Determination of ultra-low concentrations of gaseous ¹⁴C-bearing hydrocarbons produced during corrosion of irradiated steel using accelerator mass spectrometry

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Abstract

Compound-specific radiocarbon analysis (CSRA) was developed to identify and quantify gaseous ¹⁴C-bearing carbon compounds at the pico- to femtomolar concentration range and employed in a corrosion experiment with small specimens of irradiated steel. The approach is based on gas chromatographic separation of single ¹⁴C-bearing carbon compounds, their oxidation to ¹⁴CO₂, sampling with a custom-made fraction collector and quantification by accelerator mass spectrometry (AMS). In addition to CSRA, a method allowing the quantification of the total ¹⁴C content of the gas phase was developed and tested. After validation of the two set-ups with standards, the gaseous ¹⁴C-bearing carbon compounds produced during alkaline anoxic corrosion of irradiated steel were quantified. Small hydrocarbons (HCs) like methane (¹⁴CH₄) and ethane (¹⁴C₂H₆) were the only ¹⁴C-bearing compounds identified in the gas phase above the detection limit. ¹⁴CH₄ was the main species (on average 5.4×10⁻¹⁴ mol/L gas) and contributed > 90 % to the total ¹⁴C content, whereas the concentration of ¹⁴C₂H₆ was much lower (7.9×10⁻¹⁶ mol/L gas). To our knowledge, this is the first study reporting CSRA of gaseous ¹⁴C-bearing HCs produced during anoxic corrosion of irradiated metallic radioactive waste at ultra-low concentrations.

Keywords: radiocarbon; hydrocarbons; accelerator mass spectrometry; irradiated steel; corrosion.

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1. Introduction

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Gas generation is a major concern with regard to the safe disposal of low- and intermediate-level radioactive waste (L/ILW) in deep geological repositories¹. Gas migration may enhance the release of volatile radionuclides from the repository because of the significantly faster transport in the gas phase in comparison to the diffusive transport of dissolved species^{2,3}. The release of ¹⁴C-bearing gaseous species is of particular concern as ¹⁴C ($t_{1/2} = 5730$ years) has been identified as a key radionuclide in the assessment of the safety of L/ILW repositories^{1,4,5,6}. Indeed, ¹⁴C may be present as aqueous or gaseous species which are only weakly retarded by the engineered barrier and the surrounding host rock of a repository and it can also be incorporated in the human food chain^{4,5}. Future safety assessments therefore require a better understanding of the degradation kinetics of ¹⁴C-containing wastes and the chemical forms of ¹⁴C released from degrading nuclear wastes in an L/ILW repository.

In Switzerland, the ¹⁴C present in the already existing and future arising of L/ILW is mainly associated with irradiated metallic waste components⁴. The largest portion of ¹⁴C-bearing compounds (~ 75 %) is therefore supposed to be released to the aqueous and gas phases during corrosion of irradiated steel. The presence of ¹⁴C in irradiated steel can be attributed to the activation of nitrogen impurities contained in nuclear fuel and reactor core components of nuclear power plants through the nuclear reaction ¹⁴N(n,p)¹⁴C. In the context of the Swiss disposal programme, a laboratory-scale experiment is being carrying out with the aim of identifying and quantifying the ¹⁴C-bearing carbon compounds released during corrosion of irradiated steel in anoxic and highly alkaline conditions^{7,8}. The latter conditions simulate the long-term chemical environment in a cement-based L/ILW repository. Anoxic conditions prevail after closure due to oxygen consumption in the early stage of a repository in clayey host rock⁹.

