II Sampling

It is an absolute necessity that one attempts to collect samples that are representative of the matrix under investigation. When collecting samples, one must follow predetermined sampling protocols (procedures and methods) which have been chosen (bearing in mind the sampling (collection) site, the number of samples to be collected, and the timing of the sampling) to meet the purpose of the survey, and which are appropriate to the media being investigated.

II.1 Water quality

II.1.1 Sampling timing

Time the sampling trip such that it is possible to collect a representative water sample from the designated sampling point. Take into account factors such as the weather, tides, currents, geography etc.

II.1.2 Sampling point

For rivers, the primary sampling point is in the surface water layer (0-5 cm from the surface) at the centre of the main flow. However, the top 1-2 cm of this surface layer should be avoided so as not to collect floating dust, oil, etc. In addition, further samples can be collected through the full depth of the water column if required to meet the purpose of the study.

For lakes and the ocean, the sampling point will be selected after taking into consideration such factors as geography, whether there are freshwater (rivers or streams) or wastewater inflows, depth, tides, currents etc.

For underground water, the sampling site or sites will be selected after taking into consideration such factors as water flow and geological structure (hydrogeology), and also site conditions such as factories or land use, and avoiding bias so as to be able to understand the whole area's underground water.

II.1.3. Sampling tools and containers

Sampling tools

The type of water sampling tool required will depend on the sampling site and the type of sample to be taken. Sampling can be achieved using buckets, open water grab samplers (a ladle or bottle on the end of a long pole), or vertical and horizontal messenger activated samplers (such Niskin bottles or Kemmerer water samplers). The type of material such tools should be made of will depend on the purpose (target analytes) of the study, but relatively inert materials such as stainless steel, synthetic resin such as polypropylene, polyethylene or pertetrafluoroethylene (PTFE), or glass are all acceptable.

Sample containers

The size and type of sample to be taken will determine the type of sample container required.

- For volatile organic compounds, use clear or brown bottles or vials with screw caps or stoppers lined with tetrafluoroethene resin films, or similar products, which can be closed to provide a gas-tight seal.
- For semi-volatile or non-volatile organic compounds, use clear or brown glass jars with a stoppers or Teflon lined screw caps.
- For inorganic compounds such as heavy metals, use polyethylene or glass containers.

Cleanliness

Sampling tools and containers should be contamination free. The method and extent of cleaning will be determined by one's target analyte and predetermined instrumental detection limits. However, wherever possible use tools and containers which have been cleaned thoroughly. In particular,

- For volatile organic compounds, containers should be heated at 105 °C for 3 hours and then allowed to cool in a desiccator to avoid contamination immediately before use.
- For semi- and non-volatile organic compounds, use containers which have been washed with pesticide residue analysis grade solvent, and dried immediately before use.
- For heavy metal, use containers which have been washed with 10 % v/v nitric acid, or 16 % v/v hydrochloric acid, and then rinsed several times with pure (deionised) water.

II.1.4 Sampling operation

The number and volume (size) of the samples to be collected will depend on the number and concentration of the target analytes, the difficulty and expense of analysis, and whether extra storage is required. Collect the water sample using the most appropriate sampling tool given the nature of the sampling site, the target analyte, and the instrument on which quantitative measurement will be performed. Sample containers should be washed 3-4 times with water from the exact site of sampling prior to taking the sample. The samples should be carefully and gently poured into its container without making bubbles.

For underground water, collect spring water directly into sampling bottles when the groundwater is gushing out. Artesian wells are sampled by using water samplers avoiding mixing in floating objects. For pump well, collect water samples directly with sampling bottles after first totally exchanging the water contained in the pump.

- For volatile organic compounds, sample containers should be completely filled with bubble-free water and sealed tight.
- For semi- and non-volatile organic compounds, sample container should be completely filled with water that is as free as possible of air bubbles.
- For inorganic compounds such as heavy metals, the container should be approximately 80 - 90 % filled with the water sample (the space above the surface of the water sample allows thorough mixing just prior to analysis.

