

Physical and chemical assessment

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Background to the use of passive sampling methods for trace contaminant detection

1 Purpose and scope

This document describes passive sampling concepts for monitoring trace concentrations of contaminants. Passive sampling devices (PSD) are used to:

- detect contaminants that may be present in concentrations below the limit of detection that a laboratory can reach when testing a water sample. Trace levels of contaminants are often concentrated to detectable levels by passive samplers placed in water for a controlled exposure period.
- obtain a time-weighted average concentration over a deployment period, which can vary between several days and several weeks for different passive sampler types and for different analytes.

2 Associated documents

Manufacturer's instructions for use of passive sampling devices (PSD).

3 Introduction

In principle the use of a PSD involves the deployment of a chemical-absorbing or -adsorbing material (accumulating material) in the water column (or sediments). After a period of exposure, the sorbent material is retrieved and the accumulated chemicals are extracted/eluted from the sorbent phase and analysed. The basic components of a PSD are:

- an accumulating medium for the analyte/s of interest
- a membrane to control the rate of uptake (in the case of samplers designed for polar chemicals) that can also act as a protective layer
- a mounting structure to contain and protect the other components but at the same time expose them to the environment being sampled.

Some PSDs will also have a transport medium between the membrane and the accumulating medium to ensure diffusion-controlled and consistent rates of uptake. This is more common in PSDs for inorganic contaminants, which tend to be present at higher concentrations than many organic contaminants.

Passive sampling devices can be deployed in the field in a variety of situations—hung from floats, suspended from jetties, fastened to stakes inserted in a stream bottom, embedded in sediment, or anchored to the bottom but held up into the water column by a float.

The normal requirements of Quality Assurance and Quality Control apply when sampling with passive sampling devices. These include the use of trip blanks, replicate samplers, and the use of personal protective equipment such as gloves to avoid contamination of the sampler or its housing during handling. It is also important to assess the surrounding environment for contamination as some passive samplers can adsorb compounds from the atmosphere. Further information can be obtained from the BSI Standards Publication detailing - *Guidance on passive sampling in surface waters* (BSI 2011).

The main source of variability when using a PSD is the extent to which water flow conditions around the sampler affect the degree of sorption or desorption. Several approaches are used to determine the effect of flow

on the chemical accumulation to increase confidence in the results. These include:

- The use of performance reference compounds for organic pollutants, which are introduced into the accumulating medium of sampler devices before deployment. Performance reference compounds are selected to have similar diffusion and accumulation properties as the chemicals to be sampled (i.e. similar octanol/water partition coefficients). The rate at which these compounds are lost from the sampling device are assumed to be proportional to the rate of uptake of organic analytes.
- Water flow information can be obtained from rate of dissolution of a slightly soluble compound or material (e.g. plaster of Paris) deployed alongside the PSDs.
- PSDs with a diffusional medium can deploy samplers with several different thicknesses in order to obtain an average diffusion boundary layer thickness, which also relates to flow.

4 Passive sampling for organic substances

Passive sampler devices for detecting organic chemicals in water have evolved over many years, and various devices and methods have been employed. Most of these methods fall into two categories: those that use an organic solvent as the sorbent phase, and those that use a solid sorbent phase.

4.1 Semi-permeable membrane device

The most widely used passive sampler design for non-polar chemicals in water is the semi-permeable membrane device (SPMD) (Figure 1). It consists of a length of sealed polyethylene tubing (the membrane) containing a small volume of triolein (the sorbent phase) woven around a stainless steel frame. The device is then inserted into a perforated stainless steel shroud for protection from mechanical damage during deployment. This design allows a very high surface area to maximise rates of accumulation.

An alternative to the triolein-based SPMD described above is to use a strip of silicon rubber such as polydimethylsiloxane (PDMS) placed inside the deployment shroud as the absorbent material.

