Hydroisotop

Analysis of miniature water and gas samples

WATER
GEOTHERMAL ENERGY
TRACER TESTS
POLLUTANTS
FILTER TECHNIQUES
FOOD
RENEWABLE RESOURCES
ISOTOPES
GASES
SOLIDS
ANALYSIS

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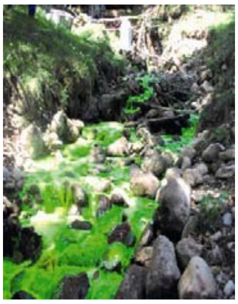
accreditated accoriding to DIN EN ISO/IEC 17025:2005

Isotopy & Chemistry in Environmental Hydrology & Food



SERVICE FOR

- **Pore water experiments**
- **Gas experiments**
- **Corrosion experiments**
- **Hydrogeological studies**
- **Hydrogeological monitoring of interim storage**

- **Analyses of gas and water samples**
- **Analyses of pore water experiments (smallest volumes)**
- **Analyses of research drillings and hydrotests**

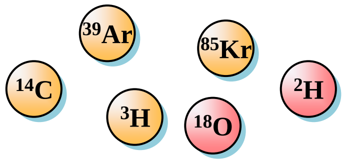
- **Sampling of gas and water samples**

- **Hydrogeological interpretation under consideration of**
  - **origin and recharge,**
  - **migration paths and**
  - **hydrochemical processes**
- **Estimation of hydrogeological investigations of monitoring programs of interim storage**

Based on several requests of clients, Hydroisotop has developed a system to organize, prepare and accomplish the multi-parameter analysis of miniature “extreme” water samples and gases.

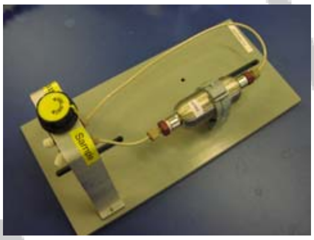
The development of complex measurements “en miniature” was started for the analysis of the Mont Terri Experiments (NAGRA) by the Pearson water. The multi-parameter analysis went into series with a collection of samples from experiments in Bure (ANDRA), but also from several boreholes drilled for geothermal energy use.
The optimisation of the applied methods, development of further analytical methods as well as reducing of the needed volume is still in progress.

Development of multi-parameter analysis of „miniature“ water and gas samples



Special tracer tests of water and gas in dense rock materials as well as water samples of horizons with low permeability provide the need for complex analysis of hydrochemistry, inorganic and organic contents and isotope values. These samples are also in need of measurement of the dissolved gases.

Based on the natural conditions pore waters from low permeable rocks can be sampled only in small amounts over long time periods. Often those samples are primarily influenced by processes of the exploration and exploitation such as the contamination by drilling fluid and disinfection fluid or cement-water interactions.

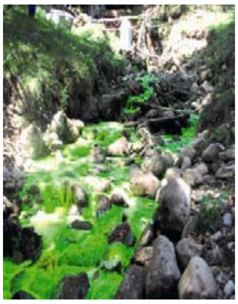



Sophisticated equipment for circulation experiments allows the sampling of gas and water in the original state in steel and peek cells.

The challenge though is to optimise the lab equipment and measurement techniques in a way that the physical-chemical conditions of the water can be analysed in the original state.







Micro Measurement Cells

The development of special micro measuring cells enables the analyses of physical parameters like pH value, redox potential or conductivity under very slow through-flow conditions and under protective gas to avoid oxidation processes. Additional analyses can follow subsequently without wasting any drop of the precious pore water.

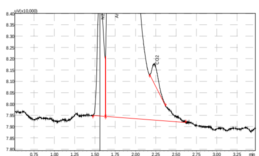


Composition of Dissolved Gases

For measurement of the dissolved gases, the cells are emptied for half of their contents by using an inert gas, disclosed of the measuring cell and lightly shaken. After a while the gas phase of the inert gas over the water phase has reached equilibrium with the originally solved gases and can be analysed by the gas chromatograph. Corrections of the measurements are done using solubility coefficient by Bunsen, gas volume and pressure.

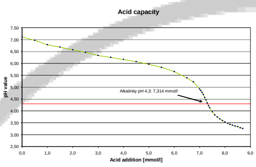
Small containers show the effect that the carbonate system of the water phase immediately degasses the very moment the inert gas is injected. Therefore even the first outflow of water is already reduced of its TIC concentration. This has been proven by several tests. The result of TIC measurement by analyser has therefore be added with the result of the CO_2 gas measurement to learn the total inorganic carbon of the sample.

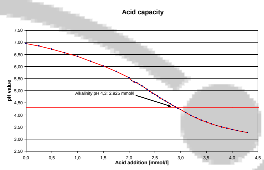
The usage of Argon as flushing gas of boreholes provides significant problems in quantifying CO_2 because of overlaid peaks including the isotope analysis of CO_2.

