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TECHNICAL NOTE

A self-made tube cracker coupled to an EA-IRMS-AGE3 system

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Abstract

The automatic graphitization system (AGE3) by IonPlus is very popular among radiocarbon dating laboratories. Usually, solid samples are burnt in an elemental analyzer (EA), and the gaseous CO_2 is transferred for graphitization. Our system is coupled also with an isotope ratio mass spectrometer (IRMS), which measures the $\delta^{13}C$ and $\delta^{15}N$ of that gas. Some less routine pretreatment protocols require the production of gaseous samples and prevent the possibility of using the EA-AGE3 system, as the EA is used for solid samples only. In order to use that system, including the measurements of stable isotopes, we developed a glass tube cracker that connects to the EA. The device is routinely used in our laboratory and is mainly built from Swaglok catalog parts. We show that the background (blank) levels of a marble standard are indistinguishable between using the cracker and burning solid marble using the EA. We further demonstrate that the $\delta^{13}C$ values are consistent and that the extraction efficiency when using the device is above 93%. Full descriptions, drawings, and working protocol are supplied.

Introduction

A tube cracker is a standard device in radiocarbon laboratories, mainly when the combustion of the sample to form CO_2 is performed in seeled quartz tubes in the presence of CuO (e.g. Seiler et al. 2019; Steinhof et al. 2017; St-Jean et al. 2017). However, the growing popularity of the EA-AGE3 system (an elemental analyzer, coupled with a 3rd generation of automatic graphitization equipment made by Ionplus company) (Wacker et al. 2010) makes the use of a tube cracker a rare occasion. Yet, in some sample pretreatments, there are hardly any alternatives to a tube cracker. Such cases include step-combustion pretreatment procedures for dating the mineral phases of ash (Toffolo et al. 2017) or lime plaster (Toffolo et al. 2020), carbon extraction from metal objects (Hüls et al. 2011), dating sediments with very low carbon content, and CO_2 extraction from water samples. Our laboratory has used an EA-IRMS-AGE3 system (also coupled to an isotope ratio mass spectrometer) in the past six years. It is composed of a "vario ISOTOPE SELECT" (by Elementar) elemental analyzer, isoprime precisION IRMS (by Elementar), and the AGE3 graphitization equipment (by Ionplus). The system is used for almost all of our samples. However, at times, a special pretreatment procedure is required, which results in a gaseous sample. IonPlus is offering a tube cracker, but the device is connecting directly to the AGE3 instrument. As we would like to measure the $\delta^{13}C$ values of our gaseous samples, we designed a tube cracker that connects to the elemental analyzer and enables us to transfer the gaseous CO_2 from the tube through the IRMS and into the AGE3 for graphitization.
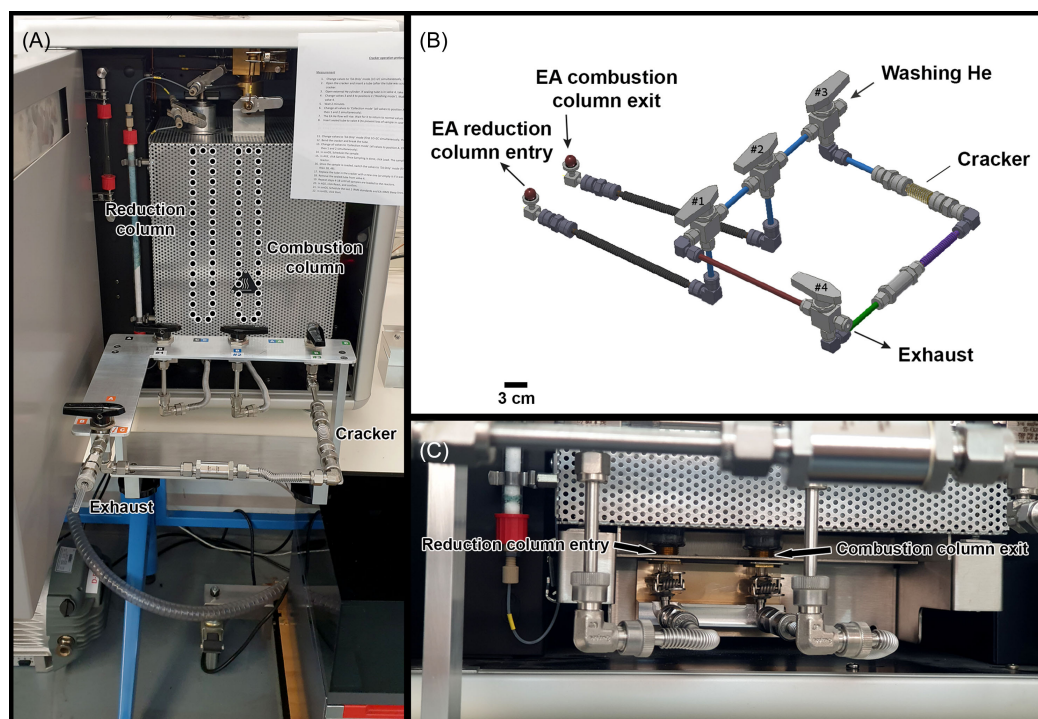
Figure 1. *The cracker device. (A) The cracker device as installed and connected to the EA. Note that the additional He cylinder for washing is not connected. (B) A drawing of the cracker device. (C) A close-up image of the connection of the device to the EA columns.*

