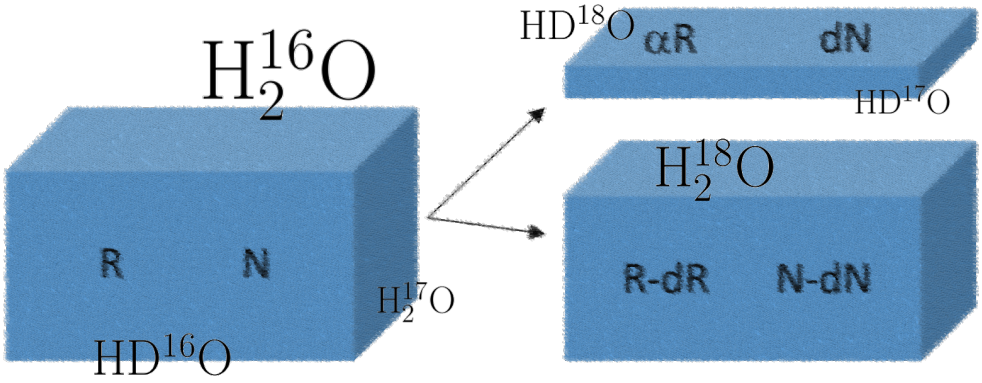
Advanced Lab Course (F55)
Rayleigh Fractionation



Institute of Environmental Physics

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If you find any mistakes or typos in the script or have suggestions for improvements, please send an email to `stherre@iup.uni-heidelberg.de`.

Location and Preparation

The experiments are carried out at the Institute of Environmental Physics (Institut für Umweltphysik), Im Neuenheimer Feld 229, lab 516 on the fifth floor and can be completed in three afternoons or mornings.

Before starting the experiment, please come to your workplace in office 506 on the same floor. There, you can store your bags, jackets and also snacks or drinks. For safety reasons, please do not let your things in the hallway and do not take any of it inside the lab.

Make sure you have thoroughly read the entire script and understand the fundamental processes of fractionation and isotope hydrology as well as the used measurement methods. You should be able to answer all the questions in the questionnaire before you begin the experiment.

The PC in office 506 is equipped with all the software you need to calibrate and evaluate your raw data from the water measurements. In addition, various software like Python, R or Excel is installed on said PC in case you want to do the complete data evaluation in the institute. You are of course free to do this part at home or wherever you like.

Safety Notes

Before starting the experiment, you must familiarize yourselves with the laboratory regulations and must have read the instructions in the script. A printed version of the lab regulations can be found next to the laboratory entrance.

- Please do not eat or drink inside the lab. You can **store any snacks or drinks and also your bags and jackets in office 506** at your PC working space on the same floor. You will also get a short introduction into lab safety from your supervisor.
- Besides the instruments used for this FP experiment, there are also several other experiments and analyzers set up in the laboratory, as well as pressurized gas bottles. Since neither the other instruments nor the gas bottles are needed for this experiment, **please do not touch them**.
- The laser spectroscopy analyzer in this experiment uses near-infrared laser light which does not escape the optical cavity in the configuration for this experiment. Therefore, you are not required to wear special laser goggles during the experiment. Nonetheless, **please do not try to open the instrument** to take a look inside, since this might severely damage the spectroscope or allow laser light to escape the cavity.
- During the experiment, you will have to use **magnetic stirrers**. These devices generate a rotating magnetic field which might be a potential hazard to anyone with a cardiac pacemaker.

Contents

1 Introduction

At the Institute of Environmental Physics, one focus of research among many others is the investigation of the cycling of meteoric or atmospheric water and other greenhouse gases such as CO_2, CH_4 or nitrous oxides. Determining the atmospheric concentrations and isotopic compositions of these constituents is an essential step towards the quantification of their transport fluxes, sources and sinks.

The growing world population poses increasing stress on freshwater availability and distribution due not only to an expanding need for drinking water, but also agricultural and industrial demand. In order to be able to provide sufficient and efficient freshwater supply in the future, it is crucial to gather information on the hydrological cycle and be able to interpret it.

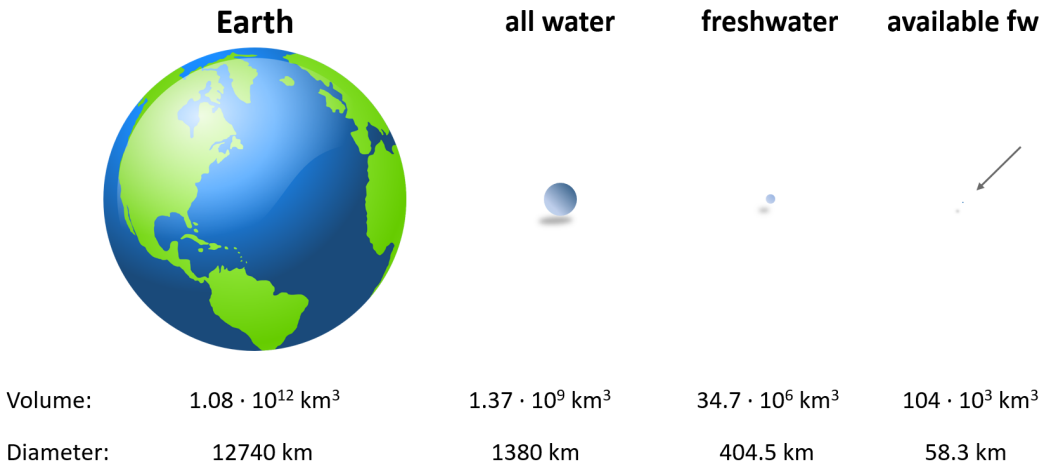


Figure 1.1: Graphic representation of water on Earth in comparison to the planet as a whole. Only 2.5 % of water on Earth is freshwater, of which only 0.3 % is liquid and readily accessible.

Stable isotopes in water, both in liquid and gaseous form, can be a valuable tool in their role as tracers of phase changes of water in the atmosphere. During phase transition processes in the hydrological cycle, such as evaporation or precipitation,

isotopic fractionation causes shifts in relative abundances of water isotopes. Since their relation was discovered to establish a crucial feature of atmospheric water cycling during precipitation, a special focus in hydrology is placed upon the stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H).

The findings from isotope and fractionation research have found applications in various fields of science and beyond. For instance, in climatology stable isotope records of ice cores from glaciers and polar regions allow for climate reconstruction over hundreds of thousands of years and provide knowledge over climate transitions from ice ages to warmer periods like it has last happened 11 700 years ago when our current warm age, the Holocene, began. Apart from many other direct applications in environmental science, isotope hydrology is even used in forensics and criminology, when for example the isotopic signature in the hair of murder victims can be matched to their places of origin.

This lab course is designed to give an insight into state of the art technologies employed in environmental hydrology and climate science and to show the implications of spectroscopic measurements of the isotopic composition of water samples. You will use Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS), a special form of laser absorption spectroscopy, specifically designed for this field of research, in order to determine the isotopic compositions of various water samples. With the results from these measurements, you will be able to calculate fractionation factors and their respective dependencies on external parameters like temperature. By analyzing and comparing mineral water samples from various places and rain water from Heidelberg you will see the isotopic characteristics of rainfall as an exemplary Rayleigh process and gain qualitative insight into isotope effects occurring during precipitation.

2 Theoretical Background

The theoretical introduction into isotopes and fractionation processes in this script mainly follows the first volume of Mook (2000). This book is also recommended if you are interested in learning more about isotope hydrology and its application. It can be read in the open-access area of the institute's library on the fourth floor.

2.1 Isotopes and Notation

Isotopes are atoms of the same element which differ in their number of neutrons and therefore also in their masses. The name "isotope" is from the greek words ísos (*equal*) and tópos (*place*) and means *at the same place* (in the periodic system). An element can have one (or more) heavy rare isotopes. For example, in addition to its common light isotope, ^{1}H, hydrogen has two heavy isotopes: deuterium (^{2}H or D) and tritium (^{3}H or T). Different isotopes of the same element can be either stable or radioactive, as is the case with deuterium (which is stable) and tritium (which is radioactive). The abundances of stable isotopes of hydrogen and oxygen are shown in table 2.1.

	Hydrogen		Oxygen		
Isotope	^{1}H	^{2}H	^{16}O	^{18}O	^{17}O
Abundance in %	99.9885	0.0115	99.757	0.205	0.038
1 part per	≈1	8696	≈1	488	2632

Table 2.1: Abundance of stable isotopes of hydrogen and oxygen.

Isotopologues are molecules that differ only in their isotopic composition, i.e. they have at least one atom substituted by a different isotope. Examples of isotopologues of water and their abundances are shown in table 2.2. In this script, for the sake of simplicity, the term isotope is used synonymously for isotopologue and the correct meaning can be deduced from the context. As the concentration of molecules containing multiple heavy isotopes is relatively tiny, in the context of measurement, the quantitative difference between molecular and atomic isotopic ratios is negligible.

Isotopologue	relative abundance	1 part per
$H_2^{16}O$	9.973×10^{-1}	≈1
$H_2^{18}O$	1.999×10^{-3}	500
$H_2^{17}O$	3.719×10^{-4}	2 689
$HD^{16}O$	3.107×10^{-4}	3 219
$HD^{18}O$	6.230×10^{-7}	1 605 000
$HD^{17}O$	1.158×10^{-7}	8 636 000

Table 2.2: Abundances of six isotopologues of water.

The following sections aim at familiarizing you with the common nomenclature in isotope hydrology.
The **isotope ratio** R is the ratio of the abundance of a considered rare isotope to the abundance of the most common isotope:

$$R = \frac{\text{abundance of rare isotope}}{\text{abundance of common isotope}} = \frac{\text{abundance of heavy isotope}}{\text{abundance of light isotope}} \tag{2.1}$$

As an example, for the heaviest stable oxygen isotope the ratio of ^{18}O to ^{16}O is $R = \frac{0.205}{99.757}$ which is approximately 0.002. The absolute isotope ratio R is not to be confused with the **isotope concentration** or **mixing ratio**, which is the abundance of a given isotope relative to *all* isotopes of the element. For example with isotopes of hydrogen, the isotope mixing ratio is 99.985% for ^1H and 0.0115% for ^2H, whereas the isotope ratio is $R = {}^2H/{}^1H = 0.015\,\%$.
There are several reasons why isotope ratios are in general not given as their absolute ratios R: From the examples above it is already clear that R is usually a rather small number, unwieldy for reporting. Absolute ratio results from one instrument or lab may be shifted with respect to those obtained by others, and a single instrument may show a similar shift over time, making direct comparison of absolute results meaningless. Additionally, interest generally lies not necessarily on absolute ratios themselves but rather in their variations during phase changes and among environmental reservoirs.

Therefore isotope ratios are measured and reported as a relative deviation from a reference material or a standard, commonly called the **δ-notation**:

$$\delta := \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \tag{2.2}$$

For example the ratio of the heavy ^{18}O isotope is expressed as

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{standard}}} - 1$$

Since these δ-values are very small numbers, they are usually reported in per mil (‰): Instead of $\delta^{18}O = -0.0085$ one writes $\delta^{18}O = -8.5\,‰$. It is important to keep in mind that δ is just a small number and not *defined* in per mil, i.e. per mil is not a unit. This is particularly relevant when using mathematical equations.
A positive delta value thus indicates the sample being "heavier" than the standard, meaning it is enriched in the rare (heavy) isotope relative to the standard, whereas the standard is "lighter" or depleted in the rare isotope abundance relative to the sample. When two samples are compared in terms of their isotopic composition, it is clear from equation 2.2, that $\delta_A > \delta_B$ indicates that the sample A is enriched in the rare isotope relative to sample B, and B is depleted in the rare isotope relative to A. One can also simply say that A is "heavier" than B.

The above definition of delta notation in eq. 2.2 obviously requires some standard material. For isotopologues of water, common international standards are VSMOW (*Vienna Standard Mean Ocean Water*) and SLAP (*Standard Light Antarctic Precipitation*), where VSMOW is a mixture of ocean waters and SLAP was obtained from water samples from the Antarctic. Both of them were created and are distributed by the IAEA (*International Atomic Energy Agency*) in Vienna.

In addition to international or external standards which are indispensable for reporting, in-house standard samples are used to calibrate the measurement setup and assess the stability and reproducibility of isotope measurements. For this experiment, these in-house standards consist of particular water samples spanning the range of isotopic values investigated during research. They are *Alpen* (a sample from the Alps), *Colle* from a glacier in Southern Switzerland, *Sammelprobe* and *VE* which is deionized water (German: "**v**oll**e**ntsalztes Wasser") from the institute's water system.

