1. LOCATION OF SAMPLING POINT (COORDINATES)

The groundwater well sampling location must be recorded as accurately as possible, preferably using a handheld GPS, or a topographic map. Record the geographic coordinates (latitude, longitude) altitude/elevation, and helpful descriptive landmarks. Coordinates are preferably recorded from the GPS in decimal degrees (to four decimal places). Record time and date of sampling.

2. WELL WATER DEPTH MEASUREMENT

Before sampling, the static water level of the well should be recorded in meters below top of the casing, or known datum. Ideally, the top of the casing has been previously surveyed to elevation (m) above sea level. Depth to water (record in meters to 2 decimal places) is best determined using a low-cost commercial electric water level tape. Record the depth, and any other information about the well (total depth, screen length section(s), etc.).

3. PURGING OF WELL

After recording the static water level, purge the well using a pump or bailer. In general, at least three well volumes should be removed, or by continuous pumping, until stable parameters are observed (T, pH) before isotopic or chemistry samples are taken.

4. FIELD PHYSICO-CHEMICAL MEASUREMENTS

After purging, unstable and in-situ geochemical parameters should be taken and recorded. These parameters may include pH, temperature, electrical conductivity (EC), alkalinity and dissolved oxygen. Continual pumping of a sample through a flow-through cell gives the best results.

Electrical conductivity and temperature

The electrical conductivity meter must be calibrated in the laboratory before field use. A calibration standard with an EC of 1413 μS/cm at 25°C is sufficient for most groundwaters. To measure conductivity, the sample can be poured into a beaker, or use a flow-through cell with conductivity electrode inserted. Once the EC readings are stable, record the conductivity and temperature of the water sample.

pH

All pH meters should be operated according to the manufacturer’s instructions, and calibrated prior to field sampling. Two standard pH buffer solutions are typically used for this calibration that encompasses the expected range (pH 4, 7, and 10). To measure the pH of a sample, insert the electrode into the sample (beaker or preferably a flow-through cell), and wait for the pH readings to stabilize. Record pH to 2 decimal places. After completing measurements, rinse and wipe the electrode and store in an appropriate storage solution.

Alkalinity

Dissolved inorganic carbonate (DIC) alkalinity (as mg/L CaCO₃) is usually measured by chemical colorimetric titration using commercially available alkalinity field kits. Instructions
Dissolved oxygen
Dissolved oxygen (DO) is measured using a commercial membrane or optical sensor, or by Winkler titration. DO sensors are most convenient for the field use, these are either calibrated in the field (membrane sensors using 100% RH chambers), or do not require any calibration at all (optical DO sensors). Samples pumped through a flow-through cell are optimal to attain stable readings. DO is recorded in mg/L and % O$_2$ saturation (if temperature sensor is included).

5. FILTRATION, ACIDIFICATION AND LABELLING OF SAMPLES FOR CHEMISTRY

Field filtration of samples is essential for laboratory measurement of cations and anions. The filter should be a 0.45 micron (or smaller) membrane filter, which is available in many convenient configurations (e.g. syringe filters, vacuum, barrel, cartridge filters). For turbid waters, the use of a pre-filter (100–300 µm) aids in reducing 0.45 µm filter plugging.

After the sample is filtered, pour the filtered sample into 125 mL cation and a 125 mL anion HDPE sampling bottles. For cations, acidify the sample by adding a few drops of concentrated nitric acid, gently agitate the sample, and ensure the pH <2 (pH papers are suitable). For anions, the water sample is not acidified.

Tightly cap and label the sample bottles and store cold, if possible.

6. STABLE ISOTOPES

For $^{18}$O and $^2$H no filtration or preservation is required. Fill a 50 mL HDPE bottle directly with the groundwater sample. Clearly label the sample with all details, and tightly cap to avoid evaporation of the sample. For saline samples, recording EC data with the sample is useful.

7. TRITIUM

For tritium a 500 mL un-preserved groundwater sample is sufficient. Depending upon the tritium content and measurement technique, a 1 L sample may be required. HDPE or glass bottles are suitable for tritium sampling. Label bottles clearly and tightly cap to ensure no leakage.

8. CARBON ISOTOPES IN DIC

Field measurements of temperature, pH and alkalinity are essential for the interpretation of $^{14}$C and $^{13}$C data, and additional parameters, such as dissolved oxygen, redox potential may also be useful. For alkalinity, please verify the format reported by your equipment (i.e. alkalinity as HCO$_3$ or CaCO$_3$; reporting in mg/L or meq/L, etc.).