II.1.5 Field records

On a form which has been prepared in advance, record all pertinent details e.g. the sampling date, sample name (code), sampling site's name (code), an accurate position for the sampling site (map of G.I.S. position), general environmental conditions such as the nature of the surrounding landscape, the state of the tide or river flow, weather conditions such as cloud cover and air temperature, and general water conditions such as colour, water temperature, pH, and dissolved oxygen content, etc.

II. 1.6 Labelling of samples

Label each sample unambiguously, i.e. write on the sample bottle in water-resistant ink details of the name or code of the sample, the sampling date, the sampling site name etc. Alternatively, one may attach a label to the sample bottle detailing the same information.

Remember also to record these details in the field record mentioned earlier. This provides a back-up record of the sampling sequence and allows cross-checking of the analytical results with field data, and reduces future problems with identification (confusion) of stored samples. Finally, record on each sample and in the field record details of transport methods, storage methods, etc.

II.1.7 Transport and storage of samples

Procedures for handling the sample during transport will depend on the nature of the sample matrix and the target analytes. However, ideally all samples should be cooled in ice soon after collection, and then transported to the laboratory packed in ice. If samples must be stored for any significant period of time, refrigerate or freeze samples as soon as possible after collection or arrival at the laboratory.

II.2 Sediment

II.2.1 Sampling timing

If only sediment is to be sampled, time the sampling trip such that it is possible to collect a representative sample from the designated sampling point taking into account factors such as the weather, tides, currents, geography etc. If sediment sampling is linked to a study of the overlying water, then collect the sediment sample at the same time as the water samples.

II.2.2 Sampling point

In rivers, the sampling point will be (a) the point where water samples are taken if the sediment study is linked to a water quality study, or (b) if only sediment is being studied, that part of the river where sedimentation is occurring (the places in the river where sediment is being deposited such as the outside of bends).

For lakes and the ocean, the sampling point will be selected after taking into consideration such factors as geography, whether there are freshwater (rivers or streams) or wastewater inflows, depth, tides, currents etc.

II.2.3 Sampling tools and containers

Sampling tools

The type of sediment sampling tool required will depend on the sampling site, the nature of the sediment, and the type of sample to be taken. Sampling can be achieved using gravity, hand or messenger activated core samplers, or for larger samples use grab dredges (such as Peterson or Ekman dredges).

Sample containers

The size and type of sample, the nature of the target analytes and their detection limits will determine the type of sample container required.

- For volatile organic compounds, use clear or brown bottles or vials with Teflon lined screw caps or stoppers which can be closed to provide a gas-tight seal.
- For semi-volatile or non-volatile organic compounds, use clear or brown glass jars with a stoppers or Teflon lined screw caps.
- For inorganic compounds such as heavy metals, use polyethylene or glass containers.

Cleanliness

Sampling tools and containers should be contamination free. The method and extent of cleaning will be determined by one's target analyte and predetermined instrumental detection limits. However, wherever possible use containers which have been cleaned thoroughly.

- For volatile organic compounds, containers should be heated at 105 °C for 3 hours and then allowed to cool in a desiccator to avoid contamination immediately before use.
- For semi- and non-volatile organic compounds, use containers which have been washed with pesticide residue analysis grade solvent, and dried immediately before use.
- For heavy metal, use containers which have been washed with 10 % v/v nitric acid, or 16 % v/v hydrochloric acid, and then rinsed several times with pure (deionised) water.

II.2.4 Sampling operation

The number and volume (size) of the samples to be collected will depend on the number and concentration of the target analytes, the difficulty and expense of analysis, and whether extra storage is required. Collect the sediment sample using the most appropriate sampling tool given the nature of the sampling site, the target analyte, and the instrument on which quantitative measurement will be performed. In rivers, take the sediment sample from three equidistant

positions within a 50 m diameter circle. Pool (mix) the samples. Cylindrical samples may be taken depending on the survey's purpose. Take cylinders of mud about 10 cm deep every meter.

In lakes and in the ocean, take sediment (mud) samples from three equidistant grid positions. The number of sampling points may be increased if there are special circumstances, such as the inflow of fresh or waste waters nearby. Samples may be taken through the full depth of the sediment should the survey require such sampling.