2.2 Fractionation

According to the assumption of classical chemistry, the chemical properties of different isotopes, isotopologues or molecules with isotopes at different positions (*isotopomeres*) are equal. Although this is true to a large extent, there are, however, measurable differences in physical and chemical properties of isotopes or isotopic molecules due largely to their differing mass.
The resulting temporal and spatial variations in isotopic abundance ratios and the processes leading to them are called ***isotope fractionation***. Fractionation

standard	δD [‰]	δ^{18}O [‰]
Alpen	-176.076	-22.653
Colle	-49.656	-8.013
VE	-60.545	-8.476
Sammelprobe	1.455	7.923
VSMOW 2	0.0 ± 0.3	0.0 ± 0.3
SLAP 2	-427.5 ± 0.3	-55.50 ± 0.02

Table 2.3: Isotopic values of the in-house and international water standards.

occurs for example during a phase transition of a compound – the most significant one for this lab course and many branches of environmental research being the transformation of liquid water to water vapor and vice versa. Other processes in which fractionation occurs include chemical reactions such as the organic transformation from carbon dioxide into other carbon compounds as it occurs during photosynthesis in plants or the difference between the isotopic signatures of two compounds in chemical equilibrium (e.g. dissolved bicarbonate and carbon dioxide at the sea surface) or in physical equilibrium (liquid water and water vapor).

For a theoretical derivation of isotope fractionation, the thermodynamical equation from kinetic gas theory for the kinetic energy of a molecule with mass m in three dimensions is considered:

$$\frac{3}{2}k_B T = \frac{1}{2}m\overline{v^2} \tag{2.3}$$

with the Boltzmann constant k_B, absolute temperature T and the average molecular velocity v. From this equation it is clear that $v \sim \sqrt{m^{-1}}$ for a constant temperature T, implying that isotopes of the same element at the same temperature have differing molecular velocities. Explicitly: heavier molecules on average move slower than lighter ones. This has direct consequences for molecular diffusion velocities (lighter molecules diffuse faster) and by extension a prerequisite for chemical reactions: collision frequencies of lighter molecules are significantly higher, they therefore generally react faster.

Besides the reduced mobility of molecules with higher masses, the second major cause of fractionation are differences in binding energies, which are generally higher for heavier molecules. To understand this relation, we consider the diatomic molecule H_2 with its reduced mass $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$, rotational energy levels

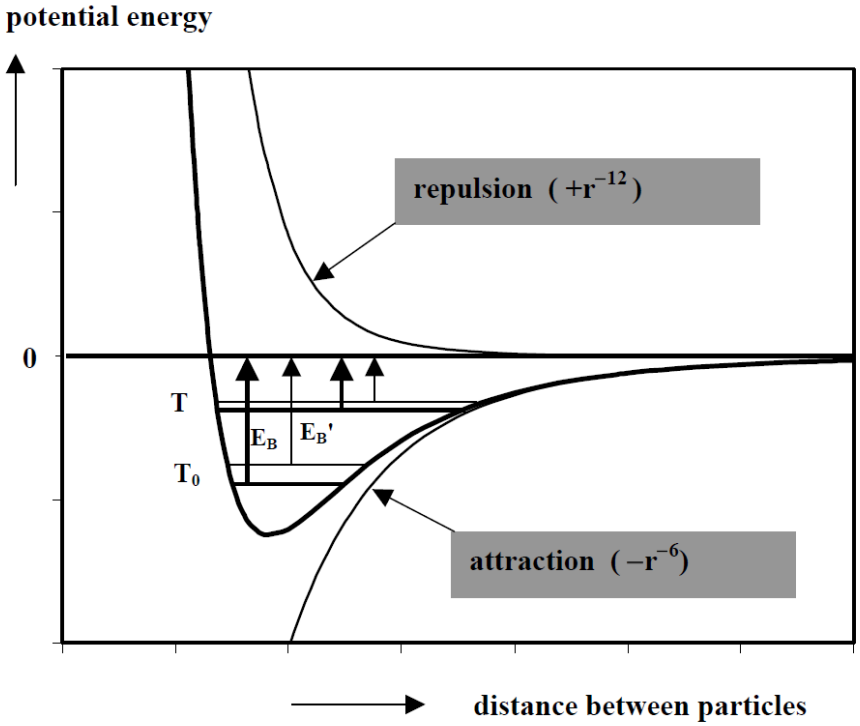


Figure 2.1: Schematic representation of the potential energy distribution of a diatomic molecule. The resulting shape of the energy well is caused by the counteracting repulsive and attractive forces between the two particles. The arrows indicate the binding energies for the considered heavy/light isotopic molecule. Figure taken from Mook (2000).

$$E_{rot} = \frac{\hbar^2}{2I} J\,(J+1) \tag{2.4}$$

and vibrational energy levels

$$E_{vib} = \hbar\omega_0 \left(n + \frac{1}{2}\right) \tag{2.5}$$

where $I = \mu R^2$ is the moment of inertia, J is the rotational quantum number, $\omega_0 = \sqrt{D/\mu}$ is the vibrational frequency and D is the force constant.
For heavier molecules with higher μ, the zero-point, vibrational and rotational energies are lower, whereas the dissociation energy is higher. This can be seen in Fig. 2.1 where the lines represent the energy levels of a molecular binding at different temperatures for a molecule with heavy and light isotopes. The heavier isotopic particle is situated deeper in the energy well than the lighter (heavy

line in Fig. 2.1) and therefore escapes less easily: The heavier isotopic particle (atom or molecule) generally has a higher binding energy going along with slower diffusion and reaction rates.

An important example from the hydrological perspective is the lower vapor pressure of heavy water isotopes $H_2^{18}O$ and HDO resulting in inhibited evaporation compared to H_2O which causes an enrichment of the heavy isotopes in the condensed phase due to preferred evaporation of the lighter H_2O molecules.

Another effect visible in Fig. 2.1 is the decreasing difference between the energy levels of two different isotopes at increasing temperatures: In warmer conditions, the binding energy decreases and the energy levels of the considered isotopologues converge. This already implies that for higher temperatures isotopic fractionation effects are less significant than for lower temperatures. Some properties for different water isotopes are given in table 2.4.

	H_2O	D_2O	$H_2^{18}O$
density at 25 °C [g cm^{-3}]	0.9970	1.107	1.110
melting point [°C]	0.00	3.81	0.28
boiling point [°C]	99.98	101.42	100.14

Table 2.4: Several properties of H_2O, D_2O and $H_2^{18}O$ emphasizing the difference between isotopologues of the same chemical compound.

2.2.1 Kinetic and equilibrium isotope fractionation

Establishing a mathematical description for fractionation processes requires a quantification of the isotope ratios of two compounds in chemical equilibrium ($A \Leftrightarrow B$) or of the compounds before and after a one-way physical or chemical transition process ($A \Rightarrow B$). This is achieved by invoking the **isotope fractionation factor** which is a ratio of two isotope ratios:

$$\alpha_A(B) = \alpha_{B/A} = \frac{R(B)}{R(A)} = \frac{R_B}{R_A} \tag{2.6}$$

This factor describes the ratio in phase or compound B relative to A. Since fractionation effects are generally small, α usually has values very close to 1, which is why another formulation is sometimes used, known simply as **fractionation**, which is defined as the deviation of α from 1:

$$\varepsilon_{B/A} = \alpha_{B/A} - 1 = \frac{R_B}{R_A} - 1 \tag{2.7}$$

Consequently, fractionation of $\varepsilon > 0$ represents an enrichment of the rare isotope with respect to phase B, whereas $\varepsilon < 0$ describes depletion.

Based on the boundary conditions of the considered process, two basic kinds of fractionation can be distinguished:
During **kinetic fractionation** an irreversible process takes place, like the evaporation of water with immediate removal of the vapor phase from contact with the remaining liquid water. Other examples for this type of process include gas diffusion and absorption. In general, lighter molecules tend to react faster in chemical reactions and evaporate more easily in phase transitions.
The second basic type of isotopic reactions is called **equilibrium fractionation** which represents the process involved in an equilibrium reaction. As an example, consider an isotope exchange reaction between two phases A and B

$$^{*}\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{A} + {}^{*}\mathrm{B} \tag{2.8}$$

where the asterisk indicates the rare isotope, the fractionation factor α is equal to the equilibrium exchange reaction constant of that very reaction:

$$K = \frac{[A] \cdot [{}^{*}B]}{[{}^{*}A] \cdot [B]} = \frac{R_B}{R_A} = \alpha_{B/A} \tag{2.9}$$

In natural processes like the evaporation of water, the occurring fractionation process is not entirely represented by either of the aforementioned types, since there will always be exchange to a certain amount between the two phases, albeit limited by the characteristic residence time of the different phases (e.g. how long water vapor is in contact with the liquid phase before it is carried away by wind). As a matter of fact, the condensation of evaporated water on a larger scale (rainfall) already shows that evaporation from ocean water cannot be a purely kinetic one-way process.

2.2.2 Rayleigh process

In hydrology, particular interest lies on the change in isotopic signature of a reservoir which is subject to continuous removal of water by, for example, evaporation, since this process is very often representative of naturally occurring processes in lakes, clouds or other reservoirs.

Invoking a simple box model describing a reservoir with a water sink representing evaporation (see Fig. 2.2) allows for quantification and mathematical interpretation of this process. In this model, N is the total number of molecules, and R is the isotopic ratio.

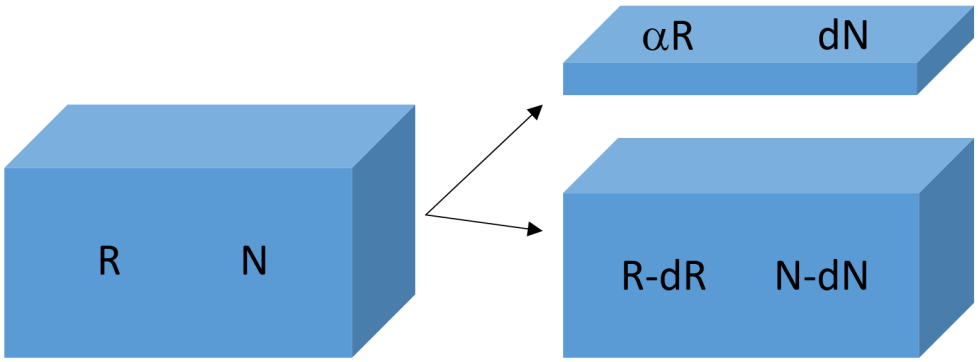


Figure 2.2: Schematic view of a Rayleigh fractionation process considering an initial reservoir with N molecules and isotopic ratio R. During evaporation, an infinitesimal $\mathrm{d}N$ is removed and its isotopic signature is altered by the fractionation factor α.

The mass balance of the rare isotopic species before and after the removal of an infinitesimal $\mathrm{d}N$ by evaporation with the fractionation factor α, which is assumed to be constant, is described by:

$$R\,N = (R - \mathrm{d}R)(N - \mathrm{d}N) + \alpha R\,\mathrm{d}N. \tag{2.10}$$

Neglecting the products of differentials, this can be rearranged to the differential equation

$$\frac{\mathrm{d}R}{R} = (\alpha - 1)\frac{\mathrm{d}N}{N} \tag{2.11}$$

with the general solution

$$\ln R = (\alpha - 1)\ln N \tag{2.12}$$

The boundary conditions to solve this differential equation are the initial values of the reservoir before fractionation: R_0 and N_0. The solution is then given as

$$\frac{R}{R_0} = \left(\frac{N}{N_0}\right)^{\alpha-1} \tag{2.13}$$

or in δ values with respect to a standardized reference and with $\varepsilon = \alpha - 1$

$$\delta = (1 + \delta_0)\left(\frac{N}{N_0}\right)^{\varepsilon} - 1 \tag{2.14}$$

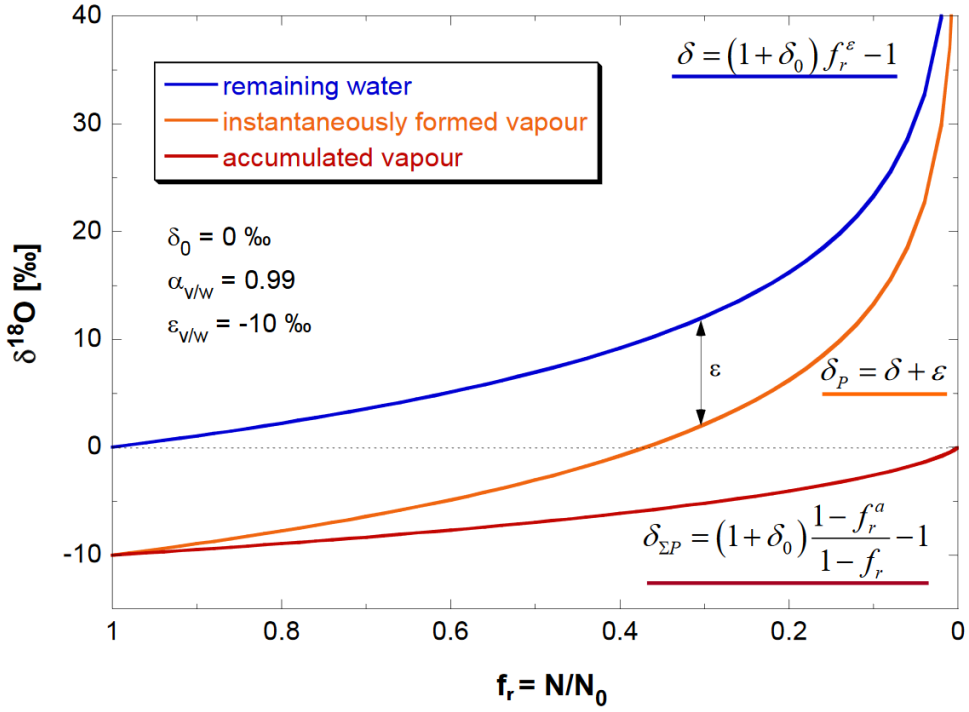


Figure 2.3: Changes in isotopic composition during Rayleigh fractionation process in a closed system. The reservoir has an initial isotope ratio δ^{18}O. The fractionation factor is $\alpha = 0.99$.