Accelerator mass spectrometry (preferable method)

For AMS (accelerator mass spectrometry) analysis of $^{14}$C (includes $^{13}$C), about 2 mg of inorganic C is required, therefore 100–500 mL of filtered water is typically needed depending
on the dissolved inorganic carbon (DIC) concentration. For duplicate measurements and ensuring sufficient volume in case of low DIC concentration, a 500 mL sample is recommended. Sample bottles should be HDPE and must be fully filled with no headspace and tightly sealed.

Results of field and laboratory experiments show that atmospheric CO$_2$ uptake can occur rapidly during direct precipitation of dissolved inorganic carbonate in hyperalkaline solutions, resulting in elevated $\text{^{14}C}$ contents. Uptake of CO$_2$ may also induce depletion in $\delta^{13}\text{C}$ due to kinetic isotope fractionation. Groundwater samples for $\text{^{14}C}+\text{^{13}C}$ analysis by AMS should be collected in the field by using plastic bottles submerged in an overflowing container. Dissolved inorganic carbon should then be extracted in the laboratory in a closed system for further measurements.

Samples should be preserved to eliminate microbial activity by adding 5 drops of I$_2$–KI solution per 100 mL sample. This I$_2$–KI solution can be prepared by dissolving 1.5 g I$_2$ and 3 g KI in 100 mL of demineralized water. Another possibility is to add 2 to 3 drops of saturated HgCl$_2$ solution. Unpreserved water samples should preferably be refrigerated and should be analysed within 30 days.

**Conventional liquid scintillation counting method (LSC)**

For $\text{^{13}C}$ and $\text{^{14}C}$ analyses, about 2.5 g of carbon are required. This amount of carbon may be obtained from a 40–60 L sample volume, depending upon the alkalinity of the water.

Fill the container up to the top with groundwater. Insert the stirrer and close the lid.

Add about 50 mL of carbonate-free concentrated sodium hydroxide to raise the pH of the sample to about 11 units. If necessary, confirm the raised pH of the sample by using pH testing paper or a pH meter. Carbonate-free sodium hydroxide solution should be prepared and aliquots bottled in a laboratory prior to the sampling campaign.

After adding sodium hydroxide, minimize exposure to the atmosphere so that atmospheric carbon dioxide does not contaminate the sample. Stir the sample using the stirrer. Add about 5 g of iron sulphate to the sample. This will facilitate formation of carbonate precipitate.
Add about 150 g of strontium chloride or barium chloride powder to form a fine cloud of carbonates. Close the lid and stir the sample.

Check for complete precipitation by adding a small amount (25–30 g) of chloride powder to the top of the tank without stirring. If any cloudiness appears, indicating further precipitation, more chloride powder and possibly sodium hydroxide solution must be stirred in to ensure complete precipitation.

Add 40 mL of Praestol solution to the sample. It is a polyacrylamide and is used as a coagulant to speed up this process. 

After addition of all these reagents, the precipitate quickly starts to settle to the bottom of the apparatus, filling the 1 L bottle attached to the bottom of the container. When all the precipitate settles, a rubber stopper fitted at the end of a steel rod is inserted and the container is closed at the bottom, so the filled 1 L bottle can be removed. If necessary, more bottles should be attached and all of the precipitate collected. Tightly cap and properly label the bottles, indicating the sample number, date, and other relevant details.

Typically 250 mL of filtered sample is sufficient, depending on the dissolved inorganic carbon concentration of the groundwater. Collect samples in HDPE or glass bottle with a tight seal. If the sample will be stored for more than a few weeks, I₂-KI solution or mercury (II) chloride (HgCl₂) may be added to eliminate microbial activity. Generally, 5–10 mg of carbonate is sufficient.

### 9. DISSOLVED NOBLE GAS ISOTOPES

Groundwater samples for noble gas isotope analysis are collected in copper tubes with specially designed clamps. Three different types of samplers are available from the IAEA — consult the IAEA staff about the choice of appropriate samplers. In either case, in order to avoid gas exchange with the atmosphere and degassing by pressure release, carefully establish a connection from a water outlet to samplers. It is recommended that water be pumped from the well or spring using a transparent plastic tube to visibly ensure that there is no entrapped air bubbles in flowing water.

**Cu-tube sampler**

Connect the plastic tube to the copper tube. Allow the water to flow through the copper tube. It is important to tap the frame lightly with the spanner to remove any air bubbles that may be trapped inside the copper tube. When ready to collect the sample, first close the outflow end of the copper tube by tightening the clamp properly and then close the clamp at the inflow end of the tube.

Label the sample using a waterproof marker on adhesive tape or on the metallic frame. Record sample number, date, time and temperature.