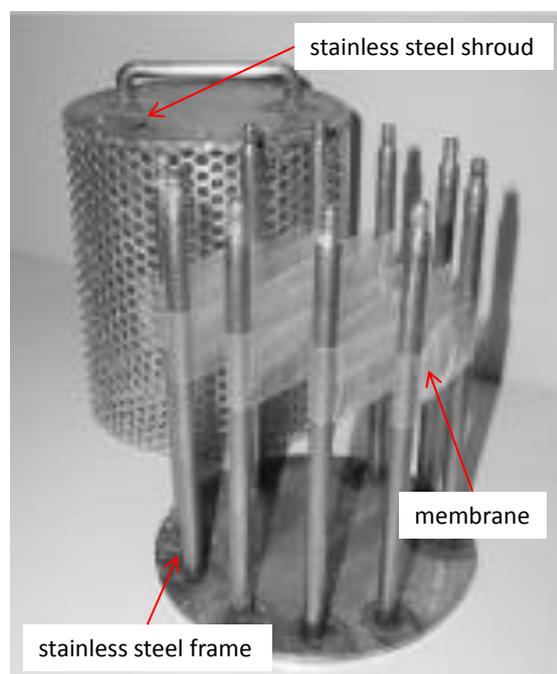


Figure 1: Housing and components of an SPMD passive sampler. The protective shroud covers the absorbent strip during deployment

4.2 Chemcatcher®

This device is a very robust PSD that employs solid phase extraction disks (e.g. Empore™ disks by 3M™) such as bonded silica (e.g. C18) or poly(styrenedivinylbenzene) copolymer (e.g. SDB-RPS) as the sorbent material, combined in most cases with a polyethersulfone (PES) membrane that allows diffusion of polar chemicals. One of these devices based on the Empore disk (Figure 2).

The sampler consists of three interlocking sections (2, 3, 9) manufactured from polytetrafluoroethylene (PTFE) that screw together during deployment to form water-tight seals (4, 10). Integral to the device is a 50mm rigid PTFE disk (7) designed to support both the sorbent material (Empore) (5) and the diffusion-limiting membrane (6). On the reverse is a lug (1) for attaching the device during deployment. The outer surface of the diffusion-limiting membrane is protected from mechanical damage during deployment by a mesh (8) of either stainless steel for organic analytes or nylon for inorganic analytes. This mesh is held in place during deployment by a removable PTFE ring (9). A PTFE screw cap (11) replaces the ring (9) during transport to and from the deployment site.