The Challenge

The analytical challenge is to obtain an extensive set of parameters which is considered representative for the in-situ conditions using only a few milliliters of water. The parameter analysis includes the determination of the composition of the water (main and trace elements) in very high quality, the isotopic compositions of the water and the dissolved constituents as well as their gas concentrations and isotopic signatures. So far the smallest sample volume needed for an analysis of a full set of parameters including the gas composition was 9 ml of water.

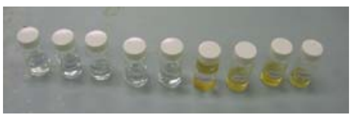




Specialities are the plotting of the titration curve to get additional information about the influences of organic acids.

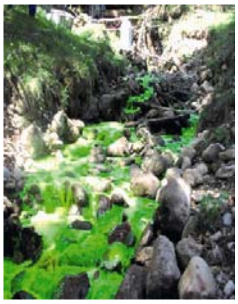
Pore waters and samples from experiments could show rather extreme compositions which strongly differ from usual natural water and gas samples. The water samples may have high salinities, high DOC contents, high contents of acids, high pH values, or high concentrations of trace elements. The control of ion balance for example has to consider all these unusual specialities. The chemical analyses by ion chromatography, ICP-MS, ICP-OES, and DOC analyser often require repetitive runs for several different dilution factors to achieve a proper calibration window for each parameter.

Though modern analytical techniques provide sophisticated methods for the analysis of very small volumes, any aliquot has to be treated with care and consideration, beginning with a sensory investigation of smell, turbidity and colour which gives you hints to organic components, H2S and trace metals.



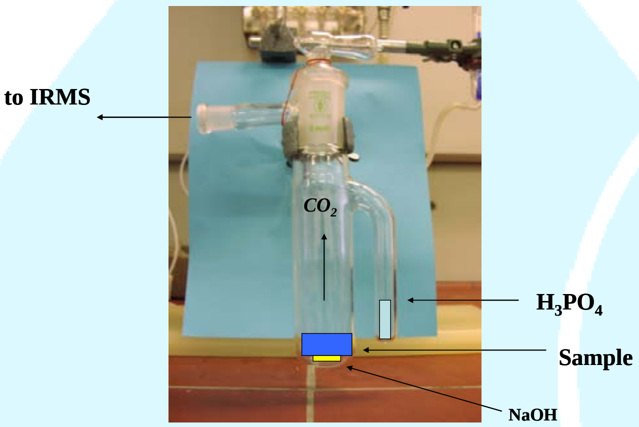






Infrastructure and Organisation

Obviously, the analysis requires a highly sophisticated infrastructure and organisation within the laboratory. Typical analyses are conducted without any waste or alteration of sample material. In case the analysis is not consuming the sample volume (e.g. 18O/2H by IRMS or conductivity by probe), it is used for other analyses subsequently (e.g. trace elements by ICP-MS or sulphate isotopes). Also special provisions are necessary for immediate post measurements of fragile parameters like sulphide, nitrogen components, alkalinity, or others. Very small fractions of water have to be divided and transferred into glass vessels protected by inert gas and fixated with special chemicals according to the intended analyses.



Gas Composition by GC

- H_2, O_2, He, Ar, Ne, CO_2, N_2
- Hydrocarbons

Gas isotopes by GC-MS-IRMS

- δ^2H-H_2
- δ^{13}C / δ^2H of hydrocarbons
- δ^{13}C / δ^{18}O-CO_2
- δ^{15}N-N_2

Parameter set for a 100 ml water or gas sample

Physical Parameters

- Redox potential
- pH value
- Conductivity
- Alkalinity at pH 4.3 and 8.2 (titration curve)

Sensoric Parameters

- Colour
- Smell
- Turbidity
- Particles, flakes, precipitates
- Oil phases

Chemical Parameters

- H_2S, NH_4, NO_2, PO_4 photometrically
- TIC, TOC, DOC by analyser
- Main ions and halogenides by IC
- trace elements by ICP-MS / -OES
- Organic acids e.g. acetate, formate by IC
- Organic compounds e.g. BTEX by GC and HPLC

Isotope Parameters

- δ^{18}O / δ^2H-H_2O by IRMS or CDRS
- δ^{13}C-TIC / -TOC by IRMS
- ^{14}C-TIC by AMS
- δ^{37}Cl by IRMS
- δ^{34}S / δ^{18}O-SO_4 by IRMS
- δ^{34}S-H_2S by IRMS
- δ^{15}N-NH_4 by IRMS
- ^{87}Sr/^{86}Sr by TIMS
- etc.