- For volatile organic compounds, take samples into the sealed container without gap and seal up.
- For semi-volatile and non-volatile organic compounds, place the sample on a clean, stainless steel tray, remove large impurities such as stones, shells, flakes of animals and plants, thoroughly mix the remaining sample, and place the sample in its container.
- For heavy metals, use a clean polyethylene, polypropylene or PTFE tray, remove large impurities, mix the remaining sample, and place the sample in its container.

II.2.5 Field records

On a pre-prepared form, record such details as the sampling date, sample name (code), sampling site's name (code), an accurate position for the sampling site (map of G.I.S. position), general environmental conditions such as the nature of the surrounding landscape, the state of the tide or river flow, weather conditions such as cloud cover and air temperature, and general water conditions such as water temperature, pH, dissolved oxygen content, and colour (visually) etc. In addition, record information such as sediment temperature, appearance and colour, odour, any obvious animal or inanimate particulate matter, and mud rate.

II.2.6 Labelling of samples

Label each sample unambiguously, i.e. write on the sample bottle in water-resistant ink or attach a label to the sample bottle detailing the name or code of the sample, the sampling date, the sampling site name etc.

II.2.7 Transport and storage of samples

Procedures for handling the sample during transport will depend on the nature of the sample matrix and the target analytes. When samples arrive at laboratory,

- Samples for volatile organic compound analysis should be weighed and analysed as soon as possible.
- Samples for semi-volatile and non-volatile organic compound analysis should be screened with a 1 mm mesh sieve (16 mesh), or centrifuged to remove larger particles, and thoroughly remixed prior to analysis. If samples must be stored, refrigerate or freeze samples after sieving.
- Samples for heavy metal analysis are sorted with non-metal sieve after air dry, thoroughly mixed and analysed.

In all cases, the mud rate (the ratio of sample weight passing through the sieve : total sample weight prior to sieving) should be calculated. And the interstitial moisture content should be determined by drying part of the samples in the oven (105-110 °C, about 2 hours). Finally, the total organic content of the sediment should be calculated by heating (ashing) the sample in the oven (600 ± 25 °C, about 2 hours).

II.3 Soil

II.3.1 Sampling timing

There are fewer restrictions on when soil samples may be collected. However, one should still time the sampling trip so that it is possible to collect a representative soil sample from the designated sampling point. Take into account factors such as the weather, season, geography etc.

II.3.2 Sampling point

The sampling point will be selected after taking into consideration such factors as local geography, soil vegetation coverage, whether there are freshwater or wastewater channels or subsurface drains, etc.

II.3.3 Sampling tools

Sampling tools

The type of water sampling tool required will depend on the sampling site and the type of sample to be taken. Sampling can be achieved using trowels, spades, or augers. Such tools are normally made of stainless steel.

Sample containers

The size and type of sample to be taken will determine the type of sample container required.

- For volatile organic compounds, use clear or brown bottles or vials with Teflon lined screw caps or stoppers which can be closed to provide a gas-tight seal.
- For semi-volatile or non-volatile organic compounds, use clear or brown glass jars with a stoppers or Teflon lined screw caps.
- For inorganic compounds such as heavy metals, use polyethylene or glass containers.

Cleanliness

Sampling tools and containers should be contamination free. The method and extent of cleaning will be determined by one's target analyte and predetermined instrumental detection limits. However, wherever possible use tools and containers which have been cleaned thoroughly. In particular,

