


TECHNICAL GUIDANCE

Groundwater Sampling Version 2.1

September 2023

Title: Groundwater sampling			
			
Document type: Technical guideline ISBN: 978-87-7871-353-7	TG. no.: G02	Version: 2.1	First Created: 10/10/2012
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	Pages: 41		
	Last update: 12/06/2023		
TG references	G01, G03, Technical Guideline groundwater data		

Contents

1 Introduction.....	2
2 Method	2
2.1 Time, place and period.....	3
2.2 Equipment	3
2.3 Procedure	9
2.3.1: Well inspection	9
2.3.2: GRUMO sampling	9
2.3.3: LOOP sampling	15
2.3.4: Filtration.....	16
2.3.5: Field analysis: pH, conductivity, oxygen, temperature and redox potential	22
2.3.6: Submission and storage of samples	26
2.3.7: Sampling for dating purposes	27
2.3.8: Discarding samples	27
2.4 Checklist	27
2.5 Maintenance of instruments	27
2.6 Special precautions – pitfalls.....	28
3 Data processing.....	28
4 Quality assurance	28
4.1 Quality assurance of method.....	28
4.2 Quality assurance of data and data submission.....	29
5 References	30
List of associated technical guidelines	31
6 Appendices	32
Appendix 6.1. Pumping table for electricity-driven pumps and montejus pumps	32
Appendix 6.2 Sampling vehicle equipment.....	35
Appendix 6.3. Overview of rules on handling of samples etc. of main components and trace elements	36

1 Introduction

Objectives

This technical guideline (TG) stipulates unambiguous instructions for the sampling, field analysis and submission of groundwater samples. The samples collected are a source of knowledge about the groundwater's chemical characteristics. Furthermore, the instruction serves to document the conditions under which groundwater monitoring is performed.

The EU directive on analysis quality in connection with groundwater monitoring – which supplements the Water Framework Directive, etc. (EU, 2009) – stipulates that field analyses must be performed to known standards and using a quality control system equivalent to the guidelines established in ISO 17025. The guidelines of this TG comply with the directive's field analysis requirements.

Principle

Water samples must reflect the water quality in the groundwater-bearing formations in which the well was established. Therefore, sampling activities must be performed in accordance with good sampling practice, and the technical design of the wells must be adequate (see G01 monitoring network). Good sampling practice is to be based on this TG and on the experience that the sample collector builds concerning site-specific conditions. Optimization of the sampling technique depends on a combination of technical decisions and the well's technical design, including the amount of particulate matter and the drawdown created during pumping.

2 Method

The sampling procedure is comprised by a total of four steps:

- Planning.
- Preparing the field vehicle by loading the needed equipment.
- Sampling.
- Submission of the samples collected.

Prior to the first sampling using the methods described in this TG, the well is to have been subject to thorough and prolonged pumping to decontaminate it (\neq purging) to conclude the construction of the well, see G01. The objective of decontaminating the well is to minimize any disturbance of the water's geochemical composition caused by the construction of the well.

When a new monitoring point is established, a series of specific items of information describing the technical characteristics of the point are recorded in Jupiter, and in MST's annual overview of station monitoring, see G01. This information is used during the planning of the sampling activities.

2.1 Time, place and period

Sampling may be performed all year round. However, at some monitoring points (typically terrain-near monitoring points), considerable variation in water chemistry is seen over the course of a year. To ensure inter-annual comparability, annual samples collected from a monitoring point should be taken in the same quarter every year.

Samples may be collected in most weather conditions. At below-zero temperatures, it is important to avoid that the water freezes in the pumps, tubing and in the “flow-cell kit”, and to store electrodes and other electronic equipment in frost-free conditions and may be calibrated to measure correctly at low temperatures.

If the terrain is very muddy and soft, e.g. following prolonged periods of rain, it is important to minimize any damage made to the fields when driving in the terrain, and to be aware of the risk of getting stuck and needing assistance to free the vehicle. It may be expedient to delay sampling to a period with prolonged frost or dry weather to improve the bearing capacity of the ground for heavy vehicles.

When sampling in high winds at risk of soil drifting, any handling of sample bottles, filtration equipment, etc. is to be done in a sheltered environment, e.g. inside the vehicle, to avoid contamination of the samples. Correspondingly, when sampling in heavy rain, it is important to avoid sample contamination by rainwater.

2.2 Equipment

Groundwater sampling requires much equipment as groundwater may only be sampled through wells from which water is extracted by use of pumps, which depend on electricity or other propellants (e.g. air) to raise the water. Well construction is described in TG: G01-monitoring network.

Groundwater sampling depends on various types of equipment as detailed below:

- Field vehicle (sampling vehicle, see Appendix 6.2)
- Batteries or generators to produce electricity
- Compressed air containers or other equipment to produce compressed air
- Pumps
- Hoses and hose trolleys
- Manual water level meters
- Field analysis equipment
- Filtration equipment
- Rubber gloves
- Plugs
- Padlocks
- Fittings and couplings
- Toolbox with fittings, etc., to maintain wells in good working order

All of these types of equipment are prepared before every sampling and maintained continually. Equipment used for sampling clean groundwater must be kept separate from equipment used for point source investigations.

Field vehicle (Sampling vehicles)

As groundwater monitoring requires much equipment, efficient planning and execution of sampling activities requires specially adapted field vehicles to allow for transport of propellants, hoses, screening equipment, boxes with rubber gloves and field analysis equipment. The collected samples must be stored at a low temperature, and therefore the field vehicle needs to have a refrigerator built in or the capacity for safe transport of cooling boxes. When fitting the vehicle, care should be taken to minimize the risk of contamination of sampling equipment and the collected samples. Consequently, petrol for generators, etc., should be kept well separated from hoses and bottles. Furthermore, the vehicle must enable the continual cleaning of hoses, filtration and field measurement equipment.

It is often useful to carry a simple camping table as part of the vehicle's standard equipment so that sample bottles may be placed on a table during sampling to avoid contact with mud and hence contamination of the sample when it is handled in the field or subsequently at the laboratory. This is particularly relevant if many (>4) subsamples are collected.

It is a good idea to include a brush cutter in the field truck's equipment, so that the work area around the well can be kept clear of tall-growing vegetation and scrub.

Adapting and outfitting the vehicle are beyond the scope of this guideline.

Power supply, e.g. with generators and propellants

Solutions with batteries or mobile generators can be used, possibly built into the car. The choice of generator depends on the force needed, as greater lift heights or a need for high performance require large amounts of energy. Technologies with battery and frequency converters are now so developed that they should be preferred for most tasks.

When a mobile generator is needed, the working environment in the field must be considered, as there may be a lot of heavy lifting involved. Lifting can be reduced by either using a lift when there is insufficient power from the battery, or a generator built into the sampling vehicle.

The vehicle or generator is placed so that the wind removes exhaust gasses from the sampling area, as samples may otherwise become contaminated by organic micro-pollutants.

Rechargeable batteries are used as an energy source in e.g. peristaltic pumps. It is important to make sure that batteries as well as spare batteries are fully charged before a field trip.

The field working environment should be considered when choosing generators, as a lighter model or a built-in generator may serve to avoid a great number of heavy lifts in future. The amount of heavy lifts can also be reduced, by a built in crane to move the mobile generator in and out of the field wagon.

The need for propellants in the form of compressed air delivered by a compressor or compressed nitrogen container also depends on the pumps selected for the task. It is very important that any propellant (gas) that may come into direct contact with the water samples during sampling has a high degree of purity, i.e. nitrogen of grade 4.6 or above. This means that the oxygen content should not exceed 5 ppm. Poorer grade nitrogen contains considerable quantities of oxygen which may change the sample's chemical composition during sampling. There may also be a risk of clogging with precipitated iron oxides in the sampling chamber in-between samplings if the chamber holds oxygenic air and reduced water.

Pumps

The choice of pumps is described in the Technical Guidance on construction of monitoring networks, G01.

The choice of pump is generally made when the well is constructed, but technical conditions and technological advances may make it appropriate to replace the pump if it results in a more efficient sampling of the well in question. The decision on pump type is a trade-off between the economic costs derived from replacing the pump on one hand, and the amount of working hours saved on the other, as well as the expected sample quality if the pumping strategy changes. Finally, it should be assessed if sample quality will change as a result of changing the pump. A pump with a lower performance may, e.g., reduce the content of particulate matter and decrease an otherwise problematic drawdown of the water table. In wells with much particulate matter, this may lead to a higher sample quality, and in some cases the increased pumping time may be compensated through a reduction of filtration costs (time and materials).

Built-in pumps are standard equipment at all monitoring points unless special circumstances apply. This ensures an effective sampling procedure while cross contamination issues are avoided as contaminated water is not transferred from one well to the next.

Not every pump type is equally suitable for every parameter type. A suction pump can be used for some "non-volatile compounds", but suction pumps are unsuitable for a considerable number of parameters, as the sample's content of decomposed gasses is changed, which causes changes in the pH value and oxygen content of the sample. Additionally, there is a risk of losing volatile compounds. Suction pumps may, e.g., be used for purging after which the sample is extracted using another type of pump.

