.

Figure 2 **Quality control samples involved in passive sampling**

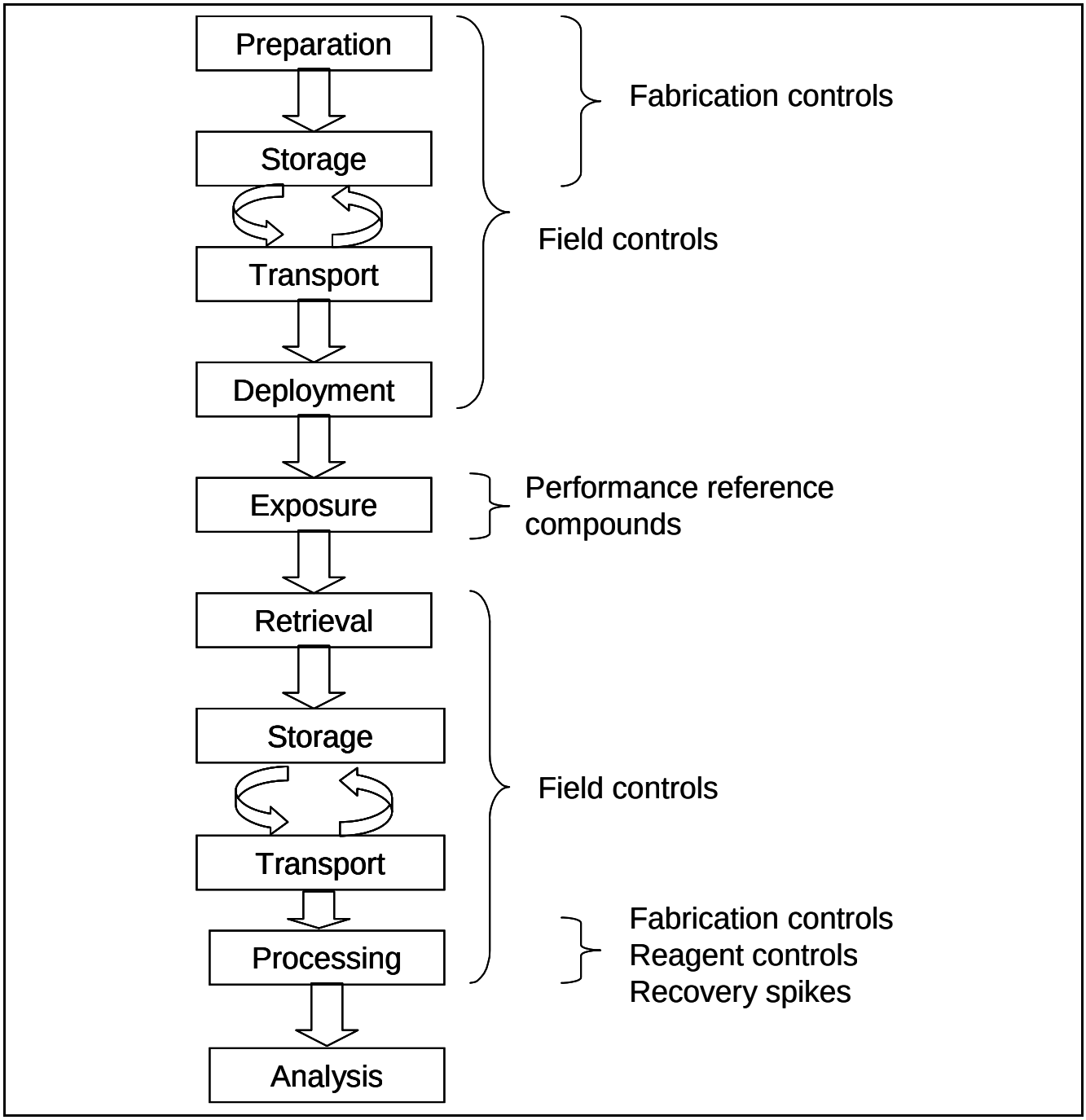


Table 1 **Sampling device control requirements**

Control type	**Number per sampling device set**	Treatment of controls
Fabrication control	At least 3 per sampling device class	Separate fabrication controls out from sampling devices manufactured and/or delivered together. Store fabrication controls in the laboratory at <5 °C [A)] in sealed containers during deployment of the sampling device set. Process and analyse fabrication controls concurrently with and identically to sampling devices of the same class in the sampling device set.
Field control	At least 1 per sampling site (2 per sampling site are recommended for quality control purposes)	Separate field controls out from sampling devices manufactured and/or delivered together. Transport field controls between the sampling site and laboratory with the sampling device set. Expose field controls to the air at the sampling site during deployment and retrieval of the sampling device set, but only during manipulation. Expose in the same way as the set of sampling devices up to/from the moment when the sampling starts/ends. Process and analyse field controls concurrently with and identically to the sampling device set.
Shipping control (optional)	At least 1 per sampling device class (2 per sampling site are recommended for quality control purposes)	Separate these controls out from sampling devices manufactured and/or delivered together. Transport shipping controls between laboratory and the sampling site with the sampling device set but do not expose them to air at the sampling site during deployment and retrieval of the sampling device set. Store shipping controls in the laboratory at <5 °C[A)] in sealed containers during deployment of the sampling device set. Process and analyse shipping controls concurrently with and identically to sampling devices of the same class in the sampling device set.
Reagent control	At last 1 per sampling device set of analysed sampling devices	Process and analyse reagent controls concurrently with and identically to sampling devices of the same class in the sampling device set.
Recovery spike	At least 3 per sampling device set of analysed sampling devices	Prior to processing of a sampling device, fortify control sampling devices of the same quality as fabrication controls with a target compound mixture. Process and analyse reagent controls concurrently with and identically to sampling devices of the same class in the sampling device set.

[A)] Precise storage temperature should be selected in accordance with manufacturer's instructions.

9 Selection of sampling site and safety precautions

9.1 Selection of sampling site