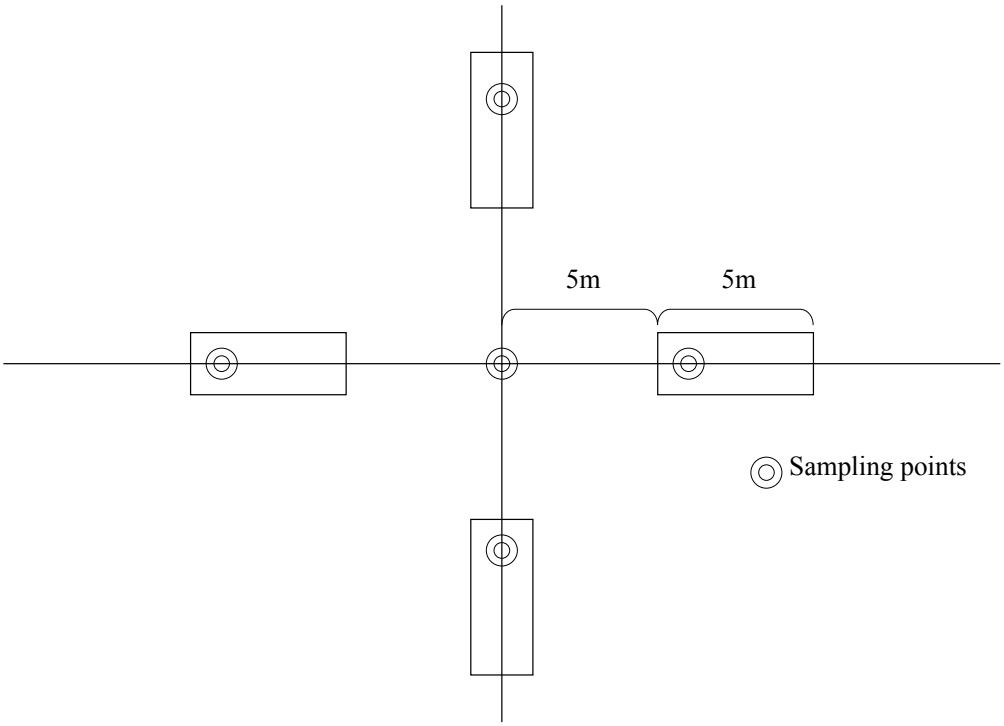
- For volatile organic compounds, containers should be heated at 105 °C for 3 hours and then allowed to cool in a desiccator to avoid contamination immediately before use.
- For semi- and non-volatile organic compounds, use containers which have been washed with pesticide residue analysis grade solvent, and dried immediately before use.
- For heavy metal, use containers which have been washed with 10 % v/v nitric acid, or 16 % v/v hydrochloric acid, and then rinsed several times with pure (deionised) water.

II.3.4 Sampling operation

The number and volume (size) of the samples to be collected will depend on the number and concentration of the target analytes, the difficulty and expense of analysis, and whether extra storage is required. Take sufficient, appropriately spaced surface soil samples (top 5 cm of the soil profile) using a geographical map to meet the survey's requirements. For each sampling point, take 3-5 samples from the same area, and mix them well to form one pooled sample. Take sub-surface

soil and soil column (profile) samples where required by the survey using an auger. Since soil and ground water pollution are closely related, combine soil and groundwater surveys where possible.

A typical sampling method for dioxin analysis (**Figure II-3-1**) is shown for reference material.



Note : Sampling is conducted by the 5 points mixture method from a 10 m square plot of bare land. Make samples by mixing 5 samples ; one taken from the centre of the plot, and the others from points between 5 to 10 m in each of four directions.

Figure II-3-1 Reference example of 5 sampling points method
(cited from "Provisional manual for soil survey related to dioxins", Soil and Pesticide Division, Water Quality Reservation Bureau, Japan Environment Agency, Jan. 1998)

II.3.5 Field records

On a form which has been prepared in advance, record such details as sampling date, sample site, an accurate map position, height above sea level, sampling location at the site, soil depth, sample's name or code, general environmental conditions, any obvious pollution sources in the surrounding locality, land use patterns, geographical features, and weather conditions. In addition, record such details as vegetative coverage at the site, drainage patterns, local geology, and soil characteristics such as colour, any obvious impurity, muddiness or dryness etc.

II.3.6 Labelling of samples

Label each sample unambiguously, i.e. write on the sample container or attach a label detailing the name or code of the sample, the sampling date, the sampling site name etc.

II.3.7 Transport and storage of samples

Procedures for handling the sample during transport will depend on the nature of the sample matrix and the target analytes. However, ideally all samples should be cooled in ice soon after collection, and then transported to the laboratory packed in ice. If samples must be stored for any significant period of time, refrigerate or freeze samples as soon as possible after collection or arrival at the laboratory.

II.4 Air

II.4.1 Sampling timing

Timing of the sampling will to a large extent depend on the purpose of the survey. However, endeavour to ensure that as representative an air sample as possible is collected i.e. sample only during stable climatic conditions. The time period over which the sample is collected will depend on the concentration and stability of the target chemicals.

