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CONTENTS
NO 33 * 2020

1. **Nguyen Thanh Giao, Ly Van Loi, Tran Do Bao Tram:** Preliminary study on influence of fire to physical and chemical characteristics of soil at Tram Chim national park, Dong Thap province..... 3
2. **Do Manh Tuan, Vu Thi Hong Cam, Van Hung Tien, Ho Van Thanh:** Some analytical results of rock slope surface stability on the road around the Hon Ngang island in Kien Hai district, Kien Giang province, Vietnam..... 13
3. **Nguyen Thu Huyen, Nguyen Thi Binh Minh:** Application of IWM2 software for environmental efficiency assessment of solid waste burning scenarios in Hai Duong city..... 25
4. **Nguyen Thanh Giao:** Evaluating soil and water quality in Phu My species and habitat conservation area, Kien Giang province..... 32
5. **Nguyen Phuong Tu, Bui Thi Thanh Thuy, Truong Duc Canh:** Transfer of renewable energy in the structure of the electricity sector and policies to promote the development of renewable energy in Vietnam..... 42
6. **Nguyen Quang Minh, Phi Truong Thanh, Do Manh Tuan, Tran Xuan Truong, Le Trung Kien, Nguyen Thi Phuong Thanh, Vu Thi Hong Cam:** Block theory analyses for rock slope stability. A case study along 3b high way, Xuat Hoa area, Bac Kan province 49
7. **Nguyen Thanh Giao:** Application of multivariate statistical techniques in selecting surface water quality monitoring sites at Bung Binh Thien reservoir, An Giang, Vietnam..... 57
8. **Nguyen Thi Bich Ngoc, Tran Van Tinh, Thi Van Le Khoa:** Application of remote sensing and gis to determine the riverbank changes in An Giang province 68
9. **Truong Duc Canh, Nguyen Phuong Tu, Bui Thi Thanh Thuy:** Comparison of the feasibility of ultrafilration and nanofiltraiton membrane in drinking water treatment at household scal 78
10. **Bui Thi Thuy Dao, Pham Thi Thuong Huyen, Quach Thi Chuc:** Application of gis for assessing adaptation of ecological scenery to serve priority spatial orientation for cassava development at Kon Tum province 85
11. **Hoang Ngoc Khac:** Species composition and key to species of subclass pteriomorphia in the mangrove forest ecosystem of Xuan Thuy national park, Giao Thuy district, Nam Dinh province..... 91
12. **Pham Thi Mai Thao, Nguyen Thi Lan:** Study on plastic waste status in mangrove forests at the coastal area of Hau Loc district, Thanh Hoa province..... 98
13. **Luong Thanh Tam, Vu Kim Hanh:** Study of the current situation of technical infrastructure related to environmental protection in Thuong Tin general hospital 107
14. **Bui Thi Hoa, Nguyen Xuan Huan, Nguyen Thanh Nam, Le Thu Ha, Le Xuan Tuan, Nguyen Thuy Lien**Water quality of Co Chien estuary, Tien river..... 114
15. **Tran Thanh Le, Nguyen Thi Thuy, Tran Vu Long:** Development of internal lab samples standard for isotopic analyses using cavity ringdown spectroscopy method 120

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DEVELOPMENT OF INTERNAL LAB SAMPLES STANDARD FOR ISOTOPIC ANALYSES USING CAVITY RINGDOWN SPECTROSCOPY METHOD

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Abstract

Water stable isotopes are a good tool for the estimation of the water cycle over the basin and tracer for the origin of the water. Analysis of stable isotope compositions nowadays mainly focuses on estimating the difference between the samples isotope compositions with the known standards isotope compositions. One of the most used methods is Cavity ringdown Spectroscopy method. The known standards are very limited and expensive then internal laboratory standards (ILS) should be prepared with a larger amount for further normal daily samples analysis. This paper described the methods and procedures for preparing the ILS of HUNRE Water Laboratory. Three water samples from three different locations were taken as the candidates' ILS. Those samples were passed procedures to determine the isotope composition's value and uncertainties. The results show that those three samples had covered a wide range of values and were well fitted to linear regression. Those ILS candidates are suited to use as the ILS for further sample analysis.

