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Performance of Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) for direct measurement of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ in water samples- Application to bottled mineral water

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Abstract: The precision, accuracy and memory effect of direct measurement of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ in water samples were evaluated using Off-Axis Integrated Cavity Output spectroscopy, and values comparable to Isotope Mass spectrometer were obtained. An injected volume correction factor is determined for each isotope and was applied to get more accurate data. Application of the method to mineral water bottles sold in India showed that it is possible to trace the origin of water. National meteoric water line was constructed, with a slope of approximately 7.46 for δ^2H and $\delta^{18}O$ and 0.54 for $\delta^{18}O$ and $\delta^{17}O$.

Keywords: *OA-ICOS, Stable Isotope, Memory effect, Injected volume correction, Mineral Water, Meteoric Water Line.*

1. Introduction

India is among the top ten countries in terms of bottle water consumption. Number of mineral water bottles from different regions is available throughout the country. Due to increase in demand of mineral water consumption, some mineral water bottle cause concern about their provenance. Isotopes represent a potential tool for detecting fraud related to bottled mineral water as δ^2H, ^{18}O, $\delta^{17}O$ reflects the water source (Godoy et. al 2012; Brencic and Vreca, 2006; Bowen et al. 2005).

Here we present a Fourth generation Cavity Enhanced Absorption Spectroscopy (CEAS) called as Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) for direct determination of δ^2H, $\delta^{18}O$, $\delta^{17}O$ from water samples (Berman et al. 2013). Accuracy and Precision of the Laser Spectroscopy was evaluated by using internal lab standards.

2. Materials and Methods

Twenty mineral water samples were collected from different parts of India and were analyzed using a commercially available; OA-ICOS laser absorption spectrometer (Los Gatos Research (LGR) Triple Isotope Water Analyzer (TIWA-45EP)) for simultaneous direct measurement of the 2H/1H, 18O/16O, and 17O/16O stable isotopes in liquid water. To provide highly accurate quantification of δ^2H, $\delta^{18}O$, $\delta^{17}O$ in injected water samples, the OA-ICOS instrument employs near-infrared tunable diode laser absorption spectroscopy with the laser coupled off-axis to a high-finesse optical cavity (Figure 1). Water samples were introduced without sample conversion into the OA-ICOS instrument via a PAL HTC-xtautoinjector (CTC Analytics) equipped with a heated (≈85 °C) injector block (LGR), where the water samples were evaporated for isotope analysis directly on the water vapor. Liquid water samples were injected into the injector block using a Hamilton 1.2 µL, zero dead volume syringes. The syringe was cleaned prior to every run using distilled water and it was lubricated using NMP (1-Methyl-2-pyrrolidinone) syringe lubricant (Berman et al. 2013), which helped to reduce injected volume fluctuations during the sample run. Syringe was allowed to settle down by running dummy samples prior to each run.

We used three internal lab standards (STD1, STD2 and STD3) (Table 1) calibrated for δ^2H and $\delta^{18}O$ using Mass Spectrometer along with IAEA primary standards VSMOW2, GISP and SLAP2 to determine the Accuracy of the analyzer. Each sample was measured for 18 injections to determine the measurement stabilization and memory effect of the analyzer by running each sample in sequences after SLAP2. Measurement was carried out in high throughput mode, each sample was analyzed for a single time (18 injections).

The raw data from the OA-ICOS was processed using data processing software. An injected volume correction called as linearity correction was applied and an improvement in accuracy and precision for all the

isotopes were observed (IAEA, 2009). Injected volume correction slopes were constructed by measuring an intermediate sample at different injected volumes between 600nl and 1200nl. A clean water sample was placed at the end of the sequence to clean the syringe.