Device design

We chose to connect the cracker device to the EA by replacing the quartz bridge between the combustion and reduction columns of the EA (Figure 1). In doing so, we exploit the EA helium flow, water drying tube, adsorption column, and the system's synchronized workflow with the IRMS and AGE3 instruments.

The device is mainly built of Swaglok catalog parts (Table 1), with few custom-made pieces: several stainless-steel tubes (Figure 2B and Table 1, parts 7, 16, 18), the holder device (parts 19–23), the brace (part 24, not shown in this figure. See Figure 2), and most importantly, the two caps (part 3), connecting the device to the EA combustion and reduction columns. The drawings of all custom-made parts are in the online supplementary material.

The device enables several working modes: "EA Only," "Washing Mode," and "Collection Mode" (Figure 2A).

EA Only Mode: In "EA Only" mode, the EA-IRMS-AGE3 system can work as before, with solid samples, even when the cracking device is connected to the EA. It also enables inserting a new glass tube for cracking. In this mode, valves 1 and 2 are both in position C, flowing the helium back to the EA in the shortest path (Figure 2A, blue path) and enabling the processing of solid samples. Valves 3 and 4 are closed (on B position). The device pictured in Figure 1A is in this mode.

Washing Mode: this mode is used once a new glass tube is inserted into the cracking device. By rotating valves 3 and 4 to position C (Figure 2A, red path. Valves 1 and 2 remain on position C as well), an external helium source flows through the device's part that was open to the air while inserting the new tube. We use another helium cylinder (not the one connected to the EA) but from the same grade (we use 99.999% purity). The washing helium enters through valve 3 and exhausts through valve 4 to the room.

Table 1. *Part list of the cracker device. The part numbers correlate with Figure 2B*

