

On-line technique for preparing and measuring stable carbon isotope of total dissolved inorganic carbon in water samples ($\delta^{13}\text{C}_{\text{TDIC}}$)

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Abstract

A fast and completely automated procedure is proposed for the preparation and determination of $\delta^{13}\text{C}$ of total inorganic carbon dissolved in water ($\delta^{13}\text{C}_{\text{TDIC}}$). This method is based on the acidification of water samples transforming the whole dissolved inorganic carbon species into CO_2 . Water samples are directly injected by syringe into 5.9 ml vials with screw caps which have a piercible rubber septum. An Analytical Precision «Carbonate Prep System» was used both to flush pure helium into the vials and to automatically dispense a fixed amount of H_3PO_4 . Full-equilibrium conditions between produced CO_2 and water are reached at a temperature of 70°C ($\pm 0.1^\circ\text{C}$) in less than 24 h. Carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) were measured on an AP 2003 continuous flow mass spectrometer, connected on-line with the injection system. The precision and reproducibility of the proposed method was tested both on aqueous standard solutions prepared using Na_2CO_3 with $\delta^{13}\text{C} = -10.78$ per mil versus PDB ($1\sigma = 0.08$, $n = 11$), and at five different concentrations (2, 3, 4, 5 and 20 mmol/l) and on more than thirty natural samples. Mean $\delta^{13}\text{C}_{\text{TDIC}}$ on standard solution samples is -10.89 per mil versus PDB ($1\sigma = 0.18$, $n = 50$), thus revealing both a good analytical precision and reproducibility. A comparison between average $\delta^{13}\text{C}_{\text{TDIC}}$ values on a quadruplicate set of natural samples and those obtained following the chemical and physical stripping method highlights a good agreement between the two analytical methods.

Key words carbon isotope composition – Total Inorganic Carbon Dissolved in water (TDIC) – stable isotopes – continuous flow IRMS measurements – on-line extraction technique

1. Introduction

The stable carbon isotope ratios of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{TDIC}}$) have been successfully applied in studies aimed at the evaluation of

sources, sinks and fluxes of carbon taking place in natural waters (Atekwana and Krishnamurthy, 1998). In active volcanic areas, on the basis of the carbon isotope balance among dissolved carbon species in solution ($\text{CO}_{2\text{aq}}$, HCO_3^- and CO_3^{2-}), the pristine carbon isotope composition of CO_2 interacting with thermal waters has been estimated (Favara *et al.*, 1999; Inguaggiato *et al.*, 2000). Temporal variations observed in the isotopic composition of TDIC in some geothermal waters of Ischia Island were recognized as significant for volcanic surveillance (Caliro *et al.*, 1999).

The determination of $\delta^{13}\text{C}_{\text{TDIC}}$ is based on isotope measurements of carbon dioxide extracted from the samples. The most common reactions to produce CO_2 from water samples are: i) reaction of 100% H_3PO_4 with solid carbonate

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precipitated from the water sample and ii) direct injection of phosphoric acid onto the liquid sample. Both these methods include the use of an expensive vacuum line and/or dedicated sampling and analytical devices.

The first procedure implies the use of a large water sample. Furthermore, it requires several steps for sample preparation including precipitation of carbonates by using $\text{Ba}(\text{OH})_2$ or $\text{Sr}(\text{OH})_2$, filtering and drying under a controlled (carbon-free) atmosphere, homogenization of the precipitate and finally its reaction with acids to form a CO_2 gas phase into a vacuum line and gas extraction. All these laborious preparation procedures comprise several potential sources of error and they lead to slow analysis time.

A more rapid procedure consists of the addition of phosphoric acid onto the liquid sample. The chemical equilibrium among dissolved carbon species in the solution is shifted towards CO_2 . The carbon dioxide produced by means of this process can be extracted into a vacuum line (Atekwana and Krisnamurthy, 1998; Favara *et al.*, 2002) or dynamically extracted under a re-circulating flow of high-purity inert gas (Mc Nicol *et al.*, 1994).

