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### 3 GAS ION SOURCE PERFORMANCE OF THE ENVIRONMICADAS AT HEKAL 4 LABORATORY, DEBRECEN, HUNGARY

5 Mihály Molnár<sup>1\*</sup>  • Marianna Mészáros<sup>1</sup> • Róbert Janovics<sup>1</sup> • István Major<sup>1</sup> •  
6 Katalin Hubay<sup>1</sup> • Botond Buró<sup>1</sup> • Tamás Varga<sup>1,6</sup>  • Titanilla Kertész<sup>1,6</sup>  •  
7 Virág Gergely<sup>1,6</sup> • Ádám Vas<sup>1,6</sup> • Gergely Orsovski<sup>2</sup> • Anita Molnár<sup>2,6</sup> •  
8 Mihály Veres<sup>2</sup> • Martin Seiler<sup>3</sup>  • Lukas Wacker<sup>4</sup>  • A J Timothy Jull<sup>1,5,7</sup> 

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9 <sup>1</sup>Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/C, Debrecen, H-4026, Hungary AQ2

10 <sup>2</sup>Isotoptech Zrt., Debrecen, H-4026, Hungary

11 <sup>3</sup>National Laboratory for Age Determination, NTNU, Trondheim, NO-7491, Norway

12 <sup>4</sup>Laboratory for Ion Beam Physics, ETH Zürich, Zürich, CH-8093, Switzerland

13 <sup>5</sup>University of Arizona AMS Laboratory, University of Arizona, Tucson, AZ 85721 USA

14 <sup>6</sup>University of Debrecen, Debrecen H-4001, Hungary

15 <sup>7</sup>University of Arizona, Department of Geosciences, Tucson, AZ 85721 USA

17 **ABSTRACT.** A coupled accelerator mass spectrometer–gas interface system has been successfully operating at the  
18 Hertelendi Laboratory of Environmental Studies, Debrecen, Hungary, since 2013. Over the last 6 years more than  
19 500 gas targets were measured below 100 µg carbon content for carbon isotopic composition. The system was tested  
20 with blanks, OxII, IAEA-C1, IAEA-C2, and IAEA-C7 standards. The performance of our instrumentation shows  
21 good agreement with other published gas-interface system data and also shows a quite good agreement with the  
22 nominal value of international standard samples. There is a measurable but quite small memory effect after modern  
23 samples, but this does not significantly affect the final results. Typical ion currents at the low energy side were  
24 between 10–15 µA with a 5% CO<sub>2</sub> in He mixing ratio. The relative errors average ±6% for samples greater than or  
25 equal to 10 µgC sample with mean count rates of 300 counts per microgram C for OxII. The blank is comparable  
26 with other systems, which is 0.0050 ± 0.0018 F<sup>14</sup>C or 34,000–47,000 yr BP, which allows for the routine measurement  
27 of both of small environmental and archeological samples.

28 **KEYWORDS:** AMS, gas interface system, gas ion source, MICADAS, radiocarbon.

### 29 INTRODUCTION

30 EnvironMICADAS, the first accelerator mass spectrometer (AMS) in Hungary, was installed  
31 in the summer of 2011 (Molnár et al. 2013). EnvironMICADAS was developed and built by AQ3  
32 ETH Zürich (ETHZ), as an improved version of the first MICADAS (Mini Carbon Dating  
33 System) of ETHZ, and was designed specifically for environmental studies (Molnár et al.  
34 2013). Details of the MICADAS AMS-concept and GIS measurements can be found in  
35 Fahrni et al. (2013), Synal et al. (2007), and Wacker et al. (2010a).

36 Our first measurements directly from gaseous CO<sub>2</sub> started in 2013, but routine CO<sub>2</sub> gas sample  
37 measurements by gas ion source (GIS) have been performed since 2015. Since then, more than  
38 500 archeological and environmental gas samples have been measured with the instrument.  
39 Thanks to the gas interface system (GIS), EnvironMICADAS is able to analyze samples  
40 with mass smaller than 100 µg carbon content, such as aerosols, collagen, carbonate, and  
41 water samples, avoiding the graphitization step in CO<sub>2</sub> form.

42 The aim of this study is to report our data and results of GIS measurements performed by  
43 EnvironMICADAS over the past 4 years. It is important to point out that the GIS used in  
44 the Hertelendi Laboratory of Environmental Studies (HEKAL) is one of the first gas  
45 handling systems for the MICADAS AMS developed in ETHZ. The first samples were

\*Corresponding author. Email: [molnar.mihaly@atomki.mta.hu](mailto:molnar.mihaly@atomki.mta.hu).

46 introduced from gas tanks and sealed glass ampoules. Results of graphite and micro-graphite  
47 measurements can be found elsewhere (e.g. Molnár et al. 2013; Rinyu et al. 2015).