Table 1: *Internal Standard values*

ID	*δ^2H ‰*	*$\delta^{18}O$‰*	**$\delta^{17}O$‰*
STD1	-9.57±1.0	-2.89±0.1	-1.43±0.08
STD2	-50.06±1.	-7.06±0.1	-3.69±0.08
STD3	-111.92±0.9	-15.53±0.09	-8.39±0.1

** $\delta^{17}O$ was calibrated using OA-ICOS*

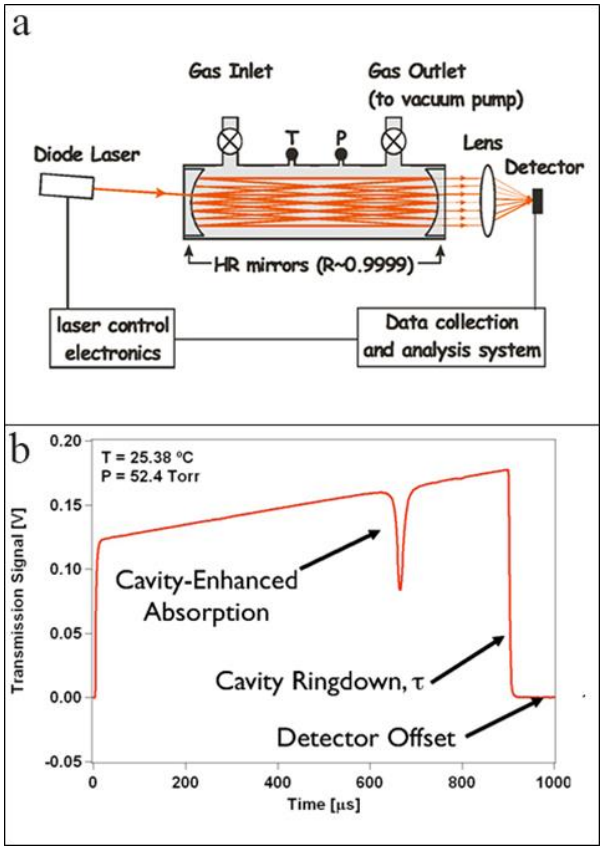

Figure 1 *(a) Off-Axis ICOS cavity enhanced absorption technique (b) Typical raw data trace*

3. Results and Discussions

In recent studies poor accuracy was related between-sample memory effects. We performed a memory effect quantification test to determine the number of injections the OA-ICOS took for measurement stabilization using IAEA primary standards. The internal lab standard was measured in a sequence followed by IAEA primary standards, each primary standard were measured after every single sample. Each sample was measured for 18 injections and it was found that first 4-5 injections were suffered by memory effect (Figure 2) .This was because of the huge isotopic difference between the SLAP2 and the sample. Memory Effect was minimal for samples whose isotope values were close to each other in the sequence (Penna et al. 2012; Penna 2010).

Accuracy and Precision of the spectrometer was evaluated from the results (Table 2). Average accuracy of OA-ICOS is better than 0.3‰ for δ^2H and 0.05‰ for $\delta^{18}O$ and $\delta^{17}O$. Average precision was better than 0.3‰ for δ^2H and 0.09‰ for $\delta^{18}O$ and $\delta^{17}O$.

Table 2: *Achieved accuracy for δ^2H and $\delta^{18}O$*

Sample Code		**STD1**	**STD2**	**STD3**
δ^2H ‰				
OAICOS measured	Mean	-10.47	-49.83	-112.09
	SD	0.32	0.46	0.26
IRMS measured	Mean	-9.57	-50.06	-111.92
	SD	1.0	1.0	0.9
$\delta^{18}O$‰				
OAICOS measured	Mean	-2.76	-7.01	-15.56
	SD	0.06	0.09	0.10
IRMS measured	Mean	-2.89	-7.06	-15.53
	SD	0.1	0.1	0.09