In the following sections, we report a rapid and simple method for collection and preparation of water samples for $\delta^{13}\text{C}_{\text{TDIC}}$ analyses. The extraction technique discussed in this paper is based on the liberation of CO_2 yielded by acidification of water samples. It requires a low amount of sample (0.5-2 ml) and an equilibrium time of about 18 h, when full-equilibrium conditions between produced CO_2 and water are established. The use of an autosampler both for acid dosing and for sample injection into the mass spectrometer reduces many potential manual errors as well as preparation and analysis time.

2. Sampling and preparation procedures

All water samples were collected in the field and dispensed into glass bottles (*ca.* 50 cc) and quickly sealed using an aluminum crimp cap and gas-tight rubber/teflon plugs, taking care that no air bubbles are present in the samples. In the laboratory, about 10 cc of pure Ar, or another carbon-free host gas, are injected with a syringe into the upturned bottles (fig. 1). The volume of water si-

multaneously withdrawn is collected in a syringe, fitted with a stopcock. The water sample is then injected through the rubber septum of a 5.9 ml screw-capped glass vial. The amount of water injected into the vials ranges from 0.2 up to 2 ml, depending on the Dissolved Inorganic Carbon (DIC) content of the sample. The lower instrument detection limit (see details in the next paragraph) allows the analysis of water samples with DIC contents greater than 4 mmoles per liter.

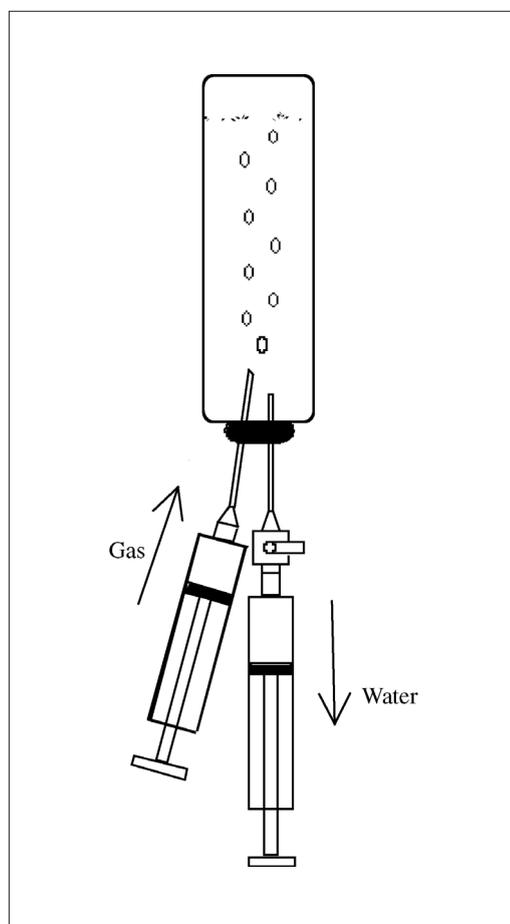


Fig. 1. Extraction of sample from sampling bottles in the laboratory. Injection of about 10 cc of pure Ar in the upturned bottles and simultaneous collection of water in a syringe with a stopcock.

However, reducing the headspace of the vials, it is possible to lower the detection limit further. This was done by inserting a glass cylinder of about 1 cc into the vials thus improving the minimum detectable DIC content to 2.0 mmol per liter.

In order to reduce any air contamination, the vials were previously flushed with ultrapure Helium (99.9996 vol%) using an Analytical Precision «Carbonate Prep System» (fig. 2a). This device consists of a modified Gilson 222XL au-

tosampler tray holding up to 132 samples kept in a thermostatic rack and equipped with a needle having three concentric capillary tubes. The same flushing needle provides the acidification of the water samples. A fixed amount (100-200 μl) of 100% H_3PO_4 is automatically dispensed into the vials by means of a valveless pump. Addition of acid decrease the pH of the sample shifting the equilibrium of dissolved carbon species towards gaseous CO_2 . This reaction takes place at 70°