In the two latter equations the term N/N_0 is the remaining fraction f_r of the initial reservoir.

Considering a closed system of evaporation where a reservoir of liquid water is successively evaporated and the resulting water vapor is confined to be analyzed, the Rayleigh process can be visualized by looking at the isotopic composition of the residual water, the instantaneously formed water vapor and the cumulating water vapor. By definition, at the moment of evaporation, the evaporating water vapor has an isotopic signature enriched or depleted by the fractionation ε, respectively. It is also clear that the accumulated vapor after completion of the evaporation ($f_r = 0$) has to have the same isotopic composition as the liquid water before ($f_r = 1$) by simple consideration of mass conservation. Fig. 2.3 visualizes the evolution of isotopic signatures of a reservoir subject to fractionation with the mentioned considerations.

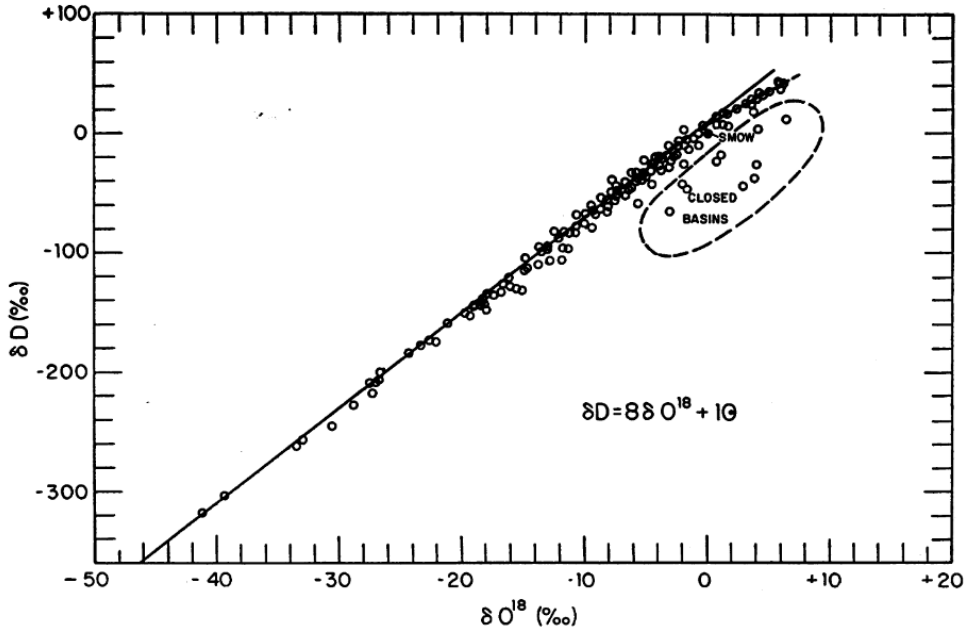


Figure 2.4: δD and δ^{18}O variations in rivers, lakes, rain and snow, expressed as per millage enrichments relative to SMOW. Points which fit the dashed line at upper end of the curve are rivers and lakes from East Africa. Figure taken from the original publication Craig (1961).

2.3 Global Meteoric Water Line

One of the most significant empirical findings of hydrology was established by Harmon Craig (Craig 1961) when the correlation of δD and δ^{18}O values of 400 meteoric water samples from many parts of the world was investigated. The linear relation expressing the strong correlation of δD and δ^{18}O is known as the **Global Meteoric Water Line (GMWL)** which is described by the equation

$$\delta D = 8 \cdot \delta^{18}\mathrm{O} + 10‰ \tag{2.15}$$

The slope in this functional relation is based on the ratio between the equilibrium isotope fractionation of hydrogen and oxygen for the precipitation condensation process. The intercept representing a deuterium excess of 10 ‰ depends on average humidity and temperature conditions in the water evaporation region.

In Fig. 2.4, the deviation from the general trend at heavier isotope values represents waters from closed basins in which evaporation is a dominant factor governing the isotopic ratios, in this case rivers and lakes in East Africa. They fit a line with a slope of about 5, in contrast to the slope of 8 found for most of the data. Studies of evaporation in the laboratory, and in areas where seasonal data

have been obtained, show that in free evaporation at ordinary temperatures the heavy isotope enrichment ratio $\delta D/\delta^{18}\mathrm{O}$ behaves differently from an equilibrium process and more similar to kinetic fractionation. This explains why these values consistently follow a smaller slope compared to the GMWL of about 5 as observed for East African basins.

2.4 Isotope Effects

In connection with the GMWL, several effects were discovered concerning the isotopic signature for meteoric waters in different geographic or orographic regions. All these effects can be explained by consideration of basic fractionation processes during the propagation of a water vapor parcel from its original source towards the eventual precipitation location. The most important of these effects are explained here:

Continental effect

The further a water vapor parcel travels inland over the continents, the longer is it subject to precipitation favoring heavier isotopes. Therefore, the longer the distance from the original recharge evaporation area at sea, the more depleted the isotopic signature of precipitation. This effect is, for example, especially significant in North America where isotopic rainfall signatures near the coasts are close to zero but become very depleted in regions close to the Rocky Mountains, where $\delta^{18}\mathrm{O}$ reaches values as low as $-18\,‰$ (see Fig. 2.5).

Latitude and temperature effect

An analysis of the investigated precipitation and meteoric water isotopic signatures that were used to establish the GMWL found a latitude effect of an approximate decrease in $\delta^{18}\mathrm{O}$ of $-0.6\,‰$ per degree of latitude for coastal and continental stations in Europe and the USA. In colder regions like the Antarctic continent, this effect is intensified resulting in an isotopic depletion of up to $-2\,‰$ per degree of latitude. Similar to the continental effect, this is due to the continuous depletion of water vapor travelling from the evaporation regions near the equator towards higher latitudes. Rainout is in this aspect not only expedited by the distance travelled by the respective water parcel, but also by the dependency of saturation water vapor pressure of air on temperature, as it is described by the Clausius-Clapeyron equation

$$p_{\mathrm{sat}}(T) = p_0 \cdot \exp\left[-\frac{L}{R_{\mathrm{m}}}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{2.16}$$

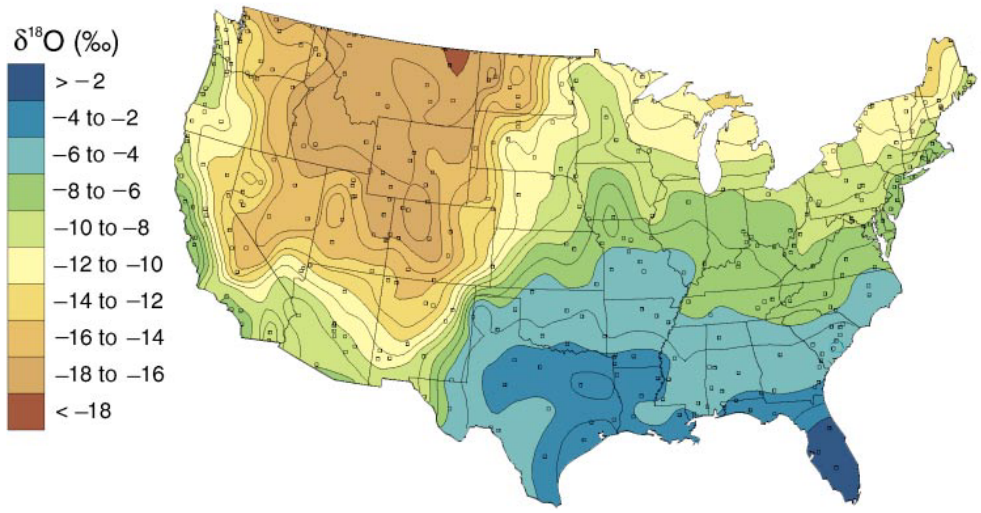


Figure 2.5: Continental δ^{18}O isotope effect of river waters in the US. The highest values are seen in the areas near the southeast coast, whereas the most depleted values are seen in the mountainous regions in the northwest. Figure taken from Kendall & Coplen (2001).

with the specific latent heat L and the gas constant R_m of water vapor and starting conditions p_0 and T_0. Thus, as an airmass is cooled on its way towards higher latitudes, more and more water vapor is forced to rain out and the remaining water is further depleted in terms of isotope ratio.

Seasonal effect

The seasonal effect is a direct consequence of latitude and temperature dependencies in precipitation formation: In northern hemispheric winter, the water that ultimately falls as rain in mid-latitude regions has, on average, traveled a longer distance from its origin due to the southward shift of Intertropical Convergence Zone (ITCZ), the region with highest insolation and evaporation. As a consequence, lower winter temperatures at a particular site are again associated with more depleted values, similar to the aforementioned temperature effect.

Other effects

In addition to the mentioned phenomena, several other aspects can be considered, when analyzing the isotopic variations in precipitation, such as the inverse correlation between the altitude of a collection site and δ^{18}O (between $-0.2\,‰$ to

$-0.6\,‰$ per 100 m) due to increased condensation during orographic uplift of a water vapor parcel, named the altitude effect.

For paleoclimatology, the amount effect is of special importance. In 1964 Dansgaard observed a relation between the amount of precipitation and $\delta^{18}O$ in that strong rainfalls (as they are for example seen during the passage of the ITCZ) are accompanied by extremely depleted values in $\delta^{18}O$ and δD.

All the mentioned effects can allow for the reconstruction of paleoclimate from archives such as sediment or ice cores, as well as speleothems, by looking at the evolution of their isotopic signature over time.

3 Measurement Methods

To quantify the isotopic composition of samples, isotope ratio mass spectroscopy (IRMS) has long been the most common method. In IRMS a beam of ions is sent through an arrangement of electric and magnetic fields where the ions are deflected and thus separated according to their mass-to-charge-ratio (Nier 1991).

Developments in the field of lasers, due largely to their use in telecommunications, made laser spectroscopic systems possible. They take advantage of the isotopologue-specific rotational-vibrational transitions to determine the isotopic composition of gaseous samples (Kerstel & Gianfrani 2008). The basic principle of laser spectroscopic instruments is absorption of laser light of characteristic frequencies by the medium of interest. Since the instrument used in this experiment is a further development of a laser spectroscopy method called Cavity Ring-Down Spectroscopy (CRDS) and actively makes use of this technique, the basic principles of laser absorption spectroscopy will be discussed first. It is emphasized that the instrument used in this experiment does not use classical CRDS.

3.1 Absorption Spectroscopy

The intensity I of a plane wave passing through a homogeneous and absorbing medium decreases by

$$dI = -\alpha I dz \tag{3.1}$$

along the traveled distance dz. The wavelength-dependent absorption coefficient $\alpha = \alpha(\lambda)$ represents the absorbed ratio dI/I. When we suppose that $\alpha(\lambda)$ is independent of I (linear absorption), integration of equation 3.1 yields the Lambert-Beer-law

$$I(\lambda, z) = I_0 \exp\left(-\alpha\left(\lambda\right) z\right) \tag{3.2}$$

According to this fundamental law of spectroscopy, the intensity of light passing through an absorbing sample decays exponentially and is dependent on the incoming intensity, the path length, the wavelength of the utilized light and the absorption coefficient of the sample which itself depends of the wavelength (Demtröder 2008). When the absorption coefficient is written as

$$\alpha(\lambda) = C\epsilon(\lambda) \tag{3.3}$$

with C being the molecular concentration of the light-absorbing species and the extinction coefficient $\epsilon(\lambda)$, the sample concentration can be determined by a measurement of the ratio I/I_0, provided that the extinction coefficient is known.

