

Measuring Isotope Fingerprints of Water through Mass and Laser Spectrometry

Tools and Techniques for Stable Isotope Measurements in Hydrology

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Isotope hydrology is a powerful tool to understand source and movement of water in environment, which is essential for water resources management. Measurement of stable isotopic ratios is the primary requirement of isotope hydrology. Stable isotopic ratios ($^2\text{H}/^1\text{H}$, & $^{18}\text{O}/^{16}\text{O}$) undergo predictable fractionation/modification during environmental processes (evaporation & condensation) and provides basis for tracing the water molecules in hydrological cycle. Since these modifications are very small, advanced analytical instruments such as mass spectrometers and laser-based isotope analyzers are required for precise measurements. This article provides a brief summary of isotope measurement techniques pertaining to stable isotopes of water molecule.

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The combined constituents of water molecule (^1H & ^2H and ^{16}O , ^{17}O & ^{18}O) can form nine isotopologues of water. Among these only $^1\text{H}_2^{16}\text{O}$ (99.76%), $^1\text{H}_2^{16}\text{O}$ (320 ppm) and $^1\text{H}_2^{18}\text{O}$ (2040 ppm) have practical importance due to their measurable abundance. During evaporation and condensation processes these natural isotopic ratios change owing to mass differentiation and these changes allow labelling of different reservoirs of water with different isotopic signatures. Stable isotope ratio measurement can distinguish among different water reservoirs (i.e. rainwater, snowmelt, surface water & groundwater) and help in deducing the dynamics. The natural isotopic ratios are indeed very small and changes due to fractionation are still smaller,

therefore measuring the absolute values of these isotopic ratios on a routine basis for a large number of samples is challenging. In addition, comparing the dataset from different laboratories would be difficult. Also, in hydrology, the change in the isotope ratio is more relevant than its absolute isotope ratio. Hence a normalized ratio is reported where relative deviation of the isotopic ratio of sample with respect to a standard is calculated and expressed by δ notation ($\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$). The δ values are reported as per mil (per thousand, ‰) instead of percent since for better readability (McKinney et al., 1950).

Isotope Ratio Mass Spectrometer

Measurement of stable isotope dates back to early 20th century when Sir J. J. Thomson and Francis William Aston developed a mass spectrograph and separated isotopes of Ne (^{20}Ne

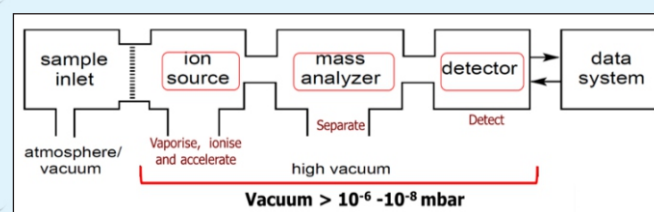


Fig.1: A block diagram of conventional mass spectrometer.

and ^{22}Ne) (Griffiths, 2008). Subsequently several advancements were made including online sample preparation, automated data analysis, micro-sized sample analysis, enhanced precision & sensitivity and simultaneous multi-isotope measurements. These developments shaped the currently used Isotope Ratio Mass Spectrometer (IRMS), which still has the same basic design of mass spectrometer comprising an inlet system, an ion source, an analyzer for ion separation, and a detector for ion quantification (Fig.1). The ions are separated in the mass analyser based on their mass to charge ratio (m/z) utilising combined magnetic and electric fields. The samples are introduced into the mass analyser as gases; hence it is required to convert the samples into gaseous form.

Sample Preparation

There are several methods of sample preparation including gas-equilibration, pyrolysis and reduction. In gas-equilibration method, the water sample is equilibrated with H_2 and CO_2 for $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ measurements respectively. For deuterium measurement, samples are equilibrated for 7 hr at 40°C in presence of Pt catalyst and for ^{18}O measurement, equilibration is done at 40°C for 2.5 hr (Horita et al., 1989). The headspace gases are then dehydrated by passing through cold finger and finally introduced into the ionization chamber. Another method for conversion of water into H_2 gas is reduction by metallic zinc in a sealed tube at very high temperature (at 450°C) (Coleman et al., 1982). The reaction completion times are typically 30 minutes, after which the reaction tube is directly attached to mass spectrometer inlet. In pyrolysis mode, the water samples are pyrolyzed over glassy carbon at high temperature ($>1400^\circ\text{C}$) to produce H_2 and CO gases, which are then introduced into ionization chamber (Gehre et al., 2003).