Keywords: Internal Laboratory Standards; Isotopic analyses

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1. Introduction

In the area of stable isotopes, metrological hierarchy and traceability of reference materials in use is the entire basis for correct uncertainty propagation. The PICARRO L2130-i isotope analyzer, which has been installed and tested at the Water Lab, Hanoi University of Natural Resources and Environment (HUNRE) since 2016, requires standards to ensure the accuracy of results for daily use. However, certified reference materials PICARRO Zero, PICARRO Mid and PICARRO Dept are only sold in small quantities. While all the good isotope laboratories do not use them for everyday calibrations because they are limited and expensive. In contrast, laboratories prepare their internal standards and calibrate those standards against certified reference materials or international standards because it is not difficult. In 2019, HUNRE was asked by the Ministry of Natural Resources and Environment (MONRE) to obtain an inexpensive set of internal standards that are calibrated

versus PICARRO Zero, PICARRO Mid, and PICARRO Dept. The laboratory measurements were conducted on three possible types of water which were candidates as materials of making for internal lab standards. This study describes the steps in the development of Internal Laboratory Standards (ILSs): standards collection and measurement, calibration, storage of standards, and reporting establishment. And this study is intended as the technical guideline for making lab isotope standards.

2. Materials and Method

Since these standards are expensive and sample limited, each lab should develop their secondary, or working, standards. Example sources for secondary standards include: Local precipitation (variable isotopic composition); Local tap water (variable, related to local precipitation) - Kona Deep, Destiny Deep Sea Water (~ 0 ‰); Snow or ice from your favorite alpine region (depleted); Tap water from your colleagues across the globe (variable) (Werner and Brand 2001) [2].

2.1. Method

The water sample candidates were passed through a procedure described below:

- *First step:* Locations selecting and samples were taken. Locations of sample candidates were carefully selected to meet with requirements.

- *Second step:* Samples preparation. Samples were taken just raw material and need to prepare before making any analysis of stable isotope components. The sample candidates were pass through suspended solid filtered and de-salting.

- *Third step:* Analysis of samples. Sample candidates were analyzed of stable isotope components by used PICARRO L2130-i isotope analyzer.

- *Fourth step:* Samples processing and statistical estimation. The results of sample candidates analysis were processing and perform necessary statistical estimation to obtain reliable values which were used as standard values.

This paper focus described some important steps to the preparations of sample candidates.

2.2. Location selecting

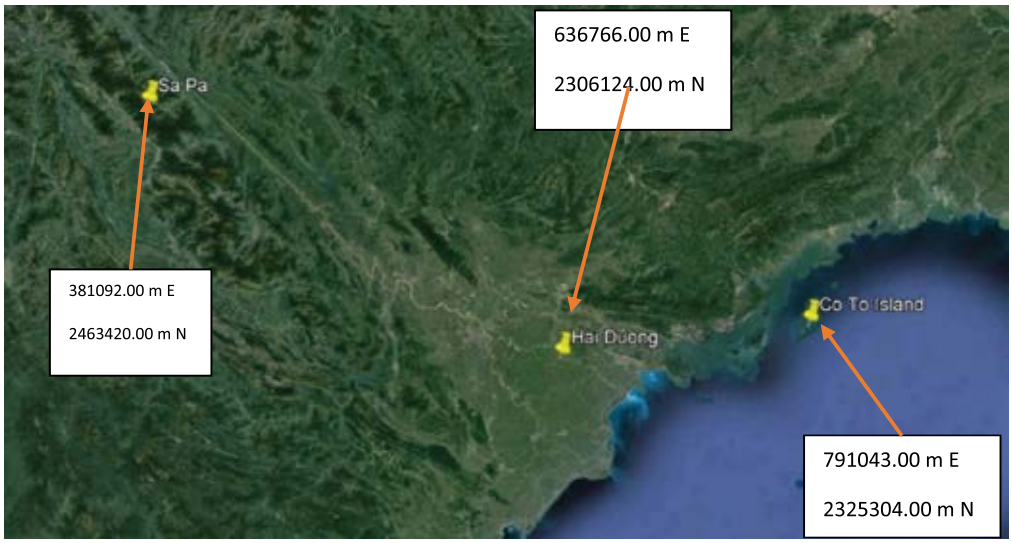

Figure 1: Positions of water standard

The HUNRE Zero ILS was taken from the seawater near Co To island, Quang Ninh province. This water type is will as close to zero of stable isotope composition as possible. The HUNRE Mid ILS was taken from rainfall water collected in Sapa with 350 km from the seashore. And the last, HUNRE Depl was taken from deep groundwater from Neogen aquifer at Hai Duong province which is almost depleted in stable isotope composition. The positions of water are depicted in the figure below (Figure 1). The raw water samples were selected to be sufficiently close to the isotopic composition of the certified reference materials PICARROs [3]. More importantly, these ILS standards were required to cover the full isotopic range of routine samples and have similar chemical properties. Two of three calibration standards include a "heavy" standard and a "light" standard breaking the range of typical sample values.