Unless special circumstances apply, the following pumps should be used for sampling:

- Submersible pumps based on the centrifugal principle with frequency adjustment
- Montejus pumps
- AP1 pumps ("bladder pumps")
- Whale pumps
- Peristaltic pumps

Cleaning of pumps

If exceptional circumstances demand that a mobile pump be used, it must be cleaned thoroughly before being moved to another monitoring point. The pump must be rinsed with groundwater free of organic compounds exceeding the drinking water threshold concentrations. The pump should not previously have been used in a well employed for monitoring or mapping of contaminated soil or landfills. In very poorly yielding wells (outputs below approx. 1 L/min), mobile pumps should generally not be used. However, for investigation or monitoring of a short duration, mobile pumps may prove more practical than built-in pumps.

Mobile pumps are rinsed through prior to sampling using one of the methods described below. The choice of cleaning method depends on the pump and the well's yield.

The pump runs for a minimum of 30 minutes, yield > 2 L/min.

A minimum of 100 L are pumped through the hoses.

In very poorly yielding wells (less than 2 L/min), hoses are rinsed through by applying at least 10 times the total hose volume.

Example calculation of water in the hoses:

Length = 50 m hose with a d = 4 cm inner diameter:

$$V = L * \pi (d/2)^2 \approx 63 \text{ litres.}$$

100 m with a 2 cm inner diameter

$$V = L * \pi (d/2)^2 \approx 31 \text{ litres.}$$

10 m hose with an inner diameter of 1 cm

$$V = L * \pi (d/2)^2 \approx 0,7 \text{ litre.}$$

Note: Rinsing is instrumental in avoiding cross-contamination with readily soluble compounds at concentrations below the drinking water threshold criteria but will not protect against risk of cross-contamination if the pump and hoses were previously used in a severely contaminated well.

Hoses used for sampling must therefore not previously have been used for sampling in connection with point source investigations.

Hoses and hose trolleys

When choosing hoses and tubes, it is essential to select materials which will neither transfer to nor absorb any matter from the samples. Comprehensive, experience-based literature is available on this subject (Sørensen, 2009, and AVJ, 2003). The risk of transfer depends on the choice of materials and on the velocity at which water flows through the hose. In poorly yielding wells, hoses with a lower degree of diffusion are needed to avoid oxygen absorption or loss of CO₂ from the surroundings, which would change the sample's chemical composition while it is being extracted.

As a general rule, VA-approved polyethylene pump hoses must be used, and in addition, for the actual sampling, short hose nozzles made of uncolored PEL, which are attached to the extension of the exit hose from the pump and have direct contact with the bottles. When taking samples for the PFAS substance group, tubes made of Teflon must NEVER be used, as the reference laboratory advises against this, due to the risk of contamination (Method data sheet, M068-2015). Instead, it is recommended to use clean, new, disposable PEL hose pieces, typically with a diameter of 10 mm, to insert into the bottle, cf. the laboratory's instructions.

Hose trolleys are used in connection with mobile pumps to keep hoses from coming into contact with the ground during sampling and to ensure a practical and efficient execution of the work.

Generally, hoses shall be kept clean and any kind of cross contamination between wells shall be avoided through due care and cleanliness during sampling. Despite such care, hoses may come into contact with the ground and in such cases, they shall be rinsed off using drinking-quality water.

Hoses, filter holders and other equipment that comes into direct contact with the samples must be washed using demineralized water and rinsed in acid between every sampling. For acid rinsing, approx. 1M HCL is used, cf. Danish Standards 2214. The acid used must be of laboratory-grade purity.

Hoses may not be stored with any volatile substances such as petrol, etc., as experience has shown that hoses may absorb petrol fumes, etc., and subsequently release these into the water samples. This e.g. applies when a petrol can is stored along with hoses in a field vehicle.

Manual water level meters

Manual water level meters are used to perform single measurements. The measurement must be registered by light or sound. Measurement accuracy is 1 cm, see also G03. The water level meter and electrical tape are kept clean to avoid cross contamination when used at several wells. Soil and dirt are removed by rinsing with drinking-quality water. Electrical tapes that were previously used at severely contaminated wells may not be used for groundwater monitoring, see G03.

Filtration equipment

Generally, filtration is done online by applying pumping pressure, the pressure overcoming the resistance of the filter. Either disposable filters are used for this or a specialized filter holder, which is placed directly onto the pump exit hose, if needed via an adapter.

At some monitoring points, e.g. points with a low yield or low pumping pressure, filtration needs to be done on a subsample by pressure filtration. This, however, requires a propellant (N_2 of grade 4.6 or above).

Furthermore, hand-operated syringes with specially designed disposable filters may also be used, see Figure 4.

The filtration procedure is discussed in Section 2.3.4.

Field analysis equipment

Field analyses are performed in flow-through cells mounted together in a practical and easy-to-operate device called a "flow-cell kit". Analyses are made using electrodes, and data on pH, conductivity, oxygen, temperature and redox potential are collected.

A series of potentiometers are used to measure the relevant parameters. The electrodes are generally sensitive to below-zero temperatures and operating these in very cold weather requires extra attention.

Field analyses are discussed in Section 2.3.5.

Safety

Field work requires the use of heavy equipment (> 20-30 kgs), electricity in a humid environment, pressure containers, pumping systems which operate at high pressure, etc. Some monitoring points are placed inside wells which the sampling staff need to enter. It is therefore necessary to be aware of the work safety measures needed to avoid accidents; see guidelines published by the Danish Working Environment Authority and the safety provisions of the workplace. The design of a safe workplace shall go hand in hand with effective planning of the work and form part of the overall planning and preparation of the field work. A presentation of work safety provisions, etc., is beyond the scope of the present technical guidance, see e.g. AVJ, 2003.

2.3 Procedure

2.3.1: Well inspection

The well is inspected upon arrival. Inspection results are noted on the pumping table.

For well inspections at which no sampling is performed, a standard pumping table or a special inspection table may be used.

- In the immediate vicinity, any grass is mowed and any shrubbery removed to facilitate future sampling. The extent of these clearing activities is noted on the pumping table. Use a brush cutter for ease.
- If there are signs of any use of pesticides/insecticides close to or on the well, this is noted.
- Next, the sampler checks if the well seems to be in good working order and free of any damage, e.g. from vehicle impact or otherwise. Any observations made are noted on the pumping table. (Collisions, removal of shrubbery, etc., all tubes closed by lids/plugs, rusty screws, etc.)
- The well is unlocked, and it is checked if the padlock needs to be greased or replaced. Use restricted (system) keys so that all installations will open using the same key.
- The well ID and any monitoring point IDs are checked by going through the signs. Missing or broken signs are replaced. A well sign template is available at the GEUS Well Data Archive website.
- The well is measured, and any measurements are recorded in the pumping table.
- Next, the upper inside of the well is inspected for casing damage and to check if the casing closes tightly (no whistling sounds in the casing) and if there are any unwanted animals or insects, etc., in the upper part of the well. Signs of stagnant water around the casing are noted.
- If the inspection identifies a need for repairs, this is noted in the pumping table. All information is entered into the relevant databases when returning from the field.

2.3.2: GRUMO sampling

Groundwater samples are taken from wells in which the water enters through a screen or, less frequently, from an open cavity in solid limestone or rock. In any case, the challenge is to achieve a sample that is representative of the chemical composition of the groundwater in the formations of the screened interval. The sample should not be affected by the sampling process nor contain water which has remained stagnant in the casing for a longer period of time (annulus water).

The sampling is prepared before going into the field; bottles are ordered, an agreement to submit the samples to the laboratory is made and the relevant equipment prepared. Preparation of field measurement equipment (calibration, etc.) is described in Section 2.3.5.

During the entire sampling process, a pumping table is used to make note of all relevant observations, see Appendix 6.1. However, some intakes may be designed so that they technically do not enable water level measurement. This especially applies in the LOOP areas.

After arriving at the well and inspecting it (2.3.1), sampling follows the following standard steps, based on available knowledge about the well:

- All monitoring points in the well are measured and measurements are noted in the pumping table. If several monitoring points are to be sampled, the uppermost point is sampled first.
- The relevant pump in the relevant monitoring point is started in accordance with the procedure and planned yield established for such work. The time, yield and type of pump are noted in the pumping table.
- The well is purged and drawdown of the water table noted in the pumping table (see below).
- The pump is wound down, if possible, and the new (reduced) yield is noted.
- Field analyses are made, and results noted in the pumping table (see below).
- The planned samples are taken. Any subsamples taken are noted in the pumping table (see procedure below).
- Check that the pumping table is filled in correctly and that all relevant information for the laboratory has been entered before filling in the laboratory requisition form, 2.3.6.
- The pump is turned off, all tubes are plugged, and the well is locked.

