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Water quality — Sampling —

Part 8:

Guidance on the sampling of wet deposition

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 5667-8 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 6, *Sampling (general methods)*.

ISO 5667 consists of the following parts, under the general title *Water quality — Sampling*:

- Part 1: *Guidance on the design of sampling programmes*
- Part 2: *Guidance on sampling techniques*
- Part 3: *Guidance on the preservation and handling of samples*
- Part 4: *Guidance on sampling from lakes, natural and man-made*
- Part 5: *Guidance on sampling of drinking water and water used for food and beverage processing*
- Part 6: *Guidance on sampling of rivers and streams*
- Part 7: *Guidance on sampling of water and steam in boiler plants*
- Part 8: *Guidance on the sampling of wet deposition*
- Part 9: *Guidance on sampling from marine waters*
- Part 10: *Guidance on sampling of waste waters*
- Part 11: *Guidance on sampling of groundwaters*
- Part 12: *Guidance on sampling of sediments*

Annex A forms an integral part of this part of ISO 5667.

Introduction

This part of ISO 5667 should be read in conjunction with ISO 5667-1, ISO 5667-2 and ISO 5667-3.

The general terminology used is in accordance with the various parts of ISO 6107, and more particularly, with the terminology on sampling given in ISO 6107-2.

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Water quality — Sampling —

Part 8:

Guidance on the sampling of wet deposition

1 Scope

This part of ISO 5667 provides guidance on the design of sampling programmes and the choice of instrumentation and techniques for the sampling of the quality of wet deposition. It does not cover measurement of the quantity of rain.

This part of ISO 5667 does not cover dry deposition or other types of wet deposition such as mist, fog and cloudwaters, since their measurements are still at research stages. However, their importance should be noted, since research results suggest that, in some cases their loading can be comparable with, or exceed, wet precipitation. Therefore, wet precipitation data alone are rarely sufficient for calculating total loadings.

The main objectives are outlined in 1.1 and 1.2.

1.1 Control of local emissions

Determination of loadings (i.e. mass/area/time) by wet deposition to a particular ecosystem requires information on emissions, transformation and transport of pollutants from point or area sources. This information, together with assessment of the relative loadings from distant and local sources, when combined with studies on the effects of the pollutant on the ecosystem, can be used to arrive at acceptable emission control regulations.

1.2 Long range transport of airborne pollutants

Determination of temporal and spatial variations in the constituents of precipitation on a regional scale requires that the stations which are selected are representative, and are remote from local point or area sources.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 5667. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 5667 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

ISO 6107-2:1989, *Water quality — Vocabulary — Part 2.*

3 Definitions

For the purposes of this part of ISO 5667, the following definitions apply.

3.1 wet deposition: Water precipitated from the atmosphere in either the liquid (rain) or solid state (snow/ice).

NOTE 1 In cold climates, winter precipitation is usually in the frozen or solid state. The precipitation may also include liquid contaminants in addition to water. Apart from the difficulties encountered with snow sampling (see 6.4.2), there

are additional factors to be considered when interpreting the results.

3.2 dry deposition: Dry deposition is the deposition of all compounds except water in the particulate, liquid or gaseous state and of particulate matter by gravitational and turbulent processes.

4 Determinants

4.1 Main components

The majority of the precipitation monitoring networks in use at the present time are designed to measure the main components such as major ions and nutrients, together with other parameters such as pH, acidity and conductivity.

4.2 Trace inorganic and trace organic compounds

Many trace inorganic materials, including radioactive materials, are released to the atmosphere during the combustion of various fuels and as a result of industrial activities. Many trace metals are adsorbed by flying ash particles, which are easily scavenged by precipitation or deposited to earth by gravitational settling.

Trace organic compounds are important in that many of them are toxic to aquatic biota. While the rate of deposition is low, the process is continuous and can lead to significant accumulation over time. Atmospheric transport is also one of the major pathways for the distribution of organic contaminants in the environment. The wet removal of airborne trace elements can occur when they provide suitable nuclei on which rain droplets can form (where the substance is in particulate or fine aerosol form), as well as by scavenging of particles and vapour partitioning in the atmosphere.