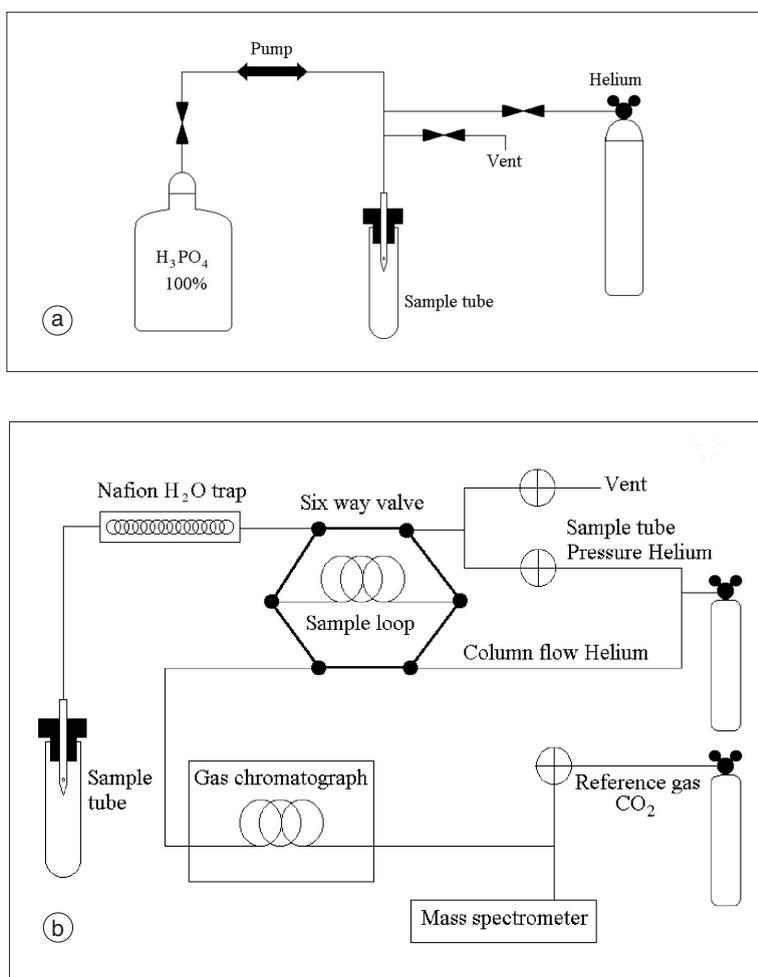


Fig. 2a,b. a) schematic of the Analytical Precision «Carbonate Prep System»; b) schematic diagram of the analytical unit (Analytical Precision AP2003).

$\pm 0.1^\circ\text{C}$. At the end of the process, the *pH* of water samples ranges between 0.5 and 1 *pH* unit.

3. Sample analysis

After 18 h, the sample vessels containing the CO_2 produced by acidification and the water sample are removed from the bath and manually transferred into the analytical unit where the vials are cooled for about 2 h (fig. 2b). The analytical unit consists of an injection apparatus (Gilson 222XL autosampler) and a purification system (Nafion[®] trap and GC column) directly connected to the mass spectrometer.

Carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) were measured on an AP 2003 continuous flow mass spectrometer using He (5.6) as carrier and CO_2 (4.8) as reference gas. By using this configuration, instrument sensitivity is calibrated on a carbon dioxide content in the range 3-10 vol%.

In order to improve the precision of the measurements, the analysis is repeated four times for each sample, resulting in a series of CO_2 peaks reaching the mass spectrometer. Within the same analysis, two pulses of reference gas bracket the sample peaks. The isotopic $^{13}\text{C}/^{12}\text{C}$ ratios (*R*) are expressed in the conventional δ -notation as follows:

$$\delta^{13}\text{C} = \left[\left(R_{\text{sample}} / R_{\text{reference}} \right) - 1 \right] * 10^3.$$

The value of $\delta^{13}\text{C}$ *versus* PDB international standard is calculated using an internal calibrated standard measured within the same batch. The entire process for each sample takes less than 10 min. The precision of the measurement is better than 0.1 permil.