## 48 **EXPERIMENTAL**

### 49 **Instrumentation, Measurements, and Data Processing**

50 The measurements, sample preparation, and combustion were carried out in the HEKAL  
51 laboratory in Debrecen, Hungary. The description of EnvironMicadas AMS is detailed in a  
52 previous status report, Molnár et al. (2013). The gas interface system allows us to measure  
53 the  $^{14}\text{C}/^{12}\text{C}$  and  $^{13}\text{C}/^{12}\text{C}$  ratio of samples even below  $< 10 \mu\text{g}$  carbon content. Both the  
54 MICADAS and its GIS system are described in detail in various studies and status reports  
55 (Fahrni et al. 2013; Hoffmann et al. 2017; Maruccio et al. 2017; Tuna et al. 2018; Welte et al.  
56 2018). Since the elemental analyzer (EA) is not routinely operating and the carbonate  
57 hydrolysis system (CHS) is not available at HEKAL, our study focuses on the results of tank  
58 and sealed gas ampoule samples. MICADAS Bats data reduction software was used for the  
59 evaluation of the results (Wacker et al. 2010b) including  $\delta^{13}\text{C}$  isotope fractionation correction.

### 60 **Samples and Sample Preparation**

61 Figure 1 shows the type and number of samples, and  $\text{CO}_2$  sample preparation methods used in  
62 this study. For the calculations, data from 88 oxalic acid 2 (OxII, NIST-SRM-4990C), 105  
63 blank  $\text{CO}_2$ , and 37 IAEA standard (C1, C2, and C7, at least 10 from each) measurements  
64 were used. Apart from simple off-line splitting from tanks (big samples), off-line hydrolysis  
65 and combustion methods were used for  $\text{CO}_2$  production at the C mass range between 10  
66 and 100  $\mu\text{gC}$ , for this study.

67 Oxalic acid 2 samples were transferred in two different ways into the syringe of the AMS  
68 (Figure 1): (1) as tank samples ( $n=45$ ); and (2) as cracker samples ( $n=43$ ) which were split  
69 fractions (sub-samples with masses of 44, 50, 70, and 100  $\mu\text{g C}$ ) of a larger sample ( $\sim 1 \text{ mg C}$ ).

70 The gas interface has a syringe, where the proper  $\text{CO}_2$  (sample) + He carrier gas mixture is  
71 produced and injected into the MICADAS ion source. In the case of our coupled  
72 GIS-MICADAS setup the ideal dilution is 5%  $\text{CO}_2$  in He carrier gas. The syringe has a  
73 variable volume, according the sample size, between 0 to 150  $\mu\text{g C}$  sample capacity.  
74 Details about our GIS interface setup are published by Molnar et al. (2013).

75 There are 3 possible ways to load the sample  $\text{CO}_2$  gas into the syringe, and all can be directly  
76 linked to the syringe using a multiport selector valve. Samples can be loaded from the  
77 normalization or blank tanks, where the  $\text{CO}_2$  (made in big quantity form Oxa-2 or fossil  
78 borehole  $\text{CO}_2$  gas) is already diluted to 5% by the pure He carrier gas.

79 For blank measurements, we used fossil  $\text{CO}_2$  gas provided by Linde Hungary Ltd. company  
80 (borehole  $\text{CO}_2$  from Répcelak, Hungary). Three types of blanks were measured (Figure 1):  
81 (1) tank blanks ( $n=25$ ) were used to check background level, i.e., to control if the system is  
82 clean enough to start measuring procedural blanks, standards, and samples; (2) cracker  
83 blanks ( $n=69$ ) were split fractions, i.e., sub-samples with masses of 19, 25, 44, 50, 70, and  
84 100  $\mu\text{g C}$  of a larger sample ( $\sim 1 \text{ mg C}$ ); and (3)  $\text{MnO}_2$  combusted blanks ( $550^\circ\text{C}$ , 12 hr)  
85 ( $n=11$ ) introduced also by the Cracker with C masses of 9, 20, 44, and 100  $\mu\text{g}$  (Janovics  
86 et al. 2018). Cracker and combusted blanks were used for correction and the latter was also  
87 used for calculation of constant contamination.

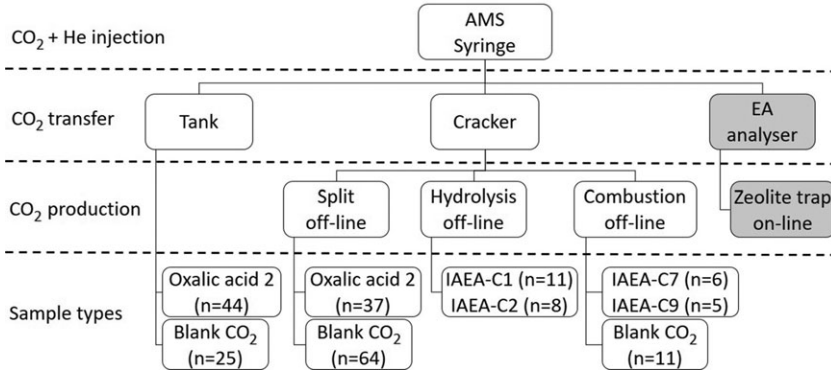


Figure 1 Flow chart and overview of sample types (with number of samples in brackets), applied off-line sample preparation methods, and modes of gas transfer into the Syringe of GIS interface for measurements discussed in this study.

88 We also report the results of 14 IAEA-C1 (marble,  $F^{14}C = 0.0000 \pm 0.0002$ ; Rozanski 1991),  
 89 11 IAEA-C2 (travertine,  $F^{14}C = 0.4114 \pm 0.0003$ ; Rozanski 1991), and 12 IAEA-C7 (oxalic  
 90 acid,  $F^{14}C = 0.4953 \pm 0.0012$ ; Le Clercq and van der Plicht 1998) standard measurements.  
 91 Standards were prepared either with hydrolysis (IAEA-C1 and -C2, 1–2 mL 85%  $H_3PO_4$   
 92 solution, 75°C, 1 hr) or combustion (IAEA-C7) and were transferred into the AMS via the  
 93 cracker unit (see Figure 1) (Molnár et al. 2013b.). Carbon masses of the standards were in  
 94 the range of 9–100  $\mu g$ .

