



EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání



Chemical methods in geology

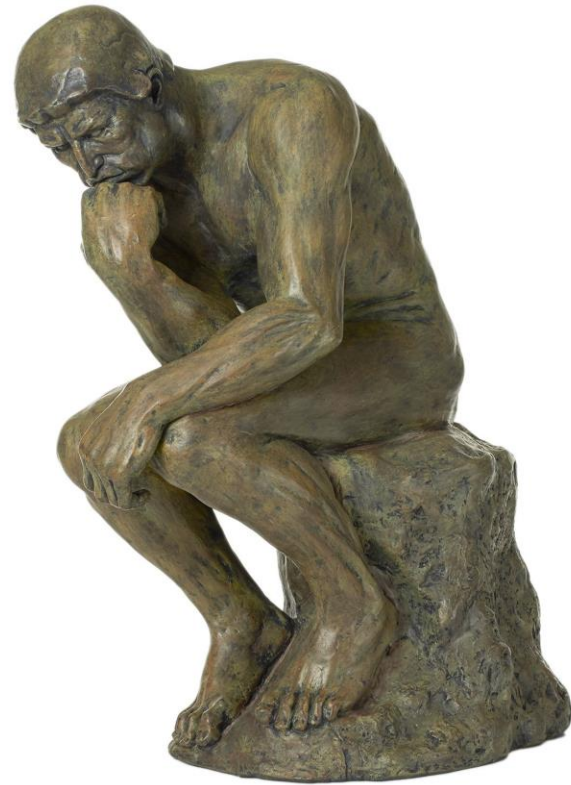
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Practical field hydrogeochemistry

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
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Principles of good practice

- How to approach the utilization of geochemical properties of water?
- How do we get quality data?
- How should we proceed?
- What to watch out for?
- Rules of good practice.



Introduction

- The use of geochemical data in hydrogeology usually requires thoughtful sampling and analysis.
- The key is to keep in mind the goal of the measurement
 - For some studies, basic parameters are sufficient, while others require a broad analytical approach
- If you are not sure about anything – the type of sample container, the amount of sample, etc. – consult with the laboratory.

Field measurements

- Properties that can easily change during transport and storage
- Temperature
 - Thermodynamic considerations, equilibria, speciation
 - EC and pH calibration
 - Usually directly via conductometer or a pH meter
 - The value is drifting (tempering of the devices)

Specific conductivity (conductivity)

- Property of a solution – a measure of the ability to conduct an electric current
- SI unit is siemens per meter (S/m)
 - In hydrogeology commonly $\mu\text{S}/\text{cm}$
- Conductivity is proportional to the content of dissolved ions in the solution
 - Water purity monitoring
 - Deionized water $0.055 \mu\text{S}/\text{cm}$
 - Drinking water $50\text{-}500 \mu\text{S}/\text{cm}$
 - Sea water $50000 \mu\text{S}/\text{cm}$
 - Simple estimation of total dissolved solids (TDS)
 - Basis for further sampling and analyses

Specific conductivity (conductivity)

- It is measured by determining the resistance of the solution between two electrodes at a known (and fixed) distance
- Alternating current (to avoid electrolysis)
- Conductometer
 - A very diverse group of devices
 - With fixed or exchangeable probe
 - Necessary maintenance – especially cleaning the electrode from deposits (calcite, dirt, bacteria...)
 - Easy storage, long battery life of basic devices
 - Choose types with automatic temperature compensation! (The water in wells is cold :-))
- Induction is also used for industrial applications...



pH

- One of the most important parameters
 - Measuring requires patience and diligence
- Necessary calibration using buffers
 - For groundwater, a two-point calibration is usually sufficient (pH 7 and 4 or 7 and 10)
- Glass electrodes – potentiometry