**Diffusion sampler**

Gas sampling for noble gas analysis can also be made by using diffusion samplers, which consist of a short piece of silicone tubing with short copper tubes on either end. Before using it, make sure that two clamps at the outer ends are closed by tightening up screws on the
clamps. Put a string to the sampler and submerge it to a desirable depth for sampling. Allow >24 hours for gas exchange through the silicone tubing to achieve equilibration of gases inside the sampler with the groundwater’s dissolved gas content. Before retrieval of samplers, record water temperature and total dissolved gas pressure at the same depth by using appropriate probes. Subsequently, retrieve the sampler and close internal clamps to seal the gas sample inside. This technique is simple and efficient, however, samplers need to be quickly removed and sealed before gas exchange occurs at the surface.

**Contact sampler**

A portable gas sampler can be provided for a direct gas sampling in the field. With this device, a direct gas sampling from groundwater is possible within 60 min without a need for external probes for water temperature and total dissolved gas pressures. A dedicated sampling manual will be provided. Contact the IAEA to consult about the use of this device.

**10. SUMMARY**

In summary, a normal set of groundwater samples obtained for the complete water chemistry and commonly analysed isotopes consists of:

- Field based measurements (conductivity, temperature, pH, alkalinity, DO, etc.);
- Two filtered groundwater samples for hydrochemistry, one acidified;
- One 500 mL (or 1 L) bottle for tritium;
- One 50 mL bottle for $^{18}$O and $^2$H;
- One 500 mL HDPE bottle for $^{14}$C-DIC by AMS, or if conventional, two 1 L bottles for wet carbonate precipitate for $^{14}$C and $^{13}$C measurements.

The field measurements and other details should be filled in the field sheets shown in the sample templates. They are also available at www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html.

*More detailed procedures on sampling can be provided by:*

*Isotope Hydrology Section*
*International Atomic Energy Agency*

*ihs@iaea.org, www.iaea.org/water*
### List of Samples for Isotope/Chemical Analysis

**Country and Project Code:** __________________________________________________________

**Submission Date:** ___/___/______

**Institute:** _______________________________________________________

**Responsible Officer:** _____________________________________________

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample ID (1)</th>
<th>Date yy/mm/dd</th>
<th>Type (2)</th>
<th>Number of bottles shipped</th>
<th>¹⁸O/²H</th>
<th>³H</th>
<th>¹³CDIC</th>
<th>¹⁴CDIC</th>
<th>Chem(3)</th>
<th>Noble gases</th>
<th>Other</th>
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<td>4</td>
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<td>x</td>
<td>x</td>
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(1) Sample ID must be unique and match the label affixed on the sample bottle.

(2) GWB-borehole; GWD-dug, shallow well; GWS-spring; SLA-lake; SRE-reservoir; SRI-river; SPR-precipitation.

(3) For water chemistry, major cations plus anions are assumed. Please indicate other parameters required.

Typical amount of sample required for analysis:
- ¹⁸O and ²H = 50 mL HDPE
- Tritium = 500 to 1000 mL, filtered, glass or HDPE
- For ¹⁴C/¹³C by AMS = filtered, 500 mL in HDPE or glass
- For ¹⁴C/¹³C by LSC = carbonate precipitate containing at least 2.5 g of inorganic carbon
- Chemistry: 125 mL for cations (filtered, acidified), 125 mL for anions (filtered, unpreserved).

Alternatively, a link to Excel Sample Submission Spreadsheet is provided: [http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html](http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html)
**SUPPLEMENTARY DATA COLLECTED IN THE FIELD**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample ID</th>
<th>Aquifer name</th>
<th>Sample depth (m)</th>
<th>GPS Location (Dec. Degrees)</th>
<th>Altitude (masl)</th>
<th>Field data</th>
<th>Alk. mg/L CaCO₃</th>
<th>Remarks</th>
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(a) For samples taken from aquifers, lakes, and reservoirs, the water or well depth field must be recorded.

(b) Coordinates can be taken with a handheld GPS, preferably in Decimal Degrees.
(please ensure your GPS is set to report Decimal Degrees using the WGS-84-datum).
Groundwater Sampling Procedures for Isotope Hydrology

Proper groundwater field sampling and accurate measurements of physicochemical and isotopic parameters are critical for scientific purposes to ensure sound data for interpretation and incorporation of results in global hydrological databases. This booklet is complementary to the IAEA video “Introduction to Water Sampling and Analysis for Isotope Hydrology”. It can be used as a field guide to ensure that procedures are performed correctly. Before starting a sampling campaign, ensure that all materials and equipment needed for field work have been properly checked (re-checked) and packed.