



**A quick guide to the collection and
sampling of water for the analysis of stable
isotopes of hydrogen and oxygen in the
water molecule**

**Final report of working group 3 of the COST
ACTION WATSON**

Søren Jessen¹, Natalie Ceperley², Ladislav Holko³ and István Fórizs⁴

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1. Copenhagen University, Denmark (sj@ign.ku.dk)
2. Bern University, Switzerland (natalie.ceperley@giub.unibe.ch)
3. Institute of Hydrology, Slovak Academy of Sciences, Bratislava, Slovakia (holko@uh.savba.sk)
4. Research Centre for Astronomy and Earth Sciences, Hungary (forizs.istvan@csfk.mta.hu)

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A quick guide to the collection and sampling of water for the analysis of stable isotopes of hydrogen and oxygen in the water molecule

1. Introduction

This document provides a short guide to sampling of water for the analysis of its stable isotopes ^2H (deuterium), ^{17}O , and ^{18}O . The text is targeted towards hydrologists who are new to the use of stable isotopes of water, but who are already familiar with field methods required to collect a sample of water, meaning the collection of a portion of water that sufficiently represents the water body being sampled with respect to one's investigative objectives (cf. U.S. Geological Survey, 2006, 2018a). As an example, these field methods in many cases involve the clean pumping of a well prior to collection of a groundwater sample that represents the aquifer pore fluid. Thus, in this guide, *sampling* refers to the act of transferring a water sample into a suitable container, and of preventing alterations during storage and transport up until its analysis.

However, to many hydrologists, the collection of meteoric waters is new. The chapter therefore will provide recommendations for collection of meteoric water in form of precipitation, snow and snowmelt, and ice. In addition, many aspects of the text below are transferable to other compartments of water in the critical zone, such as dew (Prada *et al.*, 2015) and water in vegetation (Ceperly *et al.*, 2023).

Generally, sampling for stable isotopes of water is not complicated, and laser-based analysis of stable isotopes is both fast and relatively cheap, typically at about 10-30 € per sample. These aspects are important in making stable isotopes a powerful tool for hydrologists.

2. General recommendations for liquid water sampling and sample storage

This section describes the sampling of *liquid* water, such as surface water, groundwater, and precipitation collected by rainwater collectors (Section 0). Thorough guidance on collection of representative samples of groundwater and surface water is provided by, respectively, USGS (2006) and USGS (2018b).

Generally, fractionation due to evaporation is the most critical risk to a water sample intended for analysis for stable isotopes of water. In this context, it is important to note that the natural *in-situ* evaporation from surface water bodies (lake, river, pond, precipitation, etc.) should not be prevented. Such waters can be and are often collected and analyzed. But evaporation that occurs *after* sampling has to be prevented. Post-collection evaporation would distort the isotope value from its true value at the time of sampling. Evaporation *during* sampling, i.e. the basic act of putting water into a sampling bottle, is rarely of concern though. Therefore, **evaporation during transportation and storage of the sample must always be prevented.**

To prevent post-collection evaporation several steps can be taken: i) Sample vials or flasks could be made of glass or metal, although HDPE plastic is usually adequate; non-HDPE plastic materials should be avoided. ii) Caps need to be airtight or hermetically sealed, and without septum that allows gas diffusion to become significant over the duration of sample storage. Silicone septa in particular should be avoided. iii) Temperatures during sample storage should not oscillate dramatically, for instance in a car or many storage facilities between night and day. iv) Finally, evaporation of samples can be further hindered by cooling: refrigerating to 5°C, or freezing. When freezing, it is important to keep a 15vol% headspace in the sample vial/flask to allow for expansion during freezing. If expansion causes a loss of water from the sample container, the remaining sample will likely have become useless. Due to ice-water fractionation, the lost water will have been concentrated in light isotopes while the remaining sample will have experienced a major isotopic enrichment. v) Although only a few milliliters of water is typically needed for the analysis, it is recommended to collect much larger samples, e.g. 15 mL or larger.

As a general recommendation for sampling, collect duplicate samples of, for example, 15-17 mL in a dry 20 mL HDPE vial with an airtight cover. It is recommended to filter the sample with a 0.45 µm or finer pore size before the analysis to remove particles that might be problematic for the analyzer, and to reduce biological activity in the samples. The type of filter material is not important. Filter the sample in the field, e.g. using a syringe filter, is recommended. Filtration should be quick to minimize the risk of significant water evaporation.