4. Results and discussion

The precision and reproducibility of the proposed method was tested both on aqueous standard solutions and on some natural samples. The aqueous standard solutions were prepared with Na_2CO_3 powder at five DIC concentrations (2, 3, 4, 5 and 20 mmol/l). The $\delta^{13}\text{C}$ value of the powder Na_2CO_3 was determined by reacting about 1.5 mg of solid carbonate with an excess of 100%

H_3PO_4 using the same apparatus previously described. Analytical results on eleven replicates revealed a $\delta^{13}\text{C} = -10.78\text{‰}$ *versus* PDB ($1\sigma = 0.08$).

4.1. Equilibration time and correction factor

Tests on the evaluation of the time needed for a complete reaction and the achievement of equilibrium conditions between dissolved and gaseous carbon dioxide were carried out on the aqueous standard solution with a DIC content of 4 mmol/l.

At least triplicate aqueous standard solution samples were analyzed after different equilibration times from 1 to 24 h. With increasing equilibration time, the $\delta^{13}\text{C}$ composition of CO_2 yielded by acidification tends progressively towards an equilibrium value of -10.38‰ *versus* PDB (fig. 3). Therefore the carbon isotope exchange between gaseous CO_2 and carbon dioxide dissolved in the aqueous standard solution can be considered complete after about 18 h.

Due to a carbon isotope fractionation process occurring between coexisting water and CO_2 , the obtained $\delta^{13}\text{C}_{\text{CO}_2}$ values are enriched in heavy

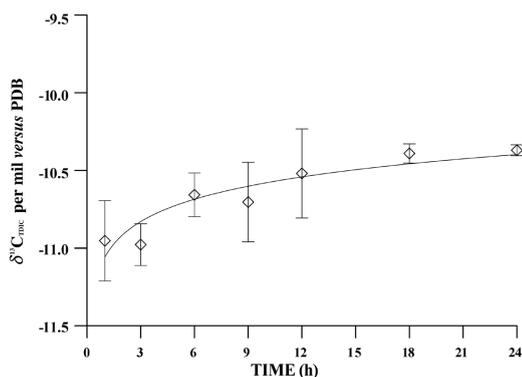


Fig. 3. Evaluation of equilibration times on the Na_2CO_3 aqueous standard solution with a DIC content of 4 mmol/l. The error bar indicates the standard deviation of at least triplicate measurements. After about 18 h the carbon isotope exchange between gaseous CO_2 and carbon dioxide dissolved in the aqueous standard solution can be considered completed reaching an equilibrium value of -10.38‰ *versus* PDB.

isotopes with respect to the carbonate used to make the standard solution. As a consequence, a correction factor to $\delta^{13}\text{C}_{\text{TDIC}}$ measurements has to be applied.

As the experiment is carried out in a closed system, the number of stable isotope carbon species remains constant. At the pH values of the solution ($0.5 \div 1$), the only carbon species present in our system are gaseous and dissolved carbon dioxide. Under these conditions, the carbon isotope balance can be expressed by the following equation:

$$\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{TDIC}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{aq}}} = \frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{gas}} \times \chi_{\text{CO}_{2\text{gas}}} + \chi_{\text{CO}_{2\text{aq}}}}{\chi_{\text{CO}_{2\text{aq}}}} \quad (4.1)$$

where ${}^{13}\text{C}/{}^{12}\text{C}_{\text{TDIC}}$, ${}^{13}\text{C}/{}^{12}\text{C}_{\text{gas}}$ and ${}^{13}\text{C}/{}^{12}\text{C}_{\text{aq}}$ stand for the carbon isotope ratios of total dissolved carbon species, gaseous CO_2 and dissolved CO_2 respectively while, $\chi_{\text{CO}_{2\text{gas}}}$ and $\chi_{\text{CO}_{2\text{aq}}}$ represent the molar fraction of gaseous and dissolved CO_2 .