Scoping calculations carried out in conjunction with the design of the corrosion experiment revealed that ¹⁴C might be present at ultra-low concentrations⁷. In fact, the first measurements of dissolved ¹⁴C species indicated concentrations around 10^{-14} mol/L⁸. The expected ultra-low ¹⁴C concentrations can

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4 51 be related to the small size and low ^{14}C content of the irradiated steel nut specimens used for the
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6 52 experiment¹⁰, the very low corrosion rate of steel under alkaline conditions (i.e. few nanometres per
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8 53 year)^{11,12,13,14} and eventually, the small volumes of samples (i.e. few millilitres) available for analysis in
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10 54 a laboratory-scale experimental set-up. Hence, these constraints required the development of a very
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12 55 sensitive analytical technique for ^{14}C quantification based on accelerator mass spectrometry (AMS)
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14 56 measurements. This approach has a significantly lower detection limit compared to the standard
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16 57 decay-counting method, i.e. liquid scintillation counting (LSC), and especially allows the determination
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18 58 of the $^{14}\text{C}/^{12}\text{C}$ isotopic ratio in the concentration range from 10^{-12} to 10^{-16} g C/L¹⁵. In a previous study,
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20 59 we reported the development of compound-specific radiocarbon analysis (CSRA) based on ion
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22 60 chromatography and ^{14}C AMS detection for water-soluble ^{14}C organic carbon compounds¹⁶. In this
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24 61 study, we describe the development and application of a CSRA method for the quantification of
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26 62 gaseous ^{14}C -bearing carbon compounds released during alkaline anoxic corrosion of irradiated steel.
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64 2. Conceptual approach

65 Previous corrosion studies on non-irradiated and irradiated metals showed the presence of small
66 hydrocarbons (HCs), low-molecular-weight carboxylic acids, alcohols and aldehydes in corroding iron-
67 water systems^{14,17}. Observed organic substances had chain lengths up to seven carbon atoms (C7) and
68 typically involved compounds between C1 and C5. Recently, small HCs (with a predominance of CH_4)
69 were identified as volatiles in corrosion experiments with non-irradiated iron powders immersed in
70 artificial cement pore water^{18,19} and with irradiated steel in 0.1 M sodium hydroxide solution²⁰. The
71 conceptual approach for the analysis of ultra-low concentrations of ^{14}C -carrying carbon compounds
72 was therefore developed on the assumption that HCs up to C7 might be formed and released during
73 alkaline anoxic corrosion of irradiated steel.
74
75 To comply with these requirements, a CSRA methodology was developed based on gas
chromatographic separation of single ^{14}C -bearing HCs, their subsequent oxidation to $^{14}\text{CO}_2$ and

trapping in sampling tubes of a custom-made fraction collector (Figure 1). $^{14}\text{CO}_2$ was finally measured by AMS (Figure 2). In brief, a gas sample containing the ^{14}C -carrying HC of interest is loaded into a first injection loop of the gas chromatograph (GC) (called "sample loop"). At the same time, a stable ^{14}C -free carbon carrier is loaded into a second injection loop of the GC (named "carrier loop") in order to achieve the amount of ^{12}C (i.e. 20 μg stable carbon) recommended for reproducible AMS analysis [Laboratory for Analysis of Radiocarbon (LARA), University of Bern, Switzerland, pers. comm.]. Both loops are simultaneously injected into the GC for chromatographic separation into single compounds. An oxidation oven is connected at the outlet of the GC column and converts the single ^{14}C -bearing HCs and the carrier into $^{14}\text{CO}_2$ and CO_2 , respectively (Figure 1). After the oxidation oven, its products (mainly CO_2) pass through a reduction oven to remove traces of O_2 and nitrous oxides (NO_x) (Figure 1). Residual water is also removed from the analyte stream by a water separator connected at the outlet of the reduction oven (Figure 1). The analyte stream (free of O_2 , NO_x and water) reaches a second short GC column for a better separation between the oxidised and non-oxidised HCs. They are detected by non-destructive thermal conductivity detection (TCD) and finally collected in the sampling tubes (metallic loops) of the fraction collector (Figure 1).

Gas Chromatography (GC)

