EXTRACTION OF DISSOLVED INORGANIC CARBON (DIC) FROM SEAWATER SAMPLES AT CEDAD: RESULTS OF AN INTERCOMPARISON EXERCISE ON SAMPLES FROM ADRIATIC SEA SHALLOW WATER

M Macchia[1] • M D'Elia[1] • G Quarta[1] • V Gaballo[1] • E Braione[1] • L Maruccio[1] • L Calcagnile[1,2] • G Ciceri[3] • V Martinotti[3] • L Wacker[4]

ABSTRACT. A dedicated sample processing line for the extraction of dissolved inorganic carbon (DIC) from seawater and groundwater for accelerator mass spectrometry (AMS) radiocarbon analysis has been developed at CEDAD, the Center for Dating and Diagnostic of the University of Salento, Lecce, Italy. The features of the new system are presented together with tests carried out to determine its functionality and background levels. The first results obtained at CEDAD for analyzing seawater samples taken from the Northern Adriatic compare well with results obtained for the same samples analyzed at ETH Zurich.

INTRODUCTION

Measurements of the radiocarbon concentration of inorganic carbon dissolved in seawater play a major role in several aspects related to global carbon cycle and ocean water mass circulation (Povinec et al. 2004; McDuffee and Druffel 2007). Since most of the carbon dioxide is dissolved in ocean water, the ocean carbonate system governs the carbon cycle largely by determining the pressure of CO_2 in the atmosphere (Emerson and Hedges 2008). Another important field in which understanding the carbonate system is of paramount importance is related to carbon capture and sequestration (CCS) studies (Feely et al. 2004). In fact, the possibility to capture carbon dioxide from industrial sources and to store it deep under the sea surface is being evaluated (IPCC 2005) and pilot projects are being planned in different countries.

In order to improve the experimental capabilities of the accelerator mass spectrometry (AMS) facility at the University of Salento (CEDAD: Centre for Dating and Diagnostics), a new preparation line dedicated to the extraction of dissolved inorganic carbon (DIC) from seawater and groundwater has been installed. This article presents the general features of the new extraction line together with the results of performance tests carried out in order to assess the background of the line and achievable recovery yields. The reproducibility of the measurements was also evaluated by comparing the results obtained at CEDAD on seawater sampled by RSE ((Ricerca sul Sistema Energetico, Sustainable Development and Energy Sources, Milan, Italy) in the Northern Adriatic with those obtained at the AMS facility at the Swiss Federal Institute of Technology, ETH, Zurich, Switzerland.

METHODS

System Description

DIC is extracted from water samples as gaseous CO_2 using a vacuum extraction line based on a modified approach of McNichol et al. (1994). The line consists of a Pyrex™ manifold to which a vacuum gauge (operating range: 5×10^{-4} to 1000 mbar) is connected in order to monitor the pressure during the different phases of the extraction process. As shown in Figure 1, the manifold consists of

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[1] CEDAD-Department of Engineering for Innovation, University of Salento, via per Monteroni, 73100 Lecce, Italy.

[2] Corresponding author. Email: Lucio.calcagnile@unile.it.

[3] Ricerca sul Sistema Energetico-RSE spa, Sustainable Development and Energy Sources, Via R. Rubattino, 54, 20134, Milan, Italy.

[4] Laboratory for Ion Beam Physics, ETH Zurich, Honggerberg 8093, Zurich, Switzerland.

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i) a system for accommodating the aqueous sample fitted with a graduated cylinder for injecting water and orthophosphoric acid; ii) an –80 °C water trap; iii) a liquid nitrogen trap for carbon dioxide freezing; and iv) up to 3 vessels used to trap and transport the extracted CO_2.