| Item	Part type	Part number	Qty.	Material	Description	Company
1	Column Ball		2	Glass	Bottom part of EA combustion and reduction columns	Existing
2	O-Ring	S05 001 302	2	Viton	O-ring, black, 7.59 x 2.62 mm for quartz bridge	Elementar
3	Cap		2	Stainless Steel 316		
4	Union	SS-4-UT-6	2	Stainless Steel 316	Ultra-Torr Vacuum Fitting, Union, 1/4 in. Tube OD	Swagelok
5	Bellow	321-4-X-6	2	Stainless Steel 321	Flexible Tubing, 1/4 in. OD, 6 in. Nominal Produced Flexible Length	Swagelok
6	Adapter	SS-304-4-XOA	6	Stainless Steel 304	XOA Adapter for Convoluted Vacuum Tubing, 1/4 in. Tube OD	Swagelok
7	Tube 1		5	Stainless Steel 316	Ø1/4'' x 0.9 x 70	
8	3-Way Ball Valve	SS-43GXS4	4	Stainless Steel 316	1-Piece 40G Series 3-Way Ball Valve, 0.90 Cv, 1/4 in. Swagelok Tube Fitting	Swagelok
9	Plate		1	Aluminum 6061		
10	Reducing Union	SS-6-UT-6-4	2	Stainless Steel 316	Ultra-Torr Vacuum Fitting, Reducing Union, 3/8 x 1/4 in. Tube OD	Swagelok
11	Bellow	321-6-X-1	1	Stainless Steel 321	Flexible Tubing, 3/8in. OD, 1 in. Nominal Produced Flexible Length	Swagelok
12	Adapter	SS-304-6-XOA	2	Stainless Steel 304	XOA Adapter for Convoluted Vacuum Tubing, 1/4 in. Tube OD	Swagelok
13	Reducing 90° Elbow	SS-400-2R-4	4	Stainless Steel 316	Tube Fitting, Reducing 90° Elbow, 1/4 in. Tube OD	Swagelok
14	Bellow	321-4-X-2	1	Stainless Steel	Flexible Tubing, 1/4 in. OD, 2 in. Nominal Produced Flexible Length	Swagelok
15	Filter	SS-4F-60	1	Stainless Steel 316	In-Line Particulate Filter, 1/4 in. Swagelok Tube Fitting, 60 Micron Pore Size	Swagelok
16	Tube 3		1	Stainless Steel 316	Ø1/4'' x 0.9 x 82.6	
17	Union Elbow	SS-4-UT-9	2	Stainless Steel 316	Ultra-Torr Vacuum Fitting, Union Elbow, 1/4 in. Tube OD	Swagelok
18	Tube 2		1	Stainless Steel 316	Ø1/4'' x 0.9 x 173.8	
19	Plate 2			Aluminum 6061		
20	Post		2	Aluminum 6061		
21	Screw		12	Stainless Steel	Slotted countersunk flathead M5 x 12	
22	Clamp		2	Aluminum 6061		
23	Handle		2			
24	Brace					
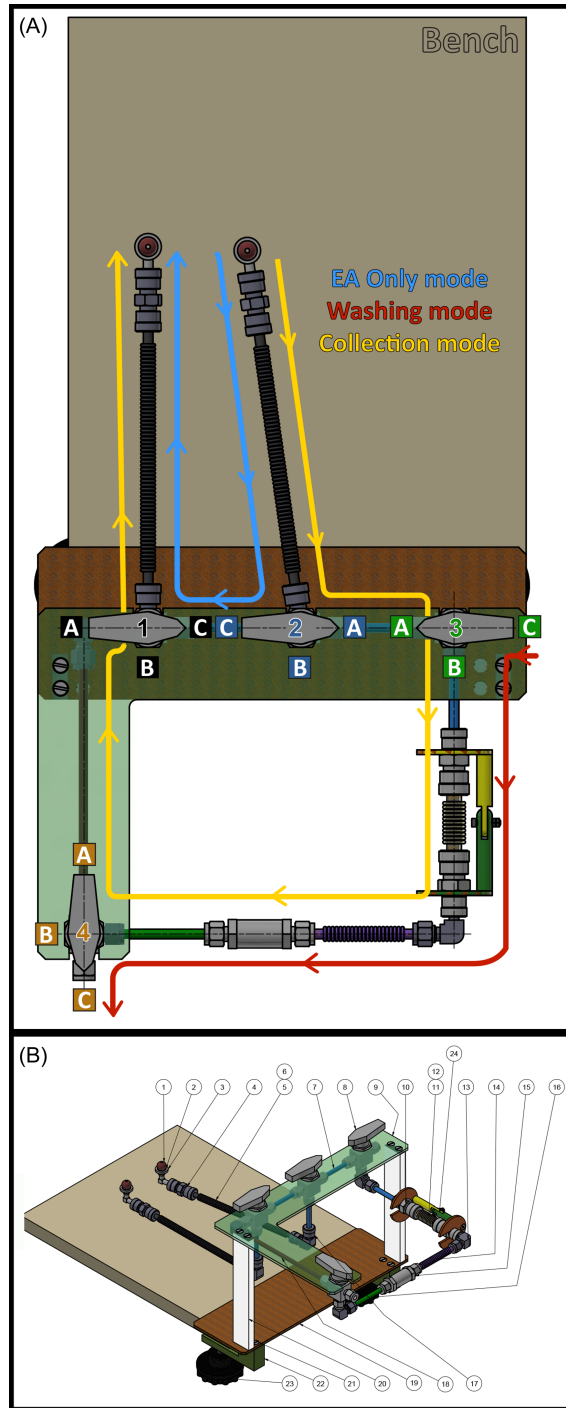
Figure 2. Operation modes and part numbers. (A) The three operation modes of the device are "EA Only" (blue line), "Washing" (red line), and "Collection" (yellow line). Note the ABC tags, marking the three positions of each valve. The black, blue, green, and orange tags relate to valves 1-4, accordingly. The tags are used to follow the operation protocol (online supplementary material). (B) An assembly drawing of the cracker device, including the item numbers, correlated to Table 1.

