UTILIZATION OF ANALYTICAL TECHNIQUE FOR EVALUATION OF $\delta^{13}C_{DIC}$ IN GROUNDWATER USING EA-IRMS UNDER THE CONDITION OF VIETNAMESE LAB

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ABSTRACT

As the demand of extraction and consumption of groundwater increases, its quality has been facing the issue of water contamination caused by industrial as well as domestic activities. Isotopic ratio analysis is a modern and effective technique widely used to trace the source of groundwater contamination. In this study, an analytical technique for carbon stable isotopic ratio of dissolved inorganic carbon in groundwater using elemental analyzer - isotopic ratio mass spectrometer was utilized under the condition in Vietnamese lab. As a result, correlation and calibration equations were established in which good reproducibility of the international standards was achieved with the value of first standard deviation less than 0.3 ‰ as well as the accuracy and precision of the measurements were obtained with errors less than 0.12 ‰. Based on these equations, 15 samples of groundwater collected from Cu Chi (Viet Nam) district were analyzed and calculated.

1. INTRODUCTION

Carbon has three isotopes that are useful tracers in the terrestrial ecosystem: stable ^{12}C and ^{13}C; and radioactive ^{14}C. Many investigations, particularly in the water management, biological sciences and climate change, have focused on quantifying variation in carbon stable isotope

ratios $^{13}C/^{12}C$ [1-3]. Although natural variations in the $^{13}C/^{12}C$ ratio are very small, the differences in this ratios are sufficient to trace various chemical, physical and biological processes; specially the source of groundwater contamination.

The relative variation of stable isotope ratio in natural compounds is expressed in term of a well-known notation δ using the unit of parts per thousand (‰) due to its quite small value. The equation is presented as:

$$\delta^{13}C\,(‰) = (R_S / R_R - 1) \times 1000 \tag{1}$$

where R_S and R_R are the isotopic ratio $^{13}C/^{12}C$ in the sample and in the Pee Dee Belemnite (V-PDB) standard, respectively [4].

According to the published data about the carbon isotopic ratio, carbonate rocks typically have $\delta^{13}C$ values of ± 5 ‰. Plants convert atmospheric carbon with $\delta^{13}C_{CO2}$ value of -7 ‰ to organic compounds via photosynthesis. Then, C3 plants (such as pine and apple trees) have $\delta^{13}C$ values in the range from -22 to -33 ‰, whereas C4 plants (e.g. corn) have $\delta^{13}C$ values of around -10 to -20 ‰. For dissolved inorganic carbon (DIC), the $\delta^{13}C_{DIC}$ value in catchment waters is generally in the range of -5 to - 25 ‰ [5].

The EA-IRMS (elemental analyzer - isotopic ratio mass spectrometer) technique has been widely accepted for the routine analysis of isotopic ratios, such as $^{15}N/^{14}N$ and $^{13}C/^{12}C$ [6-8] as well as $^{34}S/^{32}S$ [9-13]. However, the implementation of EA_IRMS technique to determine the $^{13}C/^{12}C$ ratio has not been utilized in Vietnamese laboratory. So far, the Institute for Nuclear Science & Technology in Vietnam is the only lab having EA_IRMS system which is able to support for isotopic ratio analysis. Hence, the analytical technique for determination of $\delta^{13}C_{DIC}$ in groundwater using EA_IRMS need to be utilized in order to establish the correlation and calibration equations to enhance the reproducibility of this method as well as improve the accuracy for the calculation of the $\delta^{13}C_{DIC}$ in groundwater. In this study, the international standards IAEA CO-8, IAEA CO-9 and NBS-19 were used to optimize the operation condition of EA-IRMS system by which the correlation and calibration equations were obtained and 15 samples of groundwater were then analyzed and calculated.