Single groundwater level measurements

The method used to measure the groundwater table, and the subsequently needed calculations are described in detail in G03: measurement of groundwater levels.

When single measurements of the groundwater table are made for the GRUMO and the LOOP, it is important to measure the groundwater table in all monitoring points of the well; if possible, this should be done *before* turning on the pump. These measurements are subsequently entered into Jupiter – not the operational measurements where there is ongoing pumping from intakes in the well, as the drawdown can be transmitted to other intakes.

Purging

The objective of purging is to ensure that no stagnant water from the casing (annulus water) is included in the water sample, thereby ensuring that the sample is representative of the groundwater found in the aquifer.

The same procedure should be followed every time and a description should be made for each monitoring point detailing the chosen fixed procedure, including the water volume to be removed prior to sampling. The description is brought during field work along with previous field tables (electronically, if preferred), so that information from previous samplings is at hand.

All relevant data from purging are noted in the pumping table: type of pump, yield, drawdown, appearance of the extracted water and any field analyses made. Changes in these data with respect to previous visits to the well may be an indication that the well is leaking water or that other physical conditions have changed. In such cases, the cause of the change should be determined before sampling is repeated. The issue is noted in the Comments field for the laboratory to enter into the database.

During purging, the yield is measured so that the amount of water extracted may be calculated. This is done, e.g., by filling a 10-litre bucket while timing the process with a watch to record how many seconds it takes to fill the bucket. The accuracy achieved using this method is sufficient. In poorly yielding wells, the yield is measured using a 1-litre measuring cup.

Purging is done at a higher output than sampling as the yield is reduced immediately before samples are taken, unless this is not technically possible (as is the case for montejus pumps). The difference needed between yields will depend on the drawdown of the well. By decreasing the output, the water table rises in the casing and therefore any remaining annulus water rises above the intake of the pump.

While purging, the drawdown is monitored continuously through measurements, and care is taken to avoid that the water table does not fall below the top of the screen. If this is unavoidable, a note is made stating this on the pumping table. The note is later entered into the Comments field of the analysis so that the laboratory may enter it into the database. All groundwater level measurements are noted in the field table.

If the temperature rises substantially, this may be an indication that the pump is running dry (excessive drawdown) or of a technical defect. In such case, the sampler reduces the output (causing the water table to rise once again). It may be necessary to substitute with another type of pump or to remove the pump to determine any need for maintenance.

Inevitably, the purging procedure will vary from one well to the next, as there is considerable variation in the quantity and type of particulate matter, yield and drawdown. It is particularly important to be aware of the risk of losing any gaseous components and the risk of oxygenation of water samples from aquifers with reduced conditions.

Note that several hours of purging may be needed at some very poorly yielding monitoring points. A higher yielding monitoring point may be sampled meanwhile. There must not be any hydraulic contact between two monitoring points, which are pumped simultaneously.

Field analyses made during purging

To the extent that this is technically possible, the continuous field analyses of pH, oxygen, conductivity, temperature and redox potential are made during purging. All data are noted in the pumping table and compared to previous samplings. The sample may not normally be taken until stable values of pH, oxygen and conductivity have been achieved, see Table 1. Note that the interval between measurements depends on the quantity of water extracted. Generally, it is not necessary to repeat the analysis until at least ½ a well volume has been extracted. For practical reasons, measurements may be started once the majority of the volume calculated for purging has been extracted. See technical guidance, GO1.

In a limited number of wells, it is not possible to make field measurements online. This is stated in the description of the standard sampling procedure. In these wells, sampling is done by storing the water in a container where each of the parameters can subsequently be measured using the electrodes. When measurements cannot be made online, this is noted in the pumping table.

Table 1 presents stable water quality requirements. In some very poorly yielding wells, the interval between field measurements exceeds 30 minutes as the annulus water is removed very slowly. Therefore, the chemical composition of the water in the well also changes at a modest pace compared with the requirements outlined in Table 1. This is particularly problematic if a poorly yielding well also has a large diameter or a high volume of annulus water.

Parameter	Criteria for stable water quality
pH	± 0.1
Conductivity	± 3%
Dissolved O ₂	± 0.3 mg/l
Redox potential	± 10 mV

Table 1. Stable water quality criteria for commonly used quality parameters /US-EPA, 2002/

If measurements are not stable after the calculated purge, the purging time is extended by up to 50%. If the well remains unstable, this is noted in the pumping table. The note is copied to the Comments field of the requisition form. Furthermore, the note is copied to the Danish Nature Agency's overview of well inspections.

Purging technique

Purging serves to remove any particulate matter from the well, including iron deposits. If the water is very turbid, purging shall be performed in such a manner that the particulate matter from the stagnant water in the well is removed. This should be done so gently that accumulation of new particulate matter from the formation is minimized. The removed volume of water shall be sufficiently large to ensure that there will be no annulus water left

when the sample is taken. If it is possible to raise the water table after purging and before the sample is taken, less water needs to be removed than if water is constantly abstracted throughout the sampling process. See figure 1 for well hydrology.

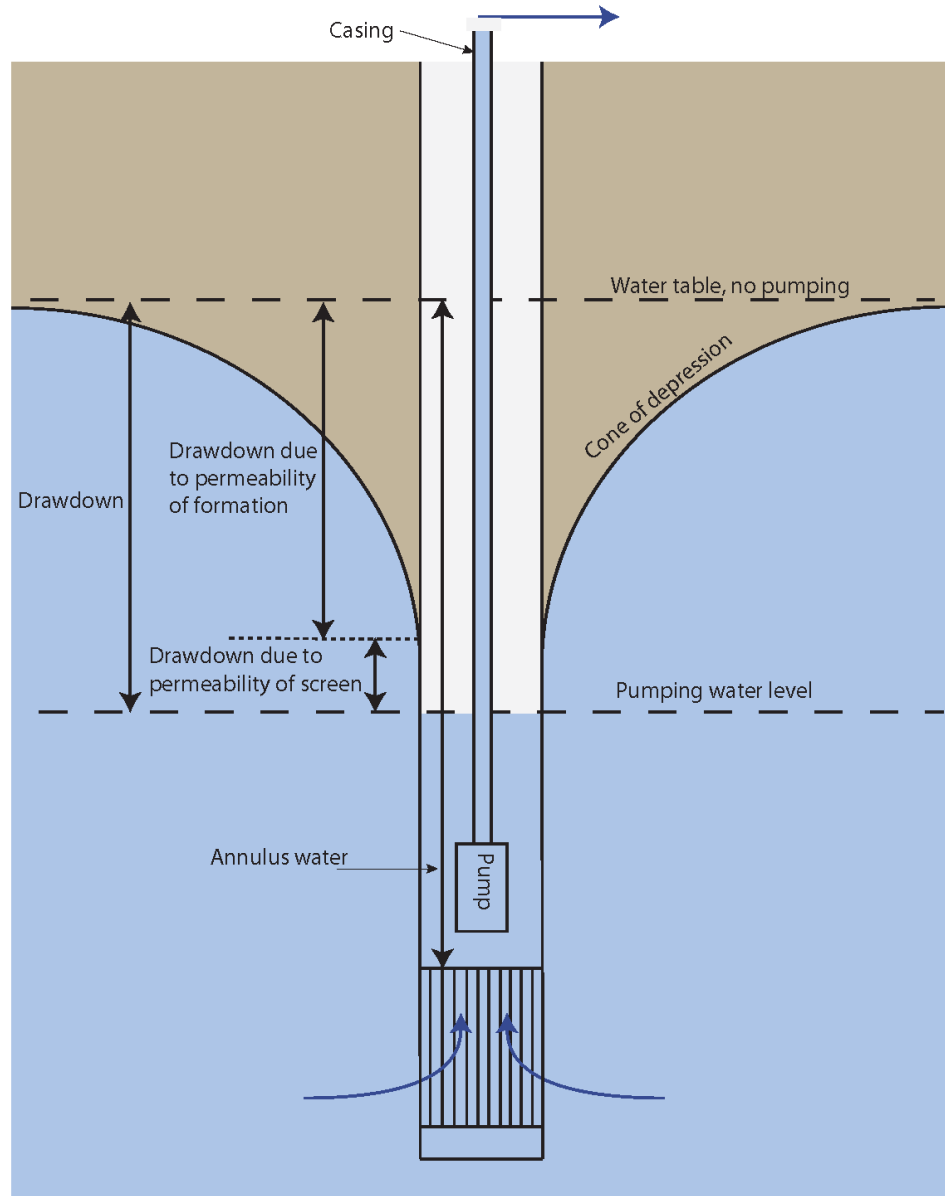


Figure 1. Principle sketch showing the well hydrology, water table, annulus water, etc., of a monitoring well. (BFN, GEUS)

If there is a sediment box below the screen, it is important to take care to avoid that matter is stirred up from the box during sampling. Stirring up particulate matter will prolong purging. Now and again, it is necessary to remove deposits and other sediments from the sediment box. The frequency varies considerably, and if a well requires frequent (annual) clean-up, this should be stated in the standard procedure. After cleaning up the sediment box, a note about this is made in the pumping table, including information about the clean-up procedure.