In most applications, one single pass through the medium of interest is not sufficient to reach a detectable signal, as the natural abundance of rare isotopes is in the range of only a few per mil. In order to increase the optical path length, cavities with (semitransparent) mirrors are used, thus the laser light passes through the medium of interest several times. Depending on the reflectivity R of used mirrors, the effective path length is $L_{\text{eff}} = L/(1-R)$, where L is the cavity length. An example: With a typical reflectivity of $R = 0.9999$ for both mirrors the path length increases by a factor of 10000.

The fundamental aspect of CRDS is the measurement of the so-called ring-down time. This is the time it takes for the light intensity leaking out of one of the mirrors to reach zero (or a fixed cut-off intensity) after the laser is switched off.

The intensity of the leaking laser light after shutoff decays exponentially according to

$$I(\lambda, t) = I_0 \, \exp\left(-\frac{t}{\tau(\lambda)}\right) \tag{3.4}$$

where I_0 is the light intensity at the time the laser is shut off, $\tau(\lambda)$ is the ring-down time constant, t is the time since shut-off and λ is the wavelength of the laser. The inverse of the the ring-down time constant $\tau(\lambda)$ is the loss rate

$$R(\lambda) = \frac{1}{\tau(\lambda)} \tag{3.5}$$

which includes the loss rate of the empty cavity $R_0(\lambda)$ and the loss rate by absorption due to the gas in the cavity $R_{\text{abs}}(\lambda, C)$:

$$R(\lambda, C) = R_0(\lambda) + R_{\text{abs}}(\lambda, C) = R_0(\lambda) + c\,C\epsilon(\lambda) \tag{3.6}$$

with the speed of light c. Equation 3.3 was used to obtain the concentration dependence. Because $c\,\epsilon(\lambda)$ is constant, $R(\lambda, C)$ is linearly dependent on the sample concentration.

When the laser is tuned to a wavelength range of interest, that is, the range which includes absorption features of the investigated isotopologues, ring-down times are recorded. By fitting the wavelength scan to the line shapes of each species and using the result of this fitting as the intensity of the observed species, the concentration can be accurately assessed. The relative intensity of the peaks for the isotopologues of interest can be converted to δ-values. Through calibration, this isotope ratio can be directly connected to the VSMOW-SLAP scale. Absorption lines of molecules can overlap, as is the case with alcohol and water. Therefore, to provide a high selectivity, it is useful to use a narrow line width laser or to apply a correction.

3.2 Off-Axis Integrated Cavity Output Spectroscopy

The instrument geometry as described in Fig. 3.1 is similar to conventional CRDS: Two high-reflective mirrors frame a temperature and pressure controlled cavity. Laser light of an intensity I_L is introduced into the cavity through one of the mirrors and a detector is positioned behind the other mirror to detect the intensity leaking out of the cavity. The absorption signal is obtained by temporal integration of the laser intensity transmitted through the cavity.

In contrast to conventional CRDS, the laser beam is directed off-axis with respect to the cavity axis, hence the name Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS). This avoids unwanted effects due to cavity resonances and the multiple reflections within the cavity are spatially separated. In fact, the multiple reflections can be seen on the mirrors as a series of spots in an elliptical pattern (Herriott et al. 1964). The per-pass rotation θ around the ellipse, i.e. the angle between two subsequent spots, is $\cos(\theta) = 1 - L/R_m$, where L is the cavity length and R_m is the curvature of the mirrors. The pattern becomes reentrant, meaning that the light retraces its path through the cavity, when the reentrant condition $m2\theta = n2\pi$ is fulfilled. Here, m is the number of optical round-trip passes and n is an integer. The properties of the cavity become similar to one that is m times longer (Herriott & Schulte 1965).

The transmitted laser intensity I through the empty cavity of length L and mirror reflectivity R and transmission coefficient T is given as

$$I = \frac{I_L C_p T}{2(1-R)}(1 - \exp(-t/\tau)) \tag{3.7}$$

where the ring-down time is $\tau = \frac{L}{c(1-R)}$. I_L is the intensity of the incident laser beam, L is the cavity length and c is the speed of light. C_p is the so-called coupling parameter which has a value between 0 and 1 and depends on geometrical factors and the properties of the light sources. When the laser is switched on, a ring-up with the same time constant τ as ring-down occurs. Steady state is reached, when half of the laser power coupling into the cavity leaves through each mirror. To record the characteristic time constant τ, the laser can be switched off just like with CRDS. When the laser is coupled continuously into the cavity, τ can also be recorded in an empty cavity or when the laser is tuned to non-absorbing wavelengths. By recording the ring-down time τ, the effective optical path length in the cavity $L_{\text{eff}} = L/(1-R)$ can be monitored. The mirror reflection coefficient, which is given as R for an empty cavity, becomes R' when an absorbing medium is present in the cavity:

$$R' = R\exp(-\alpha(\lambda)L) \tag{3.8}$$

with the wavelength-dependent absorption coefficient $\alpha(\lambda)$. A comparison with

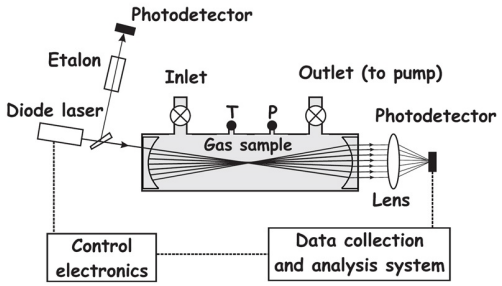


Figure 3.1: Schematic of instrument setup for OA-ICOS from (Baer et al. 2002).

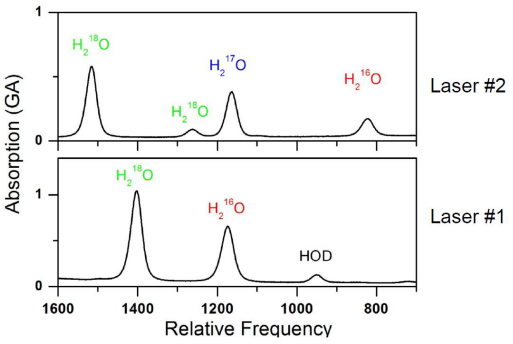


Figure 3.2: Absorption spectra of the two lasers from (Baer 2013).

the Lambert-Beer Law (equation 3.2) for a single pass yields that $I/I_0 = R'/R$.

Information about the species present in the cavity is not exclusively obtained through switching the laser off and on, as information is also contained in steady state: The change in steady state output $\Delta I = I_L - I$ is the difference of incident laser intensity I_L and the transmitted laser intensity I. ΔI is different from zero when an absorbing species is present in the cavity. The change in steady-state cavity-output is then given as

$$\frac{\Delta I}{I_0} = \frac{GA}{1 + GA} \tag{3.9}$$

with the single-pass absorption $A = 1 - \exp(-\alpha(\lambda)L)$ and $G = R/(1 - R)$.

The mole fraction of the medium of interest can be determined by integrating the measured spectra over the absorption feature. Additional measurements of cavity temperature and pressure, effective optical path length and line strength of the target species are required, since the line width of the absorption lines is temperature dependent (Sturm & Knohl 2010).

In the instrument used in this experiment, two wavelength-scanning lasers are used and allow for simultaneous measurements of the four different species:

- Laser 1: $H_2^{18}O$, $H_2^{16}O$ and $HD^{16}O$
- Laser 2: $H_2^{18}O$, $H_2^{17}O$ and $H_2^{16}O$

A sketch of the absorption features of the two lasers is shown in figure 3.2. As the extinction coefficient $\epsilon(\lambda)$ is wavelength dependent, different species are separated by tuning a laser over characteristic absorption lines. In the instrument manufactured by Los Gatos, the laser wavelength is swept at 100-1200 Hz, by

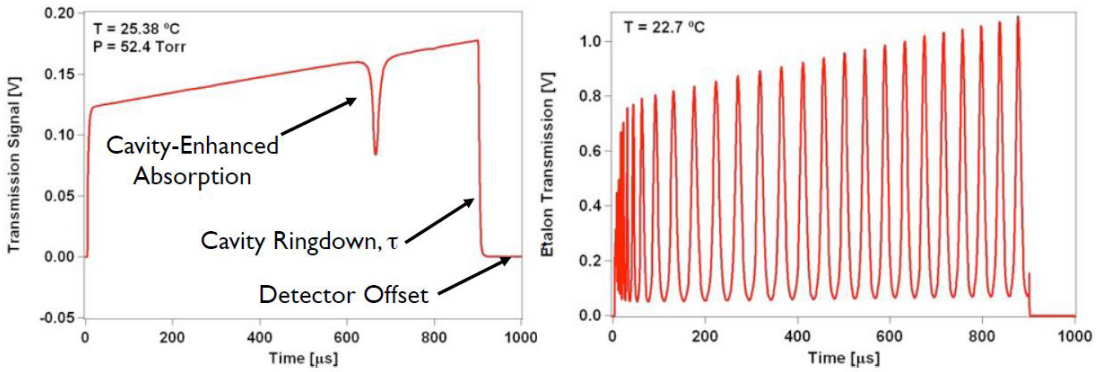


Figure 3.3: Transmission signal of the cavity and transmission through the etalon, dependent on time (Baer 2010).

applying a saw-tooth laser current ramp to the laser current source. The transmission through a solid etalon (SiO_2) is used to accurately determine the laser tuning rate and to convert time to relative laser frequency. The obtained transmission spectrum allows measurements of absorption, baseline and detector offset. The cavity-ringdown is a constituent for measurements too, as it yields the mirror loss and thus the effective optical path length $L_{\text{eff}} = L/(1 - R)$ (Baer 2013). The resulting transmission signal and the etalon transmission are shown in Fig. 3.3.

3.3 Triple Isotope Water Analyzer TIWA-45EP

The instrument used in this experiment is a Triple Isotope Water Analyzer TIWA-45EP. It consists of a Triple Water Vapor Isotope Analyzer (T-WVIA) and a Triple Liquid Water Isotope Analyzer (T-LWIA).

Measurements can either be performed for vapor or for liquid water. Whenever there are no measurements of liquid water, the instrument is set to the vapor mode. A sketch of the instrumental set-up is shown in Fig. 3.4.

3.3.1 Water vapor isotope analysis (WVIA) mode

In WVIA-Mode, the isotopic composition of water in water vapor in ambient air is measured. Ambient air enters the cavity via a heated inlet line, which is described in detail by Leinfelder (2014). Mean cavity temperature for the period from January to October 2015 was $(46.68 \pm 0.03)\,°C$ and mean gas pressure for the same period was $(40.149 \pm 0.003)\,$torr.

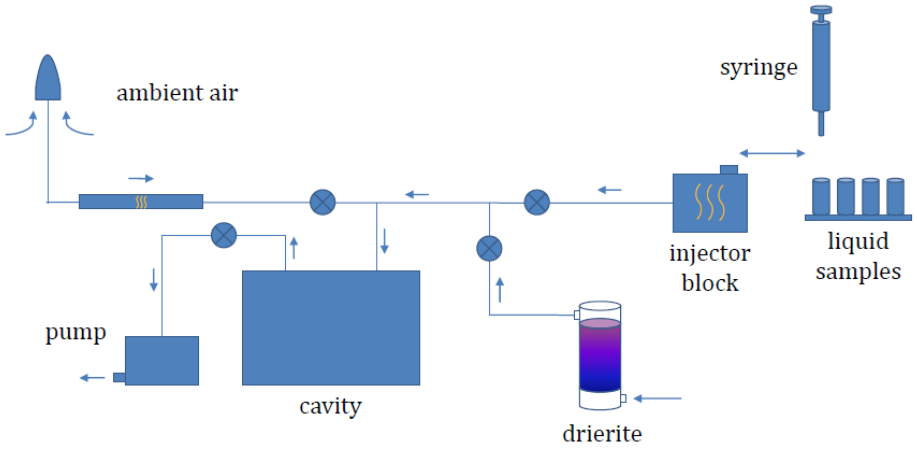


Figure 3.4: Principle of the two mode analyzer. Measurements of ambient air (left part of the set-up) and of liquid samples (right part of the set-up) are possible.

3.3.2 Liquid water isotope analysis (LWIA) mode

In the instrument's LWIA mode, δ^2H, δ^{18}O and δ^{17}O of water samples are determined. To avoid contamination of the instrumentation, water is filtered before if necessary. The water samples are filled into septum-sealed vials using a pipette and then positioned in sample trays on a tray holder of the autosampler. An autosampler syringe draws up the preset amount of water and injects it into the heater block, which is heated to approximately 100 °C to allow for evaporation and equilibration. The vaporized sample is directed to the evacuated cavity through a sample line which is 1.8 m long and made of teflon. In the cavity, the spectra are measured to determine isotopic ratios. For each injection, 30 measurements are performed. After each injection, the cavity is flushed, vented and pumped out before the next sample is flushed in. Dry air for the flushing procedure is provided by a cartridge filled with a water vapor absorbing substance. Temperature in the cavity is held constant by an internal heater. With the selected parameter settings, one injection process takes about two minutes.