5 Sampling equipment, storage and preservation

Reference should be made to ISO 5667-3 for more details on the storage and preservation of samples. Trace metals and organic compounds are present in precipitation in minute quantities, and the utmost care should be taken to avoid contamination when handling these samples.

5.1 Sample containers

The laboratory responsible for analysing the samples should be consulted for recommendations regarding the type of container to be used for sample collection, storage and transportation.

5.1.1 Organic materials

Borosilicate and quartz glass bottles with polytetrafluoroethylene (PTFE)-lined caps are recommended for containers. The utmost care should be taken when handling samples in the laboratory to avoid contamination.

5.1.2 Inorganic materials

For inorganic compounds, high quality polyethylene containers are satisfactory and are the most commonly used. However, glass, PTFE, or high quality polypropylene containers are also satisfactory in certain cases.

5.2 Contamination by sample containers

Both funnels and collection bottles should be cleaned after each sampling period. To detect any widespread contamination caused by the bottle washing process, one sample bottle for every ten of each type being used should be treated as follows.

Ultrapure distilled water should be poured through a sample funnel into the bottle. The contents of the bottle should then be analysed along with the samples, and in the same way as the samples, for all the required parameters. The results are known as "bottle blanks".

5.3 Adsorption by sample containers

Some sample constituents, most notably trace metals and organic compounds, have a tendency to adsorb onto the walls of the sample container. In the case of the trace metals, it is advisable to acidify the sample with nitric acid. This will keep the metal ions in solution. Before selecting the sample container or the preservative, consult the laboratory chemists to determine if the container and preservative are suitable for the parameters in question and also compatible with the analytical methods in use in the laboratory.

5.4 Sample transfer

Sample transfer is one of the major causes of sample contamination and should be avoided whenever possible. Sealable polyethylene liners should be used with most collectors for inorganic parameters. However, if sample transfer is to be carried out, the sample container and the funnel should be clean, and the transfer should be carried out in a dust-free area.

NOTE 2 There should be no smoking or any other form of pollution (such as gasoline or solvent fumes) in the vicinity.

5.5 Sample transportation

After collection, samples should always be forwarded for analysis as soon as possible. Before shipping, always check that all the sample bottles recorded on the field sampling forms have been placed in the carton. Indicate the shipping date and mode of transport on the field sampling form.

The investigator should also retain a copy of the field sampling forms.

5.6 Sample storage

Proper storage of samples, as specified in sampling and storage protocols (e.g. ISO 5667-3), should be provided at the site whilst awaiting shipment, containment during shipment and storage at the laboratory whilst awaiting analysis.

At the site, the sample should be stored in a cool dark location, unless otherwise specified by the laboratory.

During transportation, the samples should be contained in vapour or gas-tight vessels and stored in insulated containers.

In the laboratory, the samples should be stored in special storage facilities.

5.7 Sample preservation

ISO 5667-3 provides general guidance on sample handling and preservation. Since physical changes, and chemical and biochemical reactions may take place in the sample container between the time that precipitation is collected in the field and until the time the sample is actually analysed in the laboratory, the samples must be preserved before shipping to prevent or minimize the changes. This can be done by various procedures, such as keeping the samples in the dark or using dark containers, adding chemical preservatives, lowering the temperature to retard reaction, freezing samples, field extraction procedures, column chromatography, or by a combination of these methods. Care must be taken to ensure that the chosen method of preservation does not interfere with subsequent analysis.

5.8 Sub-sampling

Sub-sampling should be carried out by the field operator who should label each bottle accordingly. In particular, the label should indicate whether the sample was filtered and if any chemical preservative was added. This is relevant to subsequent analysis.

5.9 Field measurements

Field measurements should always be made on a separate sub-sample, which is discarded once the measurements have been made. They should never

be made on the water sample which is returned to the analytical laboratory for chemical analysis.

Specific conductance should never be measured in sample water that was first used for pH measurements. Potassium chloride diffusing from the pH probe alters the conductivity of the sample.

6 Sampling techniques

6.1 Volume of sample

Before designing a precipitation sampler, the minimum volume of sample required to perform the necessary chemical analyses, to satisfy the objectives, needs to be known by consulting the laboratory responsible for the analysis. Then, the area of the collector opening needed to give the minimum sample volume should be calculated from the minimum depth of precipitation which is considered to be an event according to the study design. Adjustments should be made to the calculation to take into account the expected collection efficiencies of the samplers. Further details on sampling of rain are given in 6.4.1.