In monitoring wells with short intakes which yield clear water, purging by extraction of 5-10 times the following volume is sufficient: $V \leq 10 \times (\text{the casing's inner cross-sectional area} \times \text{screen length} + \text{water volume of draw-down})$.

Long screens may lead to prolonged purging periods. The pump intake placement and the pump arrangement also affect the extent of purging.

It is not always possible to carry out purging correctly if the well is very low-yielding. Such wells are emptied once or twice, and the water sample is then taken, once sufficient water has returned. This is stated in the Comments field on the requisition.

During purging, pressure shocks should be avoided as rapid pressure changes cause clay and silt to dislodge from the surrounding sediments and be carried with the groundwater current into the well. By using submersible pumps with frequency adjustment (e.g. MP-1 pumps), it is possible to decrease this effect by slowly increasing the output to the desired level.

When montejus pumps are used, the drop in pressure caused by each piston pulse may dislodge matter from the geological formation outside the screen or encrustations of e.g. ochre or organic material. This may be avoided by ensuring that pressure release occurs slowly through a valve.

For further information on purging, please see the references.

The special problems associated with poorly yielding monitoring points are also detailed in "Aarhus County, 1991: Grundvandsboringer [Groundwater wells]".

How to fill sample bottles

The laboratory's filling instruction is followed. It is important to be aware of how much water needs to go in every bottle and to know the minimum volumes needed to perform the analyses with an adequate level of reliability.

Unfiltered samples:

Normally, the sample container is filled from the bottom up. A fully cleaned (see section on hoses) PEL hose is mounted on the exit hose of the pump and its free end is placed at the bottom of the bottle. When the bottle is closed, it should be filled completely or to the neck, cf. the laboratory's instructions. Some bottles should not be filled from the bottom up and should not allow for overflow as they contain acid or other substances.

NOTE: if sampling is done for PFAS, Teflon material must not be used. Good alternatives are available, for example in uncolored PEL (Method data sheet M068).

Filtrated subsamples:

The samples are filtrated according to procedure 3, see below. Some filtrated samples are filled onto bottles which already contain acid or other compounds. In such cases, overflow is not allowed, cf. guidelines from the laboratory.

Follow DS/EN ISO 5667-3 and the method data sheets from the Reference Laboratory.

The sample is stored in a cold and dark place, such as a cooling bag or refrigerator, immediately after sampling and until it may be submitted to the laboratory. Special attention should be given to ensure that subsamples kept in small bottles or subsamples from poorly yielding wells are not exposed to sunlight for prolonged periods of time before being cooled.

Labelling of groundwater samples

All sample containers are labelled in accordance with the agreement with the laboratory, in a manner ensuring unambiguous identification of every sample, e.g. using a bar code. The labelling system shall be used on the pumping table as well as on the requisition form submitted to the laboratory.

All sample containers holding subsamples from the same sampling carry the same ID and, additionally, it is be stated clearly which samples have been filtrated. In addition to date and time, the unambiguous sample IDs shall detail the well's DGU number and the monitoring point number. For further information, please see the technical guidance on groundwater data (DG-01-2).

2.3.3: LOOP sampling

LOOP sampling is performed as in GRUMO. However, it is important to take into account that the groundwater inflow to the monitoring point is, in some cases, very slow, particularly in catchments with clayey soils. Consequently, it is not possible to perform optimal pumping at all monitoring points.

Standard pumping is often not possible; instead, the individual montejus screen is (based on experience) to be emptied from three times immediately before sampling to once a few days before the sampling. Experience shows that it may be necessary to employ extra purging/emptying prior to the pumping, if the monitoring point has not been used for a prolonged period of time ($\frac{1}{2}$ -1 year or more). This trend is more pronounced in wells with problems caused by particulate matter.

As for GRUMO, a description of the sampling conditions and the optimal procedures, based on previous experience, shall be made for each monitoring point and shall be at hand when visiting the monitoring point.

If online field analyses ("flow-cell kit") or online filtration cannot be performed, the field analyses are done in a beaker that is carefully filled from

below. The beaker can be filled with nitrogen gas beforehand to avoid contamination with atmospheric oxygen. The field analyses are prioritized as follows: The most important parameter is oxygen, then pH, redox potential and conductivity. Since several of the electrodes measure the temperature, a measurement of this is always achieved in practice.

For subsequent analysis of the unfiltered subsample's main components, it is possible to use a water sample that was previously analysed for oxygen, conductivity and pH. This procedure yields as much information on the water's chemical components as possible.

Note: The special LOOP well constructions mean that at many monitoring points, oxygen analyses may best be done using a peristaltic pump rather than the built-in montejus pump. The peristaltic pump ensures a steady flow of water at the electrode. If a montejus pump is used, it is important to avoid propellant blowout through the "flow-cell kit", as the electrodes may become damaged and oxygen and pH measurements may be affected.

Filtration shall be by pressure filtration, see Figure 3, or by hand syringe, see Figure 4. Please also refer to the guidelines provided in Section 2.3.4 on filtration.

2.3.4: Filtration

Appendix 6.3 shows the parameters that require filtration before analysis. Generally, the sample is not filtered for analysis for organic pollution components such as pesticides, chlorinated aliphatics etc.

Normally, filtration is an online process as the pump creates the pressure needed for the water to pass through the filter mounted directly on the exit hose. If this is not technically possible, filtration shall be done immediately after sampling, but this increases the risk of contamination with oxygen/CO₂ degasification. When non-online filtration is performed, N₂ pressure filtration of quality grade 4.6 or superior, or a hand syringe is used.

After filtration, it must be checked that the filter is intact.

Online filtration in LOOP requires considerable caution as the built-in pumps (montejus) are not designed for high pressures. Filtration is also a working environment issue as high pressure is associated with a risk of accidents in some montejus pumps.

Equipment

For online filtration, a filter holder is placed on the pump exit hose. To ensure a constant flow, you often have to use a 3-way tap, which divides the water flow from the pump. Valves on the 3-way tap can be adjusted and ensure the necessary pressure for filtration.

If a filter of the type shown in figures 2 and 4 is used (so-called syringe filters), gloves are not necessary, as there is no risk of the filter itself being touched by fingers or otherwise contaminated.

If you use loose filters in a filter holder, you must use plastic gloves, which must be discarded after each sampling. If the sub-sample is to be used for trace substances, the filter must be placed in the filter holder using cleaned plastic tweezers and must not be manipulated by hand. The filter holder must be designed so that the filter is not damaged by the pressure from the pump. This can, e.g., be via a venting mechanism, so that air above the filter can escape and the pressure above the filter slowly increases. After sampling, check whether the filter is intact. If there are signs that the filter is damaged or has moved, the sub-sample is repeated taken again.

Filter type

It is important that the filter in no way affects the chemical composition of the sample with regard to the compounds which will be analysed in the sub-sample. When filters are acquired, it shall be checked that the filter will cause no contamination. If the laboratory supplies the filters for sampling, the laboratory shall document that the filters will not change the sample's chemical composition with regard to the relevant analysis parameters. All filters should have a pore width of 0.40-0.45 μm . If the sample contains much particulate matter, a pre-filter with a greater pore width should be inserted prior to the filter. The pre-filter shall also be of a quality guaranteeing that the subsample's content of the compounds tested for will not be affected.

The choice of filter type and material must be made after a concrete assessment and testing. General instructions cannot be given, since not all types of filter materials will be suitable.

Online filtration

If you use an online filter, the actual filter can be filters embedded in plastic, they can be loose disposable filters, or alternatively filters placed in filter holders supplied by the analysis laboratory.

Figure 2 shows an example of online filtration over a cast-in disposable filter using the pump pressure.