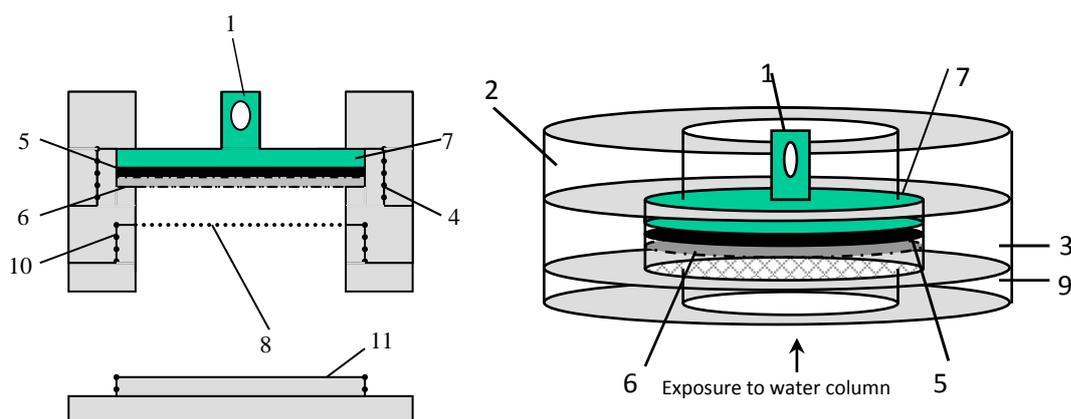


Figure 2: Housing and components of a Chemcatcher® passive sampling device

5 Passive sampling for inorganic substances

The diffusive gradient in a thin film (DGT) device employs a binding layer, which is typically a polyacrylamide hydrogel that is cast containing an accumulating material (such as a chelating resin or metal oxide adsorbent). The binding layer or gel is overlaid by a transportation medium (diffusive layer or gel) to maintain a concentration gradient over a known thickness and a filter to exclude particulates (Figure 3). Numerous binding layers have been developed to measure a range of metals (cations and oxyanions), dissolved inorganic nutrients (phosphate, nitrate and ammonium), sulphide and radioisotopes. DGT devices can also be deployed with several different diffusive gel thicknesses which allows accurate measurement under low flow conditions.

An important advantage of using DGT to measure metals in saline or marine waters is that the binding layers do not accumulate the major ions that often cause interferences in the analysis of metals. The devices sample satisfactorily over a range of pH with the range limits varying between metals – these have been well-defined for most common metal analytes. The DGT device is deployed for much shorter time periods than organic PSDs as inorganic analytes tend to be present at higher concentrations and to ensure linear uptake.

A similar PSD, known as DET (diffusive equilibrium in thin films), which does not contain a binding layer, can be deployed in sediment (as can DGT) for solutes for which there is no suitable binding layer. The DET comprises a single relatively thick sheet of gel (typically 0.8mm) supported in a holder with a membrane. Solutes in the surrounding water diffuse into the gel until concentrations equilibrate.

The University of Lancaster (UK) holds a worldwide patent on both DGT and DET devices but they are both available commercially, either pre-assembled or in kit form (gel disks and strips for local assembly). For details of supply visit the DGT for measurements in waters, soils and sediments website at www.dgtresearch.com.

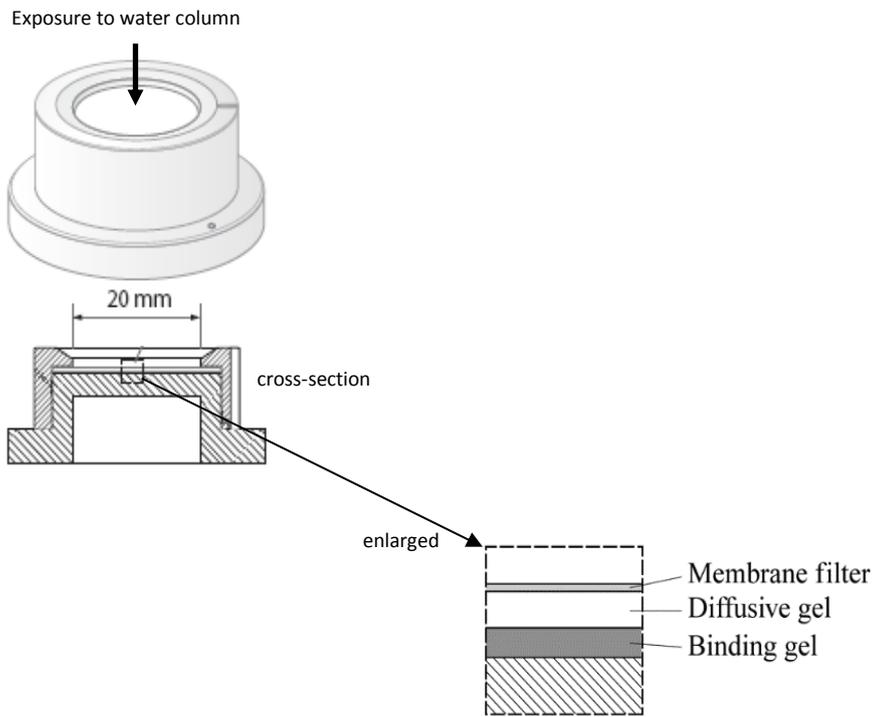


Figure 3: Housing and components of a DGT passive sampling device

6 References and additional reading

BSI 2011, Water Quality – Sampling. Part 23: *Guidance on passive sampling in surface waters* (ISO 5667-23:2011), BSI Standards Publication.