### 95 Calculation of Constant Contamination

96 To evaluate of the degree of constant contamination, we used fossil CO<sub>2</sub> gas prepared as  
 97 combusted samples. We did these calculations as follows: first, having the measured  $F^{14}C$   
 98 value ( $F^{14}C_M$ ) and mass ( $m_M$ ) of blanks, and assuming that the blank samples have  
 99  $F^{14}C_S=0.0000$ , and the contaminant is only from modern source ( $F^{14}C_C=1.0000$ ), we can  
 100 easily calculate the mass of the contaminant ( $m_C$ ), by inserting Eq. (2) into Eq. (1).

$$F^{14}C_M = \frac{F^{14}C_S * m_S + F^{14}C_C * m_C}{m_S + m_C} \quad (1)$$

101 and

$$m_M = m_S + m_C \quad (2)$$

102 Second, having the average mass of the contaminant, we applied a least square fit model  
 103 (e.g. Hanke et al. 2017; Welte et al. 2018) to control the previous calculation.

104 The calculation of constant contamination for IAEA-C7 was somewhat different. For this, first  
 105 we subtracted the nominal value from the blank corrected value, and then we did the same  
 106 procedure as mentioned above for combusted blank samples.

107 **RESULTS AND DISCUSSION**108 **EnvironMICADAS GIS Basic Parameters**

109 Comparing our system with ETH (first)MICADAS, BERN MICADAS, AixMICADAS, and  
110 MAMS, it can be stated that our performance is comparable with the above-mentioned systems  
111 (see Table 1 and references below). The efficiency of the transmission is a lower due to the N<sub>2</sub>  
112 stripper gas, but this can be improved using He as stripper gas in the accelerator (upgrade for  
113 He stripper system at Debrecen MICADAS is planned in the second half of 2019).  
114 Our maximum <sup>12</sup>C<sup>-</sup> (μA) ion current at the low energy side (10–15 μA) is also comparable to  
115 the published data from other MICADAS systems even with our lower Cs reservoir  
116 temperature (140–150°C). It is important to note that this temperature depends on the point  
117 of the temperature measurement and the geometry of the Cs reservoir, what can be unique in  
118 each MICADAS instrument. One of the most important parameters in the AMS gas ion  
119 source measurements is a proper background value. Our results show quite good background  
120 data with good agreement with the other laboratories' performance. The average background  
121 is  $0.0050 \pm 0.0018$  F<sup>14</sup>C, which is a little higher than the AixMICADAS performance ( $0.0028$   
 $\pm 0.0018$  F<sup>14</sup>C), but lower than the all the other published data shown in Table 1. Our lowest  
123 measured sample amount was 9 μgC, a bit higher than samples reported by other MICADAS  
124 laboratories (2–5 μgC). Sample size is one of the more important factors in the value of the  
125 background (Fahrni et al. 2013; Szidat et al. 2014; Hoffmann et al. 2017; Gottschalk et al.  
126 2018, and Salazar 2019 [personal communication]; Tuna et al. 2018).

127 **OxII (NIST-SRM-4990C) Results**

128 The 88 individual OxII tank and sealed glass ampoule samples were measured with a minimum  
 $\pm 1.5\%$  relative statistical error and average of 26,000 <sup>14</sup>C counts with a 15-min measurement time.  
130 The sealed glass ampoule samples were prepared in different sample sizes (44–100 μgC) in a  
131 vacuum line with a known volume to determine the amount of CO<sub>2</sub> and hence the mass of C  
132 in the sample. This system is only used for background and OxII sample handlings from  
133 tanks, not for unknown samples, to avoid cross contamination. Both tank and sealed glass  
134 ampoule samples were used for normalization of the AMS-GIS measurements. Results of  
135 OxII standard measurements are shown in Figure 2 and listed in Table 2. From the 88 OxII  
136 measurements, we obtained an average F<sup>14</sup>C and δ<sup>13</sup>C of  $1.3415 \pm 0.0101$  and  $-17.79 \pm$   
137  $5.34\%$ , respectively. For other samples, data were normalized to the consensus values (i.e.,  
AQ4 F<sup>14</sup>C =  $1.3407 \pm 0.0005$  and δ<sup>13</sup>C =  $-17.78 \pm 0.08\%$ ; Stuiver 1983), they are in agreement  
139 with those, and were used for normalization. The relatively high δ<sup>13</sup>C scatter is possibly due  
140 to fractionation in the ion source. This process has been discussed in other publications as  
141 well (Hoffmann et al. 2017), but it does not affect the final <sup>14</sup>C results, because of the  
142 simultaneous <sup>14</sup>C/<sup>12</sup>C, <sup>13</sup>C/<sup>12</sup>C measurement and <sup>13</sup>C correction (Stuiver and Polach 1977;  
143 Mann 1983). Table 2 shows an overview of our results for IAEA standards and blank  
144 samples. These data of the IAEA-C1, -C2, -C7 and blank samples will be discussed in more  
145 detail in later sections. Listed data are average values (except for sample masses).