In terms of delta notation, the eq. (4.1) begins

$$\delta^{13}\text{C}_{\text{TDIC}} = \frac{\delta^{13}\text{C}_{\text{CO}_{2\text{aq}}} + \frac{\chi_{\text{CO}_{2\text{gas}}}}{\chi_{\text{CO}_{2\text{aq}}}} \times \delta^{13}\text{C}_{\text{CO}_{2\text{gas}}}}{1 + \frac{\chi_{\text{CO}_{2\text{gas}}}}{\chi_{\text{CO}_{2\text{aq}}}}} \quad (4.2)$$

where $\delta^{13}\text{C}_{\text{CO}_{2\text{gas}}}$ is the value of measured gas, and $\delta^{13}\text{C}_{\text{CO}_{2\text{aq}}}$ is calculated considering the car-

bon isotope enrichment factor between dissolved and gaseous CO_2 ($\epsilon^{13}\text{C}_{\text{aq-gas}}$).

In vials of known volume, the molar fraction of gaseous CO_2 can be computed as a function of the DIC content in the injected sample volume and the headspace volume (table I). The molar fraction of dissolved CO_2 has been calculated taking into account the solubility of CO_2 in water (866 cc/l at 25°C calculated from Capasso and Inguaggiato 1998).

For $\delta^{13}\text{C}_{\text{CO}_{2\text{aq}}}$ the value of -1.04 δ per mil was subtracted from the measured $\delta^{13}\text{C}_{\text{CO}_{2\text{gas}}}$ according to the enrichment factor between dissolved and gaseous CO_2 ($\epsilon^{13}\text{C}_{\text{aq-gas}}$) in closed systems at 25°C found by Szaran (1998). Hence, the eq. (4.2) begins

$$\delta^{13}\text{C}_{\text{TDIC}} = \frac{(\delta^{13}\text{C}_{\text{CO}_{2\text{gas}}} - 1.04) + \frac{\chi_{\text{CO}_{2\text{gas}}}}{\chi_{\text{CO}_{2\text{aq}}}} \times \delta^{13}\text{C}_{\text{CO}_{2\text{gas}}}}{1 + \frac{\chi_{\text{CO}_{2\text{gas}}}}{\chi_{\text{CO}_{2\text{aq}}}}} \quad (4.3)$$

In a closed system, the extent of isotope fractionation between gaseous and dissolved CO_2 is a function of the headspace-water volume ratio, thus resulting in a difference between the measured $\delta^{13}\text{C}_{\text{CO}_{2\text{gas}}}$ and the values. Therefore, the $\delta^{13}\text{C}_{\text{TDIC}}$ values can be easily obtained from measured $\delta^{13}\text{C}_{\text{CO}_{2\text{gas}}}$ introducing a Correction Factor (CF) reported in table I. The CF values can be computed from eq. (4.3) fixing both the $\delta^{13}\text{C}_{\text{CO}_{2\text{gas}}}$ value and the headspace-water volume ratio.

Table I. Computed Correction Factor (CF) as a function of the DIC content and the volume of water injected for vials with internal volume of 5.9 ml. DIC contents of water samples ($[\text{CO}_{2\text{aq}}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) are expressed in mmol/l. Sample volume is expressed in milliliter. The molar fraction of dissolved CO_2 ($\chi_{\text{CO}_{2\text{aq}}}$) has been calculated by Henry's law. For DIC contents between 2 and 3.5 mmol/l, CF was computed considering the reduced headspace volume due to the insertion of the glass cylinder (see text).

DIC	Sample vol	Headspace vol	$\chi_{\text{CO}_{2\text{aq}}}$	$\chi_{\text{CO}_{2\text{gas}}}$	CF
2.0-3.5	2*	2.9	0.60	0.40	0.62
4-8	2	3.9	0.44	0.56	0.46
8.5-17.5	1	4.9	0.18	0.82	0.18
20-60	0.5	5.4	0.08	0.92	0.08
60-100	0.2	5.7	0.03	0.97	0.03

2* Samples analyzed with the glass cylinder inserted into the vial.

4.2. Tests on standard solutions

To determine the accuracy and precision of the proposed method, ten measurements were

Table II. Mean $\delta^{13}\text{C}_{\text{CO}_2}$ measurements for the aqueous standard solutions at five different DIC contents (2, 3, 4, 5 and 20 mmol/l). Each value represents the average of ten analyses. $\delta^{13}\text{C}_{\text{TDIC}}$ values have been computed according to the correction factors reported in table I. All the isotope values are expressed in ‰ versus PDB international standard.

