



## CENTRAL LABORATORY

R & D Research and Training Center

METU, Ankara

### Stable Isotope Ratio Mass Spectrometry Laboratory



Figure 1. Isotope ratio mass spectrometer in Central Laboratory.

Stable isotopes can reveal valuable information about the origin and/or the processes that have affected the material analyzed. Within the stable isotopes, the isotopes of the water molecule  $\text{H}_2\text{O}$  [ $^{18}\text{O}$  and  $^2\text{H}$ ] are used in a wide array of scientific research dealing with geological, biological, food authentication and environmental studies. Especially their utilization as tracers in the delineation of global water cycle processes (such as groundwater circulation, lake hydrology, evaporation from surface waters) and paleoclimatic reconstructions is widely accepted. An isotope ratio mass spectrometer (*ThermoFinnigan DELTAplusXP*) equipped with a continuous flow interface (*Finnigan Gas Bench II*) is used for the measurement of these isotopes in the Central Laboratory, Stable isotope facility (Figure 1).

#### BASIC PRINCIPLES

Isotopes are atoms of an element having the same number of protons but different number of neutrons. Isotopes in nature are classified into two groups as Stable and Unstable. Stable isotopes are those isotopes that do not undergo radioactive decay.

The concentration of stable isotopes in nature is controlled by a process known as isotopic fractionation. Isotopic fractionation is the distribution of isotopes between different molecular species ( $\text{CO}_2 - \text{H}_2\text{O}$ ) or different phases

( $\text{H}_2\text{O}_{\text{water}} - \text{H}_2\text{O}_{\text{steam}}$ ) during various physico-chemical processes.

The oxygen and hydrogen elements, forming the water molecule, have a total of 3 and 2 stable isotopes, respectively (Table 1). The isotopic ratios of oxygen ( $^{18}\text{O}/^{16}\text{O}$ -  $\delta^{18}\text{O}$ ; most commonly used) and hydrogen ( $^2\text{H}/^1\text{H}$  -  $\delta^2\text{H}$ ) are conventionally expressed as permil – ‰ deviation from the international water standard known as Vienna Standard Mean Ocean Water (VSMOW), distributed by the International Atomic Energy Agency (IAEA), Vienna. In addition to VSMOW, two other international water standards: GISP (Greenland Ice Sheet Precipitation) and SLAP (Standard Light Antarctic Precipitation) are also used for normalization and calibration purposes. The isotopic compositions of these standards are presented in Table 2.

Table 1. Natural abundances of oxygen and hydrogen isotopes.

Element	Abundance (%)	Isotope
Oxygen	99.76	$^{16}\text{O}$
	0.038	$^{17}\text{O}$
	0.200	$^{18}\text{O}$
Hydrogen	99.985	$^1\text{H}$
	0.015	$^2\text{H}$

Table 2. Isotopic compositions of international standards (IAEA, Vienna).

STANDARD	$\delta^{18}\text{O}$ [‰] <sub>VSMOW</sub>	$\delta^2\text{H}$ [‰] <sub>VSMOW</sub>
VSMOW	0 ± 0.02	0 ± 0.3
GISP	-24.76 ± 0.09	-189.5 ± 1.2
SLAP	-55.5 ± 0.02	-427.5 ± 0.3

#### ANALYSIS

The analyses in the Stable isotope laboratory is based on the Continuous Flow Technique, in which the sample gas is entrained in a carrier gas flow (Helium). The Gas Bench is a continuous flow interface, with autosampler assisted loop injection, coupled to a mass spectrometer for the determination of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in water samples.

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  analyses in water samples are conducted as two separate tests. The analysis of these isotopes involves the transfer of the isotopic ratio of a water sample to a gas to be sent to the mass spectrometer via water-gas isotopic equilibration. The gas to be measured (Equilibration Gas) is injected via a needle into the headspace of the exetainer vial filled with the sample. It is assumed that, after a specific amount of time, an isotopic equilibrium is reached between the gas in the headspace and the molecules in the liquid. After equilibration, the

sample gas is taken from the headspace of the exetainer vial via a sampling needle and sent into the Gas Bench for purification and separation from other gas species. Later the gases are transferred to the mass spectrometer for measurement, along with special high purity reference gases.

The gases entering the mass spectrometer are first ionized in the ion source by electron impact ionization. The ions produced are accelerated by high voltage and subsequently enter the magnetic field where they are separated according to their mass-to-charge ( $m/z$ ) ratios. Later, the ions are collected by the ion detectors (Faraday cups) assigned for different masses. Finally, the signals from the collectors are digitised and recorded by the data system (Figure 2).

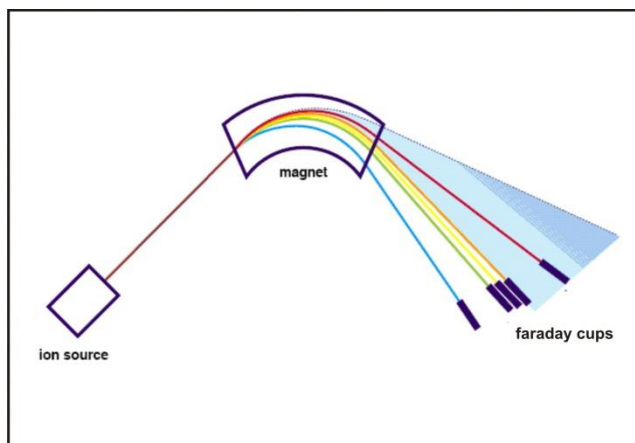


Figure 2. Schematics of the mass spectrometer.

## GASES USED IN ANALYSIS

Carrier Gas: High Purity He (5.0)

### $\delta^{18}\text{O}/^{16}\text{O}$ analysis in water

- Equilibration Gas: He + 0.3 %  $\text{CO}_2$  gas mixture
- Reference Gas: High purity  $\text{CO}_2$  gas (4.5)

### $\delta^2\text{H}/^1\text{H}$ analysis in water

- Equilibration Gas: He + 2 %  $\text{H}_2$  gas mixture
- Reference Gas: High purity  $\text{H}_2$  gas (4.5)

## LABORATORY STANDARDS

In our laboratory, internal (in-house) water standards are used for routine analyses in every sample batch. These standards, having different isotopic compositions, are periodically calibrated against the international standards (VSMOW, GISP and SLAP).

## CONTACT INFORMATION

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