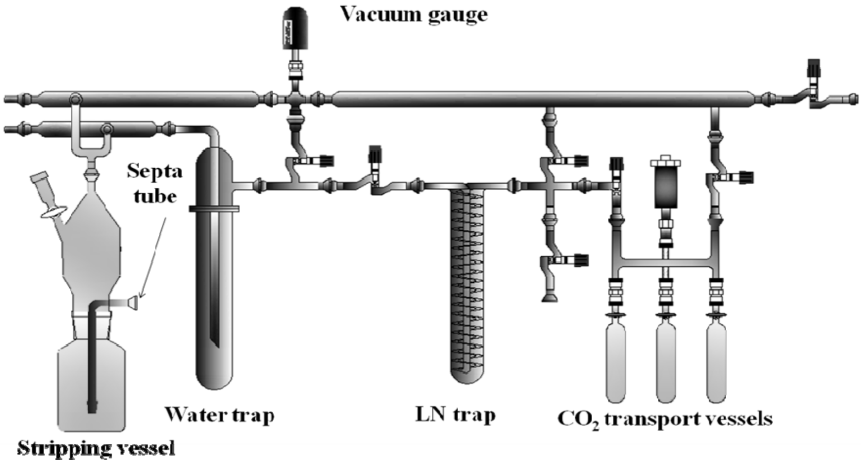

Figure 1 General scheme of the line for DIC extraction from water samples installed at CEDAD

The seawater container ("stripping vessel" in Figure 1) is attached to the vacuum line where a pressure of ~10^{-3} mbar is obtained by an oil-free rotary pump. After evacuation, 60 mL of sample are injected and DIC is extracted as CO_2 by adding phosphoric acid (2 mL of 85% H_3PO_4) with a syringe through a septa-sealed tube. The CO_2 released is then frozen into the liquid nitrogen trap, after removal of water vapor by the –80 °C trap. No carrier gas is used during the process and the complete extraction procedure is carried out under static vacuum conditions.

After the extraction process, the CO_2 produced is cryogenically transferred to an ampoule with a calibrated volume where its amount is determined by measuring the corresponding pressure with a transducer. The extracted gas is then transferred to the graphitization line to be converted to graphite at 600 °C by using hydrogen as the reducing agent and iron powder as catalyst (D'Elia et al. 2004). The graphite is then pressed into the aluminum target holders of the AMS system ion source for measurement of the ^{14}C concentration (Calcagnile et al. 2004, 2005).

Background Samples

In order to test the extraction yield and the blank level of the new line, several test samples were prepared by dissolving with acid IAEA-C1 standards (Carrara marble) with a certified ^{14}C content of 0 pMC in deionized water. Different carbonate samples with masses ranging from 0.2 to 2.2 mg were prepared in order to measure the dependence of the background on the sample mass. The extraction yield was then calculated as the ratio between the equivalent mass of carbon added as $CaCO_3$ and the mass of carbon contained in the extracted CO_2, measured in the calibrated volume.

Seawater Samples

The first measurements on seawater were carried out on 14 samples taken in the Northern Adriatic Sea at depths ranging from 14 to 30 m (Figure 2). Table 1 lists the samples together with the sampling sites and depth. Samples with the CEDAD laboratory code starting with 5 were samples from October 2010 and those starting with 8, from January/February 2011. Each sample consisted of

250 mL (from which 60 mL were used for AMS analysis at CEDAD) of seawater sampled with a benthic chamber and Niskin bottles, poisoned on-site with $HgCl_2$ to stop biological activity, and stored at 4 °C until processing. All samples showed a DIC concentration of ~ 2500 µmol/kg as determined by a flow-injection analyzer conductometric coupled system developed by RSE (Martinotti et al. 2012).