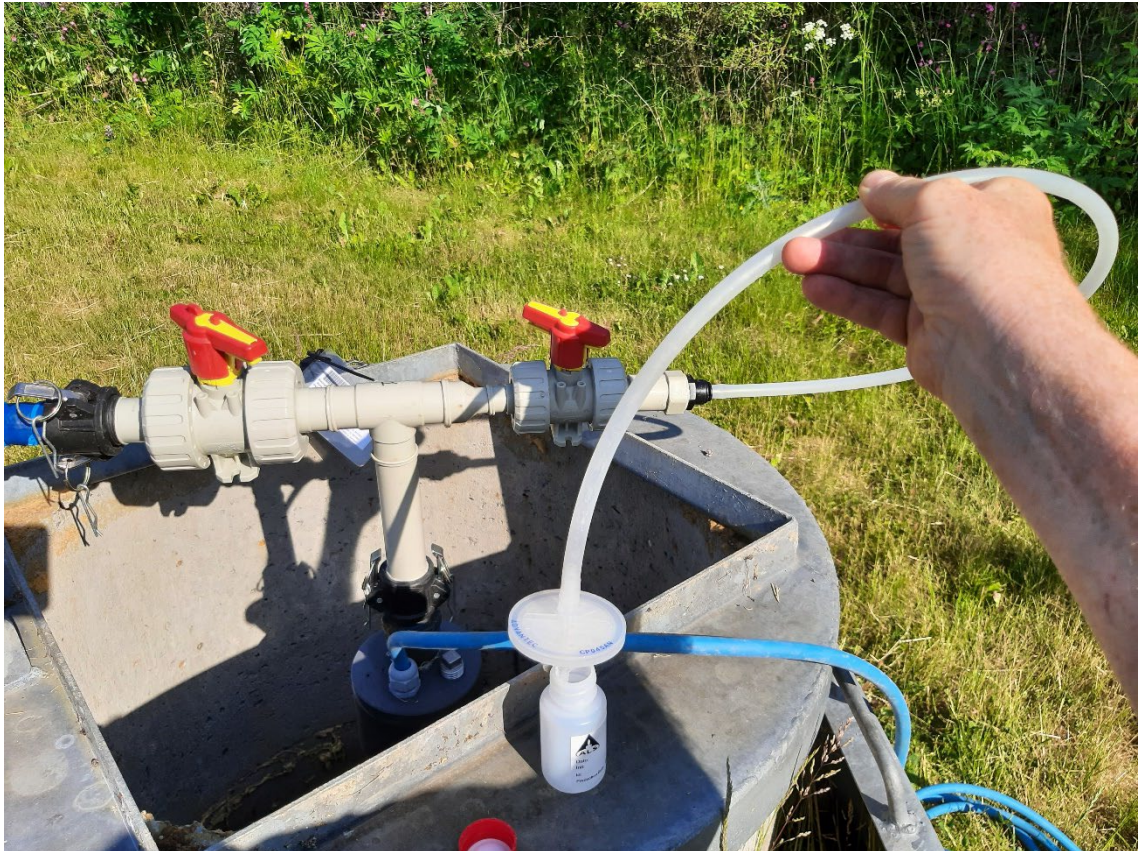


Figure 2. Online filtration over a disposable filter using the pump pressure.

If the water is very impure, a pre-filter should be placed over the filter in a filter holder in order to reduce filter consumption. This is only possible when using a filter holder, which is placed on the pump exit hose, if preferred on a subflow. If it is technically possible, vent the filter so that there is no air above the filter. This increases the durability of the filter, and the entire filter surface becomes accessible to the water.

The pumping output applied shall, if possible, be the same during filtration of a subsample as when the remaining subsamples are made. Excessive pressure should be avoided on the subflow passed through the filter holder. This may, e.g., be achieved by mounting a 3-way tap on the main flow. This also makes it possible to slowly increase the pressure above the filter.

Allow a small volume of water to pass through the filter before sampling is initiated, a minimum of 25-50 ml. Then the sample may be taken.

Change the filter in case of clogging and rinse it once again before the next sample is taken. If the water is very impure, this may be impossible. This should then be noted in the pumping table. The note is subsequently copied to the requisition form and entered in the Comments field of the analysis.

Immediately after sampling, the filter should be rinsed in demineralised water to remove any particulate matter. The filter holder is rinsed using de-

mineralized water and is cleaned in acid at least once a week – and after use, if it will not be used again for a prolonged period of time.

Acid rinsing consists in leaving the material for a period of 2 days (e.g. a weekend) in approx. 1 M hydrochloric acid (DS 2214). After acid-cleaning, the material should be rinsed thoroughly in water of drinking water quality and then in demineralized water. Once cleaned, the material is stored in clean plastic bags. This type of cleaning may be delegated to the laboratory.

Pressure filtration and hand syringe filtration

If filtration is done by pressure filtration or hand syringes, see figure 3 and 4, there is an increased risk of oxygenation of the sample prior to filtration, and of transferring precipitates to the filter. When this method is used, maximum caution must be exercised, and the method should only be used when online filtration is not an option.



Figure 3. Pressure filtration equipment from LOOP is also used in wells with insufficient pumping pressure. The figure shows the filter casing and filter holder as well as the field vehicle installation with gas for pressure filtration mounted.

When filtrating with a hand syringe, a part of the sample is transferred to the syringe. The ready-prepared filters (UFO-shaped) are then placed on the tip of the syringe and the sample is pressed through the filter by hand.

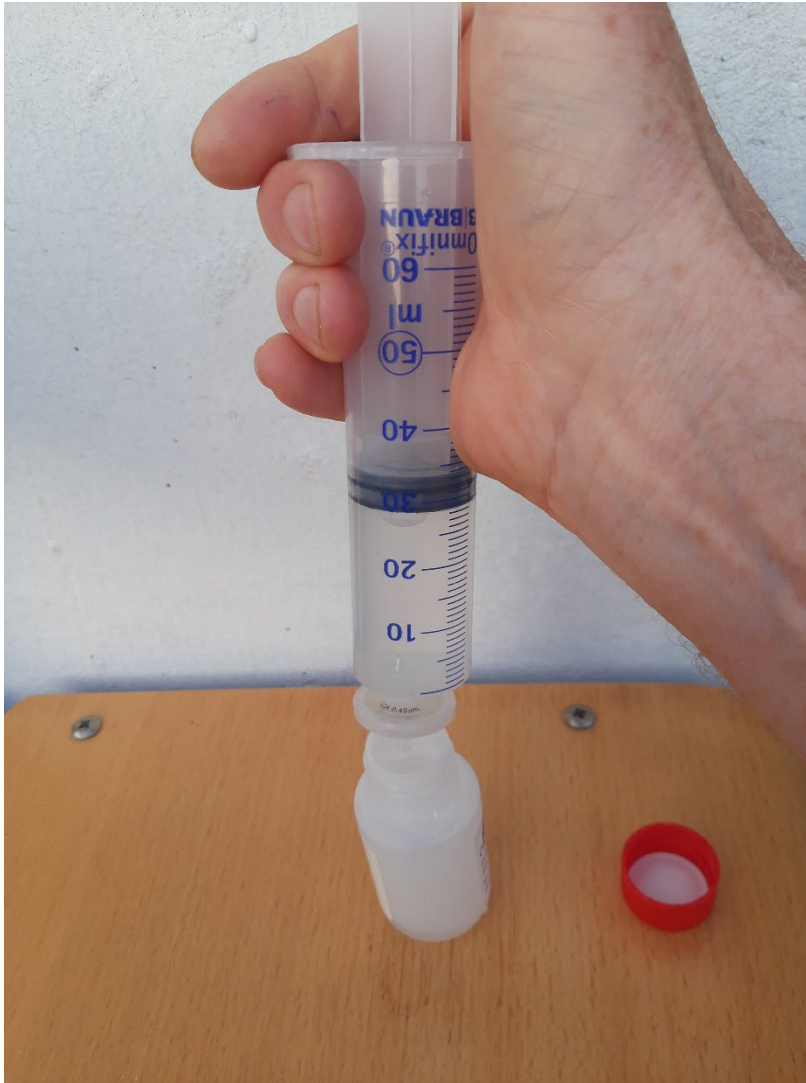


Figure 4. Filtration with a hand syringe and a small disposable syringe filter.

In pressure filtration, part of the sample is placed in the pressure chamber and then the sample is pressed through the filter by nitrogen of grade 4.6 or superior.

If the filtration is not online, the procedure is as follows:

- Before use, the filter casing and filter holder are cleaned by tap water and demineralized water, respectively, see figure 3, left-hand side.
- The filter house is rinsed using part of the water sample. Any water used for rinsing is discarded.
- A suitable amount of the water sample is poured into the filter house, which is screwed onto the filtration device using a threaded ring (figure 3, right-hand side)
- A pre-filter may be used if the sample is very sludgy.
- The pre-filter and the 0.45 μm filter are placed centrally in the filter holder's lowest part and the O ring is inserted.

- The filter holder's lower and upper parts are carefully screwed together.
- Make sure that the filters stay centred in the holder.
- The air tap at the top right of the filtration device is closed.
- The gas tap at the top left of the filtration device is opened.
- Gas pressure is set to approx. 3 bar.
- The tab placed at the bottom by the filter holder for sample flow-through is opened.
- The sample is filtrated slowly. Avoid bubbles.
- When filtration is concluded, the gas tab is closed, and the airing tab opened to depressurize the system.

Special measures concerning filtration

After sampling, groundwater samples contain particulate matter consisting of matter from the geological formation outside the screen (e.g. clay, silt, iron and aluminium hydroxide or chalk) and precipitations formed in the annulus water (typically iron and manganese oxide). The amount of particulate matter is often particularly high in groundwater samples from poorly yielding wells which are only used for monitoring purposes.

In the GRUMO, only the quantity of dissolved matter found in the groundwater is of interest. This is because the quantity of particulate matter depends widely on the sampling procedure. Particulate matter is therefore a source of error if included in the analysis result. In connection with the analysis procedure, part of the particulate matter may dissolve in e.g. acid and cause erroneous analysis results, particularly when analysing metals.