Advancements of sample preparation methods have further opened the scope of isotope measurement of individual compounds/species in water sample (compound specific isotope analysis-CSIA) by interfacing the gas or liquid chromatographic setup with sample preparation unit. In the gas chromatography (GC)-IRMS, the dissolved volatile compounds in water can be analysed. Here, the sample mixture is introduced into GC column, which allows separation of the compounds based on their volatility and affinity toward stationary phase. The separated moieties

are oxidised to corresponding gases and fed to ionization chamber. In liquid chromatography (LC)-IRMS, isotope ratios of dissolved compounds are measured. Here, the samples are injected to a stream of mobile phase maintained at high temperature ($\sim 2000^\circ\text{C}$), which moves through a densely packed column of stationary phase by means of a pump. The compounds are separated based on their polarity, which are then combusted to generate gases such as CO_2 , NO_x , SO_2 . Some gasses are reduced using Cu turnings to convert (NO_x to N_2 , & CO_2 into CO) and finally introduced into ionisation chamber.

In ionisation chamber, gaseous samples are converted to a beam of positive ions, which is focused and accelerated through a potential difference (V) so that all ions acquire same kinetic energy. Subsequently ions are subjected to a magnetic field applied perpendicular to the electrical field. Because of Lorentz force, ions take a circular path inside magnetic field and the monoenergetic ions are dispersed and separated based on their mass to charge ratio (m/z). The lighter masses follow a path with smaller radii while heavier masses have larger radii. Faraday cups are placed along the path of ion beams, which measure the ion currents and subsequently the isotope ratios are computed. Based on the inlet system IRMS are divided into (i) Dual inlet and (ii) continuous flow.

Dual Inlet – Isotope Ratio Mass Spectrometer

In this system the sample and reference gases are introduced into the ionisation chamber alternately. The heart of dual inlet system is the changeover valve that allows alternate introduction of sample and reference gases from two different reservoirs to ionisation chamber (Fig.2). The gases are fed to changeover valve by

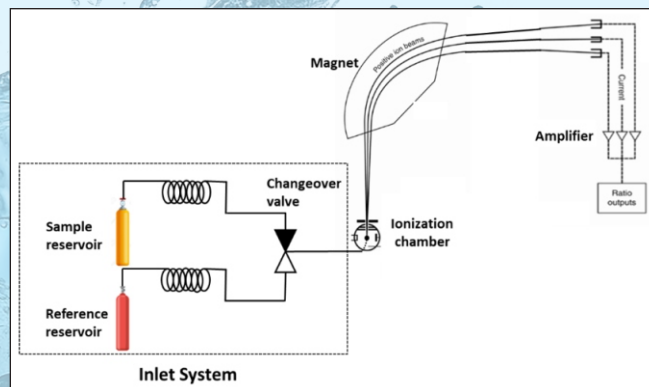


Fig.2: Schematic diagram of Dual Inlet Isotope Ratio Mass Spectrometer.

means of capillaries of around 0.1 mm diameter and about 1 m in length with crimps for adjusting gas flows at their ends. When either gas flows to ionisation chamber the other one is directed to vacuum waste chamber so that uninterrupted gas flows through capillaries. As sample and reference gases are measured under identical conditions, dual inlet systems are highly accurate and precise (Ghosh et al., 2003).

Continuous Flow- Isotope Ratio Mass Spectrometer

In continuous flow system the gases are introduced sequentially to the ionisation chamber along with He as carrier gas (Brenna, J. T. et al., 1997). The reference gas is introduced by a separate interface and pneumatic actuators quickly toggle between sample and reference gases to introduce the gases into ion analyser (Fig.3).