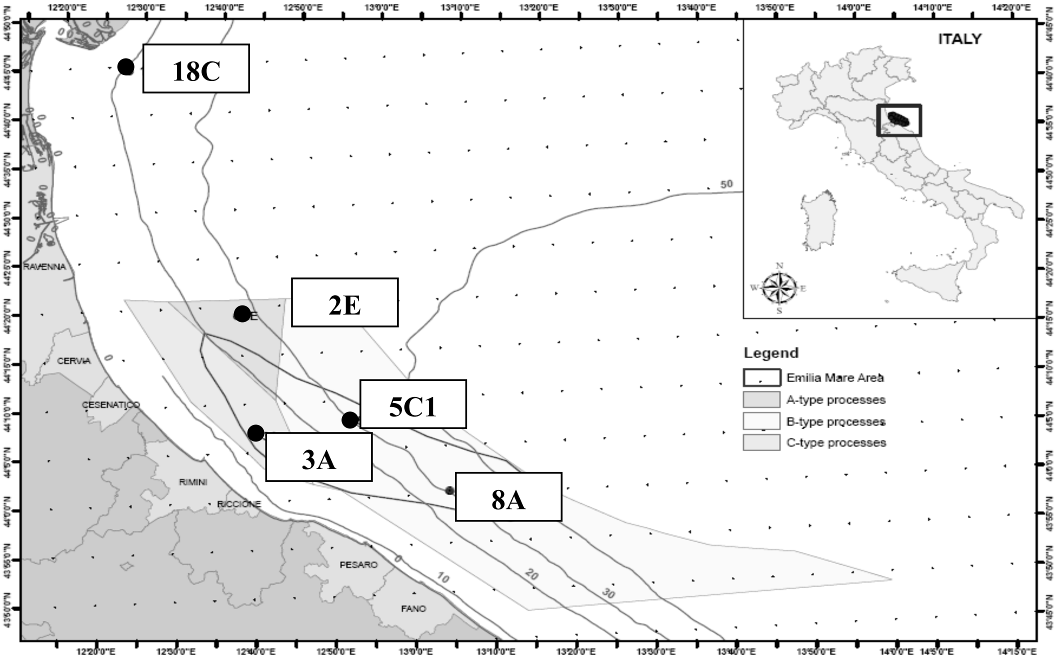

Figure 2 Sampling sites in the Northern Adriatic Sea. The sampling depths were as follows: 2E: 28 m; 3A: 14 m; 5C1: 31 m; 8A: 30 m; 18C: 20 m.

Table 1 List of the analyzed seawater samples, of CEDAD and ETH laboratory codes, sampling sites and measured radiocarbon concentrations.

CEDAD ID	Sampling site[a]	ETH-ID	CEDAD value (pMC)	ETH value (pMC)	Δ	*t*
LTL5802A	2E	45372	103.97 ± 0.59	104.25 ± 0.51	–0.28	0.36
LTL5805A	3A	45374	102.65 ± 0.50	102.47 ± 0.49	0.18	0.26
LTL5807A	5C1	45375	103.86 ± 0.50	104.13 ± 0.50	–0.27	0.38
LTL5808A	8A	45376	104.58 ± 0.50	104.79 ± 0.51	–0.21	0.29
LTL5809A	8A	45377	104.69 ± 0.87	103.69 ± 0.52	1.00	0.99
LTL5810A	18C	45378	103.30 ± 0.50	103.35 ± 0.51	–0.05	0.07
LTL8657A	2E	—	104.35 ± 0.53	—	—	—
LTL8660 A	5C1	45382	105.07 ± 0.48	104.31 ± 0.49	0.76	1.11
LTL8661A	8A	45384	104.19 ± 0.50	103.71 ± 0.48	0.48	0.69
LTL8662A	18C	45387	102.18 ± 0.50	101.65 ± 0.47	0.53	0.77
LTL8663A	3A	45380	102.48 ± 0.49	101.59 ± 0.50	0.89	1.27
LTL8664A	5C1	45381	103.58 ± 0.50	102.50 ± 0.52	1.08	1.50
LTL8665A	8A	45383	105.55 ± 1.2	104.62 ± 0.50	0.93	0.72
LTL8666A	18C	45386	104.55 ± 0.48	103.91 ± 0.49	0.64	0.93

[a] See Figure 2.

Thirteen samples were also sent to ETH Zurich for an independent analysis of the ^{14}C concentration in the DIC. At ETH, DIC was extracted from 12 mL of seawater (acidified with 1 mL of 85% H_3PO_4) in 40-mL septa-sealed vials (Molnár et al. 2013). Between 200 and 300 μg carbon were extracted as CO_2 and transported in a helium flow to the automated graphitization system (AGE), where it was converted to graphite (Němec et al. 2010; Wacker et al. 2013). The samples were measured on the MICADAS at ETH (Synal et al. 2007).

RESULTS AND DISCUSSION

Overall, an extraction yield above 90% was obtained as the ratio between the equivalent mass of carbon added as $CaCO_3$ and the mass of carbon contained in the extracted CO_2. Figure 3 shows the ^{14}C concentrations measured for the blank samples obtained on IAEA-C1 standards as a function of the added mass of carbonate expressed as the equivalent mass of carbon. The results clearly indicate a dependence of the background level on the sample mass, as expected (Tisnérat-Laborde et al. 2001). Nevertheless, for standard samples, i.e. yielding more than ~1 mg C, an overall background level of 0.3 pMC, corresponding to ~47 ka in the ^{14}C timescale, is measured. This value is comparable with the sample processing background measured on organic samples undergoing the combustion process, which is estimated to be ~0.28 pMC (D'Elia et al. 2004).