2. MATERIALS AND METHODOLOGY

2.1. Chemicals and instruments

All chemicals and instruments used for this study such as Cromium oxide (Cr_2O_3 – 99 %), silvered cobaltous cobaltic oxide (Co_3O_4/Ag), copper (99.5 %), magnesium perchlorate ($MgClO_4$- 99.5 %), quartz fused (SiO_2 – 99.5 %), tin capsule, quartz tube reactor were commercially purchased from Microanalysis (UK), and used as received without any further purification unless otherwise noted. The international standards IAEA CO-8, IAEA CO-9 and NBS-19 supplied by International Atomic Energy Agency and National Bureau of Standards have been used in this study for carbon calibrations.

All groundwater were collected from Cu Chi district, Hochiminh City, Vietnam and stored in bottles which have been sealed with paraffin to minimize atmospheric CO_2 contamination. The alkalinity of groundwater will be determined by Vietnamese standard (TCVN6636-1:2000) before going to analyze the DIC.

The instrumentations used in the study were the Elemental Analysers (EA from EuroVector, Italy) and Isotope ratio mass spectrometers (IRMS from IsoPrime, UK) together with a Reference Gas Injector system (RGI).

2.2. Methodology

2.2.1. Determination of DIC

Depending on the value of alkalinity, the volume of samples will be calculated in order to obtain at least 0.5 mg of $BaCO_3$. The calculated volume of sample is poured from the full bottle, and DIC of the water sample is precipitated by the addition of $Ba(OH)_2$. The bottle is immediately capped. The sample is allowed to precipitate at ambient temperature for at least 24 hours before further sample processing takes place. After samples have been treated with $Ba(OH)_2$, they are filtered through 0.45 μm glass filters to separate the $BaCO_3$ from the water and any excess $Ba(OH)_2$ in the sample bottle. The sample is collected on the filter paper and then flushed many time with deionized water to bring the pH of the carbonate to a neutral level (pH between 7 and 8). Once the pH is neutral, the filter paper with sample is transferred to a glass Petri dish and dried overnight at 90 °C. A representative sample is placed in a 2 ml dry, clean, air-tight vial and ready for analysis by EA-IRMS.

2.2.2. Determination of $\delta^{13}C_{DIC}$

Prepared samples are loaded in Sn tightly crimped capsules to avoid any trapping of moisture before the combustion. After O_2 pulsed injection, the capsule is dropped into a combustion furnace containing chromium oxide and silvered cobaltous oxide and operating at a temperature of 1030 °C. When O_2 is introduced, the Sn oxidation creates an exothermic reaction that ensures a complete combustion and oxidation of the sample. Then, the mixture flows into the reduction chamber containing copper and operating at 650 °C. The reduced Cu absorbs the excess O_2 and the He gas carries the products of the combustion (N_2, CO_2, and H_2O) via a water trap for subsequent phase separation on the gas chromatographic column (GC) where separation of CO_2 and N_2 is performed. It should be noticed that the background signal obtained in the elemental analyzer (showed on the thermal conductivity detector - TCD) should be set to its minimum level and a good chromatographic separation of the gases needs to be obtained with complete H_2O absorption by the water trap before going into the IsoPrime IRMS where the isotope ratios $\delta^{13}C$ are reported relative to a reference gas standard.

IAEA CO-8, IAEA CO-9 and NBS 19 are three international standards which the values of $\delta^{13}C_{V-PDB}$ are known as -5,749 ‰; -47,119 ‰ and +1,95 ‰, respectively [4]. These values will be used for carbon calibration. This calibration is obtained by plotting raw $\delta^{13}C$ values of standards measured by EA-IRMS as a function of their known isotopic compositions. Furthermore, it is necessary to determine the correlation between raw $\delta^{13}C$ values of standards and $\delta^{13}C$ value of CO_2 reference from which $\delta^{13}C_{DIC}$ (‰) of groundwater can be calculated.