It is not possible to visually determine with certainty whether a groundwater sample is free of particulate matter. Even minute quantities of particulate matter can cause substantial errors in metal analyses in some cases. This is e.g. the case for aluminium, which is normally only found in very low concentrations, but may be present in substantial amounts in particulate matter (typically 1,000 fold higher), which is essential in modern analyses such as ICP-MS, as the contribution from the particulate matter will show up in the analysis result.

In groundwater samples, there is also a risk that some of the dissolved compounds may deposit with time, as groundwater samples are generally in disequilibrium with the atmosphere, which may cause a loss of CO₂ and contamination with O₂. When a sample is depleted of CO₂, pH increases. The sample may thereby start to precipitate chalk leading to a reduction in Ca, Mg and HCO₃. Studies show that pH may change considerably, e.g. from 6 to 8 in approx. four hours in a sample stirred continuously. /Elberling et al. 1997/

If the sample is contaminated by oxygen, dissolved Fe(II) and Mn(II) will oxidize and precipitate. In this process, other trace elements may be removed from the solution, among others arsenic. Oxidation of Fe(II) can occur within minutes when pH exceeds approx. 7.

If precipitation/flocculation occurs in the groundwater sample after field filtration (during transport to the laboratory), making it opaque again, filtration should not be repeated at the laboratory. Rather, the laboratory shall re-dissolve the precipitation if the analysis concerns metals, arsenic, phosphate or other compounds that may precipitate.

When analysing compounds that do not precipitate, e.g. nitrite, chloride, pesticides, etc., the sample may be decanted or centrifuged.

Even though filtration is not strictly required when samples will be used for the analyses of certain compounds, it may be expedient to filter a subsample before analysis. Compounds which may be filtrated, but do not strictly need to be, are listed in Appendix 6.3.

For some parameters, water samples may not be filtrated before analysis, see Appendix 6.3. To this group belongs compounds for which filtration will cause erroneous analysis results either because part of the compound may be lost to filtration or due to risk of contamination. This applies to nitrite, dissolved gasses and all organic micro-contaminations, including pesticides.

If the water sample contains much particulate matter after sampling, the sample should be decanted at the laboratory before analysis. This should be noted in the pumping table as well as on the requisition form so that the note may be entered into Jupiter along with the analysis results. Note: For a number of compounds, analysis of decanted samples is not relevant as they require filtration and must therefore be discarded, see Appendix 6.3.

2.3.5: Field analysis: pH, conductivity, oxygen, temperature and redox potential

Online field measurements of the following should be performed when possible: pH, conductivity, oxygen content, temperature and redox potential, see 2.3.3 for specifics on LOOP wells. The objective is to ensure correct analysis of pH and oxygen and to verify that purging was performed satisfactorily, i.e. that the extracted water has a stable composition reflecting the conditions found in the aquifer.

Field measurements are typically performed in a series of connected flow-cells each equipped with an electrode. A subflow of the abstracted water passes through the flow-cells, see Figure 5. The flow should be sufficient to ensure that the water at the electrode is constantly replaced. Flow cells shall be sufficiently small to support field analyses based on water samples of only 500 ml from a single pulse of a montejus pump or from emptying of the chamber of a LOOP well with a peristaltic pump.



Figure 5. Example arrangement of equipment for field measurements with a montejus pump. Note the control box placed on the ground used to control the sampling process.

Once the water has passed the flow-cells, it is discarded, except if only very limited amounts of water are available, as is frequently the case in LOOP. When it is necessary to perform analysis on water that has passed the flow-cells, this is noted in the pumping table as well as on the requisition form, so that the Comments field of the analysis holds an adequate description of the issue.

Maintenance and documentation

All field analysis equipment shall be maintained and calibrated regularly. To meet the requirements of good laboratory practice, cf. ISO 17025, a log is kept of all calibrations of each electrode. When calibrations no longer meet the requirements stated in the specifications for each type of electrode and the below notes (typically the slope of the calibration or its zero point changes), more thorough maintenance or replacement of the parts is needed.

Note that the accuracy of the calibration standards has a limited durability. Do not use standards after their expiry date.

All equipment shall carry identification labels. The details pertaining to this subject are described in the Danish Environmental Protection Agency's quality assurance system. This includes the individual electrodes and pH meters.

The log shall state which items of equipment were used on each sampling day.

Finally, the degree of accuracy shall be known. Accuracy is determined through inter-calibrations of the fieldwork.

Accuracy and precision

The accuracy of the analyses is optimised through calibration of the instruments against known standards.

In the day-to-day work, the measurement uncertainty, i.e. the precision, shall remain within the values presented in Table 2.

Note: Measurement uncertainty expresses only the uncertainty associated with the analysis. It does not comprise the variation derived from natural variation in the groundwater, e.g. during the course of a sampling procedure. For oxygen and conductivity, these uncertainties are established through measurements close to the detection threshold.

Parameter	Measurement uncertainty S_{Tmax}	Uncertainty U_{abs}
pH	0.05	0.2
Temperature	3%	15%
Conductivity	1.5 mS/m	5 mS/m
Oxygen	0.03 mg/l	0.3
Redox	No requirements	No requirements

Table 2. Quality requirements for field analysis, cf. MIM, 2023, where the definition and calculation routines for S_{Tmax} and U_{abs} are detailed.

Oxygen

Online oxygen measurements are far more reliable and reproducible than laboratory analysis. The analysis is usually easy to do. However, considerable caution should be exercised then working with poorly yielding monteju pumps. Electrodes with a detection threshold of ≤ 0.1 mg/l are used.

Oxygen is reported with two decimals as mg/l.

During purging, oxygen measurements serve as quality control ensuring that no air enters. This is done by using the previously measured oxygen content as reference value.

Traditional electrochemical oxygen electrodes

It is important to stir/ensure movement in the water during measurements, as the electrode consumes oxygen. As a minimum, the electrode is calibrat-

ed daily against water-saturated atmospheric air (100% oxygen-saturated conditions). If electrodes with a detection threshold of 0.01 mg/l are used, take into account that the method is very sensitive to hydrogen sulphide, which may produce a fictive oxygen content measurement of up to 0.5 mg/l.

Optical oxygen sensors

An optical oxygen electrode does not consume oxygen and can therefore be used to measure oxygen in environments with no movement/stirring in the area around the electrode.

The electrode is pre-calibrated at the producer and therefore does not require daily calibration.

The electrode is checked weekly in saturated oxygen and in an oxygen-free nitrogen atmosphere as described in the user's manual. The result for 100% and 0% are noted in the log. If results show deviations or instability, the electrode needs to be calibrated against saturated oxygen.

pH

Online pH measurements in the field provide a far more accurate reflection of the groundwater conditions than laboratory measurements, as the majority of undesirable effects associated with carbon dioxide degassing during laboratory measurement are avoided. This is an unavoidable problem as the groundwater has a CO₂ content equivalent to a partial pressure about 10 times that of the atmosphere.

pH is always stated with two significant digits.

pH electrodes are calibrated at least once a week. The electrode is calibrated against two standards with pH values close to those expected for the sample pH, use pH 4 and 7 buffers as standard. Please note that the time needed for the electrode to reach equilibrium during calibration may be several minutes. If the time needed to reach equilibrium increases, the electrode probably needs to be replaced. The constants of the calibration curve are noted in the log. Furthermore, any signs that the time needed to reach equilibrium is excessively long, are noted.

It is important to replace electrodes not complying with the specifications set by the supplier in order to achieve a sufficiently accurate result. The design of the pH electrode shall be robust to the pressure in the flow cell (Hansen et al., 2008).

Conductivity

Conductivity is measured as mS/m and stated with one significant digit. The majority of the conductivity measuring devices presently on the market cannot be calibrated. They can, however, be set to normalise the results measured to a pre-established temperature. For groundwater, the convention is "conductivity at 25 °C". If the conductivity meter was set incorrectly,

typically to a reference temperature of 20 °C, results will not be correct. Furthermore, results in the display are often provided as $\mu\text{S}/\text{cm}$ which needs to be converted before entering the reading into the pumping table.
 $1 \text{ mS}/\text{m} = 10 \mu\text{S}/\text{cm}$

Redox potential

The redox potential is primarily measured to ensure the quality of oxygen measurements and of the sampling. It is a convention in the GRUMO that the resulting redox potential is stated NOT as the standard redox potential E_{H}^0 with hydrogen as reference state), but rather using the reading of the electrode. Platinum electrodes shall therefore be used with a built-in KCL reference electrolyte. It is important to maintain the platinum electrode polished, preferably with a rough paper napkin, to allow its surface to react with the redox-sensitive parameters of the sample. The time needed to reach equilibrium of the platinum electrode may be extraordinarily long, several hours, but as the readings from the electrode often find the correct level given the accuracy needed, the measurements will be sufficiently good to fulfil their purpose.

Redox potential is stated with +/- and using the mV unit.