Combined electrode

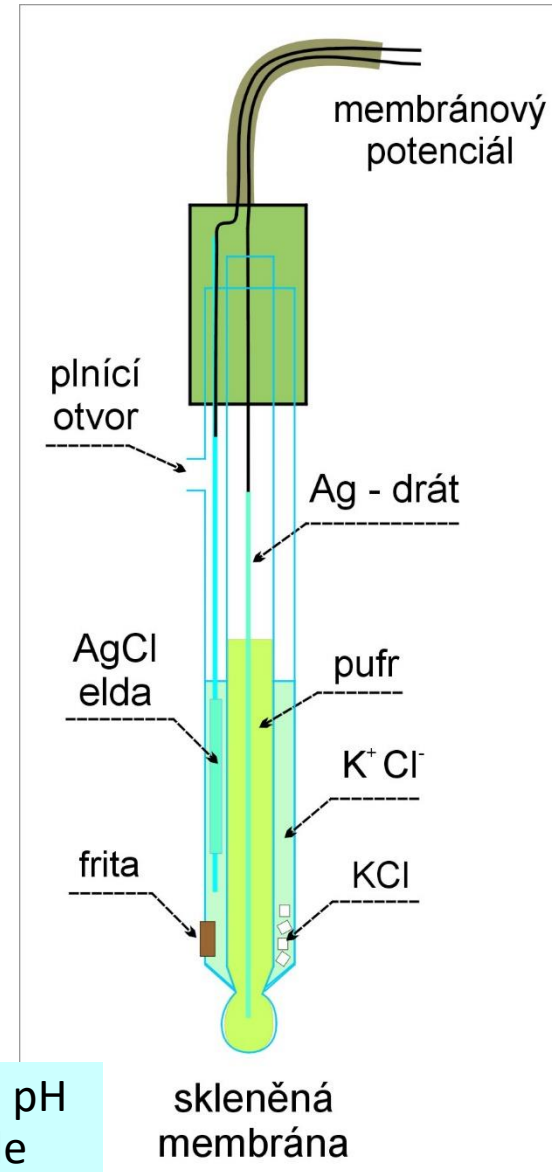
- The use of two separate electrodes (glass + reference) is extremely impractical
- Combined electrode
 - Contains both electrodes in one body
 - Reference el. of a known potential to a hydrogen electrode
 - Glass measuring electrode
- The circuit is closed using a junction/diaphragm (ceramic, Pt) – reference electrode / measured solution
- The trend of miniaturization of the glass part, plastic bodies, gel fillings

Measurement

pH meters

pH calibration – buffers

direct measurement of E – Zobell's solution



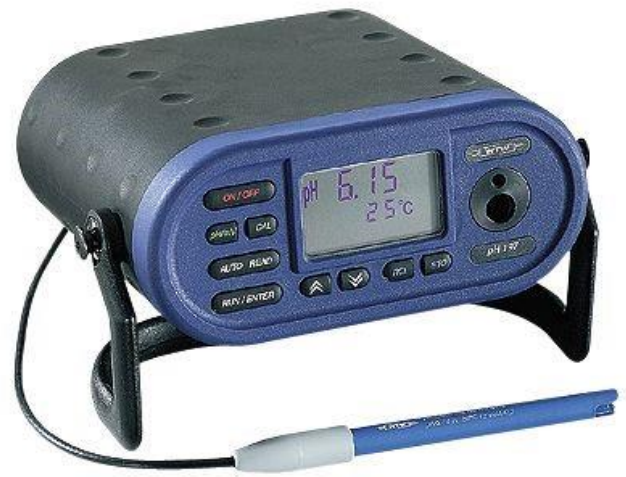
pH-electrodes

Wear and tear
Compatibility
Calibration



- **For the most accurate measurement possible:**
 - Correct electrode storage (see manuals)
 - Replace on time – monitor the quality of electrode calibration
 - Rinse the electrode between measurements
 - Gentle movement of the electrode in the solution (prevents development of potentials on the electrode)
 - For some types of water (little buffered, low TDS, low alkalinity...) the measured value can drift
 - For water degassing CO₂ or with low redox (red. Fe and S) it is advisable to avoid contact with air (e.g. using flow cells)

pH meters



Redox potential

- Electrode measures potential (electromotive force)
- No calibration
 - Checking the correctness of the measurement against a solution with a fixed Eh (e.g. Zobell's solution)

Zobell's Solution (Eh = 0.430 V at 25°C)