4 Questionnaire

The following questions aim to cover the fundamental aspects of this experiment and its underlying processes and theoretical background. You should be able to answer all of them once you have carefully read and understood the previous chapters.

- What is isotopic fractionation? When and why does it occur?
- How do you quantify fractionation? Which nomenclature is used?
- What is a Rayleigh process and why is it often used in environmental isotope hydrology?
- Do you expect a dependency of fractionation on temperature? If yes, what is the reason for it? If not, why not?
- What is the GMWL and what are its main characteristics?
- Which hydrologic isotope effects are there?
- What are the causes for the latitude effect in precipitation?
- What is the general principle of Off-Axis Integrated Cavity Output Spectroscopy?
- The mirrors in the cavity do not reflect all of the incident light. Why is this aspect fundamental for the experiment?
- Which effects enable you to use laser absorption spectroscopy for water isotope analysis?
- How – in principle – does the analyzer determine the concentration of a certain isotopologue species?
- How do you operate a pipette?

5 Experiments

The experiments are always carried out in three consecutive days.

Schedule

First day (4h):

- First part of experiment 5.1
- Experiment 5.2
- Start first overnight measurement:
  liquid samples from 5.1

Second day (4h):

- Second part of experiment 5.1
- Calibration/Evaluation of experiment 5.2 and first part of 5.1
- Start second overnight measurement:
  liquid water samples from 5.1, 5.3 and 5.4

Third day (<2h):

- Calibration/Evaluation of remaining measurements from 5.1, rainwater samples from 5.3 and unknown samples from 5.4

5.1 Evaporation at Different Water Temperatures

In this part your goal is to calculate the fractionation factors for evaporating water depending on the water temperature. Therefore the water will be heated in glass bowls to three different temperatures (40 °C, 50 °C and 60 °C) using a magnetic stirrer with a heated plate. There are only two magnetic stirrers, so you have to split the experiment into two parts.

There is a temperature and humidity data logger, which records the room temperature and the air moisture every five minutes. It should say "rec" on the display. Before you fill the glass bowls with water, weigh them together with the stirring bar. Now fill each pan with 500 ml to 700 ml of deionized water – approximately the same amount of water for each pan. Put them on the magnetic stirrer and adjust the stand so the temperature sensor is dipping into the water, but not touching the bottom. Now turn on the magnetic stirrer, adjust the temperature to the desired value and set the frequency to 100 rpm.

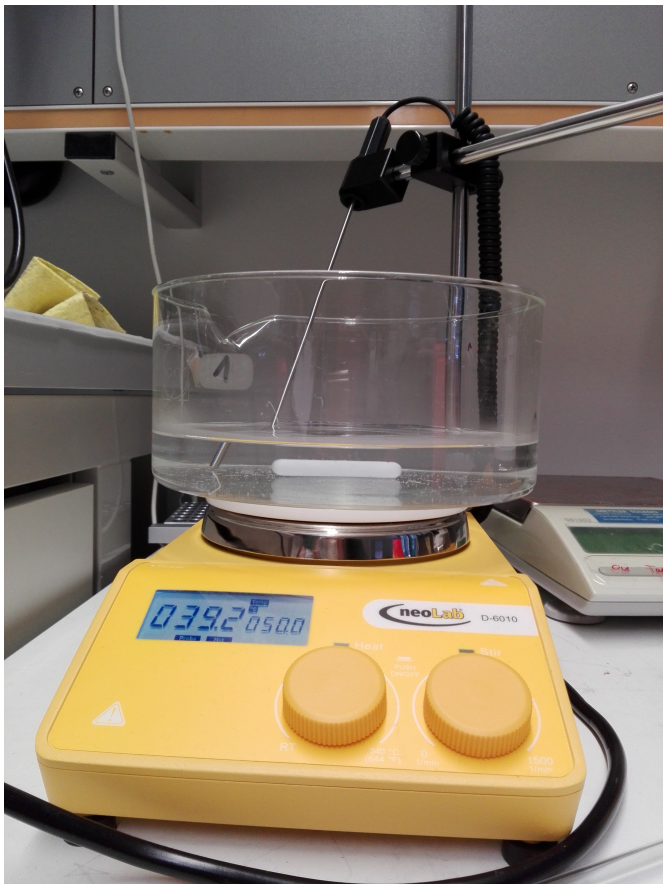


Figure 5.1: Experimental setup for experiment 5.1.

It will take about 20 min to 30 min for the water to be heated to the desired temperature. While you are waiting you can prepare the vials and caps with septa to store your samples in. Your supervisor will show you where to find them.

The septa serve the purpose to avoid evaporation of sample material prior to measurement and allow for the penetration of the autosampler syringe. They need to be manually inserted into the caps: If you squeeze the septa into the caps roughly with a glass stick or a metal rod, they will adjust themselves when you screw the cap onto the vial. Pay attention to the orientation of the septa: The red silicone side should face downwards while the white PTE side should face upwards and be visible when the cap is screwed onto the vial.

Once the desired temperature is reached, turn off both heat and stirrer and weigh the pan. Then use the pipette to take a 750 µl sample from each pan and insert them into the prepared vials. **Important: Use a new pipette tip for each sample!** Close the vials immediately but do not close them too tight! It has been seen in past measurements that vials closed too tight cause problems concerning the automatized sampling. When you're done taking the sample put the pan back on the magnetic stirrer and turn on the heat and stirrer.

You can now put your samples in one of the trays. For each sample, write down the time, the weight of the pan with the remaining water, the water temperature and the tray position. Repeat the sampling (and weighing) every 30 min to 40 min. After three hours take the final sample and turn off the magnetic stirrer.

Your samples of the first two temperatures will be measured overnight between the first and second day. The sample set of the third evaporation experiment together with the unknown and rainwater samples from experiments 5.3 and 5.4 will be measured the night after. The procedure to start a measurement run with the analyzer is described in section 5.5.

Once your liquid samples have been measured, the raw data can be found in the file `tlwiayyyy-mm-dd_f00XX`, with `XX` being the running number for the measurements started that day. To get the required files, connect the flash drive to the port and click on the button "Files", a new window opens with all the data files on the left side. To see the content of the flash drive on the right side, click "mount USB". Now look for the folder with today's date and copy it to the flash drive.

5.2 Observing Rayleigh Fractionation

In this part the fractionation process of an evaporating water drop is observed. Therefore the water vapor of the evaporating water drop will be measured directly. To set up the experiment make sure the instrument is set to the WVIA-mode (compare screen to figure 5.2) and the measurement rate to 10 seconds. Make sure to write down the computer time (on the analyzer), you will need it to find the data later.

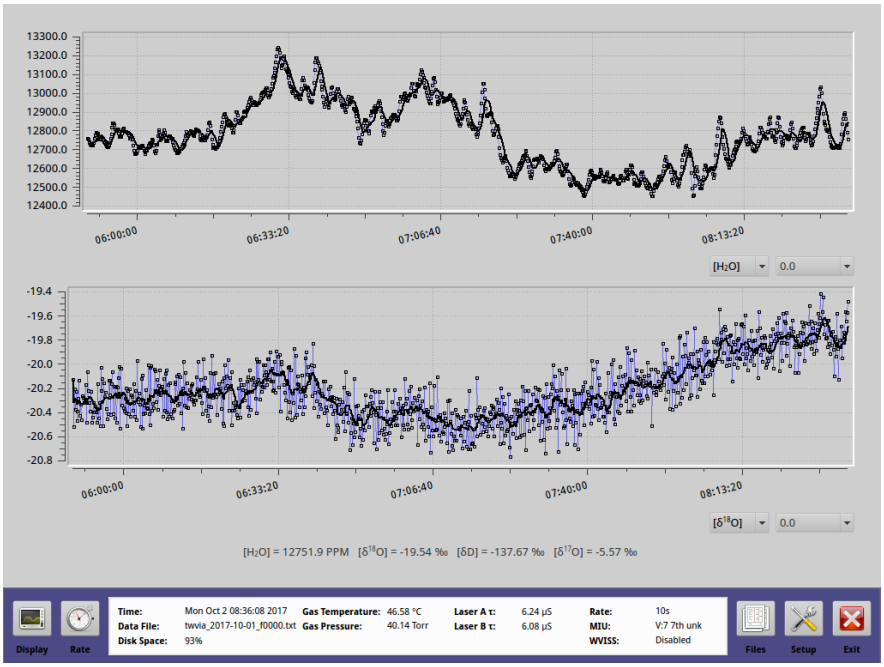


Figure 5.2: Example of a typical screen in the WVIA-mode for outside air.

To change the measurements from ambient air to room air switch the multi-way valve at the back of the instrument. There is yellow label on top saying “Aussen” (*outside*), if you switch it you will be able to read the label “Raum” (*room*). Now connect the end of the line to the glass cooling trap as is shown in Fig. 5.3.

Use a wash bottle to insert a little drop of deionized water into a thin glass tube. Cover one end with your finger and insert it into the glass tube of the cooling trap. Release the water by uncovering the tube, make sure the water doesn’t stick to the surface of the glass tube. After you have inserted the water, do not move the cooling trap!

On the monitor you will now be able to see a change in the water content and the δ-values. Since the water drop must evaporate completely to see the full effects of Rayleigh fractionation, this experiment will take longer the bigger the inserted

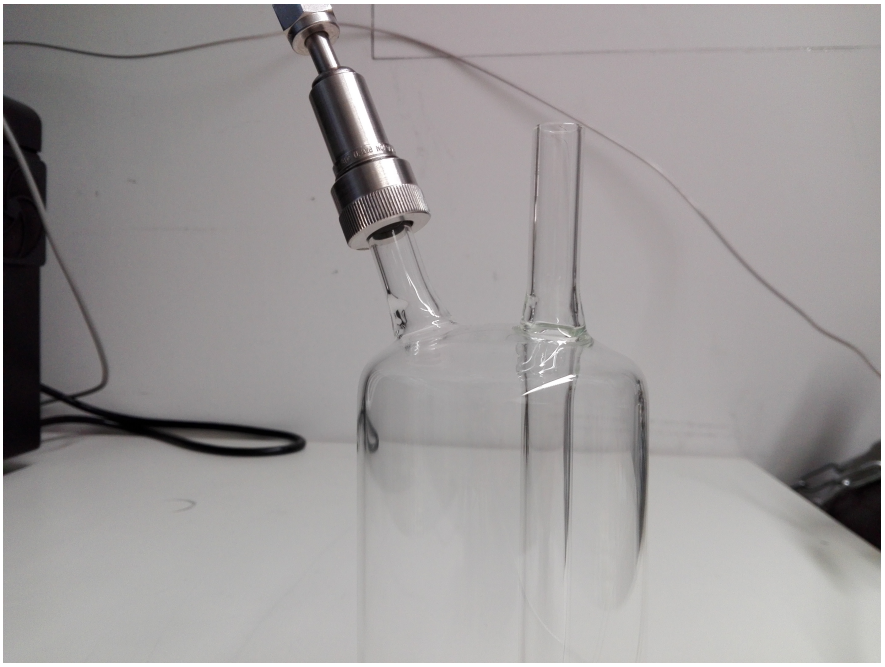


Figure 5.3: Setup for experiment 5.2: end of the instrument line connected to the cooling trap. The drop is inserted through the vertical opening.

water drop is, so do not insert too much water. When the experiment is finished, switch the valve back to ambient air and disconnect the cooling trap from the line. Again, record the computer time in your lab book. Also note the start and end time on the table sheet in the lab.

After the experiment is finished, save the file `twvia_yyyy-mm-dd_f0000.txt` to the USB drive.

5.3 Local Rainwater Samples

To investigate how the isotopic composition of rainwater can change with time, you will measure rainwater samples collected in Heidelberg during recent individual rain events, as well as one sample representing the mean value of an entire month's worth of precipitation. Ask your supervisor which samples are to be measured, as they change regularly, and be sure to note the dates which each sample encompasses. Take 750 µl samples, just as described in the previous sections.

You will later have to compare your results to measurements from the last two years, so make sure you copy the existing file of compiled previous measurements from the PC in the office (see section 6.3).

5.4 Finding the Source of Unknown Samples

In this part you will measure, along with the samples from experiment 5.1, some unknown water samples from various geographical locations. The aim is to use their isotope signature to attempt to determine where they originate from.

You can also bring your own samples, e.g. tap water from home, or mineral water from fancy places you have visited on vacation, if you happen to have any.