Laser based optical Techniques

Most molecules have absorption spectra in visible to near IR zone containing sharp peaks corresponding to roto-vibronic transition. Analysing the intensity of these characteristic IR peaks allows measurement of concentration of isotopologues. However, due to low natural abundance of isotopologues of water, the

absorption peaks are too weak and precise quantification is difficult. However, the recent advancement in laser techniques has allowed the measurement of isotopic ratios of water precisely. This is achieved by increasing the path-length of the laser beam during absorption. The laser-based techniques are non-destructive, very fast and cost-effective. Two types of laser isotope analysers are widely used for hydrological investigations.

Cavity Ring Down Spectroscopy (CRDS)

Here a particular wavelength of light is allowed to resonate with a cavity filled with analyte gas. The cavity comprises two or more highly reflective mirrors (reflectance > 99.99%), where photons can propagate for prolonged time. Optical length of the cavity is typically few kilometres. When laser enters the cavity, resonance between laser light and ring down cavity is achieved by constructive interferences as light reflects back and forth between the mirrors (Fig.4). At this point, a sudden increase in intensity is detected by photo detectors that senses small amount of light leaking via either of the mirrors. As soon as the increase in intensity is detected, the incoming laser source is cut off and the light intensity is measured outside the cavity. Theoretically, intensity of light pulse decreases after each cycle due to absorption and scattering by medium and reflective losses. A CRDS spectroscopy measures the time taken to reduce the intensity to $1/e^{\text{th}}$ of its initial value. The measured time (ring down time) is then used to calculate the concentration of absorbing substance inside the cavity (Wahl et al., 2006; Santos et al., 2019). For measuring isotopologues of water molecule, the measurements are carried out separately at three different wavelengths, 1392 nm for $^1\text{H}_2^{16}\text{O}$, 1395 nm for $^1\text{H}_2^{18}\text{O}$, and 1403 nm for $^1\text{H}^2\text{H}^{16}\text{O}$. Despite of high sensitivity, CRDS has some limitations, which

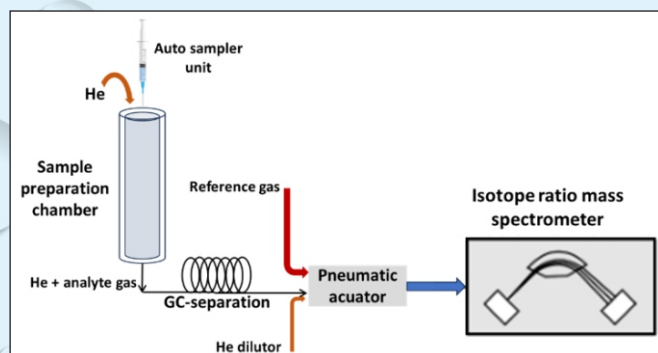


Fig.3: Schematic representation of a continuous flow IRMS system.

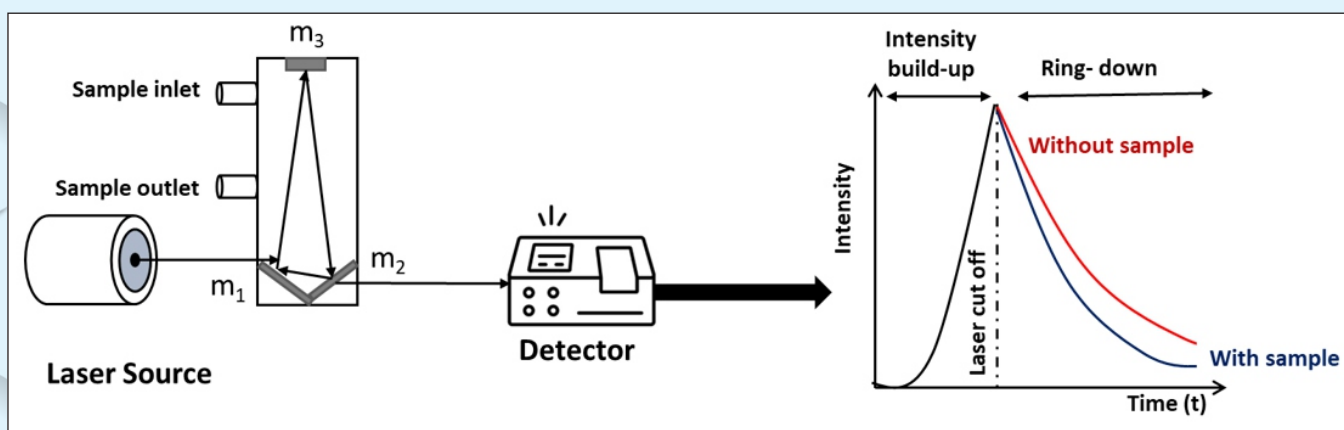


Fig.4: Instrumentation of a cavity ring down spectrometer with detector output.