2.3. Samples preparation

Before analysis, a standard laboratory distillation system was used for the preparation of internal standards (see Figure 2).

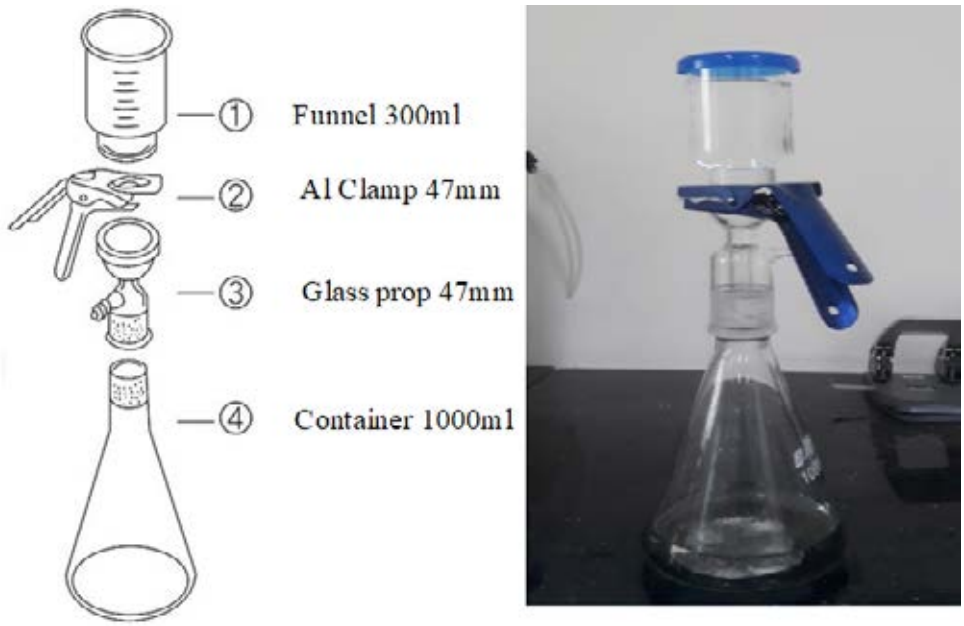

Figure 2: Water distillation

2.4. Calibration of the ILS samples

The isotopic compositions of these ILS samples were carefully calibrated versus the reference materials (RMs) PICARROs in the HUNRE Water Laboratory, Hanoi, Vietnam. The analyzer provided raw data to be ready for correction and calibration handily. 10 measurements were performed and then repeated on 3 days to derive statistically well-founded results. In the meantime, TU Delft analyzed these internal standards through the isotope analyzer (LGR, type LWIA) as an independent check.

Calibration of ILS is of utmost importance as it defines the possible accuracy of any measurement. However, the exact value of each calibration standard is not of particular importance as long as they span a representative range of values over which the analyzer will typically be operated.

Therefore, it is best to measure three available PICARRO standards, bracketed around the delta values of the unknown ILS samples, to construct a calibration line whose regression coefficients can be used to scale the unknown ILS sample data.

We obtained three unknown ILS samples numbered 1 - 3 and the three PICARRO standards S1, S2 and S3 which are representative of PICARRO Zero, PICARRO Mid and PICARRO Dept. The following arrangement of vials in the autosampler tray was performed:

S1	S2	1	2	3	S3	1	2	3	S1	S2
		1	2	3	S3	1	2	3	S1	S2
		1	2	3	S3	1	2	3	S1	S2

Plot the true values of the PICARRO standards used above (see Tab. 1) against the measured values recorded by the analyzer (see Tab. 2). Two separate plots had been made (see Fig. 3 and Fig. 4), one for $\delta^{18}O$ and one for δD. Fitting a straight line through each of the two plots yielded an equation of the form:

$$y = m.\ x + b \qquad (1)$$

where m is the slope and b is the intercept.