The mineral water bottles are stored outside the laboratory, your supervisor will show you where to find them. Choose five bottles – preferably at least one non-European – and take them back to the lab. After shaking the bottles to homogenize the water, take a 750 µl sample from each with the pipette as described before and fill them into vials. Make sure to close the bottles immediately after you took the samples. Take notes of the bottle numbers and sample positions in the tray. Measure these vials together with the samples from experiments 5.1 and 5.3.

5.5 Starting a Measurement in LWIA Mode

Since the analyzer is by default running in WVIA mode, you first have to change it to LWIA mode to be able to measure the liquid samples.

Changing the mode of the analyzer

- Click on "Exit" (red X) in the lower right corner to shut down the analyzer.
- When "you may turn off the analyzer now" is displayed, turn off the analyzer using the power switch.
- Wait for about 30 seconds and switch it back on. After a while you can choose the mode. Click on "LWIA-Analyzer".
- Ask your supervisor to assist you in changing the septum.
- Next you have to exchange the syringe placeholder in the auto sampler. Your supervisor will instruct you.

Make a test run

Before the samples can be measured, a test run is needed to ensure that the injected volume of the syringe is stable and all settings are in order:

- Fill a vial with deionized (VE) water and put it into one of the trays.
- Write the position and the tray of the VE water into the first row of the table "Available Samples" on the left side and name it "VE".
- Use the green arrow to move it to the right window "Samples To Measure".
- Set "Measured Inj/Vial" to 15. This parameter defines how often one sample is measured each time it appears in the list.
- Click on "Make Run" at the bottom and "Display" in the left bottom corner to see a list of all injections.
- Before you click on start, make sure the tray is correctly aligned in the tray holder and the vial is in the right position.
- Click on "Start" to begin the test measurements.

Wait for the results of approximately the first four injections. The volume for the first injection is usually higher than for the others. The injected volume (column "H20_N/cm3") should be between 2.8 and 3.2 $\times$ 10^{16} N/cm. If the injected volume is too high or too low after the fourth injection or if the laser is out of tune, stop the run.

Adjust the injection volume

If necessary, go to "Setup", choose the flag "Auto Injector" and adjust the "Sample Volume" in the section "Measure Fill Setting" to a value 20 µl higher or lower. Save your changes and make another test run.

Laser adjust

To check the laser, click on "Display". You can see the absorption of both lasers. The peaks should be within the shaded areas.Go to "Setup", choose the flag "Laser Adjust". If you check the box "Disable Laser Frequency Lock", you will be able to adjust the laser frequencies until the peaks are on the dotted lines.

Once you have adjusted the settings, go back to the main display and click "Make Run", "Display" and "Start" again. While you are waiting for the test run to finish, you can prepare the samples and standards.

Setting up a run configuration

Once you have all the samples in the tray, you need to pipette the water for standards. Use the standards "VE", "Alpen", "Colle" and "Sammelprobe" in the drawer below the analyzer. Shake the bottles before you open them and do not leave them open unnecessarily. Take notes of the vial positions of the standards in the tray. When the test run is over and there aren't any pressure flags and the volume is stable, you can set up the configuration of the actual measurement (see Fig. 5.4).

To set up a run configuration, follow these steps:

- On the left side, there is a window for "Available Samples" and "Available Standards". Only use "Available Samples".
- With the blue button, you can add new lines for tray positions. At the bottom you can choose for which tray the new positions are added. You can also change the tray number and position manually. Write down the names of the samples and standards in the fields with their corresponding

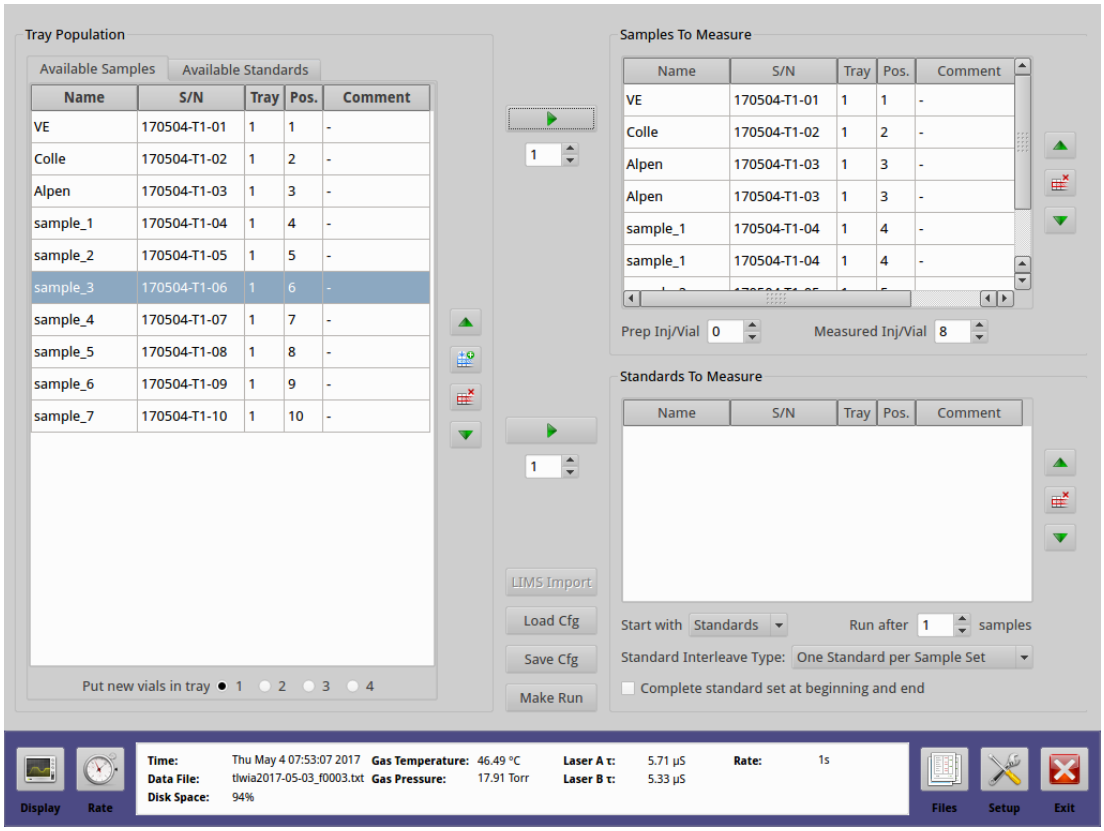


Figure 5.4: Main menu to set up a run configuration.

tray positions. Best use sample names that allow for an easy identification (e.g. “50C_33min”, “W031”).

- On the right side are two windows for “Samples to Measure” and “Standards to Measure”. Again, only use the window for samples.

- Use the green arrow to manually move the standards and samples to the “Samples to Measure” window on the right. Start with the standards. **Important:** The difference between the isotopic ratios of “Alpen” and most other samples/standards is expected to be large. Therefore always add a second consecutive measurement of “Alpen” and the following sample/standard (see Fig. 5.4).

- After every set of the four standards add a set of **five samples**. Alter the order of the standards for every set. Once you added all samples, start from the beginning and add all samples again. At the end make a set of all standards.

- Set “Measured Inj/Vial” to 8.
- Click on “Make Run” and “Display”, then let your supervisor take a look at the configuration.
- Start the measurement and if the first four injections appear OK, let it run over night.
- Write down on the table sheet in the lab how many injections you have in total (including the test run).

When you come back the next day, exchange the syringes again, your supervisor will help you. To switch back to the ambient air measurements, click on “Exit” and wait until the cavity is vented. Then turn off the power switch and after 30 seconds turn it on again. Choose the “WVIA-mode”. You can now save the files of the day of the measurement on a flash drive as described before.

6 Calibration and Evaluation

6.1 Evaporation at Different Water Temperatures

Save your data from the USB drive to the "FP" folder on the PC in room 506 and unzip the file. For the calibration of your files use the *LWIA Post Analysis* software to process your raw δ-values. A short manual for the software can be found in section 6.5.

To read out the temperature and humidity data logger, connect it to the computer and use the *Testo* software (see section 6.5). Calculate the mean temperature and the mean relative humidity for each experiment.

With the determined calibrated δ-values for your samples perform the following evaluation of your results:

- **δ-values**
  Plot the δ-values against the remaining fraction of water. Describe and explain the course of δD, δ^{18}O and δ^{17}O. Now plot the water line for all temperatures. Compare the observed slope in the data sets to the GMWL and find reasons for the differences.

- **Fractionation Factors**
  Calculate the fractionation factor of the Rayleigh evaporation process for each temperature by relating the measured δ-values to the remaining water fraction. Plot α over water temperature for the measured isotopes and explain the different values of the fractionation factors.

6.2 Observing Rayleigh Fractionation

For this section, the evaluation is only qualitative, i.e. you are supposed to describe the processes visible in the humidity and δ-value data during the evaporation of the drop.

The file `twvia_yyyy-mm-dd_f0000.txt` contains time, water concentration (ppm), raw δ-values and raw isotope ratios as well as some internal parameters like temperature and gas pressure. Extract the data for your experiment and plot both water concentration and the δ-values. If the file you saved doesn't appear

to contain your data, it could be that your data is included within the previous day's file. Describe and explain the temporal evolution of the δ-values.