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3 92 Figure 1: Schematic representation of the chromatographic system and the fraction collector used for
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6 93 sample preparation for CSRA of the ^{14}C -carrying HCs. The inset on the right shows a picture of the
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8 94 fraction collector.
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12 96 Once the sampling loops are filled with up to seven $^{14}\text{CO}_2/\text{CO}_2$ samples, the fraction collector is
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14 97 disconnected from the GC system and transferred to LARA for ^{14}C AMS measurements. There, the
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16 98 fraction collector is connected to the 200kV MIni CARbon DAtIng System (MICADAS) via a Gas System
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18 99 Interface (GIS) (Figure 2). A He flow is applied to purge the $^{14}\text{CO}_2/\text{CO}_2$ from the sampling loops onto
20 100 the zeolite trap of the GIS^{21,22}. After $^{14}\text{CO}_2/\text{CO}_2$ collection, the zeolite trap is heated up and $^{14}\text{CO}_2/\text{CO}_2$
21 101 is directly released into a syringe. By knowing its volume, it is possible to measure the amount of total
22 102 CO_2 that will be released into the gas ion source of the MICADAS. Accuracy and precision of the ^{14}C
23 103 measurements by MICADAS are comparable to both LSC and large AMS systems²³, while the detection
24 104 limit of AMS is several orders of magnitude lower than that of LSC. The instrument offers further
25 105 advantages due to its user-friendly operation, low requirements of sample material and short process
26 106 time²³. In the secondary ion mass spectrometry-type ion source of the MICADAS, the CO_2 is sputtered
27 107 by a primary beam of thermally ionised Cs vapour (Cs^+) and negatively charged ions (i.e. $^{12}\text{C}^-$, $^{13}\text{C}^-$ and
28 108 $^{14}\text{C}^-$) are extracted from the sample and fed into the accelerator. There, the high-energy collisions with
29 109 a gas contained in a charge-exchange device (stripper tube) destroy molecular bonds, remove most
30 110 interferences (isobars: ^{13}CH , $^{12}\text{CH}_2$) and changes the charge of the ions from negative to positive. The
31 111 electric field after the stripper tube accelerates the ions further²⁴. The beam is again filtered on the
32 112 high-energy beam line before ion detection and counting by the Faraday cups (for $^{12}\text{C}^+$ and $^{13}\text{C}^+$) and
33 113 the ionisation chamber detector (for $^{14}\text{C}^+$)²⁵.

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Figure 2: Scheme of the connection of the fraction collector to the ion source of the AMS via the GIS.

3. Material and Methods

3.1. Gas sampling

The set-up and operation of the reactor used for the corrosion experiment with irradiated steel consists of two 1 g specimens prepared from an irradiated steel nut, which had been exposed to radiation in the reactor of nuclear power plant Gösigen (Switzerland) for about two years^{7,10,26}. They are immersed in artificial cement pore water at pH 12.5 in a gas-tight autoclave-type reactor. The gas phase has been sampled at 1114 and 1252 days of corrosion. To this end, a sampling tube was connected to the gas outlet of the reactor, purged with N₂ (Carbagas, AG, Basel, Switzerland, grade 5.0) and evacuated. A volume of ~ 50 mL gas was collected by opening the valves in-between the reactor and the sampling tube. After gas collection, N₂ was injected into the reactor to re-adjust the initial operating conditions at 4 bar overpressure.

3.2. Analysis of gaseous HCs and sample preparation for CSRA

3.2.1. Identification and quantification of HCs

Gaseous HCs were identified with a TRACE™ GC Ultra gas chromatograph (Thermo Fisher Scientific Inc., Waltham, USA) equipped with an ISQ mass spectrometer (MS) (Thermo Fisher Scientific Inc., Waltham, USA) operated in the electron ionisation (EI) mode. First, a volume of 10 mL was withdrawn from the sampling tube and injected into a purged and evacuated 20 mL headspace vial with a gas-tight syringe (Hamilton AG, Bonaduz, Switzerland). To allow pressure compensation, a gas sampling bag filled with N₂ was connected to the headspace GC vial for 5 seconds. The samples were then injected into the GC by using a headspace method. Briefly, the headspace vial containing the sample was incubated under agitation during 120 s at 50 °C. Afterwards, a gas-tight syringe, pre-heated at 85 °C, sampled 2 mL of the gas phase which were injected into the GC in split mode (split ratio of 1:18; splitless time of 1 min) using He (Carbagas, AG, Basel, Switzerland, grade 5.0) as carrier gas at a constant flow rate of 2.0 mL/min. Well-resolved separation of the HCs was achieved by using a Restek Rt®-Msieve 5A GC column (30 m × 0.32 mm with 0.025 mm film; named column 1) in combination with a specific programme, starting at 45 °C (hold 4 min) and heating up to 290 °C (hold 10 min) at a rate of 20 °C/min (overall run time ~ 26 min) (retention time as listed in Table 1). The individual HCs were identified by MS, which was operated at standard EI parameters (70 eV collision energy; 1860 V EM voltage; 230 °C MS source temperature). Data were acquired in the selected ion monitoring (SIM) mode. Thermo Xcalibur 3.0.63 (Thermo Fisher Scientific Inc., Waltham, MA, USA) and the PAL Sample Control (PAL3 System software, CTC Analytics AG, Switzerland) are the software controlling the system, the data acquisition and processing.