146 **Blank CO<sub>2</sub> Results**147 *Tank and Cracker Blanks*

148 To calculate the degree of memory effect (or level of cross contamination), we used the average  
149 F<sup>14</sup>C of 21 blank CO<sub>2</sub> samples measured first, second, and third in order after OxII samples  
150 (Figure 3). The obtained memory effect is  $0.34 \pm 0.05\%$  for the first blank, and  $0.10 \pm 0.06\%$  for

Table 1 Summary of typical measurement parameters and settings of EnvironMICADAS and comparison with MICADAS systems at other laboratories.

	EnvironMICADAS (Debrecen, Hungary)	ETH MICADAS <sup>1</sup> (Zürich, Switzerland)	BERN MICADAS <sup>2</sup> (Bern, Switzerland)	AixMICADAS <sup>3</sup> (Aix-en-Provence, France)	MAMS <sup>4</sup> (Mannheim, Germany)
Number of GIS measurements	>500 (2015–2019)	>2500 (2009–2013)	~5000 (2013–2018)	>2600 (2014–2018)	>400 (2014–2017)
Cs reservoir temp. (°C)	140–150	175 (185)	127-130	160	160–167
Carbon mass flow (µg/min)	3.5	1.6 (2.5)	1.5-2.5	2.8	3.5
CO <sub>2</sub> in He (%)	5	2.5 (5)	5	5	4
Injection pressure (mbar)	1600–1800	—	—	1300	1600-1800
Max. <sup>12</sup> C <sup>-</sup> ion current (µA)	25	30	17	—	18
Average <sup>12</sup> C <sup>-</sup> ion current (µA)	10–15	12 (15)	10-15	5–15	5–15
Background current (nA)	≤110	70	—	<110	—
Transmission (%)	36.6 ± 3.0	—	~40	48.1 ± 0.6	—
Average Meas. time (min)	13 ± 7	10–12	20	12	—
Sample size (µg)	9–120	2–100	5-200	5–120	2–100
Average blank F <sup>14</sup> C	0.0050 ± 0.0018	<0.01	0.01-0.03	≤0.0028 ± 0.0011	0.0081 ± 0.0027

<sup>1</sup>Fahrni et al. 2013; <sup>2</sup>Szidat et al. 2014; Gottschalk et al. 2018, and Salazar 2019 (personal communication); <sup>3</sup>Tuna et al. 2018; <sup>4</sup>Hoffmann et al. 2017.

Table 2  $F^{14}C$  results of OxII, IAEA standards, and blank  $CO_2$  samples, and comparison with nominal values.

Sample type	$F^{14}C$	$F^{14}C$ reference	Mass range ( $\mu g$ )	Measurement time (min)	Number of samples
OxII	$1.3415 \pm 0.0101$	$1.3407 \pm 0.0005$	44–100	$15 \pm 7$	88
IAEA-C1	$0.0029 \pm 0.0020^{1,2}$	$0.0000 \pm 0.0002$	19–100	$8 \pm 3$	14
IAEA-C2	$0.4105 \pm 0.0049^1$	$0.4114 \pm 0.0003$	33–94	$15 \pm 4$	11
IAEA-C7	$0.4957 \pm 0.0116^{1,2,3}$	$0.4953 \pm 0.0012$	9–100	$5 \pm 4$	12
Blank $CO_2$ tank	$0.0058 \pm 0.0022^2$	0.0000	100	$12 \pm 5$	25
Blank $CO_2$ cracker	$0.0050 \pm 0.0018^2$	0.0000	19–100	$13 \pm 6$	69
Blank $CO_2$ combusted	$0.0000 \pm 0.0029^3$	0.0000	9–100	$6 \pm 4$	11

Listed data are average values (except for sample masses). Given uncertainties are  $1\sigma$ . <sup>1</sup>Blank corrected. <sup>2</sup>Memory effect corrected. <sup>3</sup>Constant contamination corrected. Reference values of IAEA-C1 and -C2 from Rozanski (1991), IAEA-C7 from Le Clercq et al. (1998), and OxII from Stuiver (1983).