Collection Mode: In this mode, all valves are set to position A, enabling the EA helium to flow through the whole device and collect the CO_2 sample from the cracked tube into the EA adsorption column (Figure 2A, yellow path).

Operation protocol

The full protocol can be found in the online supplementary material. The concept is that the EA-IRMS-AGE3 system works in "Auto" mode as usual, without manual software intervention. We arrange the samples in the EA carousel with an empty spot between each two samples. Running an empty spot is called a "RunIn" in the EA software. We use each RunIn to change the glass tube in the cracking device and wash the line.

In short, the protocol starts with inserting all the sample data into the IRMS ionOS software, with a RunIn before each sample, and starting the EA-IRMS-AGE3 as usual (by the "Auto" button in the AGE3 software). Due to the additional path of the helium through the cracker in "Collection Mode," we altered the EA and IRMS Methods to fit that change. Our cracker Methods parameters can be found in the online supplementary material as well.

The default mode for the cracker is "EA Only." The IRMS calibration standards can be run in this mode while the AGE3 is conditioning the iron catalyst. During each RunIn, a new glass tube is inserted into the cracker, and the device is washed from the air using the "Washing Mode." At a specific time, a short while before the sample collection starts, the line is rewashed, and then the tube is cracked. At this point, the system should be changed to "Collection Mode," and the CO_2 from the glass tube is transferred into the EA adsorption column. From there, it is released to the IRMS and AGE3 as any solid sample. As the software is working on "Auto" mode and unaware of the additional cracking device, keeping the designated times for sample exchange, washing, and cracking the tubes is essential. However, using this setting, combining samples from the cracker device with standard solid samples through the EA carousel in one graphitization and the additional measurement of IRMS standards is possible and fluent.

## Tested samples, pretreatment, and ^{14}C measurement

We tested the cracking device using the ^{14}C background-level marble sample IAEA-C1 standard. We compared samples in the 0.17–1 mgC size range between solid samples using the EA carousel (Steinhof et al. 2017) and CO_2 gaseous samples using the cracker. The latter was prepared by dissolving powdered marble in 85% phosphoric acid at 40°C overnight and then distributing the gas to ampules. The CO_2 levels of the gaseous samples were prepared using a calibrated volume in the laboratory's glass system. The solid samples were weighted and run using the EA carousel with tin foil capsules (Elemental Microanalysis Ltd. 5 x 3.5 mm #D1015). The combustion column temperature was set to 950°C (our routine temperature), and oxygen was injected for 120 seconds. The graphitized samples were pressed into aluminum cathodes using a pneumatic sample press (PSP, Ionplus), and the ^{14}C content was measured at the DANGOOR Research Accelerator Mass Spectrometry Laboratory at the Weizmann Institute of Science (Regev et al. 2017).