Select a sampling site in accordance with BS EN 25667-1 (ISO 5667-1) and either BS 6068-6.4 (ISO 5667-4) for lakes or BS ISO 5667-6 for rivers and streams.

Before deployment and prior to retrieval of sampling devices, carefully inspect sampling site for:

a) sources of vapour-phase contaminants, including engine fumes, oils, tars, gasoline, diesel fuel, paints, solvents, cigarette smoke and asphalt pavement, if organics sampling devices are to be used;

b) sources of metallic contamination, if metals sampling devices are to be used;

c) oily films or biofilms on the surface of the water;

d) adequate water depth to keep the sampling device submerged throughout deployment under all conditions;

and record any findings for the site.

NOTE 1 Some shallow streams or pools could become dry after a short period of time in dry weather conditions. In tidal waters, sampling devices should be deployed at a suitable distance beyond the spring tide low water mark.

NOTE 2 The reduction of atmospheric exposure time during deployment and retrieval is particularly important when vapour phase contaminants are present. At some sites, atmospheric levels of certain target compounds may be higher than concentrations in receiving waters and once the sampling device is exposed to site air, sampling begins.

NOTE 3 Where surface layers of chemicals are visible, precautions may be needed to reduce contamination during aqueous insertion of deployment devices.

9.2 General safety precautions

The enormously wide range of conditions encountered in sampling surface waters can subject sampling personnel to a variety of safety and health risks.

Personnel responsible for the supervision of passive water sampling operations should ensure that sampling personnel are informed of the necessary precautions to be taken during sampling operations. BS EN 25667-1 (ISO 5667-1) specifies certain safety precautions, including sampling from boats and from ice-covered waters. BS ISO 5667-6 specifies safety precautions to be considered when sampling from river banks.

NOTE 1 Attention is drawn to the requirements of health and safety regulations.

NOTE 2 Precautions against accidents might need to be taken.

10 Sampling device deployment and retrieval

10.1 Materials and apparatus

10.1.1 *Sampling devices*, labelled in accordance with BS EN 25667-1 (ISO 5667-1), and BS ISO 5667-6.

10.1.2 *Control devices*, as required.

10.1.3 *Cool box*, with freezer blocks.

10.1.4 *Gloves*, as defined in **5.1.2**.

10.1.5 *Gas-tight containers*, of inert materials, having low permeability to external contaminants and labelled with the sampling device identification.

10.1.6 *Camera.*

10.1.7 *Water quality assessment equipment*, such as thermometer, temperature logger, pH meter, flow rate meter, as necessary.

10.1.8 *Depth measuring device.*

10.1.9 *Deployment device*, to hold the sampling devices in the water.