3. RESULTS AND DISCUSSION

3.1. The recovery of DIC

As mentioned in the determination of DIC, the volume of samples needs to be calculated in order to obtain at least 0.5 mg of $BaCO_3$. To do that, after the alkalinity of the samples are measured in the range of 400-600 mg HCO_3^-/L (not shown in this paper), the recovery of DIC needs to be determined. The procedure for precipitation of DIC is applied for the samples with known concentrations. The results presented in Table 1 show that the recovery of DIC can reach an average value of 93.14 %. Hence, the minimum volume of samples is calculated as 40 ml to ensure required amount of samples ready for analysis by EA-IRMS.

Table 1. The recovery of DIC.

N_o	Samples	Volume (ml)	m_{BaCO3} known (mg)	m_{BaCO3} measured (mg)	The recovery (%)
1	$NaHCO_3$	15	49.335	46.129	93.50
2	$NaHCO_3$	15	49.335	46.585	94.43
3	$NaHCO_3$	15	49.335	46.326	93.90
4	Na_2CO_3	15	45.0478	41.903	93.02
5	Na_2CO_3	15	45.0478	41.205	91.47
6	Na_2CO_3	15	45.0478	41.678	92.52

3.2. Isotopic ratio analysis of international standards

Before starting isotopic analyses of the samples, the operation of EA-IRMS system needs to be optimized such as the reference gas carried by He should generate a stable signal in the mass spectrometer source, the background signal needs to be obtained in the elemental analyzer, a good chromatographic separation of the gases and completed H_2O absorption by the water trap are required.

Measured $^{13}C/^{12}C$ ratios are obtained by comparing integrated peak areas for atomic number 44 and 45 of the sample CO_2 pulses compared to those for the sample and reference gases. The final isotopic ratio measurements of IAEA CO-8, IAEA CO-9, NBS 19 and CO_2 reference gases are expressed in term of $\delta^{13}C_{V-PDB}$ and $\delta^{13}C_{CO2-ref}$. The results together with the known values of IAEA CO-8, IAEA CO-9 and NBS 19 are presented in Table 2.

Table 2. $\delta^{13}C$ values of the C isotopic standards used for the EA-IRMS technique.

Isotopic standards	Nature	$\delta^{13}C_{V-PDB}$ known [4] (‰)	$\delta^{13}C_{V-PDB}$ measured (‰)			$\delta^{13}C_{V-PDB}$ average (‰)	Standard deviation (σ_1)	$\delta^{13}C_{CO2\_ref}$
			1st	2nd	3rd			
IAEA-CO 8	calcite	-5.749	-5.55	-5.7	-5.8	-5.68	0.13	18.11
IAEA-CO 9	$BaCO_3$	-47.119	-47.35	-47.31	-46.86	-47.17	0.27	-22.63
NBS-19	calcite	1.95	1.79	1.91	1.8	1.83	0.07	26.50

The average values of $^{13}C_{V-PDB}$ measured for IAEA CO-8, IAEA CO-9 and NBS 19 samples are obtained as 5.68 ‰, -47.17 ‰ and 1.83 ‰, respectively. The reproducibility of the standards is acceptable as shown by value of the first standard deviation in the range of 0.07 to 0.27.

Furthermore, the accuracy and precision of the EA-IRMS isotopic ratio measurements can be observed by comparing the measured values with the known values of $\delta^{13}C_{V\text{-}PDB}$ (error < 0.12 ‰).

3.3. Correlation and calibration

3.3.1. The correlation of $\delta^{13}C$ values

Based on the analysis results, a plot of $\delta^{13}C_{V\text{-}PDB\text{-}avg}$ and $\delta^{13}C_{CO2\text{-}ref}$ can be performed and shown in Figure 1. A correlation equation for this relationship can be obtained as in equation (2):

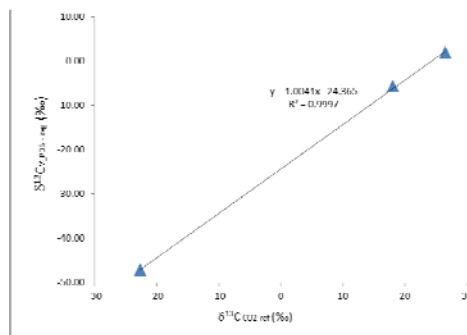$$\delta^{13}C_{V\text{-}PDB\text{-}avg} = 1.0041\ \delta^{13}C_{CO2\text{-}ref} - 24.365 \tag{2}$$

Figure 1. Correlation of $\delta^{13}C$ values of the isotopic standards.