Table 1. Known values of PICARRO standards

	S1 (PICARRO Zero)	**S2 (PICARRO Mid)**	**S3 (PICARRO Dept)**
$\delta^{18}O$	0,3	-20,6	-29,6
δD	1,8	-159,0	-235,0

For each plot, the equations correspond to:

$$\delta^{18}O_{calibrated} = m_{\delta 18O}.\ \delta^{18}O_{measured} + b_{\delta 18O} \qquad (2)$$

$$\text{and } \delta D_{calibrated} = m_{\delta D}.\ \delta D_{measured} + b_{\delta D} \qquad (3)$$

Use the slopes and intercepts (see Tab. 3) in the equations above to calculate the calibrated isotope ratios of ILS samples from the measured values.

Re-calibrations were conducted regularly 2 times per week(s)

2.5. Calibration of stable isotope data

SICalib (GRÖNING 2018) [1], a calibration excel template provided free of charge by IAEA, was used in HUNRE and TU Delft to ensure comparability of data between two selected laboratories.

The reported final values in Tab. 5 were calculated from the entire set of data from all two interlaboratory comparison exercises following a two-step statistical treatment performed by SICalib. In the statistical treatment, the stated standard uncertainty at the 1σ- level is based on the standard deviation derived from the individual laboratory mean values as provided from the interlaboratory comparison exercises. The second step was modified by using an exclusive sigma criterion: interactively, the most extreme value is excluded in the calculation of the standard deviation and the appropriateness of the exclusion is verified retroactively by calculating the standard deviation of the remaining data set. The iteration was stopped when the last excluded value stayed within a 2σ standard deviation interval of the mean value of the remaining data.

In Tab. 4, data in the 1st row is within the 2σ - the range of all reported values. Data in the 2nd row are the results of the two-step statistical treatment. Data in the 3rd row is an interquartile rejection criterion.

2.6. Storage

Based on the calculated isotopic compositions, 15 liters of three samples produced at HUNRE were stored in three

specially constructed large containers. Three containers were filled with 5 liters of HUNRE each using the slight gas overpressure of pure Nitrogen and an attached dispenser (see Fig. 3). It is not recommended to store unused fractions of the materials for further use due to the strong possibility of evaporation losses with significant isotope fractionation. Therefore, the reference values in this reference sheet (see Tab. 2) do not apply anymore for such retained portions. Under no circumstances may any portion of the material be used for repeated isotope measurements due to the isotopic exchange and corresponding shift of the isotopic compositions of the material during the preparation process.

Figure 3: Metal barrels under gas overpressure

3. Results and Discussion

3.1. Calibration line for the Picarro water isotope analyzer

To obtain the highest desired level of accuracy, the number of repetitions of three ILS samples between the PICARRO standards S2 and S3 and between S3 and S1 was 5, as well as the number of injections measured per sample was 10. According to the manner described above, all corresponding results are shown below:

Table 2. Analyze measurements of PICARRO standards

	S1 (PICARRO Zero)	S2 (PICARRO Mid)	S3 (PICARRO Dept)
$\delta^{18}O$	0.23	-20.66	29.67
δD	1.39	-158.99	236.21

Use the data in Tab. 1 and Tab. 2 to calculate the slope and the intercept of two equations (see Tab. 3) corresponding to two separate plots for $\delta^{18}O$ and δD.

Table 3. Regression coefficients

	Zero	Mid	Dept
$\delta^{18}O$ slope	0.924	0.924	0.924
$\delta^{18}O$ intercept	-2.0	-2.0	-2.0
$\delta^{2}H$ slope	1.08	1.08	1.08
$\delta^{2}H$ intercept	2.9	2.9	2.9

In the meantime, two separate plots were made (see Fig. 3 and Fig. 4), one for $\delta^{18}O$ and one for δD.

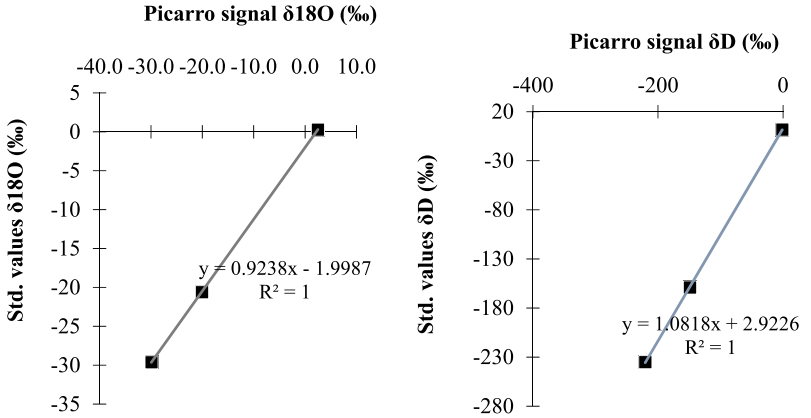

Figure 4: The calibration line for $\delta^{18}O$ and $\delta^{2}H$ of the true values of the standards against the measured values