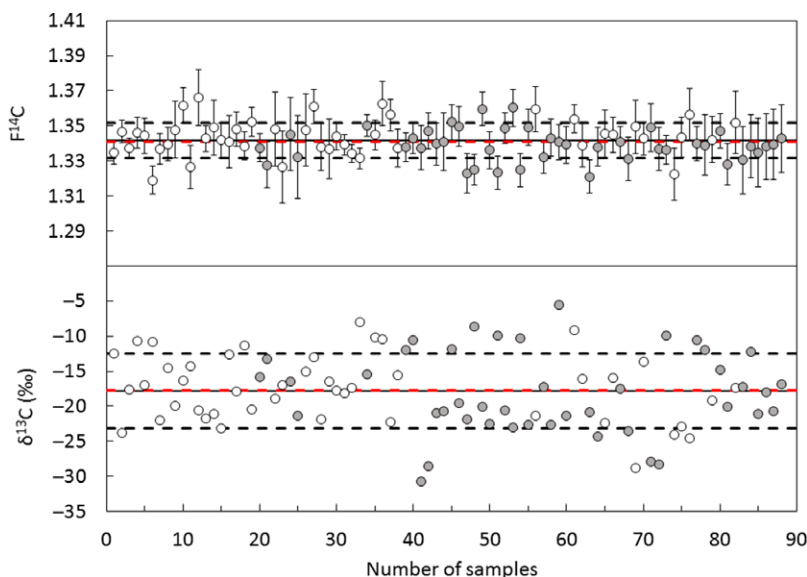


Figure 2  $F^{14}C$  and  $\delta^{13}C$  results of OxII tank ( $n=45$ ) and OxII cracker ( $n=43$ ) measurements. Open symbols are tank samples, and solid symbols are cracker samples. Solid black lines show the average values, and dashed black lines mark the associated  $1\sigma$  standard deviations. Dashed red lines represent the nominal values ( $F^{14}C = 1.3407 \pm 0.0005$  and  $\delta^{13}C = -17.78 \pm 0.08\text{‰}$ ; Stuiver 1983). (Please see electronic version for color figures.)



151 the second blank measured after a modern sample. The average  $F^{14}\text{C}$  after correction for  
152 memory effect is  $0.0058 \pm 0.0022$  and  $0.0050 \pm 0.0018$  for fossil tank and cracker samples,  
153 respectively (Figures 4 and 5, Table 2). These results in conventional  $^{14}\text{C}$  age are in the  
154 range of 34,000–47,000 yr BP, typical for the achieved background with graphite samples  
155 in the HEKAL (Molnár et al. 2013).

156 The blank value can be corrected by the memory effect (Figure 4), but without this correction, our  
157 results are still comparable with other GIS performance as mentioned in Table 1 (Szidat et al.  
158 2014; Hoffmann et al. 2017; Gottschalk et al. 2018; Tuna et al. 2018). The blank tank  
159 samples have slightly higher  $F^{14}\text{C}$  values, probably because the tank samples are generally  
160 measured at the beginning of the GIS measurement campaign, or alternatively due to a small  
161 leakage at the tank or fitting problems around the connections or accumulated  
162 cross-contamination effects in the capillary and gas handling system. These small differences  
163 cannot greatly affect the final  $F^{14}\text{C}$  results, but have to be taken into account (Hoffmann  
164 et al. 2017).

165 Figure 5 shows the  $F^{14}\text{C}$  values as a function of sample mass. The most commonly measured glass  
166 ampoule samples used the cracker in the GIS are the 50 and 100  $\mu\text{gC}$  samples, because the mean  
167 size of the measured unknown samples in HEKAL is between these values. The difference  
168 between the different sample masses is small but variable. The best achievable blank strongly  
169 depends on the condition of the Cs sputtering ion source. It is recognizable that GIS  
170 measurements increase the stress on the ion source because they apply more ionized Cs to the  
171 ion source box, which can contaminate the system and worsen the background signal in the  
172 long run.

### 173 *Combusted Blanks*

174 For fossil  $\text{CO}_2$  blanks prepared by combustion, we calculated a constant contamination of  $0.57$   
 $\pm 0.09$   $\mu\text{g C}$ . The validity of this value was also confirmed by the least square fit method  
176 (reduced chi square = 0.91). This value is comparable with a coupled GIS+EA system as  
177 mentioned in Tuna et al. (2018). In that paper, the coupled AGE+CHS system was  
178 reported to have  $1.74 \pm 0.42$   $\mu\text{gC}$  constant contamination. Thanks to the low volume of  
179 our system, we can keep the constant contamination as a lower level. The resulting average  
180 corrected  $F^{14}\text{C}$  is  $0.0000 \pm 0.0029$  (Figure 6 and Table 2).

### 181 **IAEA Standards**

182 IAEA standards (C1, C2, and C7) were used as internal standards and treated as unknowns in  
183 our measurements, therefore they were not used for normalization. IAEA-C1 and -C2  
184 standards were prepared by off-line hydrolysis, and since the average  $F^{14}\text{C}$  results of  $0.0029$   
 $\pm 0.0020$  and  $0.4105 \pm 0.0049$ , respectively (Table 2), are in good agreement with the  
186 nominal values (Figures 7 and 8;  $0.0000 \pm 0.0002$  and  $0.4114 \pm 0.0003$ ; Rozanski 1991), we  
187 assume that this type of sample preparation does not introduce any significant contamination.

188 Figure 7 shows that the disagreement between the nominal and measured, corrected values  
189 appear to be independent of the mass of the sample, at least between 20 and 70  $\mu\text{g}$ .  
190 As the IAEA-C1 is a blank standard for AMS measurements, the  $0.0029 \pm 0.0020$   $F^{14}\text{C}$   
191 value indicates quite good agreement and implies that the off-line hydrolysis does not add  
192 high levels contamination to the prepared samples. The agreement in case of the IAEA-C2  
193 samples is quite convincing (Figure 8).