10.1.10 *Anchorage device.*

10.1.11 *Ropes.*

10.1.12 *Buoy or floats.*

10.1.13 *Weights.*

10.2 Deployment procedure

10.2.1 Transport the labelled sampling devices (**10.1.1**), and required control devices (**10.1.2**) to the sampling site in sealed containers (**10.1.5**) [inside a cool box (**10.1.3**) where necessary].

10.2.2 Take a photograph of the sampling site (**10.1.6**). Record any water quality parameters significant to the study such as water temperature, pH, clarity, turbidity, estimated water flow rate in cm/s (**10.1.7**).

10.2.3 Put on gloves (**10.1.4**) and remove each sampling device from its container in accordance with manufacturer's instructions. Treat field control devices in exactly the same way as the field deployed devices, but do not deploy them. Where shipping controls are used, do not open their containers.

NOTE For some sampling devices the containers might have to be opened under water.

10.2.4 Where possible, take care not to touch the membrane of the sampling device, unless the type of sampling device so requires. Prepare each sampling device as necessary and install in the deployment device (**10.1.9**). Where photodegradation of organic chemicals is of major concern, protect the sampling device from direct light during deployment.

NOTE The use of photolysis surrogates (such as PRCs) added to the sampling device can help determine any potential chemical loss due to photodegradation.

10.2.5 Anchor the deployment device to the river, lake, or sea bed (**10.1.10**) at the sampling point and suspend it below the surface from the buoy or floats (**10.1.12**). Attach weights (**10.1.13**) to the deployment device if necessary to keep it submerged at this depth. Record the sampling depth (**10.1.8**). Take account of fluctuations in water level, such as tide. Ensure sampling devices are deployed, so that no air, or sediments may become trapped on the device, where they can reduce sampling efficiency, or contaminate the device.

NOTE 1 The deployment device should be positioned such that it is as inconspicuous as possible in order to guard against tampering or vandalism.

NOTE 2 The sampling device should be adequately secured and protected against damage and loss during flood events, or storms.

10.2.6 At the time the sampling device set is being deployed, close the containers that contain the field control(s).

10.2.7 Close the empty sampling device containers and place in the cool box, where used, for transport back to the laboratory along with the field control(s) and shipping control(s).

10.2.8 Record the date and time of deployment, weather conditions and name of the person executing the deployment.

10.2.9 Where necessary, check the integrity of the deployment device and sampling devices at intervals. Measure and record relevant water quality parameters at deployment and retrieval (see **10.2.2**).

NOTE For some investigations, it may be necessary to recover devices sequentially throughout the deployment period

10.3 Retrieval procedure

10.3.1 Take a photograph of the sampling site (**10.1.6**). Record any water quality parameters significant to the study such as water temperature, pH, clarity, turbidity, estimated water flow rate in cm/s (**10.1.7**).

10.3.2 Retrieve the deployment device. Put on gloves (**10.1.4**) and retrieve sampling devices in accordance with manufacturer's instructions, taking care not to touch the membrane surface.

10.3.3 At the time the sampling devices are being retrieved, open the container housing the field control(s) (**10.1.2**).

10.3.4 Check integrity of each sampling device. Record any damage, e.g. ruptured membrane, and the extent of biofouling.

10.3.5 Prepare each sampling device as necessary. Return each sampling device to its original container (**10.1.5**). Close the container housing the field control(s).

10.3.6 Seal each container and place immediately in the cool box (**10.1.3**) along with the shipping control(s) and field control(s) (**10.1.2**).

10.3.7 Record the date and time of retrieval, name of the person executing the retrieval and weather conditions.

10.3.8 Transport and store sampling devices in their sealed containers at temperatures recommended by manufacturers prior to analysis (typically $<5\ ^{o}C$ for organics sampling devices).

11 Extraction of analytes from sampling devices and preparation for analysis

When preparing sampling devices and controls for analysis, follow the handling instructions given in Clause **5**.

Prepare the receiving phase for analysis in such a way as to avoid contamination from fouling on the sampling device surfaces.

NOTE This can be achieved via preparations such as cleaning of the membrane surface or careful disassembly of sampling devices.

Use techniques such as dialysis, solvent extraction, acid digestion or thermal desorption to extract the analytes, residual performance reference compounds and residual analytical performance compounds for analysis.