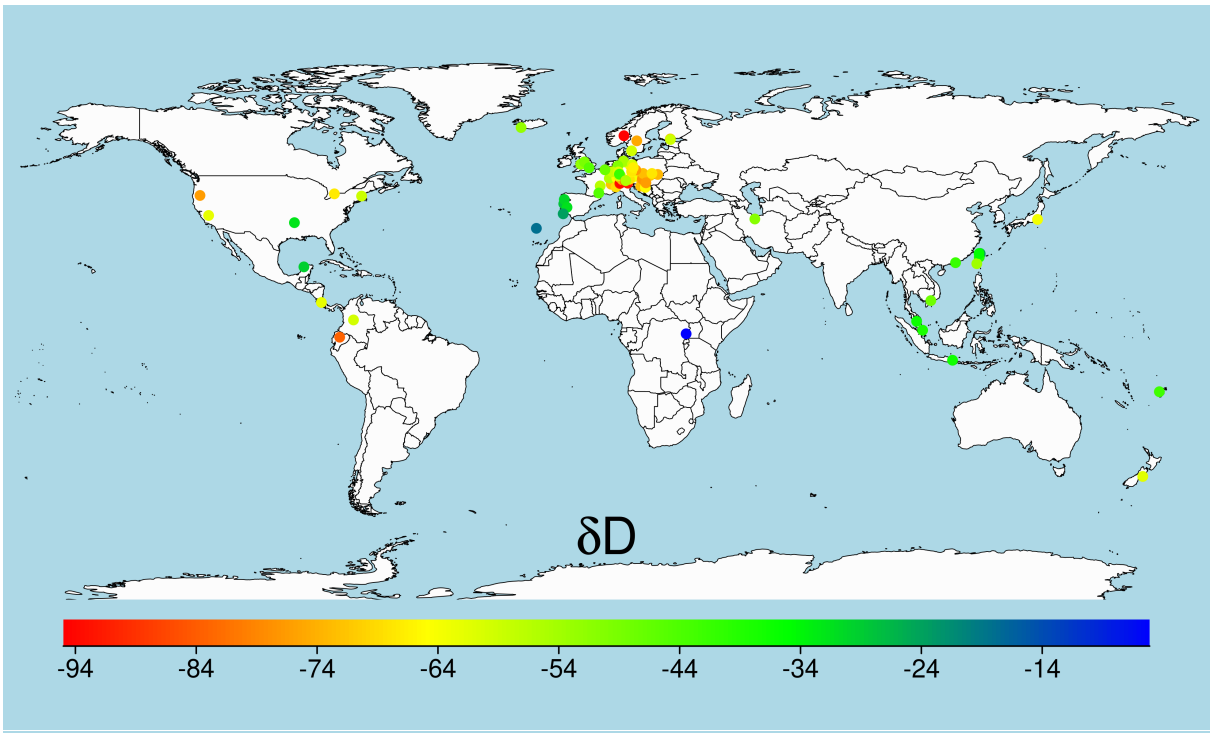
6.3 Local Rainwater Samples

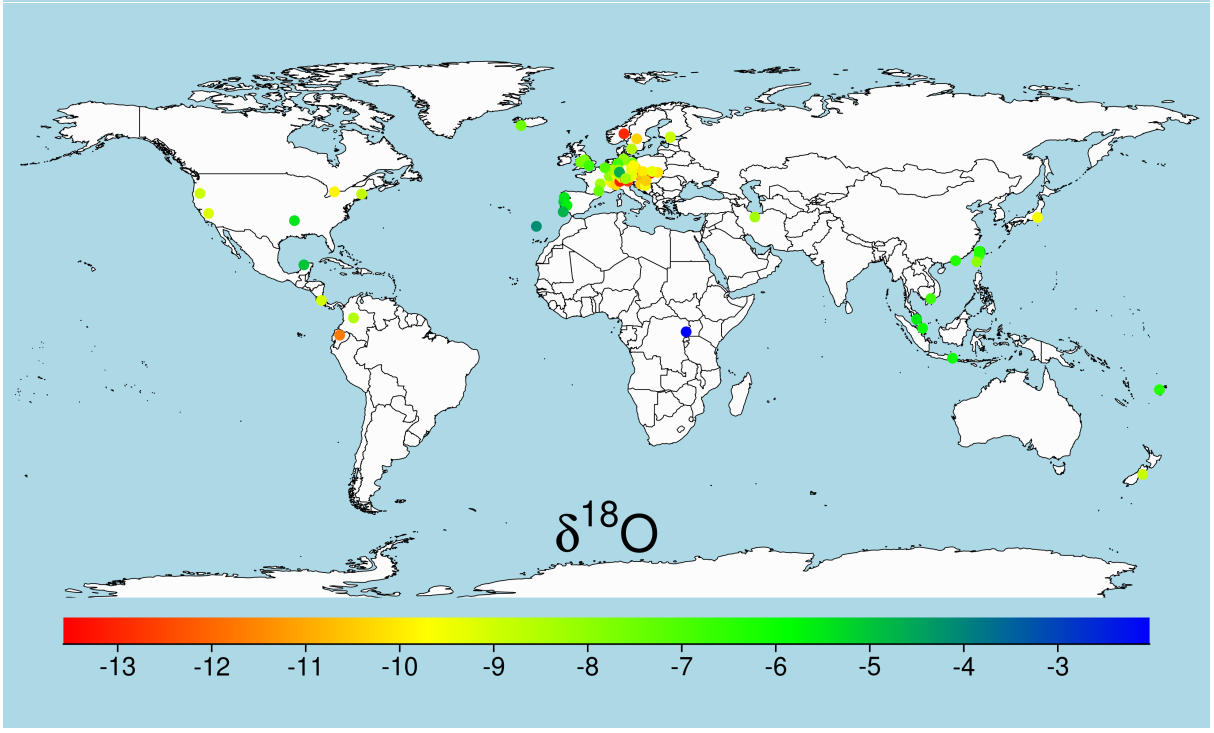
On the PC desktop in room 506 you will find a folder named "Rainwater Data" which contains an excel file with two years of Heidelberg rainwater isotope data. Note that there are two sheets in the excel file: one for individual rain events and one for monthly mean values. Use your measured rainwater data in combination with the previous data to plot δ-values over time, and explain any effects which can be seen. Also, plot δD over δ^{18}O as a local meteoric water line (LMWL) for Heidelberg and compare the result to the GMWL.

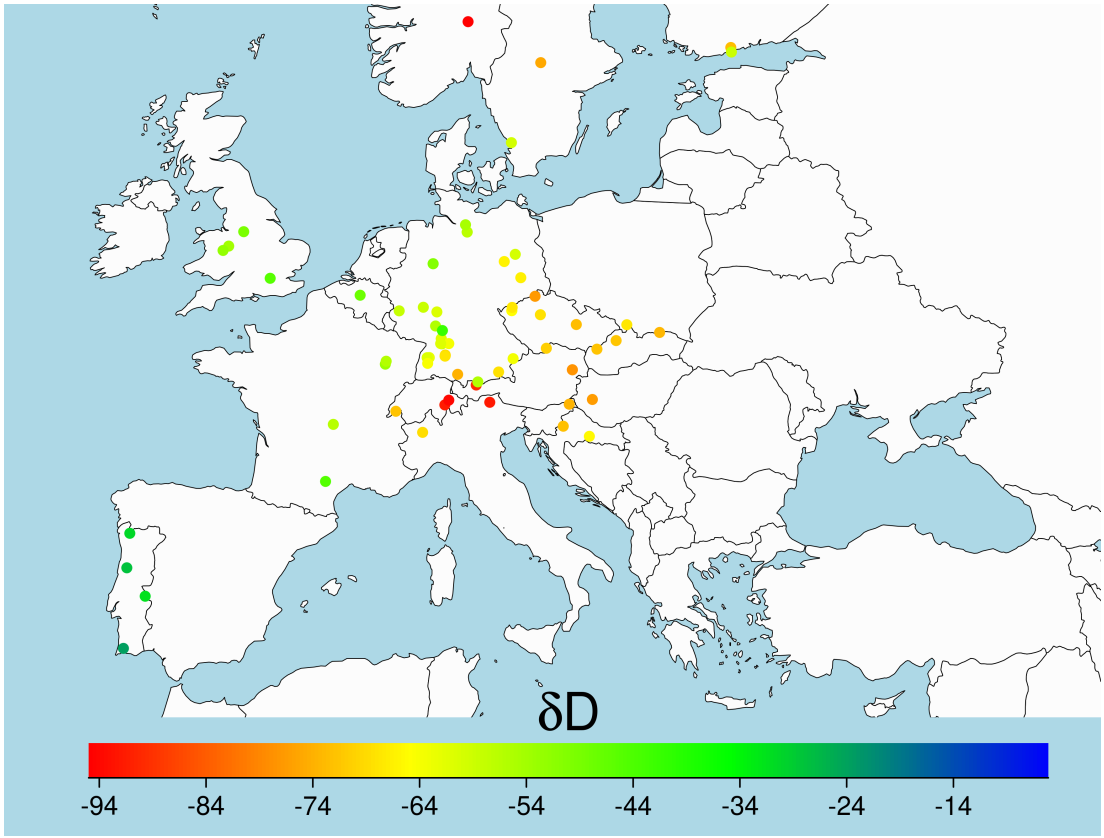
6.4 Finding the Source of Unknown Samples

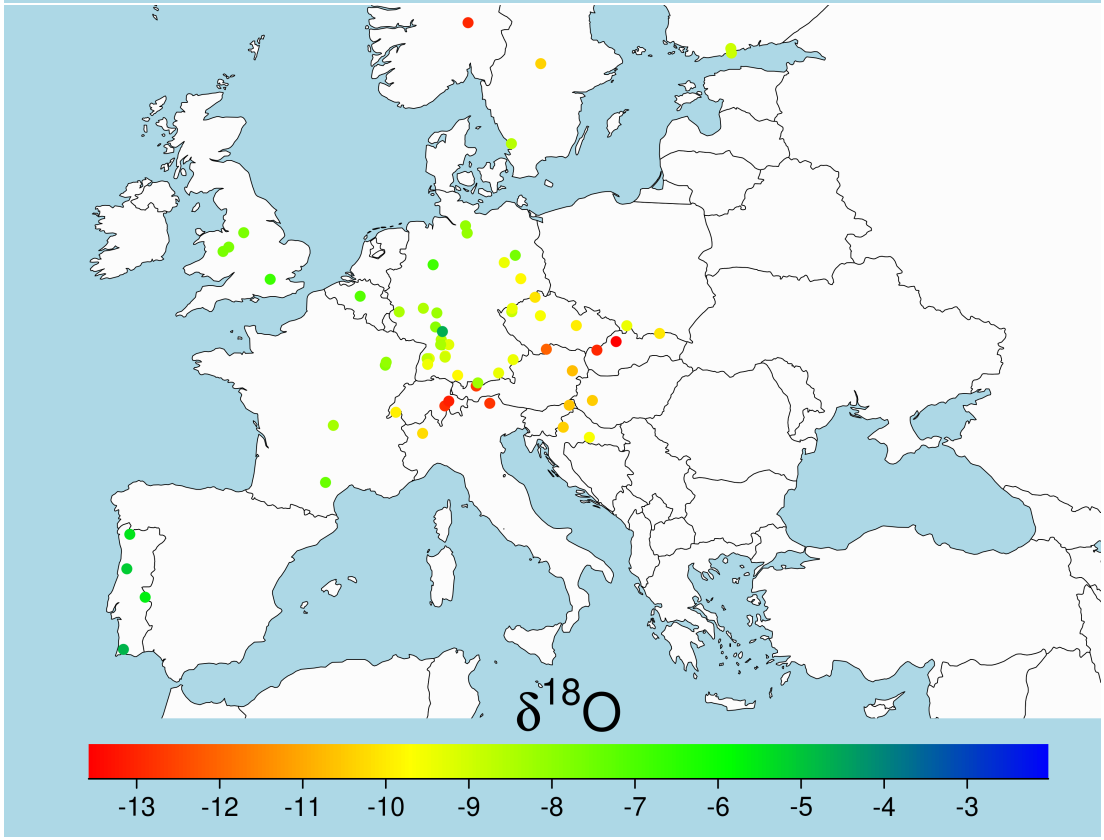
Use the maps for δD and δ^{18}O on the following pages to identify the source of your water samples. Comparing your results to the previously measured sample data in Tab. 6.1 might help you find the correct location. Please note that some of the data points are not represented on the maps, but can still be found in the tables. Think about the following questions:

- Looking at the map: What is the general geographical trend in isotopic values from European samples? What is the reason for this trend?
- Which samples from the European data set are lowest in isotope ratios? What is the explanation for these high levels of depletion at their respective location?
- What range of values do you expect for the regions that are not yet covered by our data? Where do you think you would find the highest/lowest values in water from meteoric sources?


δD
-94
-84
-74
-64
-54
-44
-34
-24
-14


δ18O
-13
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3


δD
-94
-84
-74
-64
-54
-44
-34
-24
-14


δ18O
-13
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3

Name	Region	Country/Territory	δD	δ^{18}O	δ^{17}O
Vöslauer ohne	Europe	Austria	-77,518	-10,735	-5,774
Vöslauer	Europe	Austria	-77,734	-10,693	-5,792
Tap water from Tervueren	Europe	Belgium	-48.198	-7.239	-3.781
Studenac	Europe	Croatia	-65,847	-9,627	-5,104
Mattoni Neperlivá	Europe	Czech Republic	-65,622	-9,370	-5,098
Korunní	Europe	Czech Republic	-68,384	-9,645	-5,553
Basic still water	Europe	Czech Republic	-70,716	-12,071	-4,666
Jana	Europe	Czech Republic	-72,310	-10,455	-5,871
Aqua Anna	Europe	Czech Republic	-72,616	-9,998	-5,382
Aquila první voda	Europe	Czech Republic	-64,958	-8,901	-4,827
Dobrá Voda	Europe	Czech Republic	-76,811	-10,136	-5,475
Magnesia Perlivá	Europe	Czech Republic	-67,841	-9,408	-5,241
Rainwater from Helsinki	Europe	Finland	-58.963	-8.960	-4.800
Tap water from Helsinki	Europe	Finland	-72.598	-8.954	-4.847
Contrex	Europe	France	-53,279	-7,916	-4,055
Evian	Europe	France	-72,081	-9,942	-5,201
Vittel	Europe	France	-56,129	-8,112	-4,651
eau de la reine	Europe	France	-45,096	-7,468	-4,123
Volvic	Europe	France	-56,468	-8,365	-4,567
Aqua Mia Still	Europe	Germany	-58,848	-8,174	-4,445
Eiszeit Quell	Europe	Germany	-68,918	-9,505	-4,973
ViO medium	Europe	Germany	-56,780	-8,083	-4,482
Christinen Naturelle	Europe	Germany	-53,265	-7,840	-4,949
Gemminger Mineralquelle	Europe	Germany	-60,993	-8,726	-4,770
Wüteria Schlossbrunnen	Europe	Germany	-60,997	-8,633	-4,860
Eiszeit Quell still	Europe	Germany	-69,016	-9,475	-5,383
Odenwald Quelle Naturelle	Europe	Germany	-55,983	-7,906	-4,065
Griesbacher still	Europe	Germany	-63,720	-9,466	-5,010
Black Forest still	Europe	Germany	-62,691	-9,344	-5,051
Christinen Carat Naturelle	Europe	Germany	-66,302	-9,467	-5,178
Staatl. Fachingen still	Europe	Germany	-58,628	-8,509	-4,621
ViO still	Europe	Germany	-57,058	-8,147	-4,368
ARIWA aus der Renchtalquelle	Europe	Germany	-60,827	-8,728	-4,739
Nestlé Pure Life	Europe	Germany	-54,744	-8,093	-4,136
Hornberger Lebensquell naturelle	Europe	Germany	-64,264	-9,502	-4,877
Quelle St. Leonhard Das lebendige Wasser	Europe	Germany	-68,612	-9,398	-5,053
Schönrain Quelle 29	Europe	Germany	-67,984	-8,997	-5,009
Aqua Vitale naturelle	Europe	Germany	-58,609	-8,184	-4,635
K-Classic natürliches Mineralwasser	Europe	Germany	-60,095	-7,624	-4,221
Frische Brise Marius Mineral Quelle	Europe	Germany	-63,793	-9,283	-5,048
Christinen Naturelle	Europe	Germany	-50,682	-6,825	-3,984
Krumbach Naturell	Europe	Germany	-74,212	-9,794	-5,650
Ensinger Sport	Europe	Germany	-61,215	-8,406	-4,617
Gerolsteiner	Europe	Germany	-58,463	-8,470	-4,950
Elisabethen Quelle	Europe	Germany	-60,904	-8,250	-4,763
SpreeQuell	Europe	Germany	-66,746	-9,803	-5,159
Stream Water from Zugspitze	Europe	Germany	-90,26	-12,689	-7,092
Stream Water from Zugspitze	Europe	Germany	-55,734	-8,297	-4,696
Theodora Balaton-felvideki Nemzeti Park	Europe	Hungary	-77.058	-10.513	-5.685
Plose	Europe	Italy	-91,950	-12,770	-6,736
Lauretana Das leichteste Wasser Europas	Europe	Italy	-68,924	-10,262	-5,517
Imsdal	Europe	Norway	-94,997	-12,985	-6,798
Żywiec Zdrój	Europe	Poland	-67,664	-9,428	-4,894
Kropla Beskidu	Europe	Poland	-73,267	-10,097	-5,539
Nestlé Pure Life Poland∗	Europe	Poland	-71,876	-9,97	-5,242
Naturalna Woda Mineralna∗	Europe	Poland	-69,955	-9,642	-5,018
Luso	Europe	Portugal	-27,959	-5,125	-2,700
Fastio	Europe	Portugal	-30,636	-5,456	-2,897
Madeira river water	Europe	Portugal	-18.962	-4.3	-2.284
Serra de São Mamede	Europe	Portugal	-31,654	-5,649	-3,032
Monchique	Europe	Portugal	-23,748	-4,733	-2,522
Lucka	Europe	Slovakia	-72,136	-12,965	-4,801
Rajec Kojenecká Voda	Europe	Slovakia	-71,672	-13,578	-4,708
Rajec Patentované Prírodou	Europe	Slovakia	-69,257	-9,511	-5,116
Radenska Classic	Europe	Slovenia	-73,799	-10,570	-5,978
Premier Källvatten	Europe	Sweden	-75,319	-10,418	-5,584
Vichy Vatten	Europe	Sweden	-59,574	-8,623	-4,948
Valser Classic	Europe	Switzerland	-91,565	-12,858	-6,846
Arkina	Europe	Switzerland	-94,070	-13,108	-7,000
essential Waitrose	*Europe*	United Kingdom	-54,036	-7,719	-4,352
coop still Fairbourne Springs	*Europe*	United Kingdom	-52,189	-7,692	-4,116
Buxton	*Europe*	United Kingdom	-49,652	-7,732	-4,121
Heathrow Airport tap water	*Europe*	United Kingdom	-45,433	-6,803	-3,407