0.0033 M $K^+ - Fe^{2+} - CN^-$ solution

0.0033 M $K^+ - Fe^{3+} - CN^-$ solution

0.01 M K^+/Cl^- solution

Quinhydrone Solution

pH 7 solution = 86 ± 20 mV

pH 4 solution = 263 ± 20 mV

$\Delta 3$ pH (difference between the two solutions) =
 177 ± 4 mV

Redox potential

- When measuring:
 - Gentle movement of the electrode in the solution (prevents the development of static voltage on the electrode)
 - Wait a few minutes for stabilization
 - If the readings fall and then start to rise, there is O₂ contamination from the atmosphere – record the lowest value reached

Redox potential

- Correcting the measured E to Eh :
 - Add the standard electrode potential to the measured value
 - Standard potentials of argent-chloride electrodes:

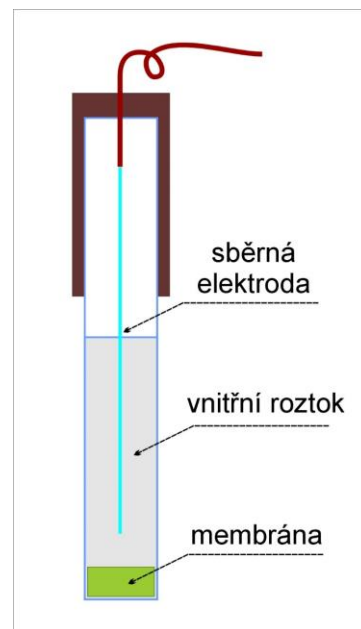
T (°C)	0	5	10	15	25	35	50
E_R	220	216	213	209	202	195	184

Redox potential

- Determination problems
 - Volatile values and long settling
 - Clean the electrode (soapy water and a soft brush)
 - Soaking in the preservation solution
 - Measurement in a sealed container (constant solution concentration)

Ion Selective Electrodes (ISE)

- Membrane potentials – solid/liquid membrane
- Direct quantitative determination according to the Nernst equation – calibration line
- For anions: F^- , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} ...
- Metals: Ca, Ag, Pb, Cd, Na, K...
- Alkali metals – membranes contain molecular cavities with the exact dimensions of the given element
- Degradation of electrodes (relatively limited lifetime) – more intensive than for pH and ORP
- Typically for frequent measurements of e.g. nitrates or sodium (measurement of water quality, spread of pollution, passage of contamination cloud, etc.)



Examples of measuring range:

0.1 to 14000 mg/L	NO_3^-
0.002 to 23000 mg/L	Na^+
1.8 to 35500 mg/L	Cl^-
0.02 to 40100 mg/L	Ca^{2+}

Multimeters

Measurement of conductivity, temperature, pH, redox , oxygen, ISE

WTW marketers idea
of using a multimeter
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Logger functions (data recording), direct connection with a PC
Generally applies to all devices – the more functions, the greater the demand on the battery
Simplicity could lead to pure perfection