According to this figure, the values of $\delta^{13}C_{V\text{-}PDB\text{-}avg}$ vary from 1.95 ‰ to -47 ‰ while the values of $\delta^{13}C_{CO2\text{-}ref}$ change from 26.50 ‰ to -22.63 ‰ and the correlation equation has a very good R-squared value ($R^2 = 0.9997$) which indicates the regression line fit well the data. Later on, this correlation equation will be used to calculate the values of $\delta^{13}C$ measured from the samples of groundwater.

3.3.2. The carbon calibration

The calibration can be obtained by plotting $\delta^{13}C_{V\text{-}PDB\text{-}avg}$ values of international standards (IAEA CO-8, IAEA CO-9 and NBS 19) measured by EA-IRMS as a function of their known isotopic compositions, as shown in Figure 2.
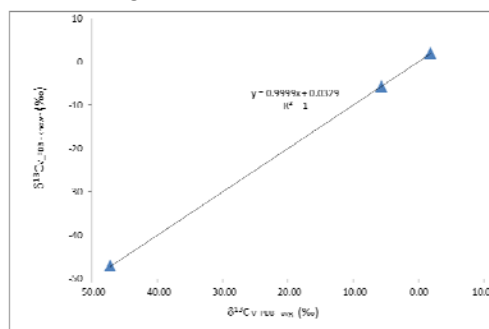

Figure 2. Calibration determined using $\delta^{13}C$ values of the isotopic standards.

A good calibration equation can be generated based on these data. Later on, all measured data will be corrected by the following equation:

$$\delta^{13}C_{V\text{-PDB (corrected)}} = 0.9999 \, \delta^{13}C_{V\text{-PDB (measured)}} + 0.0329 \qquad (3)$$

It is important to have standards with a wide spread of isotopic compositions in order to generate an accurate and robust calibration equation. All measured results show very good agreement with the known values of $\delta^{13}C_{V\text{-PDB}}$, the error is around 0.05 ‰ to 0.12 ‰. Here, the good calibration obtained offers a precise correction along all of this range (from -50 ‰ to +5 ‰) for a wide spread of sample C-isotopic values.

3.4. Isotopic ratio analysis of groundwater

The optimized condition used in the procedure of isotopic ratio analysis of international standards was applied similarly to analyze the samples of groundwater collected from Cu Chi district, Ho chi minh City, Vietnam. Using the correlation and calibration equations obtained, the value of $\delta^{13}C_{DIC}$ were determined and corrected for 15 samples of DIC in groundwater, as reported in Table 3.

Table 3. $\delta^{13}C$ value of groundwater collected from Cu Chi district.

N_o	Samples	$\delta^{13}C_{CO2\text{-ref}}$ (‰)	$\delta^{13}C_{DIC(measured)}$ (‰)	$\delta^{13}C_{DIC(corrected)}$ (‰)
1	N5	5.90	-18.44	-18.41
2	N6	9.44	-14.88	-14.85
3	N13	18.53	-5.76	-5.73
4	N16	6.38	-17.95	-17.92
5	N17	5.04	-19.30	-19.27
6	N18	7.48	-16.85	-16.82
7	N20	7.98	-16.35	-16.32
8	N21	8.35	-15.98	-15.95
9	N22	6.14	-18.20	-18.17
10	N23	5.79	-18.55	-18.52
11	N24	5.60	-18.74	-18.71
12	N25	6.77	-17.56	-17.53
13	N26	6.96	-17.37	-17.34
14	N27	7.17	-17.16	-17.13
15	N28	5.49	-18.85	-18.82

The results show that the values of $\delta^{13}C_{CO2\text{-ref}}$ are in the range of 5.04 ‰ to 18.53 ‰ and $\delta^{13}C_{DIC}$ in groundwater are corrected as varying from -19.27 ‰ to -5.73 ‰, respectively. The results are consistent with previous studies of the isotopic ratio of DIC in groundwater [5]. These values will provide information for tracing the source of carbon dissolved in groundwater which may come from carbonate rocks, degradation of organic matter, or human pollution sources.