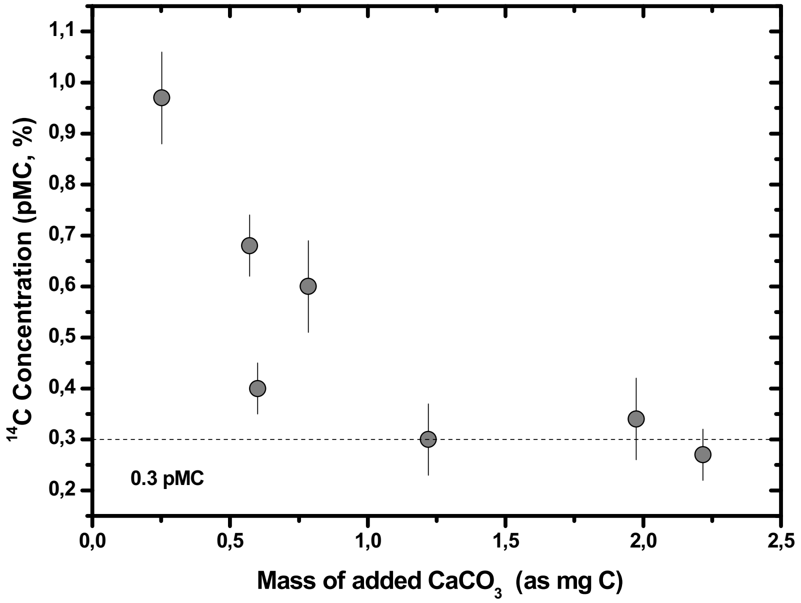

Figure 3 Radiocarbon concentration measured on "blank" samples obtained by dissolving IAEA-C1 Carrara marble in deionized water as a function of the added mass of carbonate.

The results obtained in the analysis of the North Adriatic seawater samples at CEDAD and ETH are listed in Table 1 and shown in Figure 4 with the corresponding 1σ error bars. The difference between the values measured in the 2 laboratories is also given (Δ in Table 1) together with the discrepancy (*t* in Table 1) calculated as Δ divided by the square root of the sum of the squares of the corresponding uncertainties. It should be noted that the calculated values of the *t* term are all smaller than 1.96, which indicates agreement between the measurements performed in the 2 laboratories at the 95% level.

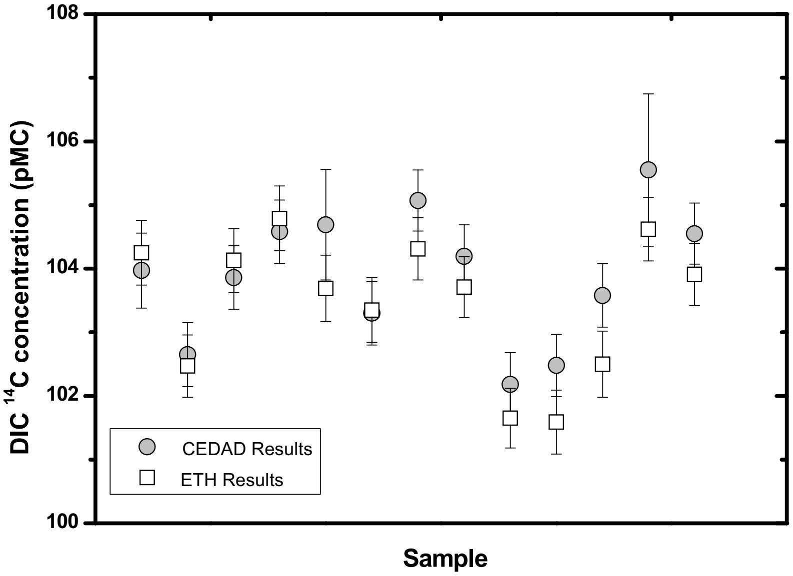

Figure 4 Comparison between the values measured on seawater samples taken in the Northern Adriatic Sea at CEDAD and ETH.

CONCLUSIONS

A new line installed at CEDAD for the extraction of DIC from water samples has been presented. The general features of the line have been described together with the results of blank tests and of an intercomparison exercise on shallow seawater sampled in the Northern Adriatic Sea. Blank tests were carried out by analyzing samples obtained by dissolving ^{14}C-free IAEA C-1 standards into deionized water and showed a background level of ~0.3 pMC for samples with a mass of ~1 mg C. For smaller samples, an increase of the measured background was highlighted as the sample mass decreases. The results of the intercomparison exercise carried out with the AMS group at ETH Zurich are in very good agreement and show good reproducibility of the obtained results.

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