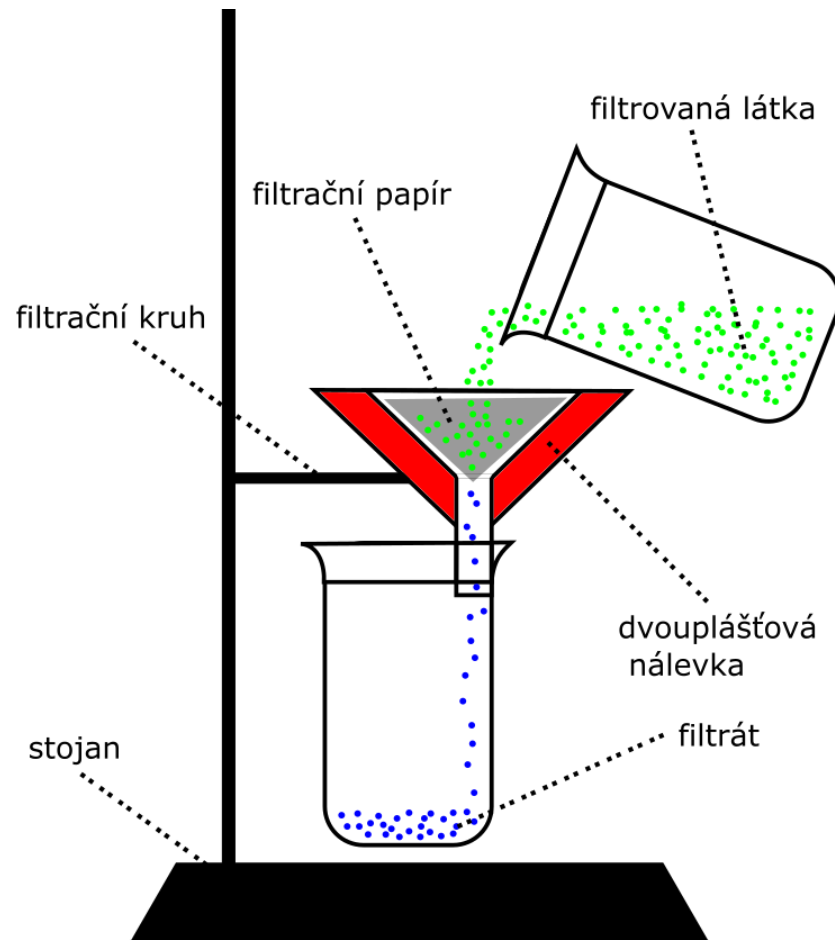
Less common properties

- Radioactivity of water
 - Dissolved gases (Rn)
 - Activity [Bq]
- Amount of dissolved oxygen
 - Oxidation-reduction properties
 - Biota
 - Electrochemically (electrodes)

CHEMICAL ANALYSES

Filtration

- Water contains unsuitable particles (suspension)
 - Chemical interactions may occur
 - Filtration directly in the field
 - Syringe attachment (various sizes)
 - Most commonly 0.45 μm
 - Particles, clays, part of oxohydroxides Fe and Mn
 - Bacteria
 - Does not capture viruses and most organics (e.g. fulvic and humic acids)
 - For colloids up to 0.1 μm
 - Suction can cause degassing - forcing is better



Major anions

- **Laboratory measurements**
- Gravimetric (sulphates), titration (nitrates), liquid chromatography, possibly also MS (sulfur)
- Carbonates by titration (determination of alkalinity)
- **Direct field measurement**
 - Briefcase sets
 - ISE
 - Portable photometers
(*Cl* 0.01-10 mg/L, **ammonia** 0.01-50 mg/L, **NO₃⁻** 0.2-133 mg/L)
 - Lower accuracy – suitable for orientation measurements, rapid development monitoring or routine measurements



Samples for anion analysis

- Usually 5 mL is enough for one analysis, better around 50 mL (repetition)
- PE or PP bottles, rinse with sampled water, filter
- Store in a cool and dark place – microbial activity (oxidation-reduction of sulphur), precipitation

Sulfides and sulfates

- H_2S and HS^- very soluble
- They are formed under reducing conditions from sulfates
- They oxidize quickly – even O_2 diffusing through the plastic of the bottle
 - Necessary stabilization during sampling – precipitation as Zn and Cd sulfides
- Distortion of sulfate content – it is necessary to separate also for the determination of SO_4^{2-}

Major cations + trace elements

- Field determination via ISE (Na^+ , K^+ , Ca^{2+} , Mg^{2+})
- Today usually ICP-AES, ICP-MS, AES or AAS
- Spectrophotometry (complexing cations)
- High precision, small samples (limit ca. 25 mL)
- Samples can be acidified – preventing precipitation of carbonates and oxides (typically small amounts of HNO_3)
 - Keeps metals in solution
- The acidified filtered sample is stored in a PP or PE bottle

Sampling for isotopic analyses

- $\delta^{18}\text{O}$ and $\delta^2\text{H}$
 - Not subject to significant chemical and biochemical processes – can withstand long-term storage
 - High content in water – resistance to dilution and interaction (isotopic exchange)
 - A large air space above the water
 - Tightly closed bottle with minimal bubbles – depending on sample volume
 - No filtration, tightly sealed (due to evaporation), refrigeration recommended
 - Various methods (LRS; IRMS)
- Tritium
 - Depending on the method, it may not require special sampling (LSC scintillation methods)



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Resources

- Most pictures are public domain or taken from manufacturer's catalogues