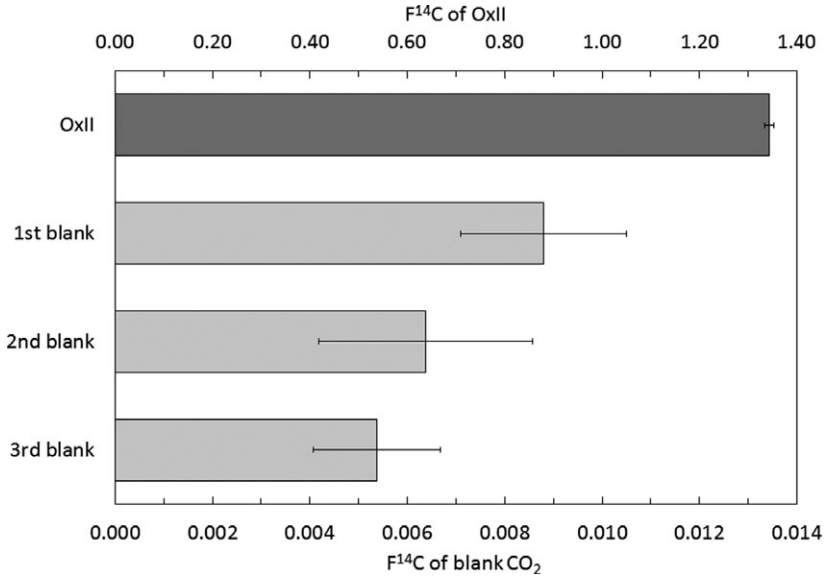


Figure 3 Diagram showing the memory effect after measuring three successive blank samples (blank CO<sub>2</sub>) after a modern sample (OxII). The dark grey bar shows average F<sup>14</sup>C of 21 OxII samples, and light grey bars show average F<sup>14</sup>C of 21 blank CO<sub>2</sub> samples (6 tank and 15 cracker blanks). Note the 2-magnitude order difference between the two x-axes (i.e., OxII and blank samples). Error bars show 1σ standard deviation.

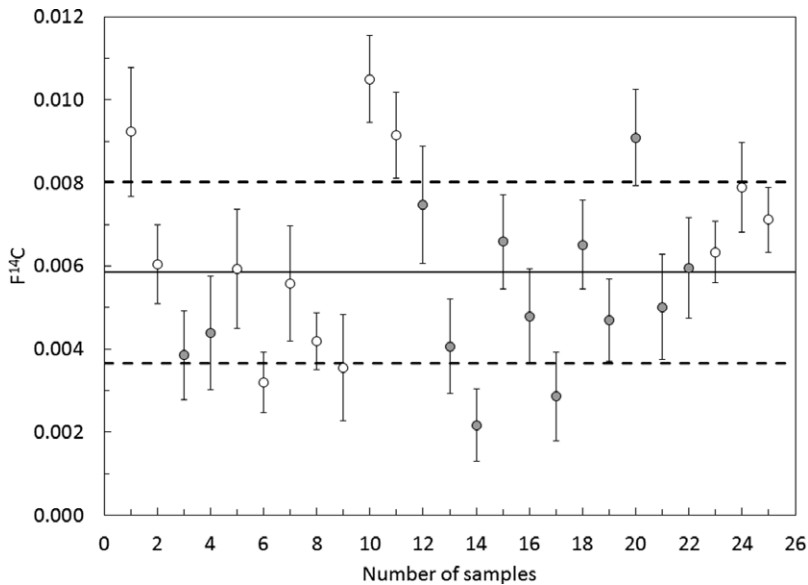


Figure 4 F<sup>14</sup>C results of blank CO<sub>2</sub> tank samples (n=25). Open symbols are measured values, and solid symbols are values after memory effect correction. Solid black line shows the average F<sup>14</sup>C (0.0058 ± 0.0022), and dashed black lines mark the associated 1σ standard deviation.

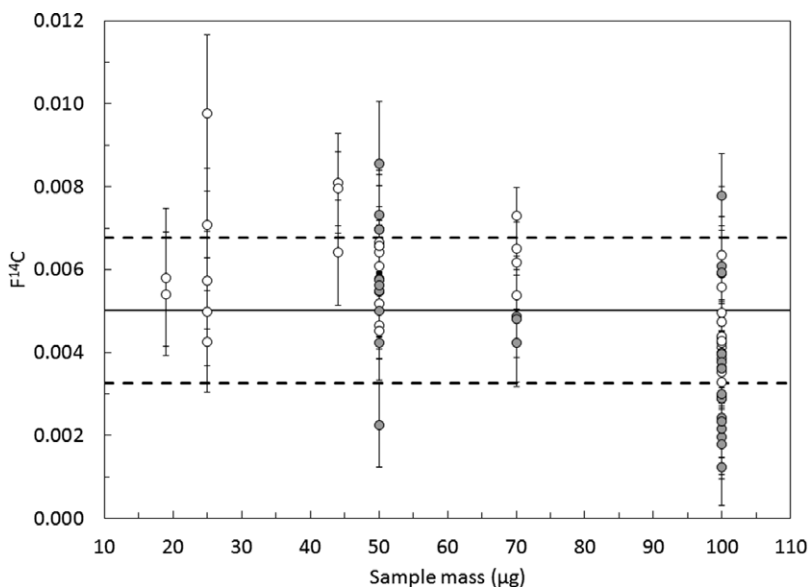


Figure 5  $F^{14}C$  results of blank  $CO_2$  cracker samples ( $n=69$ ). Open symbols are measured values, and solid symbols are values after memory effect correction. Solid black line shows the average  $F^{14}C$  ( $0.0050 \pm 0.0018$ ), and dashed black lines mark the associated  $1\sigma$  standard deviation.