DIC	$\delta^{13}\text{C}_{\text{CO}_2\text{meas}}$	$\delta^{13}\text{C}_{\text{TDICcorr}}$	Standard deviation (1σ)
2	-10.34	-10.96	0.29
3	-10.39	-11.01	0.20
4	-10.47	-10.93	0.14
5	-10.40	-10.86	0.05
20	-10.63	-10.71	0.05

Average $\delta^{13}\text{C}_{\text{TDICcorr}}$ -10.89

Standard deviation (1σ) 0.18

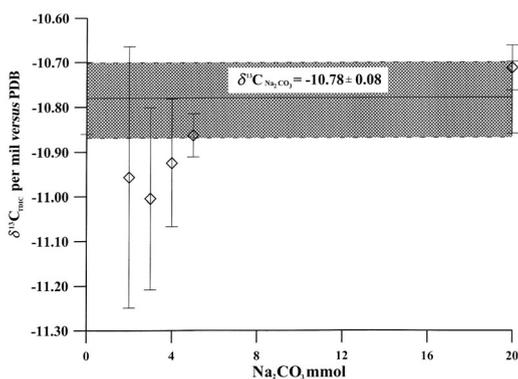


Fig. 4. Comparison between isotopic composition of solid Na_2CO_3 and Na_2CO_3 aqueous standard solution at different DIC concentration (2, 3, 4, 5 and 20 mmol/l). The error bar indicates the standard deviation of at least eight measurements for each of the aqueous solutions. Mean $\delta^{13}\text{C}_{\text{TDIC}}$ values are corrected according to eq. (4.2) and table I. All the resulting $\delta^{13}\text{C}_{\text{TDIC}}$ values are very close to the carbon isotope composition of the Na_2CO_3 powder (dark area) the maximum difference being 0.23 ‰ per mil.

carried out for each of the prepared aqueous standard solutions having five different DIC contents (2, 3, 4, 5 and 20 mmol/l). Mean $\delta^{13}\text{C}_{\text{CO}_2}$ measurements and corrected $\delta^{13}\text{C}_{\text{TDIC}}$ values are reported in table II together with their standard deviation (σ). The average value of $\delta^{13}\text{C}_{\text{TDIC}}$ is only 0.11 ‰ per mil lighter with respect to the carbon isotope composition of the Na_2CO_3 powder ($\delta^{13}\text{C}_{\text{Na}_2\text{CO}_3} = -10.78\text{‰}$ versus PDB). As can be seen in fig. 4, all the $\delta^{13}\text{C}_{\text{TDIC}}$ values are very close to the $\delta^{13}\text{C}_{\text{Na}_2\text{CO}_3}$ value, the maximum difference being 0.23 ‰ per mil for the 3 mmol/l solution. Furthermore, on the basis of the number of analyses ($n = 50$), the obtained results also highlight excellent reproducibility of the measurements. The standard deviation values decrease with increasing of DIC content in the prepared standard solutions. Using this method, the carbon isotope reproducibility is better than ± 0.14 for DIC content higher than 3 mmol/l.

4.3. Tests on natural water samples

To test the proposed method on natural waters more than thirty water samples were sampled and analyzed in replicate. The main physical-chemical features of these waters are reported in table III together with the analytical results. The water samples were collected from springs or domestic wells belonging to different geologic environments, from active volcanic systems (Vulcano Island, Etna, Stromboli, Popocatepetl-Mexico) to carbonate sedimentary aquifers (Western Sicily) to cover a wide range of carbon isotope composition. For comparison on the same samples $\delta^{13}\text{C}_{\text{TDIC}}$ values were also determined using the methodology proposed by Favara *et al.*, (2002) based on chemical and physical stripping of CO_2 from water samples. The $\delta^{13}\text{C}_{\text{TDIC}}$ values reported in table III are graphically shown in fig. 5 highlighting comparable results giving very small differences in the whole range of isotope values.