12 Analysis

Analyse samples from the sampling devices and controls using a suitable analytical technique for determining the amount of each analyte, performance reference compound and analytical performance compound in the receiving phase, e.g. gas chromatography mass spectrometry (GC-MS) or liquid chromatography mass spectrometry (LC-MS) for organic analytes, atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) for metal analytes.

*NOTE 1 Before commencing analysis it is essential, using laboratory tests, to establish overall precision, bias and LOD of the methods (see **B.2**). These procedures should be used each time an analysis is performed.*

As far as possible, use methods specified in European and International Standards and that have been validated in your laboratory.

NOTE 2 European Standards giving analytical methods for determination of pollutants are listed in Annex A.

NOTE 3 Where there is a need to measure very low trace levels of a pollutant, extracts from multiple devices can be pooled prior to analysis.

13 Calculation

Calculate the time-weighted average concentration C_W of analytes in water over the deployment time as follows:

$$C_W = \frac{M}{k_o A t} \quad (1)$$

where:

M is the amount of analyte accumulated in the sampling device after an exposure time t (kg);

t is the exposure time (s);

k_o is the overall mass transfer coefficient of the analyte from water to the sampling device (m s^{-1}); and

A is the effective area of the sampling device (m^2).

NOTE This is a very general statement of the calculation, assuming an integrative uptake of the analyte during the whole deployment period.

The value of the overall mass transfer coefficient for any analyte is in general a device- and site-specific calibration parameter. It is obtained in a variety of ways, depending on the specific sampling device used and deployment conditions. It is a substance specific value depending on the physicochemical properties of the analytes and environmental variables such as water temperature and hydrodynamic conditions.

The mass transfer coefficient can be obtained in a number of ways including the use of empirical calibration data or from theoretical considerations where the parameters are provided by the manufacturer. In addition, for some sampling devices, PRCs can be used to correct the mass transfer coefficients for fluctuations in environmental conditions.

The errors associated with the estimates of C_w can be determined from the use of appropriate quality control measures (see Annex B). Examples of calculation and quality control measures for the various types of sampling device are provided in relevant references cited in the bibliography.

14 Test report

At least the following information shall be included in the test report for each analyte in the sampling device set:

a) sampling device manufacturer;

b) sampling device batch number;

c) sampling device field identification;

d) sampling device uptake rate and the method used to determine it;

e) sampling location, date and time of deployment and retrieval of sampling devices, site characteristics and name of person deploying and retrieving the device;

f) where applicable, further information on the sample site, e.g. previous levels of any pollutants found;

g) water quality parameters recorded at deployment and retrieval;

h) any performance reference compounds used and their levels in sampling devices before and after exposure;

i) analytical performance compounds used;

j) sample preparation method;

k) analytical method;

l) levels of target analytes quantified in quality control samples;

m) time weighted average concentration of analyte in the surface water, with its estimated uncertainty.

Annex A (informative)

Relevant analytical methods (European and international standards)

BS 6068-2.47:1995, ISO 11083:1994, *Water quality – Physical, chemical and biochemical methods – Determination of chromium (VI) – Spectrometric method using 1,5-diphenylcarbazide*

BS EN 903, *Water quality – Determination of anionic surfactants by measurement of the methylene blue index MBAS*

BS EN 1233, *Water quality – Determination of chromium – Atomic absorption spectrometric methods*

BS EN 1483, *Water quality – Determination of mercury*

BS EN ISO 6878, *Water quality – Determination of phosphorus – Ammonium molybdate spectrometric method*

BS EN 12260, *Water quality – Determination of nitrogen – Determination of bound nitrogen (TN_b), following oxidation to nitrogen oxides*

BS EN 12673, *Water quality – Gas chromatographic determination of some selected chlorophenols in water*

BS EN 14207, *Water quality – Determination of epichlorohydrin*

BS EN ISO 5961, *Water quality – Determination of cadmium by atomic absorption spectrometry*

BS EN ISO 6878, *Water quality – Determination of phosphorus – Ammonium molybdate spectrometric method*

BS EN ISO 9562, *Water quality – Determination of adsorbable organically bound halogens (AOX)*

BS EN ISO 10301, *Water quality – Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic methods*

BS EN ISO 10304-1, *Water quality – Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions – Part 1: Method for water with low contamination*

BS EN ISO 10304-3, *Water quality – Determination of dissolved anions by liquid chromatography of ions – Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate*

BS EN ISO 10304-4, *Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 4: Determination of chlorate, chloride and chlorite in water with low contamination*