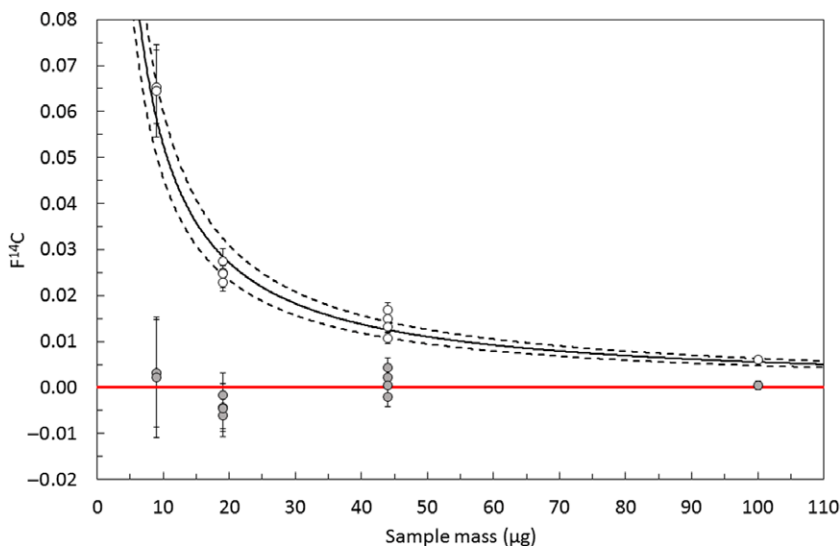


Figure 6  $F^{14}C$  results and constant contamination model of combusted blank samples ( $n=11$ ). Open symbols mark the measured values, and solid symbols represent the constant contamination corrected values ( $F^{14}C=0.0000 \pm 0.0029$ ). The solid black line shows the best fit and dashed black lines mark the associated  $1\sigma$  standard deviation. The red line shows the reference value ( $F^{14}C=0.0000$ ). Error bars mark  $1\sigma$  uncertainty.

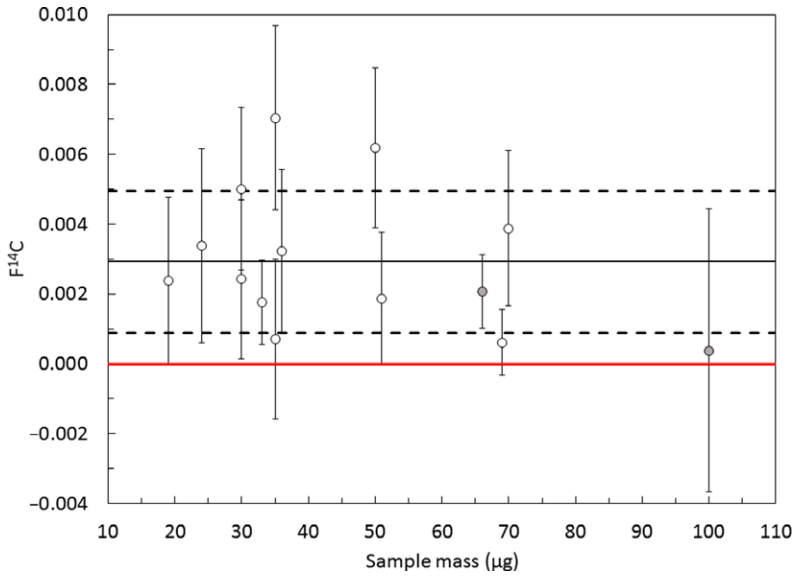


Figure 7  $F^{14}C$  results of IAEA-C1 samples ( $n=14$ ). Open symbols represent blank corrected values, and solid symbols show blank and memory-effect corrected values. Solid black line shows the average  $F^{14}C$  ( $0.0029 \pm 0.0020$ ) and dashed black lines mark the associated  $1\sigma$  standard deviation. The red line represents the reference value ( $F^{14}C=0.0000 \pm 0.0002$ ; Rozanski 1991). Error bars mark  $1\sigma$  uncertainty.

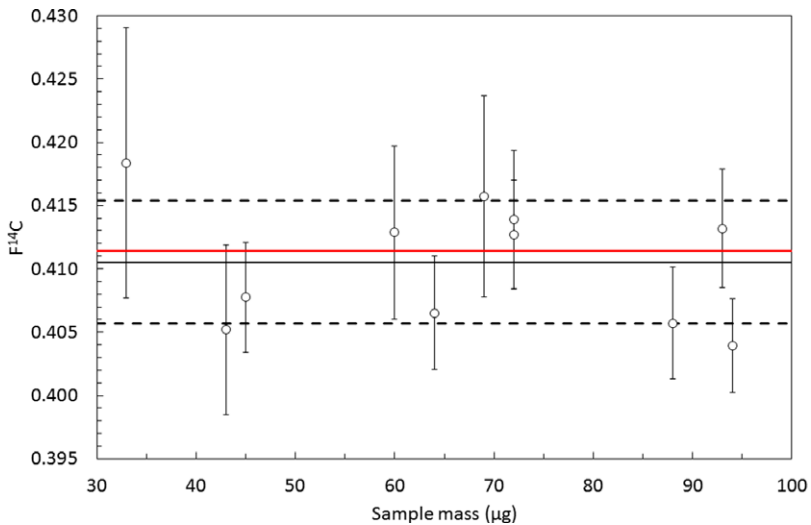


Figure 8  $F^{14}C$  results of IAEA-C2 samples ( $n=11$ ). Open symbols mark blank corrected values. Solid black line shows average  $F^{14}C$  ( $0.4105 \pm 0.0049$ ) and dashed black lines mark the associated  $1\sigma$  standard deviation. Dashed red line represents the reference value ( $F^{14}C=0.4114 \pm 0.0003$ ; Rozanski 1991). Error bars mark  $1\sigma$  uncertainty.