4. CONCLUSIONS

Analytical technique for $\delta^{13}C_{DIC}$ in groundwater using EA-IRMS was utilized under the condition in Vietnamese lab. As a result, the recovery of DIC in groundwater can reach an average value of 93.14 %. Good reproducibility of the international standards were achieved with the value of first standard deviation less than 0.3 ‰ as well as the accuracy and precision of the EA-IRMS isotopic ratio measurements can be obtained with the error less than 0.12 ‰ as comparing the measured values to the known values of $\delta^{13}C_{V\text{-}PDB}$. Furthermore, the correlation and calibration equations were established, contributing to standardize and improve the accuracy for the calculation of the $\delta^{13}C_{DIC}$ in groundwater. Consequently, 15 samples of groundwater were analyzed and the values of $\delta^{13}C_{DIC}$ were determined in the range of -5.73 ‰ to -19.27 ‰, being consistent with the previous studies in the literature.

REFERENCES

1. Peterson B. J., Fry B. - Stable isotopes in ecosystem studies. Annu. Rev. Ecol. Syst. **18** (1987) 293.

2. Sharp Z. - Principles of Stable Isotope Geochemistry. Prentice Hall, New Jersey, 2005.

3. Dawson T. E., Siegwolf R. - Stable Isotopes as Indicators of Ecological Change. Academic Press, London, 2007.

4. Gonfiantini R., Stichler W., Rozanski K. - Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements. Proceedings of a consultants meeting held in Vienna, 1-3 December 1993, p.13-29.

5. Kendall C., McDonnell J.J. - Isotope Tracers in Catchment Hydrology, Elsevier Science, Oxford, UK, 1998.

6. Preston T., Owens N.J.P. - Interfacing an automatic elemental analyzer with an isotope ratio mass-spectrometer – the potential for fully automated total nitrogen and N-15 analysis. Analyst **108** (1983) 971–977.

7. Barrie A., Bricout J., Koziet J. - Gas-chromatographystable isotope ratio analysis at natural abundance levels. Biomed. Mass Spectrom. **11** (1984) 583–588.

8. Lichtfouse E., Budzinski H. - 13C analysis of molecular organic substances, a novel breakthrough in analytical sciences. Analysis **23** (1995) 364–369.

9. Giesemann A., H.-J. Jager, Norman A.L., Krouse H.R., Brand W.A. - On-line sulfur isotope determination using an elemental analyzer coupled to a mass spectrometer. Anal. Chem., **66** (1994) 2816–2819. laboratories by CF-IRMS. Technical Note 309/LA version 2. Micromass UK, 1996.

10. Morrison J., Fourel F., Churchman D. - Isotopic sulphur analysis by CF-IRMS. Technical Note 509/LA. Micromass UK, 2000.

11. Grassineau N.V., Mattey D.P., Lowry D. - Rapid sulphur isotope analysis of sulphide minerals by C-GC-IRMS. Eighth Annual V.M. Goldschmidt Conference, Toulouse.

12. Morrison J., Fallick A., Donelly T. - d^{34}S measurements of standards from several

13. Mineral. Mag., 62A, Part 1 (1998) pp. 537–538.

14. Grassineau N.V., Mattey D.P., Lowry L. - Rapid sulphur isotopic analyzes of sulphide and sulphate minerals by continuous flow-isotope ratio mass spectrometry (CFIRMS). Anal. Chem. **73** (2001) 220–225.Grassineau N.V. - High-precision EA-IRMS analysis of S and C isotopes in geological materials. Applied Geochemistry **21** (2006) 756–765.