Table 3: *Delta values obtained for bottled mineral water (values as ‰)*

Brand	**City**	**$\delta^{18}O$ ‰**	**δ^2H ‰**	**$\delta^{17}O$ ‰**
Railneer	Hyderabad	-3.54	-24.80	-2.07
Railneer	Hyderabad	-3.51	-24.21	-1.90
Aquafina	Chittoor	-5.40	-34.48	-2.89
Aquos	Guwahati	-5.97	-35.82	-2.94
Sheetal	Jorhat	-5.71	-37.69	-3.24
Pura	Tinsukia	-5.81	-38.16	-3.34
Dew Drops	Sivasagar	-4.16	-21.94	-2.17
Aquafina	Delhi	-6.58	-47.04	-3.62
Aquafina	Delhi	-6.65	-47.20	-3.61
Kinley	Gujarat	-1.57	-11.60	-0.47
Kinley	Hirebaganal	-1.41	-2.29	-0.59
Kinley	Bangalore	-1.59	-6.37	-0.86
Bisleri	Pune	-1.41	-7.95	-0.64
Aquafina,	Roha	-1.55	-3.06	-0.73
Kinley	Amritsar	-7.24	-52.14	-4.01
Kinley	Amritsar	-7.20	-52.36	-4.10
Aquafina	Chennai	-5.99	-37.74	-3.16
Water Tech	Chennai	-3.98	-26.95	-2.23
Bisleri	Roorkee	-8.83	-59.84	-4.57
Bisleri	Roorkee	-8.83	-59.29	-4.43

The data obtained for δ^2H, $\delta^{18}O$, $\delta^{17}O$ for Indian bottled mineral water are presented in Table 3. The values follow a straight line with a slope 7.46(R^2=0.9766) for δ^2H - $\delta^{18}O$ and a slope 0.55 (R^2=0.9839) for $\delta^{18}O$ - $\delta^{17}O$ (Figure 3(a) and 3(b))