Strict demands on the accuracy of redox potential (i.e. deviation from true value) are meaningless as the majority of groundwater samples are in internal disequilibrium with regard to redox potential. This applies e.g. to the following redox pairs: N_2/NH_4 , $\text{NO}_3^-/\text{NO}_2^-$, $\text{NO}_3^-/\text{NH}_4$, $\text{Fe(II)}/\text{Fe(III)}$, $\text{SO}_4/\text{H}_2\text{S}$.

Temperature

The temperature of the extracted water will be affected by the heating caused by the pump and the interaction with air temperature occurring around the hoses, which in cold weather are at risk of freezing and at higher temperatures may cause water temperatures around 20° C. Temperature measurement is not calibrated. The results are stated with one significant digit using the °C unit. Temperature is mainly measured to check the pump's technical condition.

The correct groundwater temperature can only be determined by measuring directly in the well, see G3-Measurement of Groundwater Levels.

2.3.6: Submission and storage of samples

Upon collection, all samples are stored in a dark and cold place. Specifically, samples may be stored in a cooling bag from the laboratory or in the refrigerator of the field vehicle.

The deadlines for handing in the various sample types are stated in the method data sheets from the Reference Laboratory. No groundwater laboratory analysis currently has a durability below 24 hours, provided sampling, storage and preservation have been performed as described by the laboratories. It is therefore possible to hand in samples at the end of the working day, after which the samples can be analysed the next day.

All samples are handed in to the laboratory along with a requisition form detailing the samples' ID (as a minimum: DGU no., screen no., date and time, sampler's staff ID) and the results of the field analyses so that these may be transferred electronically to Jupiter along with the analysis results. See the data-technical guidance on groundwater data. Note! Remember to fill in the Comments field if there are any relevant comments to the sample.

2.3.7: Sampling for dating purposes

Samples which will be used for groundwater dating purposes are taken by specially trained staff. The procedure used depends on the dating method employed, and a description of these is beyond the scope of this technical guidance. To the extent possible, samples used for groundwater dating shall be taken while sampling with a view to determining the groundwater's main components. Thorough and adequate purging is required before dating samples are taken. /Hinsby et al. 1997/

2.3.8: Discarding samples

If samples cannot be filtrated due to excessive content of particulate matter, only the subsamples, which are to be used for parameters that do not require filtration, should be submitted.

2.4 Checklist

Before any field work is initiated, sampling equipment, etc., needs to be prepared.

- Bottles are ordered, and the time and place at which the samples will be handed in is agreed with the laboratory.
- All equipment is cleaned before initiating any field work, including hose trolleys and filtration equipment.
- All field instruments should be fully charged.
- Calibration liquids should be brought, and their "valid until" dates checked.
- Check that any pressure containers hold sufficient amounts of gas, and order replacement containers if this is not the case.
- Remember to bring all relevant information recorded at previous sampling sessions and the description of the standard procedure, on paper or electronically.

2.5 Maintenance of instruments

Adequate maintenance of all instruments and equipment is a prerequisite to an efficient day in the field.

Generators and other electrical equipment require continuous maintenance, and at least once a year; all field equipment should be revised and checked.

Some maintenance work can be done while wells are being purged. Other maintenance tasks require workshop facilities and, in some cases, specific competences, e.g. to handle power current, etc.

Not all pumps are equally durable, and pumps may need to be replaced or to undergo maintenance, e.g. in case of excessive sand passage, as suspended sand increases the wear on any movable parts of the pumps.

Technical issues concerning the maintenance of pumps are handled in collaboration with the supplier.

2.6 Special precautions – pitfalls

Sampling in groundwater requires two types of professional competences. Firstly, the technical competences including the use and maintenance of the many types of equipment and also the ability to optimize the work process by opting for the optimal pumping strategies, etc. Secondly, a certain knowledge of groundwater chemistry is required, including and in particular, the fact that groundwater is not normally in chemical equilibrium with the air of the atmosphere. The CO₂ content is about ten-fold higher in groundwater than in the atmosphere, and the content of oxygen is frequently considerably lower than that of the atmosphere. If groundwater is exposed to air, both pH and redox conditions will change.

Sampling at times when pest control or liquid manure is being spread, or in an environment with airborne contamination from exhaust fumes, etc., entails a risk of contaminating the sample with organic micro-contamination. In such cases the sampling staff should assess if sampling activities should be postponed. If sampling is continued, a note is made on the requisition slip so that it may be stored in Jupiter along with sampling results. The comment should also be included in the overview of station inspections.

3 Data processing

Please see the data-technical guidance on groundwater data. Field measurement results should be converted into the correct units of measurement, cf. Appendix 6.2.

4 Quality assurance

4.1 Quality assurance of method

Quality assurance of field work is based on thorough use of pumping tables and logs for field analysis and the instructions in this technical guidance, as the quality system needs to comply with ISO 17025.

All relevant observations are noted as described above in the pumping tables and logs, including observations which require follow-up, i.e. maintenance tasks or comments for the analysis form.

The log covering the field measurements will show when electrodes are not working optimally, and it will continuously provide the opportunity to see if samples can be taken at the required level of quality.

Specifically, the eH analyses are used to quality assure oxygen measurements, as a high eH equals a high oxygen content, and negative eH is normally only observed in anaerobic environments. If the measured eH and oxygen measurements do not concur during a sampling session, this is an indication that the sampler should revise calibrations and pumps to look for errors or leaks in the system.

As the continued maintenance of propellants and pumps is of great significance for sampling quality, logs are to be kept detailing the technical equipment (preferably in electronic format). This is particularly relevant if several staff members use the same equipment.

Non-electronic logs are kept for a minimum period of 5 years after their last use.

4.2 Quality assurance of data and data submission

Please see the data-technical guidance on groundwater data.

It is important to observe that all chemical data from samplings are transferred by the laboratory, while all measurement data and observations concerning changes in the well technical conditions are entered directly into Jupiter or reported to the Well Data Archive after sampling.

Typical error types

The carbonate system, Ca, Mg and HCO_3 : If CO_2 is lost to the air during sampling, pH increases and chalk precipitations may occur. This may occur at all steps from sampling to conclusion of the analysis. Significant deviations from one sampling to the next or problems with ion equilibrium may often be explained by problems that have to do with the carbonate system.

Erroneous units on field measurement results, particularly conductivity: Check that the correct scale was read; quite a few measurement instruments use $\mu\text{S}/\text{cm}$ instead of mS/m .

Erroneous statement of oxygen units: Oxygen is to be stated as mg/l and not %, even though some instruments may state %.

Erroneous statement of monitoring point or field measurements on the requisition form: Thoroughly check that the correct values are handed over to the laboratory.

5 References

Statutory material and guidelines

Miljøministeriet 2011: Bekendtgørelse om kvalitetskrav til miljømålinger udført af akkrediterede laboratorier, certificerede personer m.v. BEK nr. 900 af 19/08/2011. The Danish Executive Order on Analysis Quality.

Dansk Standard DS/EN ISO 5667-3 Vandundersøgelse Prøvetagning Del 3: Retningslinjer for konservering og transport af prøver.

Dansk Standard DS 2214 Vandundersøgelse Prøvetagning af vand til analyse for spormetaller.

Europæisk standard EN ISO/IEC-17025 om generelle krav til prøvnings- og kalibreringslaboratoriernes kompetence rummer egnede internationale standarder for validering af de benyttede analysemetoder

EU, 2009: The Directive on Analysis Quality 2009/90/EF of 31 July 2009 concerning technical specifications for chemical analysis and monitoring of water quality as described in the European Parliament's and the Council's Directive 2000/60/EF.

Lossepladsprojektet, 1989: Grundvandsprøvetagning og feltmåling. Lossepladsprojektet. Udredningsrapport U3. April 1989

Inga Sørensen ed., 2009: Environmental Sampling – Groundwater. Leonardo da Vinci. EU report. Published by VIA University College, Horsens.

U.S. Environmental Protection Agency, 2002: Ground-water Sampling Guidelines for Superfund and PCRA Project Managers

The Reference Laboratory's method datasheets, see the Links section below.

Professional literature

County of Aarhus, Environmental Office, October 1991: Grundvandsboringer, Technical report.

GEUS, 2002: Grundvandsboringers egnethed til analyse. Work report of the Groundwater Monitoring Programme.

Bo Elberling, Lærke Thorling and Per Misser 1997: Det kan være surt at måle pH. Vand og jord, vol. 4, no. 4, Aug. 1997, pp 150-152.

Hinsby, K., Laier, T. & Dahlgaard, J. 1997: Datering af grundvand – ved hjælp af CFC. Geologisk Nyt no. 2, 1997. The Trade and Industry Group (Erhvervsgruppen) at Department of Geoscience, Aarhus University.

Birgitte Hansen and Lærke Thorling, 2008: Interkalibrering af grundvandsprøvetagningen 2007, NOVANA. GEUS report. [Link to report](#)

Relevant links

General information on nature and environment monitoring is available in Danish on the Danish Environmental Protection Agency website: [Link to MST](#)

Method datasheets from the Reference Laboratory are available here: [link to Method datasheets \(in Danish\)](#).