6.2 Organic materials

Sample collectors designed to collect precipitation samples for organic chemical analysis should be constructed of materials "inert" to organic materials. Materials which are recommended are stainless steel, glass, and PTFE. All other plastics materials should be avoided. When using stainless steel, care should be taken to ensure that any welding or brazing does not present a surface of absorption to the sample. Certain fluxes used in these techniques can contaminate the sample. It should be noted that only event samples, which are collected or extracted shortly after the precipitation, lead to representative results needed for the determination of organic parameters.

6.3 Physical parameters and inorganic compounds

For sampling precipitation for inorganic chemical analysis, a plastics or glass collector is recommended. Since trace metals may be adsorbed onto the sides of the plastics collectors, it is recommended to collect trace metal samples separately in a collector containing a measured quantity of nitric acid to prevent adsorption and to preserve the sample. If a distinction is required between dissolved and particulate phases of rainfall, the sample should be filtered (e.g. < 0,5 μm membrane filter) prior to acidification.

6.4 Sample collection

Precipitation samples can be collected in anything from a simple container to an automatic wet-only collector, provided that the criteria concerning the material of construction and siting are taken into

consideration. If accurate representative information on the chemical content of precipitation is required, wet-only collectors are recommended. However, bulk collectors can be used if it can be proven that the results obtained from them differ insignificantly from results from wet-only collectors. Some form of guard should also be incorporated in the design, to prevent contamination by bird droppings.

6.4.1 Rain

The principle of a rain collector is that rain is caught in the funnel or mouth of the bucket and stored until removed. The area of the necessary collection orifice should be determined. This will depend on the sampling strategy. For example, if the network is based on event sampling and the minimum event considered of interest is 1 mm of rainfall, then the area of orifice should be such that 1 mm of rainfall will provide 60 ml to 80 ml of sample. This is generally the minimum sample volume required for analysis. However, with the use of modern methods of analysis, a smaller sample volume may be adequate. A precipitation measuring gauge should be used as an indication of the collector efficiency, by comparing the actual precipitation measurement with that measured by the collector.

6.4.2 Snow

The collection of a representative sample of snowfall in all but calm conditions is difficult. This is due to the displacement and acceleration of the airflow caused by the aerodynamic blockage of the collector. This results in falling precipitation being displaced away from the collector opening.

The effect is more important for snow than rain, due to its lower falling speed.

Since wind eddies inside the collector can often remove collected snow from the collector, any shielded deep cylinder in which snow can accumulate should be used as a collector. Furthermore, since wet-only snow collectors are similar to the rain collectors, except that they are heated to thaw and store the entrapped snow as liquid in a compartment beneath the sampler, a standard snow gauge should be located adjacent to a snow collector to measure snow quantity.

6.5 Samplers

There are many commercially available precipitation samplers on the market today. It is not the intention of this part of ISO 5667 to provide details of all types of samplers. Operating instructions and maintenance guides contained in the manuals provided by the equipment suppliers should be used for guidance.

6.5.1 Event sampling

Where operators are on site or can sample on a daily basis, a clean bucket positioned at the onset of an event and removed immediately on cessation of the event is recommended as a minimum requirement. However, for off-site sampling, automatic wet-only samplers fitted with moisture sensing grids and solid state control circuits to operate their motor driven covers are recommended. These sensors have heaters to evaporate the moisture off the sensing grids at the end of the precipitation.

In the case of an automatic sampler, event sampling can be approximated by daily sampling, i.e. by emptying or changing the collector bucket every 24 h.

6.5.2 Composite samples

The automatic sampler described briefly in 6.5.1 should be used for composite sampling. The lid automatically opens for each event during the sampling period. The sample can be accumulated in the collector bucket itself or in a bottle attached to the funnel/bucket. At the end of the sampling period, the collector should be emptied or the bottle detached and the sample forwarded to the laboratory for chemical analysis.

Where automatic samplers are not available, the same effect can be achieved by sampling each event individually using a bucket and compositing the sample in a large bottle. The sample in the bucket is emptied into the bottle after each event. The funnel and the bucket should be cleaned after each rainfall event. At the end of the period, the bottle is forwarded to the laboratory for analysis.