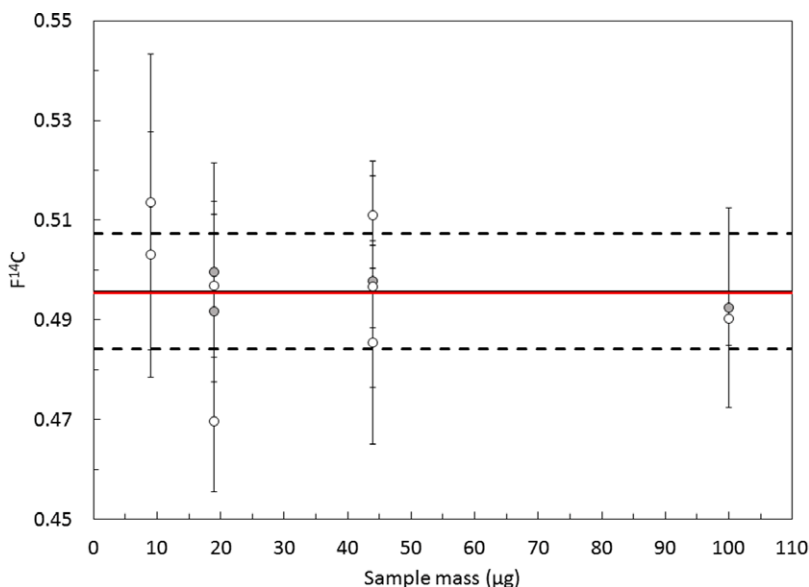


Figure 9  $F^{14}C$  results of IAEA-C7 samples ( $n=12$ ). Open symbols show data which were corrected for blank, memory effect and constant contamination, while solid symbols mark values which were corrected only for blank and constant contamination. Solid black line shows average  $F^{14}C$  ( $0.4957 \pm 0.0116$ ) and dashed black lines mark the associated  $1\sigma$  standard deviation. The red line marks the reference value ( $F^{14}C=0.4953 \pm 0.0012$ ; Le Clercq and van der Plicht 1998). Error bars mark  $1\sigma$  uncertainty.

194 IAEA-C7 standards were prepared by combustion, and it was necessary to correct the  $F^{14}C$   
 195 values for constant contamination (Figure 9), as was previously discussed for combusted  
 196 blank samples (see above). IAEA-C7 standards appeared to have a contamination of  $0.29$   
 198  $\pm 0.09 \mu\text{g C}$  (reduced chi square = 0.38), which is less than for combusted blanks ( $0.57 \pm$   
 199  $0.09 \mu\text{g C}$ ), but they are in agreement within  $1\sigma$  uncertainty. After correction for constant  
 200 contamination (and memory effect), an average  $F^{14}C$  of  $0.4957 \pm 0.0116$  agreed well with  
 the nominal value of  $0.4953 \pm 0.0012$  (Le Clercq and van der Plicht 1998).

## 201 CONCLUSION

202 The Gas Interface System (GIS) at the Hertelendi Laboratory of Environmental Studies  
 203 (HEKAL), Hungarian Academy of Sciences, Debrecen has been operating successfully  
 204 since 2013. The system is one of the first GIS equipment which has successfully applied for  
 205  $^{14}C$  measurements from  $CO_2$ , originally developed by the ETHZ. After more than 500 gas  
 206 target measurements, we can conclude that our system has high stability and  
 207 reproducibility. This conclusion can be confirmed by the comparison of other laboratories'  
 208 performance. Both the blank, OxII and IAEA standard measurements demonstrate the  
 209 reliability of the gas target measurements at the HEKAL. This reliability is achievable even  
 210 below  $20 \mu\text{gC}$ . The investigation of memory effects shows a low but visible  
 211 cross-contamination based on measurements of OxII and a series of 3 consecutive blank  
 212 sample measurements. The level of the cross contamination is  $0.34 \pm 0.05\%$  for the first  
 213 blank, and  $0.10 \pm 0.06\%$  for the second blank measured after the OxII standard. For  
 214 samples greater than or equal to  $10 \mu\text{gC}$  relative errors of 6% could be achieved. Relative

error is defined as absolute error (1 sigma) of fM result divided by the actual fM value. It is about  $\pm 6\%$  (six percent) in the case of very small (10–20  $\mu\text{g C}$  sized  $\text{CO}_2$  samples). The  $^{12}\text{C}$  ion current at the low energy side is between 10–15  $\mu\text{A}$  with  $13 \pm 7$  min average measurement time and about 300 counts per microgram C for OxII. The applied  $\text{CO}_2$  in He mixing ratio was 5%. The blank is comparable with other MICADAS GIS systems, that is  $0.0050 \pm 0.0018 \text{ F}^{14}\text{C}$  or a range 34,000–47,000 radiocarbon years BP, which is feasible for dating both of archeological and environmental samples. In the future, we plan to attach the gas-ion source inlet to elemental and organic carbon measurements (EC and OC) with a coupled Sunset ECOC analyzer-GIS system and introduction of EA-GIS measurements. This will extend our capabilities to use the gas ion source for environmental studies.

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