II.4.2 Sampling point

Choose a sampling point where the local atmosphere conditions are well understood, and avoid places which are directly influenced from specific fixed or mobile pollution sources. Place the air intake of the sampling device at least 1 m away from any floor or wall surface.

II.4.3 Sampling tools and methods

Use either a high volume air sampler or low volume air sampler within a shelter. Trap particles in the air using filters made of quartz fibre, fluorine resin, or nitro-cellulose. Measure air flow at both the start and end of sampling, and calculate the amount of absorbed air. In addition, weigh the filters before and after sampling. Weigh the filters at 20 °C and a relative humidity of 50%. Calculate the sample weight and concentration of medium size particle substances in the air.

Choose a sample collection system based on the chemical nature of the target analyte, its concentration, and the nature of the sampling site. Suck the air sample into either stainless steel containers inactivated by electrolytic polishing or coated by oxidation or with silica, glass vacuum bottles, elasticised gas sampling bags (10 - 30 L), single or multiple use cartridges filled with absorbent polymer beads such as Tenax GC, Chromosorb, XAD, carbon molecular sieve or activated charcoal, or gas washing bottles filled with freshly prepared absorbent liquid. Suck the air through cartridges or the liquid in gas washing bottles at a flow rate optimised to trap the greatest amount of sample without break-through or contamination.

Wash sample containers, cartridges or gas washing bottles well prior to sampling. Use only equipment which has been shown not to contaminate the sample above predetermined instrumental detection limit. Use piping made of materials which has been shown not to contain or absorb the target chemicals, such as glass lined stainless steel, glass lined aluminium or aluminium with an oxidised coating, fluorine resin, or polyimide. Use a pump to pressurise the system and check for air leakage before use.

Figure II-4-1～II-4-4 shows a typical sampling apparatus. If possible, place all of such apparatus indoors, except for the sampling pipe. If it is not possible to set up the apparatus indoors, set up apparatus on a sturdy tripod, or use weights to prevent the apparatus falling over, and cover the trap and tubing or sampling bottle with aluminium foil etc.

Bearing in mind the chemical nature of the target chemicals and the atmospheric conditions at the air intake, use a dehumidifier which doesn't absorb the target substances at high percentage humidity, and use filter materials which traps dust but not the target substance. Finally, use an umbrella or other such glass or stainless steel funnel shaped cover to avoid rain ingress.