6.5.3 Directional sampling

Directional sampling should be conducted to determine from which direction the pollutants in wet precipitation originate. Equipment designed for directional sampling near the ground usually consists of a funnel and wind vane. The outlet at the bottom of the funnel should direct the precipitation to one of a number of bottles, depending on the orientation of the wind vane. A detailed analysis of meteorological data is required, since the wind direction near the ground may differ from the direction of storm passage.

7 Sampling locations

7.1 General considerations

Before commencing to design a precipitation sampling network, the objectives need to be well defined. These determine the scale and density of sampling required. The design needs to be specific, applicable and responsive to the study objectives (e.g.

measurement of a local source, measurement of long-range transport, number of sources etc.).

7.2 Guidance on siting criteria

7.2.1 Introduction: urban and remote

Urban and industrial sites are generally used to study local problems or urban area sources and have short distances, ranging from a few hundred metres to a few kilometres, between the pollution sources and the environment that they affect.

Remote sites are used to study regional or continental scale issues. A regional issue has a source-receptor distance in the order of tens or a few hundreds of kilometres, whereas a continental or large scale issue has a source-receptor distance in the order of hundreds or a few thousands of kilometres.

The primary purpose of regional stations is to assess long-term changes in atmospheric deposition which may be related to changes in pollutant emissions or regional land-use practices or other man-induced activities. These stations should be in representative locations within the region and in essentially rural areas, so as not to be unduly influenced by fluctuations in pollution from built-up areas or other local sources as determined by background surveys.

Remote sites selected to address large scale concerns should be selected carefully, taking into account climatological and meteorological patterns and source characteristics. Furthermore, the sites should avoid the influences of any point or regional diffuse sources including changes in land use, or construction during the proposed sampling period. These can be determined through background monitoring or surveys of the area.

The siting criteria which follow are recommended for monitoring precipitation on a regional scale. General siting criteria for local sources are not given, since these should be determined on a case-by-case basis. A regional scale will usually encompass a rural area of reasonably homogeneous geography and climatology. It may extend from tens to hundreds of kilometres and may be expected to receive a fairly uniform impact from sources outside the region. Data characteristics of this scale provide information on larger scale processes of pollutant emissions, transformation, losses, and transport as they relate to precipitation deposition chemistry.

The siting criteria should be followed to the maximum extent possible, to ensure representative collection of data. It is recognized that there will be situations where these criteria cannot be followed in their entirety. In these cases, a rationale for identifying deviations from the criteria needs to be employed.

7.2.1.1 Distance from known man-made sources

In the case of regional and continental studies, preferably there should be no anthropogenic (man-made) emission sources which could affect precipitation chemistry within 50 km of the sampler. Sources farther than 50 km from the site are considered to exert a regional influence.

NOTE 3 For most or all smaller industrialized countries, it may be difficult to find suitable sites and this may influence the kinds of studies they can undertake.

Sites should not be considered to be regionally representative if

- a) there is a continuous industrial source, a town or suburban area located within 10 km;
- b) there is a major point source (e.g. > 10,000 tons of SO₂ per year) located within 50 km; or the sum of point source emissions within 50 km is greater than 10,000 tons per year, unless this is typical of the region;
- c) there is a surface pollutant storage facility (e.g. salt pile) located within 1 km;
- d) there are major transportation sources, furnaces, incinerators or sewage works located within 1 km, or minor sources or mobile sources such as air transport, shipping or other surface transportation located within 100 m.

7.2.1.2 Accessibility of site

The site should have year-round accessibility, preferably by road, and a supply of electricity (if possible).

7.2.1.3 Topography

The sampler should be installed over flat undisturbed land, which is open where possible but surrounded by trees which provide shelter from the wind. Any surface gradient in the vicinity of the sampler should be noted.

Buildings and trees may contribute to local problems by disturbing the airflow and generating additional turbulence. This can affect the collection efficiency of samplers, and, if they are too close, may also contaminate the sample. It is difficult to determine the minimum distance to avoid these effects but, as a general guideline, it is suggested that they should not be closer to the sampler than 5 to 10 times (preferably) their height. Local topographic factors are generally more important for snow collection than for rain.

The location chosen should be protected against vandalism by the provision of appropriate security measures.