Fitting a calibration line through each of the two plots yielded the equations:

$\delta^{18}O_{calibrated} = 0.924\ \delta^{18}O_{measured} + 1.99$ (4)

and $\delta D_{calibrated} = 1.08\ \delta D_{measured} + 2.92$ (5)

3.2. Reference values for the reference material HUNRE Zero, HUNRE Dept, HUNRE Mid

The δ-values for HUNREs are based on statistically evaluated laboratory results from two intercomparison exercises (see Tab. 4).

Table 4. Intercalibration mean values of the accepted data and uncertainties based on the standard deviation of the dataset (1σ)

$\delta^2H_{PICARRO}$			δ²H-standard uncertainty			Number of accepted results n (reported results)			$\delta^{18}O_{PICARRO}$			δ¹⁸O-standard uncertainty			Number of accepted results n (reported results)		
Zero	Mid	Dept	Zero	Mid	Dept	Zero	Mid	Dept	Zero	Mid	Dept	Zero	Mid	Dept	Zero	Mid	Dept
1.99	-158.43	-235.86	1.27	0.96	0.86	40	40	40	0.2	-20.64	-29.77	0.08	0.06	0.12	40	40	40

Reference values for the relative difference in hydrogen and oxygen stable isotope-amount ratio for the reference materials (HUNRE Zero, HUNRE Dept, HUNRE Mid) are listed in Tab. 5.

Table 5. δ²H and δ¹⁸O reference values relative to respective PICARRO values for the reference material HUNRE

Name	$\delta^2H_{PICARRO}$	δ²H-standard uncertainty	$\delta^{18}O_{PICARRO}$	δ¹⁸O-standard uncertainty
HUNRE Zero	-6.78	0.3	-1.15	0.17
HUNRE Mid	-53.66	0.47	-7.55	0.19
HUNRE Dept	-91.37	0.92	-12.78	0.09

The traceability chain for δD and $\delta^{18}O$ measurement results performed in the HUNRE Water Lab, using PICARRO Zero, PICARRO Mid and PICARRO Dept as calibration standards, ends with the δ-values of these three materials, serving as certified reference materials, expressed on the respective PICARRO value.

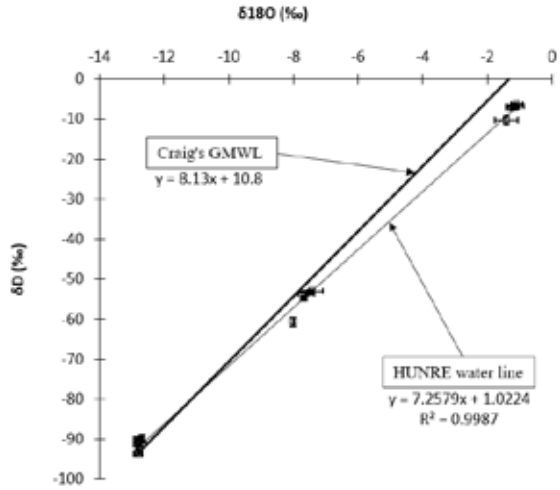

Figure 5: Values of three ILS candidates versus Craig's GMWL

No further data are available on the past individual laboratory measurements or on the laboratory performance at this time, and therefore no more accurate calculation of standards uncertainties is possible. For the future, re-assessment of isotopic values and re-determination of the associated analytical uncertainty are planned.

4. Conclusion

The traceability of the HUNRE δ-values back to PICARRO justifies its status as a reference material. The reference materials HUNREs provided three water samples with reference values for its relative difference in $^{2}H/^{1}H$ and $^{18}O/^{16}O$ isotope-amount ratios (δ-values). HUNREs as materials are used to confirm the successful calibration of internal laboratory standards by the use of the certified reference materials PICARROs. It is recommended that the materials are used in parallel to PICARROs to check the success of the calibration of internal laboratory standards immediately upon opening.

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