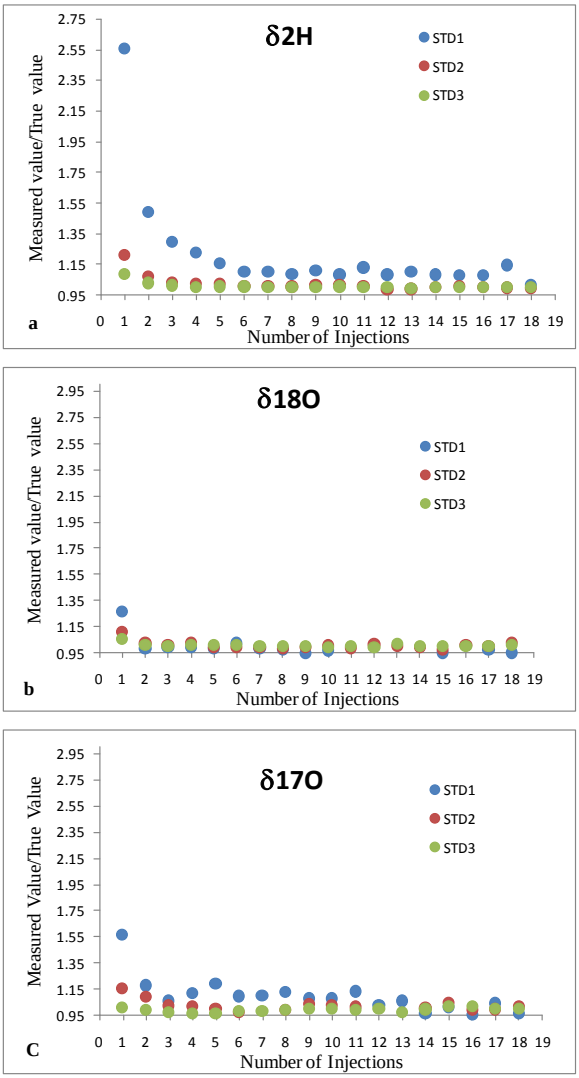

Figure 2 *Memory effect testing (a) δ^2H, (b) $\delta^{18}O$ and (c) δ^{17}*

Table 4: *d-excess values from Mineral water bottles*

City	State	d-excess ‰
Hyderabad	AP	3.53
Hyderabad	AP	3.83
Chittoor	AP	8.74
Guwahati	AS	11.95
Jorhat	AS	8.01
Tinsukia	AS	8.29
Sivasagar	AS	11.35
Delhi	DL	5.62
Delhi	DL	6.03
Gujarat	GJ	0.95
Hire Baganal	KA	8.99
Bangalore	KA	6.32
Pune	MH	3.34
Roha	MH	9.34
Amritsar	PB	5.76
Amritsar	PB	5.25
Chennai	TN	10.14
Chennai	TN	4.91
Roorkee	UK	10.81
Roorkee	UK	11.38

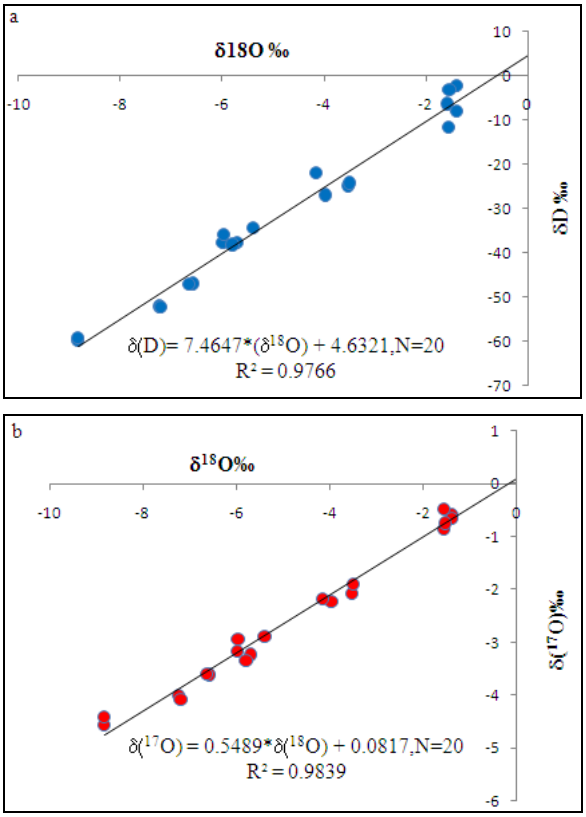

Figure 3 *Meteoric water line based on analyzed bottled mineral water samples*

The bottle mineral water from various regions has a different isotopic composition as well as in the d-excess, which allows its use for authenticity testing. The mineral water from same state had a fair unique isotopic composition. Mineral water brands from Assam have a similar isotopic composition and probably originated from the same local source.

4. Conclusion

This study was carried out in National Institute of Hydrology Roorkee, during the installation and demonstration of LGR OA-ICOS TWIA (IWA-45EP). OA-ICOS technology is a proven technique for accurate and fast determination of water isotope measurement comparable to Isotope mass spectrometer. This study demonstrates that it is possible to obtain precise and accurate isotopic ratios using OA-ICOS. Applying small correction factors "injected volume correction" and"spline calibration" improved the precision and accuracy of the measurements. This is a preliminary test

carried out to identify the source of bottled mineral water. Stable isotopes can be a potential tool to identify mineral water fraud and mislabeling. Detailed comprehensive study is required to find the exact source of each mineral water bottles available in the market. Indian meteoric water line based on bottled water samples is constructed which has a slope coefficient approximately 7.46 for δ^2H - $\delta^{18}O$ and 0.54 for $\delta^{18}O$ -$\delta^{17}O$. The isotopic composition varied between -2.29‰ to -59.84‰ for δ^2H, and between -1.41‰ to -8.83‰ for $\delta^{18}O$, and between -0.47‰ to -4.57‰ for $\delta^{17}O$. The d-excess varied between 0.95‰ to 11.95‰ with an average of 7.23‰.

5. Acknowledgements

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