Results

Ten marble samples, 0.17–1 mgC in weight, were extracted through the cracker into the AGE3 system. The pMC levels of those samples are nearly indistinguishable from the five samples of the same material combusted in the EA (Figure 3). In fact, the cracker samples resulted in slightly lower pMC levels than the EA ones. The consistent low background levels eliminate the presence of a memory effect, even though the system is being opened to air during the insertion of each new sample. The carbon percentage of the extraction through the cracker, as measured by the EA, is above 93% (Table 2). For the solid

Table 2. *Measured values of all samples*

EA/cracker	RTD	Size [mgC]	%C	pMC	pMC+/−	δ¹³C [‰]
EA	11898.1	0.259	11.5	0.437	0.021	2.4
	11898.2	0.264	12.38	0.357	0.017	2.11
	11898.3	0.276	12.36	0.372	0.018	2.76
	11898.4	0.985	12.23	0.218	0.008	2.65
	11898.5	0.997	12.18	0.219	0.011	2.62
Cracker	11888	0.616	97.26	0.187	0.016	2.86
	11889.1	0.272	98.19	0.363	0.037	2.68
	11889.2	0.268	95.33	0.319	0.024	2.89
	11889.3	0.173	93.61	0.476	0.045	2.83
	11897.2	0.823	94.57	0.186	0.008	3.22
	11897.4	0.303	102.27	0.278	0.014	2.51
	11897.5	0.277	95.47	0.268	0.019	2.61
	11897.6	0.266	96.4	0.238	0.014	2.74
	11948.1	0.95	95.16	0.183	0.007	2.41
	11948.2	0.897	94.65	0.156	0.007	2.29
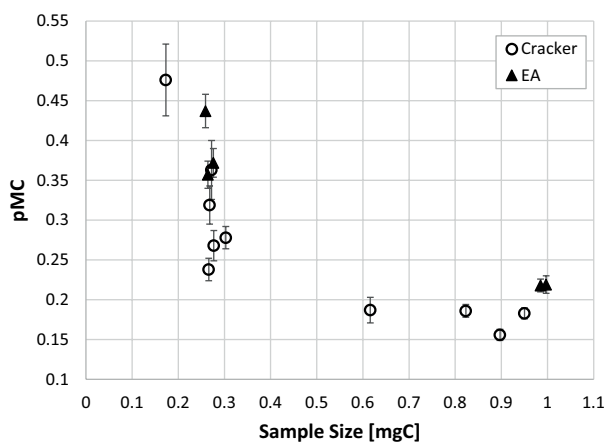
Figure 3. *pMC levels of marbles extracted through the cracker or by the EA.*

samples, the %C represents the combustion yield in the EA. As marble is $CaCO_3$, with a molecular mass of 100 g/mol, the expected %C is 12%, in accordance with the measured values (Table 2).

The $\delta^{13}C$ of all samples was measured in the coupled IRMS instrument and is indistinguishable as well (Figure 4).

Conclusions

We developed a glass tube cracker that enables graphitizing gaseous samples using the EA-IRMS-AGE3 system by Ionplus. The EA measures the carbon percentage of the gaseous sample for quality control, and the $\delta^{13}C$ value is measured by the IRMS. The device comprises mainly Swaglok catalog parts and is routinely used in our laboratory. The complete working protocol and the technical drawings of the custom-made parts are available in the online supplementary material.
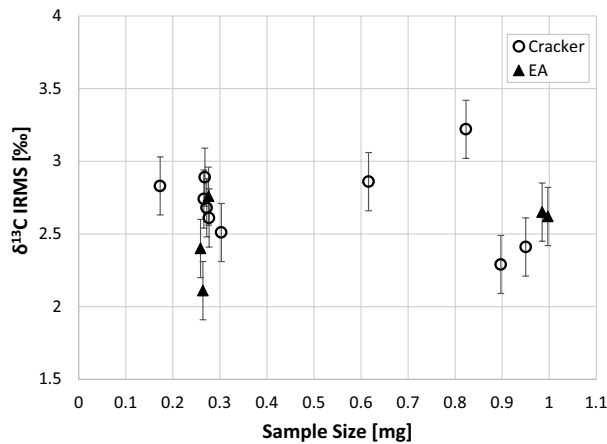
Figure 4. *δ¹³C values of marble samples extracted by the cracker or EA and measured using the coupled IRMS instrument. The δ¹³C uncertainty is 0.2‰.*

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