Name	Region	Country/Territory	δD	δ^{18}O	δ^{17}O
Rwenzori	Africa	Uganda	-5,111	-2,023	-1,112
Nestlé Pure Live Iran	Asia	Iran	-50,785	-8,339	-4,915
Tokyo tap water	Asia	Japan	-64.142	-9.626	-5.106
Taipei Beauty Hotels	Asia	Taiwan	-30,246	-5,756	-3,22
pH 9.0	Asia	Taiwan	-19,285	-5,083	-2,877
Tap water from Ji'an	Asia	Taiwan	-37,884	-6,731	-3,828
Tap water from Hengchun	Asia	Taiwan	-53,675	-7,988	-4,255
Tap water from Taipei	Asia	Taiwan	-35,222	-6,414	-3,676
Cristal Costa Rica	Central America	Costa Rica	-62,270	-9,087	-4,851
Cristal Mexico	Central America	Mexico	-29,546	-5,009	-2,664
imivik	Greenland	Greenland	-111,708	-15,449	-8,173
Stream water from Sisimut	Greenland	Greenland	-104,057	-14,416	-7,602
Meltwater from Kangerlussuaq∗	Greenland	Greenland	-216,292	-27,903	-14,88
Melted glacier ice from Ilulissat∗	Greenland	Greenland	-208,348	-27,257	-14,566
Ícelandic Glacial	Iceland	Iceland	-52,707	-7,541	-4,174
Montclair	North America	Canada	-67,484	-9,839	-5,231
Crystal Geyser Natural Alpine	North America	USA	-32,132	-5,491	-3,000
Arrowhead	North America	USA	-62,313	-9,234	-4,775
Nestlé Pure Life USA	North America	USA	-59,152	-8,810	-5,141
Crater Lake Water	North America	USA	-76.998	-9.019	-4.786
Kiwi blue	Oceania	New Zealand	-61,373	-8,845	-4,716
Fiji Natural Artesian Water	Oceania	Republic of Fiji	-42,595	-6,403	-3,388
Bogotá tap water	South America	Columbia	-59,730	-8,534	-4,421
Tesalia	South America	Ecuador	-83,337	-11,689	-6,111
Jefi Water	Southeast Asia	Malaysia	-36,498	-5,560	-3,009
La Vie	Southeast Asia	Vietnam	-48,211	-6,813	-3,407

Table 6.1: European and international mineral water samples for experiment 5.4 with measured isotopic values in ‰ (VSMOW2) and the approximate region of origin for each mineral water. Asterisked samples are not included in the maps.

6.5 Software

LWIA Post Analysis

The LWIA Post Analysis software calibrates the δ-values, using the water standards, and applies a volume correction due to the fact that the raw δ-values depend on the injected sample volume. The software also helps to identify bad or flawed measurements. This short instruction will give you an overview on how to use the software.

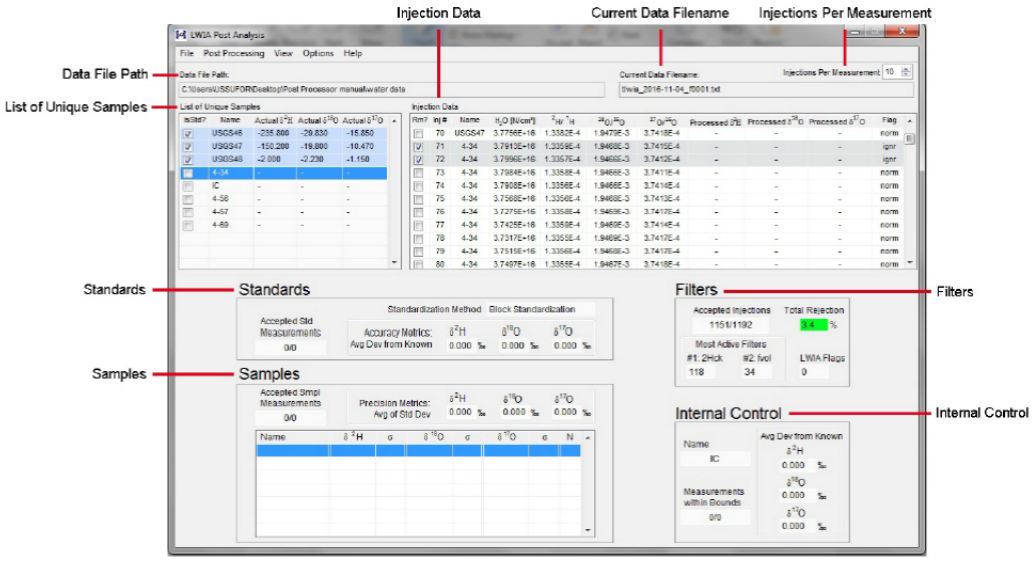


Figure 6.1: Summary screen with loaded data file.

Open the LWIA Post Analysis software (blue and white "LGR" button on the desktop). The summary screen is shown. To open your measurement, click on "File" and "Open LWIA Data File". On the left side you can see "List of Unique Samples", all the used standards should be shaded blue. If one isn't labeled as a standard, it might be spelled wrong. If so, go to the `.txt` file and change it. On the right side, you see the raw values for each injection of the samples and standards. The last column shows different flags which are all explained in Tab. 6.5 at the end of the script. The box "Filters" shows how many injections are accepted/rejected and which flags appear at most. The first four measurements of each sample will not be considered for the calibration, due to the memory effect from the previous sample.

Set "Injections Per Measurement" to 8 and switch to the dataset plots under "View". This screen shows the raw isotope ratios. The differences in isotopic ratio

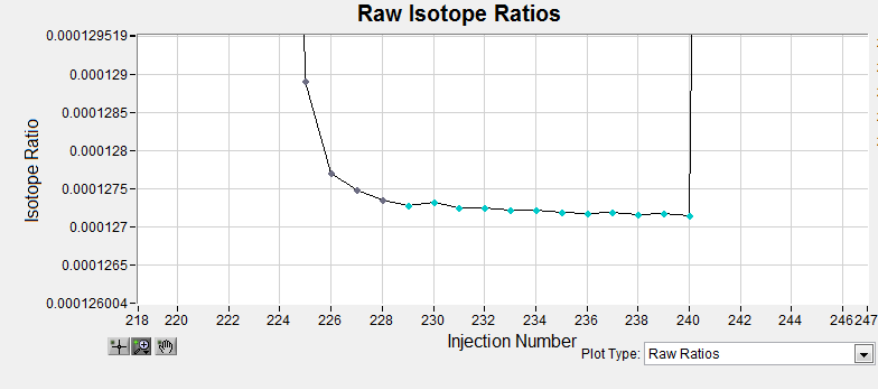


Figure 6.2: Injections with high disparity in isotopic values can cause memory effects on the raw ratios. When measured twice all injections except for the last four must be discarded manually.

between some samples and standards are large. This is why, when you have a low following a high standard, you measured the low standard twice. Zoom in to the low standard. In Fig. 6.5, you can see the ratios are still decreasing for the not ignored injections (green). Discard (check the box "Rm?") all injections except for the last four. Repeat this for all the samples/standards you measured twice.

Now uncheck Colle from the List of Unique Samples and go to "Post Processing" and click "Run Post Processor". If you go back to the summary screen, the internal control shows the average deviation from the known value for Colle. It helps to identify instrument drifts or bad storage of the samples. The deviation should be lower than 1 ‰ for δD and lower than 0.4 ‰ for δ^{18}O and δ^{17}O. Now check Colle and run the Post Processor again. If all the standards are used the calibration is more accurate. The window "Samples" shows the calibrated and volume corrected δ-values. Save the result with "File", "Save Processed Data". Two files will be saved, for the evaluation you need the `tlwiayyyy-mm-dd_f00XX-Processed` file. It contains all the important data for every sample.

Temperature and Humidity Data Logger

To read out the data logger, connect it to the computer and open the testo software (orange ball). Go to "Instrument" and connect your logger. Go to "Evaluating", "Import measurement data". Under "Evaluate measurement data" you find an overview of the recorded data. Select the data you want to save, click on the little orange arrow in the corner, "Export table lines", "Copy to clipboard". The data can now be pasted to an editor program and saved.

Flags

Flag	Meaning
norm	Indicates that there are no issues with the injection
user	Rejected by user: The user can manually check the "Rm?" box to exclude injections, and the flag column will then display "user". The injection data will not be included in the calculation of the processed values. The entire row will appear yellow.
incl	Rejection overwritten by user: The user can manually uncheck the "Rm?" box to include an injection that has been rejected, and the Flag column will then display "incl". The injection data will be included in the calculation of the processed values.
temp	Generated by the analyzer. The temperature of the water vapor is changing too rapidly during a single measurement.
dens	Generated by the analyzer. The water number density inside the measurement cell is not stable during a measurement.
pres	Generated by the analyzer. The pressure within the measurement cell is rising during a measurement.
2hsd (18/17sd)	Generated by the analyzer. The D/H ($^{18}O/^{16}O$, $^{17}O/^{16}O$) ratio is excessively noisy.
aftr	Rejects injections that follow analyzer pres and dens flags.
ignr	The first injections of each sample are ignored to reduce the memory effect.
avol	These injections have too much or too little water. It is typically caused by syringe malfunction or empty vials.
fvol	The injected volume deviates excessively from a running average of injected volumes of surrounding injections.
svol	The injected water volume standard deviation exceeds the threshold.
tvar	The temperature variation exceeds the recommended standardization conditions.
2Hnc (18/17nc)	Identifies statistical $^{2}H/^{1}H$ ($^{18}O/^{16}O$, $^{17}O/^{16}O$) outliers in each injection average group that deviate more than the specified number of standard deviations.
intf	The spectral contamination filter identifies spectral interferences in the measured absorption spectra.
2Hck (18/17ck)	Identifies entire injection average groups if the standard deviation of the measured values is larger than the specified value.

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