BS EN ISO 10695, *Water quality – Determination of selected organic nitrogen and phosphorus compounds – Gas chromatographic methods*

BS EN ISO 11732, *Water quality – Determination of ammonium nitrogen – Method by flow analysis (CFA and FIA) and spectrometric detection*

BS EN ISO 11969, *Water quality – Determination of arsenic – Atomic absorption spectrometric method (hydride technique)*

BS EN ISO 12020, *Water quality – Determination of aluminium – Atomic absorption spectrometric methods*

BS EN ISO 15680 (BS 6068-2), *Water quality –- Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption*

BS EN ISO 15681-1, *Water quality – Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) – Part 1: Method by flow injection analysis (FIA)*

BS EN ISO 15681-2, *Water quality – Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) – Part 2: Method by continuous flow analysis (CFA)*

BS EN ISO 16588, *Water quality – Determination of six complexing agents – Gas-chromatographic method*

EN ISO 23631, *Water quality – Determination of dalapon, trichloroacetic acid and selected haloacetic acids – Method using gas chromatography (GCD-EC D and/or GC-MS detection) after liquid-liquid extraction and derivatization*

BS EN ISO 17353, *Water quality – Determination of selected organotin compounds – Gas chromatographic method*

BS ISO 18857-1, *Water quality – Determination of selected alkylphenols – Part 1: Method for non-filtered samples using liquid-liquid extraction and gas chromatography with mass selective detection*

Annex B (informative) Quality control measures

B.1 Recovery

Recovery is evaluated on the basis of mean analyte recovery from recovery spikes. Percentage recovery is determined by:

$$\%\ \text{recovery} = \frac{\text{mean measured analyte concentration}}{\text{recovery spike concentration}} \times 100 \qquad \text{(B.1)}$$

Control limits and warning limits for spike recoveries are established by:

$$\text{WL} = \bar{x} \pm (2 \times s) \qquad \text{(B.2)}$$

$$\text{CL} = \bar{x} \pm (3 \times s) \qquad \text{(B.3)}$$

where

WL is the warning limit;

CL is the control limit; and

s is the standard deviation of measured spike concentrations.

B.2 Method detection limits (LoD)

In order to limit false negative results for samples containing some of the analyte in question replicate recovery spikes are analysed to determine the limit of detection (LoD) that is given by:

$$\text{LoD} = \left(2\sqrt{1+\frac{1}{n_B}}\right)t_{(n-1,\,\alpha)} \times s \qquad \text{(B.4)}$$

where

t is the one-tailed Student t value for a significance level α with n–1 degrees of freedom;

n is the number of replicate spiked samples analysed;

s is the standard deviation of the measured analyte concentration in replicate spikes; and

n_B is the number of blank determinations used to correct sample results when using the method for analysing samples from the sampling devices.

To get realistic values of s, the spiking levels should not be significantly greater than 5 to 10 times the expected s-value. The user will need to decide the level of protection required against false negative results and use the appropriate values of n and t.

B.3 Precision

Precision of sampling devices is determined by comparison of replicate, field-exposed sampling devices. Relative percent differences (RPD) are calculated as:

$$\text{RPD} = \left[\frac{|x_1 - x_2|}{0.5(x_1 + x_2)}\right] \times 100 \qquad \text{(B.5)}$$

where

x_1 and x_2 are analyte concentrations in replicate sampling devices.

RPD can also be assigned control and warning limits. As RPDs approach zero, precision increases.

Control limits and warning limits are established by:

$$\text{WL} = \bar{x} \pm (2 \times s) \qquad \text{(B.6)}$$

$$\text{CL} = \bar{x} \pm (3 \times s) \qquad \text{(B.7)}$$

where

s is the standard deviation of recovery spike concentrations determined; and

$\bar{x}$ is the mean recovery concentration.

The spike level should be close to the expected determinand level.

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Standards publications

For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

BS EN ISO 14644-1, *Cleanrooms and associated controlled environments – Part 1: Classification of air cleanliness*

DD ENV ISO 13530, *Water quality – Guide to analytical quality control for water analysis*

Other publications

[1] EUROPEAN COMMUNITIES. Council Decision 2455/2001/EC of the European Parliament and the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Luxembourg: Office for Official Publications of the European Communities.

[2] EUROPEAN COMMUNITIES. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Luxembourg: Office for Official Publications of the European Communities.

Further reading

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