Jupiter and the Well Data Archive are available here: [link to Well Data Archive and Jupiter](#).

<http://www.grundvandsovervaagning.dk>

<http://www.jordforurening.info/>

GEUS, 2017: Datateknisk anvisning for grundvandsdata (DG-01-2). ([Can also be found on the Danish Environmental Protection Agency's website](#))

List of associated technical guidances

G01 – Monitoring networks, Technical guidance for monitoring networks, groundwater ([link to, in Danish](#))

G03 – Measurement of Groundwater Levels – a Field Guide, Technical guidance for the national groundwater table networks and soundings ([link to](#))

6 Appendices

Appendix 6.1. Pumping table for electricity-driven pumps and montejus pumps

A PDF version of these pumping tables is available for download at the GEUS webpage, where the tables are placed alongside the technical guidelines.

The first figure is a pumping table for a submersible pump and then follows a pumping table for a montejus pump.

DGU no.- ID in Jupiter:		Screen no.:		Name of location			Init:		Date:	
Well no.:		Surroundings and weather:								
Reference point (rp): In Jupiter [] Other please describe [] :							Time and sounding before purging			
Type of Pump: Built in MP1 [] Built-in SQE [] Mobile MP1 [] Mobile SQE [] Other type:										
Starting time of pumping (hh:mm):				Sampling hose Opaque PE [] Other [] :						
Time	Conductivity	Temperature	Oxygene	pH	Redox	Comments	Yield	Transformer	Sounding	
(hh:mm)	mS/m	°C	mg/l		mV		l/min	Hz / %	m.b.rp	
Sampling time(hh:mm):										
Water sample smell[] sandy/clayey [] opaque[] other comments:							Suitability	yes	maybe	no
Filter type (note):							Well:			
Number og filters used: filtrer couloring : No [] Yes [] Colour:							Sample			
Program: Main cont.		Redox	Pesticides	Halogenated	PFAS	Trace elements	Screening	GEUS isotope	TFA	
Sample barcode:						Comments:				

DGU no. -ID in Jupiter:		Screen no.:		Name of location:			Init:		Date:		
Well no.:		Surroundings and weather:									
Reference point (rp): In Jupiter [] Other please describe [] :							Time and sounding before pruging				
Type of Pumpe Montejus [] Bladder pump [] Other type [] which:							Gas type		Pressure (bar):		
Starting time of pumping (hh:mm):				Sampling hose Opaque PE [] Other [] :							
Time	Conductivity	Temperature	Oxygene	pH	Redox	Comments	air inflow	Yield	Pause	Air outflow	Sounding
(hh:mm)	mS/m	°C	mg/l		mv		min	l/step	min	min	m.b.rp
Samling time(hh:mm)											
Water sample smell[] sandy/clayey [] Opaque[] other coments:							Suitability	yes	maybe	no	
Filter type (note): Number of filters used: filtrer couloring : No [] Yes [] Coulor:							Well:				
							Sample:				
Program: Main cont. Redox Pesticides Halogenated PFAS Trace elements. Screening GEUS isotope. TFA											
Sample barcode						Comments:					

Appendix 6.2 Sampling vehicle equipment

In a sampling vehicle, the following tools and equipment shall be available:

- Hand tools; screwdrivers, single-head wrenches, pliers, etc.
- Fittings and adaptors for various water work exit taps
- Filtration equipment
- Cooling unit for sample storage
- Hoses for pumps, exit hoses and tubes, adaptors, etc.
- Hose trolley
- Tissues
- Demineralized water
- Rubber gloves, various sizes
- Manual water level meters
- Extra batteries for the equipment
- Generators
- Pressure containers for sampling of montejus screen
- A compressed air device with air filters, if needed

Desirable equipment:

- Lightweight camping table
- Brush cutter (electrical)

Appendix 6.3. Overview of rules on handling of samples etc. of main components and trace elements

Analysis methods, sampling, etc., shall be performed in accordance with the method data sheets of the Reference Laboratory. The choice of analysis methods, sample bottles and preservation techniques is the responsibility of the laboratory used, and the laboratory shall perform any work in accordance with the instructions of the method data sheets of the Reference Laboratory.

No organic substances are filtrated. Only PFOS is included in this table.

The table in this appendix only presents conditions relevant to the sampling and quality assurance of data.

Main components

Substance:	Specific problems concerning type of pump and sampling equipment	Filtration	Method data sheet, pre-treatment, preservation	Results are reported as:
Aggressive carbon dioxide	Do not use suction pumps	No	See method data sheet, M031. Calcium carbonate is added to the sample bottle at the lab before the field work.	mg/l (agg.) CO ₂
Ammonium	Suction pumps and pumps causing oxygenation of the water are not to be used	YES	See method data sheet	mg/l NH ₄ ⁺
Hydrogen-carbonate		YES		mg/l HCO ₃ ⁻
Calcium		YES		mg/l Ca ⁺
Chloride		May be filtrated		mg/l Cl ⁻
Fluoride		May be filtrated		mg/l F ⁻
Residue after evaporation		YES		mg/l

Substance:	Specific problems concerning type of pump and sampling equipment	Filtration	Method data sheet, pre-treatment, preservation	Results are reported as:
Iron, total, dissolved	Pumps which cause oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling	mg/l Fe
Potassium		May be filtrated		mg/l K ⁺
Conductivity		No	Performed as a field analysis	milliS/m
Magnesium		YES		mg/l Mg ⁺⁺
Manganese	Pumps which cause oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling	mg/l Mn ⁺⁺
Methane	Pumps using the suction principle are not to be used	No		mg/l CH ₄
Sodium		May be filtrated		mg/l Na ⁺
Nitrate		YES	See method data sheet	mg/l NO ₃ ⁻
Nitrite		No	See method data sheet	mg/l NO ₂ ⁻
NVOC Non-volatile organic carbon	Oil-greased pumps may not be used	YES	The laboratory adds acid to the sample bottle before sampling	mg/l C
Orthophosphate		YES	See method data sheet	mg/l PO ₄ -P
pH	Pumps using the suction principle are not to be used	No	See method data sheet, M050. This is always a field analysis	PH units

Substance:	Specific problems concerning type of pump and sampling equipment	Filtration	Method data sheet, pre-treatment, preservation	Results are reported as:
Total phosphorus, dissolved		YES	See method data sheet. The laboratory adds acid to the sample bottle before sampling.	mg/l P
Silicon dioxide		YES	See method data sheet. The laboratory adds acid to the sample bottle before sampling.	mg/l SiO ₂
Sulphate		May be filtrated		mg/l SO ₄ ²⁻
Hydrogen sulphide	Pumps using the suction principle are not to be used	No	May be performed as field analysis or laboratory analysis	mg/l H ₂ S

Organic pollutants. All should be stated using the unit µg/l.

Substance	Specific problems concerning type of pump and sampling equipment	Filtration	Method data sheet, pre-treatment, preservation	Results are reported as
PFAS, Perfluoro-alkyl substances	Do NOT use Teflon when sampling	No	See method data sheet M068.	Specific substance, unit µg/l
All other substances		No		Unit µg/l

Inorganic trace elements. All should be stated using the unit µg/l.

Substance	Specific problems concerning type of pump and sampling equipment	Filtration	Method data sheet, pre-treatment, preservation
Aluminium	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Antimony		YES	The laboratory adds acid to the sample bottle before sampling.
Arsenic	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Barium	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Beryllium			The laboratory adds acid to the sample bottle before sampling.
Lead	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.

Substance	Specific problems concerning type of pump and sampling equipment	Filtration	Method data sheet, pre-treatment, preservation
Boron	Plastic equipment is to be used		The laboratory adds acid to the sample bottle before sampling.
Bromide		May be filtrated	The laboratory adds acid to the sample bottle before sampling.
Cadmium	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Chrome, total	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Cobalt	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Cyanide (total)		No	The laboratory adds acid to the sample bottle before sampling.
Iodine (total)		Yes	See method data sheet, M050. No preservation
Iodide		No	No preservation
Copper	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Mercury		YES	The laboratory adds acid to the sample bottle before sampling.
Lithium		May be filtrated	The laboratory adds acid to the sample bottle before sampling.
Molybdenum	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Nickel	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Selenium		YES	The laboratory adds acid to the sample bottle before sampling.
Strontium	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.

Substance	Specific problems concerning type of pump and sampling equipment	Filtration	Method data sheet, pre-treatment, preservation
Silver		YES	The laboratory adds acid to the sample bottle before sampling.
Thallium		YES	The laboratory adds acid to the sample bottle before sampling.
Tin		YES	The laboratory adds acid to the sample bottle before sampling.
Vanadium	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.
Zinc	Pumps causing oxygenation of the extracted water should not be used	YES	The laboratory adds acid to the sample bottle before sampling.

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