A general recommendation for sample storage would be to keep the samples cold during field days of a sampling campaign in case of warm field conditions, e.g. by placing the samples on/with ice in the cooler box, but it is not absolutely necessary. As early as possible though, and when you return to your home institution, refrigerate the samples, or freeze them, if you intend to store them for several months or longer. When samples are shipped, they can be allowed to thaw during transport. The samples can be refrozen when they arrive to their destination.

3. Collection of precipitation

When collecting precipitation, preventing evaporation is less trivial. This is because precipitation is usually collected over a period of time of hours, days, weeks or one or a few months. The goal is usually to determine the average isotopic value of the accumulated precipitation without alteration by evaporation following the events of precipitation. Because precipitation collection is done accumulatively, it is necessary to note the start and end dates for each precipitation collection period.

Precipitation includes rain, snow and, in more specialized cases, also dew (e.g. Prada *et al.*, 2015). This guide first addresses the collection of precipitation in the form of rain, then it addresses the collection of snow and snowmelt.

4. Collecting rain water

Rain water collectors typically comprise a funnel connected with a thin hose to a collector flask. A small hole in the collector flask's lid allows air to escape as rain collects in the flask and the headspace volume decreases. Evaporation from the collector flask upwards through the funnel is prevented by letting the thin hose reach the bottom of the flask. In this way, the hose's lower end

becomes submerged after the first rain. Evaporation from the water surface within the hose and up through the funnel is usually ignored, due to the small water surface area within the hose and due to the sluggish diffusion along the length of the hose. Also evaporation from the much larger water surface, surrounding the thin hose, upwards through the air escape hole need to be prevented. The traditional way to prevent this important evaporation component is by the use of mineral oil in the collector flask. The oil creates a seal at the surface of the collected water, thereby preventing evaporation to the headspace of the collector flask and through the air escape hole. This methodology is effective and widely used, but it has to be considered that oil residues can cause problems in the analysis with common laser-based instruments. The use of mineral oil can be omitted by connecting the 'air escape hole' to a several meters long thin tube. The length of the tube ensures an adequately small humidity gradient along the tube so that evaporation from and fractionation effects on the collected water within the collector flask remains insignificant. This methodology was presented with the Palmex Rain Sampler RS1_ (Gröning *et al.*, 2012). The long tube is curled around the collector flask compartment resulting in an overall compact design of the rain collector. For any collector type, the product of the funnel area and the maximum amount of precipitation expected over a collection period should never exceed the collector flask volume.

As a general recommendation when sampling a rain collector, start out by recording the amount of water collected in the collector flask during the accumulation period. Then sample the collected water (as above) and, finally, empty and dry (or replace) the collector flask. Each time the collector flask is sampled, check that the collector flask has not become completely filled up during the accumulation period. Also make sure that the hose connecting the funnel to the collector flask has not become blocked: with the collector flask off, check that water can pass through the hose with ease. Then clean the hose by penetrating it with a steel wire, a straw, or a long-and-thin brush, to prevent buildup of smudge in the hose, before you remount the collector flask. If you find the collector flask completely filled up, or if the hose leading to it was not free enough from smudge, then no proper collection has been guaranteed for the whole sampling period at least for a while during the collection period, or water has only slowly seeped through the hose, allowing evaporation from the water in the funnel after the precipitation event. Always clean the hose when sampling.

5. Collecting snow and snowmelt

Snowpacks integrate precipitation from one or more precipitation events while concomitantly superimposing effects of sublimation, vapor diffusion, and thaw and freeze events. All those effects cause fractionation and mixing between the precipitation events and loss of melt water and its respective isotope concentration to the (sub)surface. Despite this complexity, occasional snowfalls that quickly melt at the study site are often collected simply as snowmelt using rain collectors. This is appropriate when the aim of the study is to characterize the (net) isotopic composition of input liquid water to groundwater and stream flow. If this sampling procedure is desired, it must be ensured that the total volume of snow between melting moments does not exceed the storage capacity of the funnel. In the case of the Palmex RS1 described above, the designers therefore recommend to increase the funnel storage by adding an additional 30 cm long tube on top of the funnel if snow is expected. Quantitative snow collection in the funnel remains strongly affected by losses attributable to wind (catch effects). Furthermore, the temperature regime controlling sublimation, vapor diffusion and freezing and thawing, and hence the isotopic composition of the melt, may be very different in a funnel compared to the natural analogue on the ground. Dedicated methods to obtain samples of snowmelt are described later.