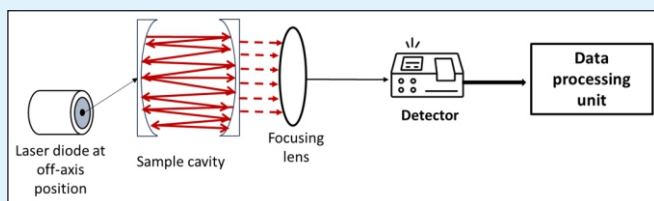


Fig.5: Schematic representation of OA-ICOS instrumentation.

includes requirement of sub-nanometre optomechanical precision, and stability of laser beam for wavelength resonance.

Off Axis - Integrated Cavity Output Spectroscopy (OA-ICOS)

In OA-ICOS, continuous scanning of laser wavelength is done to achieve a highly resolved spectrum (Fig.5). A tuneable diode laser is allowed to pass through a high-finesse cavity at an off-axis angle. Specific wavelengths are absorbed by water vapour present in the optical cavity. The intensity of transmitted light is measured by a photodiode and the difference between incident and transmitted light is utilised to calculate the concentration of each isotopologues. As wavelength scanning is possible from UV region to IR, the instrument focuses on the strongest absorption lines and this process enhances the sensitivity several times compared to CRDS. For stable isotope measurement in water sample a diode laser is used having wavelength centered at 1390 nm (Gupta., 2023).

In OA-ICOS, multiple isotope ratios (e.g. $\delta^2\text{H}$, $\delta^{18}\text{O}$) can be measured simultaneously with a single scan, while in case of CRDS measurements need multiple wavelength scanning. Though IRMS remains the gold standard for stable isotope ratio measurement in water, laser-based techniques are getting more popularised due to the advantages in providing fast results, minimal sample preparation and cost effectiveness.

Conclusions

The advancements in isotope measurement systems are broadening the role of isotopes in hydrological systems, ecological sciences, climate studies. Many new methods are being developed using laser techniques for the measurement of different isotopes, which is allowing comprehensive understanding of the complex hydrological processes.

References for this article have been consolidated and are available upon request.



Dr. M. Someshwar Rao is currently serving as the Head, Groundwater Division, National Institute of Hydrology (NIH), Roorkee & Coordinator, Regional Centre, NIH, Jodhpur. With 28 years of research experience, his expertise lies in groundwater investigations using isotopic and hydrochemical tools. Dr. Rao played a key role in establishing advanced laboratories at NIH, Roorkee; IIT, Roorkee; and PRL, Ahmedabad. He acted as member of several national-level coordinated research projects, including the Isotope Fingerprinting of Waters in India (IWIN) and National Hydrology Projects (HP-I, HP-II, and NHP), among others. He has authored over 200 publications including book chapters and edited volumes. In addition to academic achievements, he conducted many scientific outreach activities through Jal Shakti Abhiyan and water campaigns in the 'Maha Kumbh Mela'.



Ms. Anushree Ghosh is currently working in the Isotope Hydrology Section, Isotope and Radiation Application Division (IRAD), RC&IG, at Bhabha Atomic Research Centre (BARC). She joined IRAD in 2023 as Scientific Officer-C after passing out from the 66th Batch of IGCAR Training School. Ms. Anushree is specialized in the measurement of stable isotopes of water and dissolved constituents by Isotope Ratio Mass Spectrometer. She is actively pursuing her research in the field of application of environmental stable isotopes (^2H , ^{18}O , ^{13}C) and radioisotopes (^3H , ^{14}C) in hydrology.