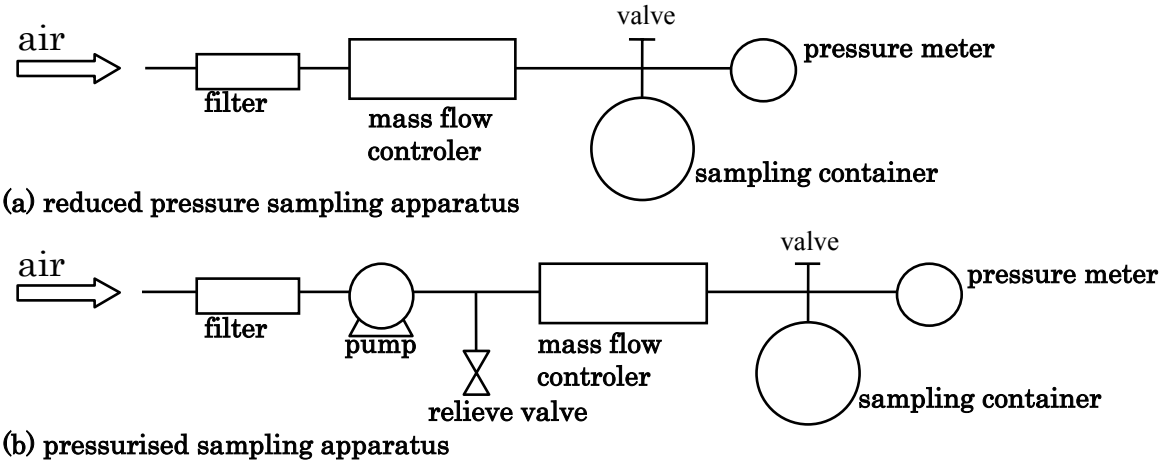


Figure II-4-1 Outline of sampling apparatus by container sampling method

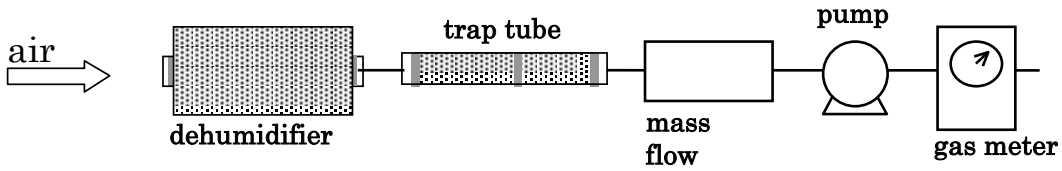


Figure II-4-2 Outline of sampling apparatus by solid phase adsorption - dissolution extraction method

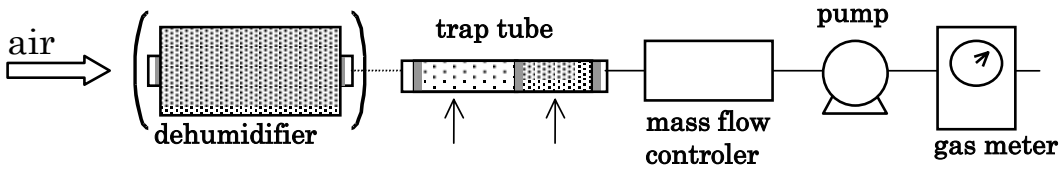


Figure II-4-3 Outline of sampling apparatus by solid phase adsorption-thermal desorption method *

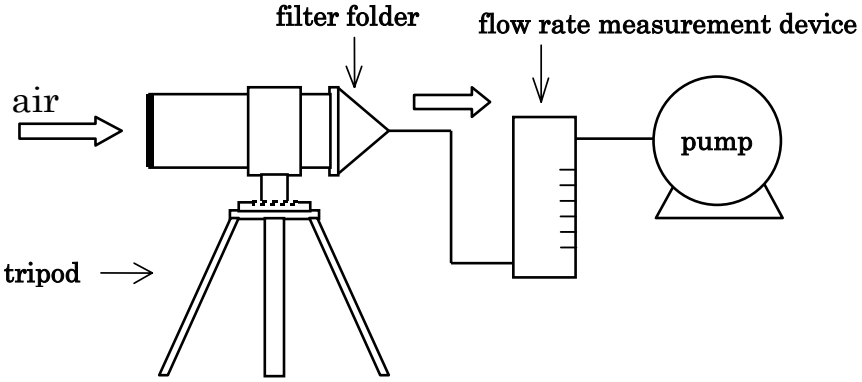


Figure II-4-4 Low volume air sampler *

* cited from "Manual of analytical method for air pollution" Japan Environment Agency, Feb1997

II.4.4 Record of field research

On a form which has been prepared in advance, record all pertinent details e.g. sampling date, sample name (code), sampling site's name (code), an accurate position for the sampling site (map of G.I.S. position), general environmental conditions such as the nature of the surrounding landscape. In addition, record climatic conditions such as temperature, humidity, atmospheric pressure, wind direction, wind velocity, the sampling method, the start time and finish time of sampling, sample temperature, pressure, sampling air flow rate, accumulated air flow amount at gas meter etc.

II.4.5 Labelling of samples

Label each sample unambiguously, i.e. write on the sample bottle in water-resistant ink, or attach a label with details of the name or code of the sample, the sampling date, the sampling site name etc.

II.4.6 How to transfer and store samples

Construct and take apart apparatus quickly to avoid contamination from surrounding air. Put filters in clean plastic bags. Cover glass vacuum bottles and gas sampling bags with black bags to prevent deformation by the sun. Close sampling containers tightly, or pressurise depending on sampling method to avoid outside influence. Seal cartridges and place in resealable containers with activated charcoal etc. In all cases, transfer the sample containers quickly after sampling and analyse as soon as possible. If it is impossible to analyse within a short period of time, store them in a dark room and avoid outside air. Analyse as soon as practicable.