Snowpack collection

Collection of samples from a snowpack or snow layers requires (i) high-quality bags that can be hermetically sealed in the field and that won't be easily punctured (commercial grade food bags work well), (ii) a controlled temperature environment (e.g., a cooler box in the field and/or a refrigerator at the home institution) to ensure a slow thaw processes at low temperature rather than a rapid phase change and corresponding evaporative fractionation, and (iii) vials for water sampling and storage (the same as described in Section 0). In the field, the snow sample can be collected vertically by a snow tube or by smaller cylinders that are inserted into discrete depths or layers of the snowpack. When the snow is placed in the sampling bags, the bags should be compressed to reduce the volume of contained air as much as possible. Once the snow has thawed completely, the bags with thawed snow should be well mixed in case of condensation on the walls of the bags. Then subsamples of the water in the bag may be filtered and collected into sample vials (Section 0).

When sampling snowpacks, one must consider which variables and values are important to the study. Which snow, in the layers of the snowpack, is of interest? New snow, old snow, or a composite value for the entire snow pack? And with which detail should snow textures, snowpack depths, layers thicknesses, temperatures, and snow density be recorded? In the case of deep snow packs, attention must be paid to pack stability to prevent collapse of the pit or local avalanche triggering. Snow sampling near a meteorological station adapted to record snow fall amount is advantageous.

Snowmelt water collection

For many hydrological applications, the isotopic composition of the snowpack is not actually of interest. It is the snowmelt water that enters the hydrological system from the melting snowpack. Except for the occasional snowfalls that melt quickly and are often sampled with a rain collector (Section 0), the dedicated sampling of the snowmelt water is not straight forward. A collector for snowmelt ideally must not change the temperature regime that controls when and how much snowmelt is generated from the snowpack. Snow lysimeters of different constructions have been proposed to collect the snowmelt water. A snow lysimeter is essentially a device that collects the meltwater from an area and directs it to a storage container (e.g., a flask) collecting the meltwater to be sampled. The lysimeter can for example be a plastic sheet, plastic or metallic drip pan, modified gutter, or rain gauge (e.g. Kattelman, 2000; Rucker *et al.*, 2019). Most snow lysimeters are designed to be sampled several times during the melting season. A passive capillary sampler (Penna *et al.*, 2014) has been developed that is especially suitable to collect just one or a few large samples that represent the entire winter, i.e. a cold season integrated sample. In many locations, snowmelt occurs at a very high rate during a short period of the year. Therefore, careful attention must be paid to ensure that the lysimeter can correctly operate/function throughout a whole season below snow cover and can handle the volume of melt that is expected during the spring melt period. Additionally, snowmelt may be accompanied by a significant debris flow, which presents another challenge to field instrumentation.

6. Automated sampling of liquid water

The use of automated sample collectors, e.g. ISCO-samplers for sampling streamwater or precipitation, has some peculiarities that need to be addressed. Autosamplers inherently store samples for a period of time before the samplers are visited by field personnel. During the in-sampler storage period, the samples may suffer evaporative fractionation or isotopic exchange via vapor mixing that will work to even out differences in isotopic composition between the collected samples. These alterations can be prevented using mineral oil or by modifying the autosampler's collection

flasks appropriately, e.g., see von Freyberg *et al.* (2020). The ideal is to make each collector flask in the autosampler act—as close as possible—as if it was a ‘small rain collector’.

7. Collecting ice

For ice sampling, an ice screw as those used for climbing can be used to obtain a cylindrical ice core that can either be placed directly into a water sampling vial or into a snow sampling bag and then treated like snow (see above). Ice samples may contain large amounts of debris and therefore samples may require filtration after thawing. In some cases an ice corer may be necessary, in order to access deeper ice (cf. Eicken *et al.*, 2014).

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