The least-squares regression line for the entire data set is: $Y = 1.011X + 0.04$, $r^2 = 0.998$.

A set of samples analyzed 30 days after sampling highlights the fact that the storage of water samples both in the glass sampling bottles and in the vials do not compromise the carbon isotopic ratio. However, some precautions have to be tak-

Table III. Tests on natural water samples together with their main physico-chemical parameters. *pH* is expressed in *pH* unit, *DIC* in *mmol/l*, *TDS* (Total Dissolved Solid) in *mg/l*. Sample volume is reported in milliliter and the corresponding Correction Factor (CF) is taken from table I. All the isotope values are expressed in $\delta\text{‰}$ versus PDB international standard. Standard deviation – std. dev. (1 σ) is calculated, at least, on four replicates.

Sample	Location	Date	<i>pH</i>	<i>DIC</i>	<i>TDS</i>	Sample vol	CF	Av. $\delta^{13}\text{C}_{\text{CO}_2}$ meas.	Std. dev.	$\delta^{13}\text{C}_{\text{TDIC,corr}}$ (°)	$\delta^{13}\text{C}_{\text{TDIC}}$ (°)
R. Campana	Etna	30.10.2002	7.45	5.5	646	2	0.46	-3.96	0.03	-4.42	-4.83
G. Pavone	Etna	13.02.1998	6.53	10.8	528	1	0.18	2.25	0.10	2.07	2.06
Ponteferro	Etna	17.01.1998	7.49	14.2	1636	0.5	0.08	1.04	0.28	0.96	1.28
Valcorrente	Etna	13.02.1998	6.92	21.3	1681	0.5	0.08	3.92	0.18	3.84	4.40
P31	Etna	30.10.2002	5.99	21.7	804	0.5	0.08	0.45	0.11	0.37	0.21
AT	Popocatepetl	18.05.2002	6.80	4.6	1728	2	0.46	-7.60	0.25	-8.06	-7.98
AX	Popocatepetl	18.05.2002	5.90	28.7	620	0.5	0.08	-2.31	0.10	-2.39	-2.65
Zurro	Stromboli	31.01.2003	6.93	5.9	30997	2	0.46	-0.08	0.28	-0.54	-0.25
Zurro	Stromboli	26.01.2003	6.93	6.3	32696	2	0.46	0.21	0.13	-0.25	-0.58
Ossidiana	Stromboli	02.02.2003	6.93	6.6	40404	2	0.46	-0.36	0.27	-0.82	-0.79
Sirennetta	Stromboli	31.01.2003	7.10	7.5	18888	1	0.18	1.10	0.22	0.92	0.91
Cusolito	Stromboli	31.01.2003	6.77	10.8	26121	1	0.18	1.54	0.25	1.36	1.37
Cusolito	Stromboli	27.01.2003	6.61	11.0	24605	1	0.18	2.07	0.14	1.89	1.75
Cusolito	Stromboli	2.02.2003	6.75	11.6	25913	1	0.18	1.84	0.12	1.66	1.74
Fulco	Stromboli	26.01.2003	6.39	19.3	24484	0.5	0.08	1.83	0.18	1.75	1.96
Fulco	Stromboli	31.01.2003	6.35	19.5	12323	0.5	0.08	0.90	0.19	0.82	0.99
Fulco	Stromboli	02.02.2003	6.45	19.7	12936	0.5	0.08	0.96	0.12	0.88	1.22
C. Sicilia	Vulcano Island	13.01.2003	7.45	7.2	6467	2	0.46	1.12	0.08	0.66	0.82
Eas	Vulcano Island	13.01.2003	8.42	19.8	2293	0.5	0.08	4.47	0.09	4.39	4.78
Bambara	Vulcano Island	13.01.2003	5.73	27.5	1038	0.5	0.08	-2.61	0.26	-2.69	-3.00
Discartica	Vulcano Island	13.01.2003	6.63	63.2	4788	0.2	0.03	0.90	0.09	0.87	0.51
C. Baida	Western Sicily	29.01.2003	8.11	2.7	367	2*	0.62	-14.96	0.16	-15.58	-15.45
C. Baida (°)	Western Sicily	29.01.2003	8.11	2.7	367	2*	0.62	-14.53	0.13	-15.15	-15.45
Scopello	Western Sicily	29.01.2003	7.87	2.7	318	2*	0.62	-12.84	0.36	-13.46	-13.56
Scopello (°)	Western Sicily	29.01.2003	7.87	2.7	318	2*	0.62	-12.87	0.26	-13.49	-13.56
Fragnesi	Western Sicily	29.01.2003	8.16	3.5	764	2*	0.62	-9.63	0.34	-10.25	-10.29
Fragnesi (°)	Western Sicily	29.01.2003	8.16	3.5	764	2*	0.62	-9.54	0.23	-10.16	-10.29
Pioppo	Western Sicily	29.01.2003	7.15	4.7	616	2	0.46	-13.95	0.20	-14.41	-14.62
Pioppo (°)	Western Sicily	29.01.2003	7.15	4.7	616	2	0.46	-14.06	0.07	-14.52	-14.62
S. Nuova	Western Sicily	29.01.2003	6.70	5.9	1695	2	0.46	-2.17	0.23	-2.63	-2.68
S. Nuova (°)	Western Sicily	29.01.2003	6.70	5.9	1695	2	0.46	-2.35	0.09	-2.81	-2.68
Merla	Western Sicily	29.01.2003	7.06	7.4	972	2	0.46	-14.00	0.21	-14.46	-14.17
Merla (°)	Western Sicily	29.01.2003	7.06	7.4	972	2	0.46	-14.01	0.28	-14.47	-14.17