II.5 Living things

II.5.1 Capture

Capture organisms at the same time every year, taking into account their breeding cycles and migration patterns. Standardise the time, place, number and size of organisms captured in order to maintain high precision. In general, choose juveniles since they are most sensitive to environmental pollution.

II.5.2 Capture method

II.5.2.1 Fish

The method of capture will depend on the type of fish to be caught e.g. one can use hand nets, drop nets, fish-traps, gill nets, seine nets, drift nets, drag nets, hook and line, or electrofishers. Whatever method is used, use equipment and sample containers which are not contaminated with the target substances to avoid sample contamination. Measure the length of each fish caught, and determine its weight. Place each sample in clean, non-contaminated artificial resin bags, or hard quality glass containers.

II.5.2.2 Shelled organisms

The method of capture will depend on the type of shelled organism. Collect shelled organisms e.g. snails, mussels, abalone etc., by hand or dredge from the substrate upon which they live i.e. plants, rocks or the river, lake or ocean floor. After collecting the organism, place the samples into clean, non-contaminated artificial resin bags, or hard quality glass containers.

II.5.2.3 Birds

The method of capture will depend on the type of bird to be collected and its habits. Capture birds by hand, net, trap or gun etc. Determine the bird's body weight and measure the length of the longest part of the wing. Put each bird in its own clean, non-contaminated artificial resin bags, or hard quality glass containers.

II.5.3 Record of field research

On a form which has been prepared in advance, record all pertinent details e.g. sampling date, sample name (code), sampling site's name (code), an accurate position for the sampling site (map of G.I.S. position), general environmental conditions such as the nature of the surrounding landscape. In addition, record the species name, the organism's body weight, length, capture number, and the total number of organisms caught, and the capture method.

II.5.4 Transfer and storage

Sacrifice (kill) the organisms at the site of capture in the appropriate, ethical manner. Freeze biological organisms on site, or chill in ice during transfer. Prepare samples and analyse them as soon as possible after arrival at the laboratory. If the samples are required to be stored, put the

samples into bags or containers which do not contain, dissolve or absorb the target substances. Weigh the samples before and after sample preparation, and freeze or refrigerate them in order to avoid contamination or decomposition.

II.5.5 Sample labelling

Label each sample unambiguously, i.e. write on the sample bottle in water-resistant ink, or attach a label with details of the name or code of the sample, the sampling date, the sampling site name etc.

II.6 Wastes

II.6.1 Sampling timing

Time the sampling trip such that it is possible to collect a representative wastewater sample from the designated sampling point. Sample at the start and finish of waste treatment, or at regular intervals, or when there are suspicions about leakage.

II.6.2 Sampling point

The place of sampling will depend on the nature of the wastewater survey, the nature of the sampling site and the type of sample to be taken. Take samples of exudate water, groundwater, overflowing water (surface run off), target area, surrounding air, leakage from intermediate treatment sites, last treatment place, landfill sites, waste disposal sites, areas which are considered likely to leak or where there is a significant risk of contamination during collection, transport, and storage of wastes.

II.6.3 Sampling tools, sampling operation, transfer and storage of samples

The type of water sampling tool required will depend on the sampling site and the type of sample to be taken. In general, sampling tools acceptable for water, air or soil sampling will be acceptable for sampling wastes. When sampling waste of homogeneous character, take samples that are consistent in character and composition of the bulk of the wastes. When sampling waste of inhomogeneous character, take multiple samples of the waste, and mix in order to gain

representative samples. In either case, crush and homogenise the final pooled sample, and then prepare the samples for analysis.

II.6.4 Record of filed research

On a form which has been prepared in advance, record all pertinent details e.g. the sampling date, sample name (code), sampling site's name (code), an accurate position for the sampling site (map of G.I.S. position), general environmental conditions such as the nature of the surrounding landscape. In addition, record details such as the purpose of sampling, the condition and treatment of wastes, the causes of any accidents, the kind of wastes, etc.

II.6.5 Display and coding of samples

Label each sample unambiguously, i.e. write on the sample bottle in water-resistant ink, or attach a label with details of the name or code of the sample, the sampling date, the sampling site name etc.

II.7 Sampling flow chart

An example of a sampling flow chart for the analysis of semi- and non-volatile compounds in river water is shown in **Figure II-7-1**.

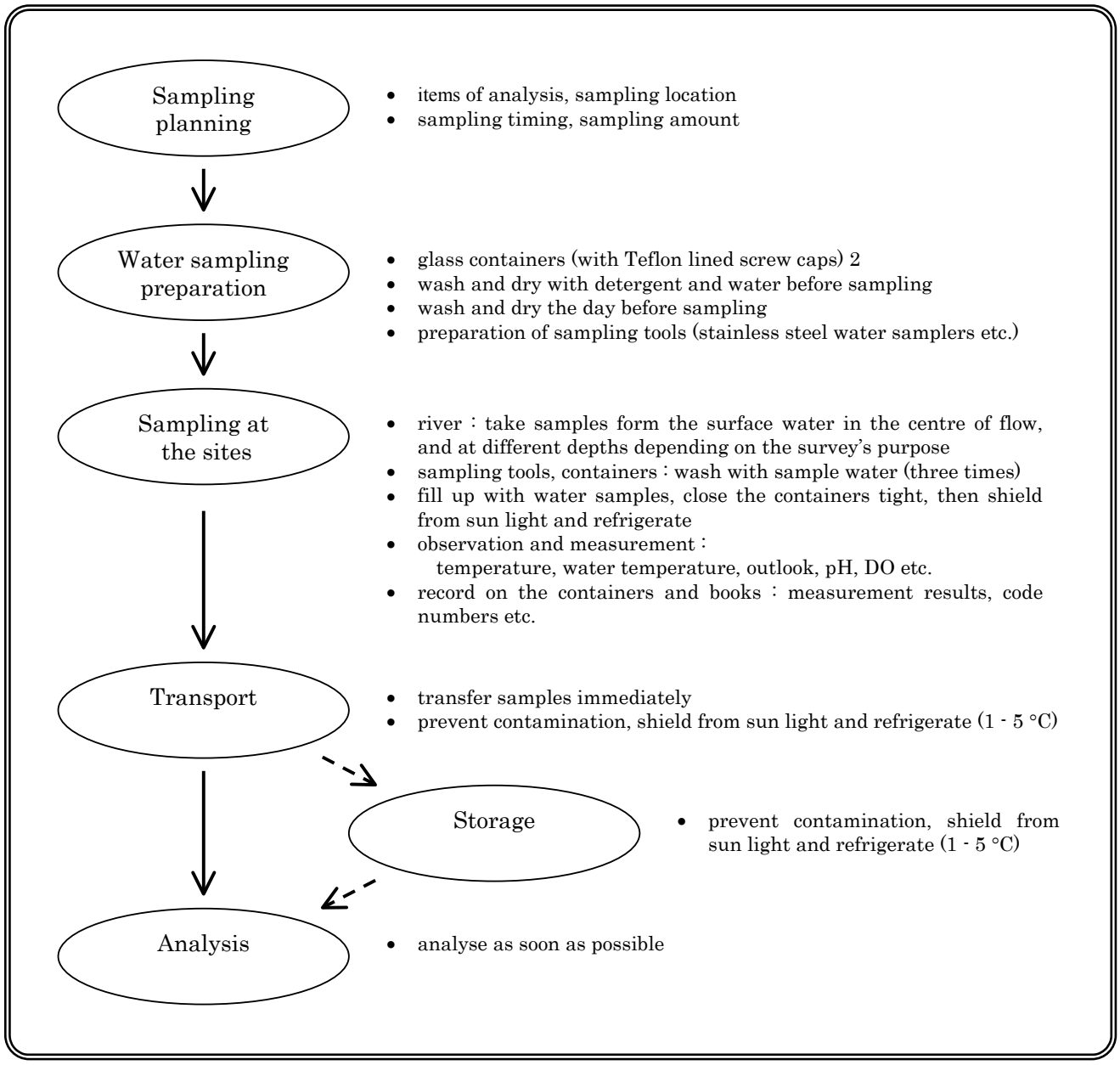


Figure II-7-1 An example of a sampling flow chart for analysis of semi- and non-volatile compounds in river water