2* Samples analyzed with the glass cylinder inserted into the vial; (°) this method; (°) samples analyzed after 30 days; (°) analyzed following the stripping method (Favara *et al.*, 2002).

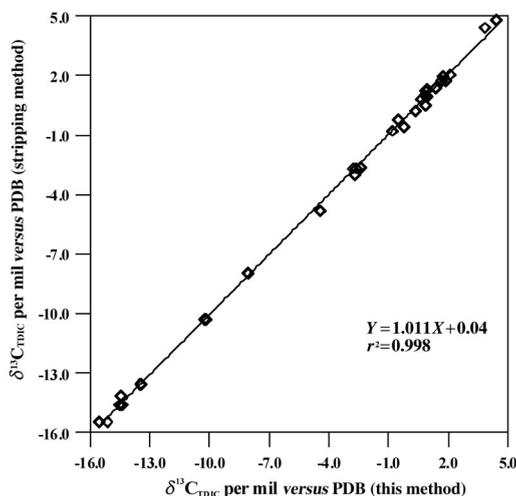


Fig. 5. Comparison between the $\delta^{13}\text{C}_{\text{TDIC}}$ values obtained using the proposed method and those carried out following the chemical and physical stripping technique (Favara *et al.*, 2002) for some natural water samples. The least-squares regression line for all the data set ($Y=1.011X + 0.04$, $r^2=0.998$) highlights comparable results over the whole range of isotope values.

en for waters saturated with respect to carbonate minerals and/or organic matter rich waters that could modify the pristine TDIC isotope composition. In the first case this is due to the precipitation of a solid carbonate phase, whereas the organic activity leads to enrichment of ^{12}C in biologically synthesised organic compounds.

5. Conclusions

An automated technique for extracting and analyzing inorganic carbon isotope ratio ($\delta^{13}\text{C}_{\text{TDIC}}$) from 0.5 to 2 ml water samples has been developed. This method, based on the release of CO_2 yielded by acidification of water samples, is a modification of the procedure previously proposed by Favara *et al.* (2002). The use of an autosampler both for acid dosing and for sample injection into the mass spectrometer not only greatly reduces a lot poten-

tial manual errors as well as reducing preparation and analysis time but also eliminates the use of expensive devices (vacuum preparation line, special grease, liquid nitrogen, etc.).

Analytical results gave good sample reproducibility and precision over a wide range of isotope composition and highlighted that this method is comparable to the other analytical procedures.

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