Standard gases like CH₄ (puriss.; 4.5 GC from Fluka Analytical, Sigma Aldrich, Switzerland) and a reference gas mixture (Westfalen AG, Germany) containing 94.8 ppm CH₄ (2.5), 98.3 ppm acetylene (C₂H₂; 2.6), 98.5 ppm ethene (C₂H₄; 2.5), 98.0 ppm ethane (C₂H₆; 2.0), 96.2 ppm propene (C₃H₆; 2.5), 94.1 ppm propane (C₃H₈; 2.5) and 101.0 ppm *n*-butane (C₄H₁₀; 2.5) were used to determine the dynamic range and reproducibility of the GC-MS measurements¹⁸. Briefly, between 0.3 and 10 mL

volume of standards were withdrawn from gasbags containing the standard gases, diluted with N_2 if necessary and injected with a Hamilton syringe into headspace GC vials. Blank samples consisting of five headspace GC vials filled with N_2 were analysed with the headspace method to quantify the limit of detection (LOD) and quantification (LOQ) (Table 1). They were based on the standard deviation of the blanks multiplied by a factor of 3.3 and 10, respectively^{27,28}.

Table 1: Retention times, limits of detection (LOD) and quantification (LOQ) of the GC-MS analysis.

	Methane	Ethane	Ethene		Propane	Propene	Butane
Retention time (min)	2.8	10.5	15.3		15.7	20.4	22
LOD (μM)	0.016	0.005	0.007		0.010	0.005	0.017
LOQ (μM)	0.047	0.017	0.020		0.029	0.017	0.052

3.2.2. Sampling of ^{14}C -bearing HCs with the fraction collector

The gas sampled from the reactor and the ^{14}C -free carrier were loaded into the sample and the carrier loops of the GC, respectively. The sample loop had a volume of 500 μL when used for blank measurements (i.e. N_2) and a volume of 40 μL when gas from the reactor was analysed. The carrier loop had a volume of 40 μL . This corresponds to a capacity of 20 μg C as CH_4 or 40 μg C as C_2H_6 at ambient pressure, which is the recommended amount of stable carbon ($^{12}C + ^{13}C$) for reliable ^{14}C AMS measurements (LARA, University of Bern, pers. comm.). Both loops were simultaneously injected into the TRACE™ GC in split mode (see section 3.2.1). The HCs were separated on the Restek Rt®-Msieve PTL-5A GC column (30 m $\times$ 0.32 mm with 0.025 mm film; column 1) using the following temperature programme: 50 $^{\circ}C$ (hold 4 min), heating up at 20 $^{\circ}C/min$ to 80 $^{\circ}C$ and subsequent heating up at 50 $^{\circ}C/min$ to 290 $^{\circ}C$ (hold 10 min). After chromatographic separation, the single ^{14}C -carrying HCs and the ^{14}C -free carrier were oxidised to $^{14}CO_2/CO_2$ in the oxidation oven (Thermo Finnigan, Bremen, Germany) (Figure 1). The oxidation oven consists of a non-porous alumina tube containing three wires of copper (Cu), nickel (Ni) and platinum (Pt) braided and centred end-to-end into a resistively heated Al_2O_3

177 furnace. Its normal operation temperature is at $T = 1000\text{ }^{\circ}\text{C}$. After oxidation, the analyte stream passes
178 sequentially through: (i) a reduction oven having a similar setting than the oxidation oven except that
179 it contains three wires of Cu and operating at $T = 650\text{ }^{\circ}\text{C}$ (Thermo Finnigan, Bremen, Germany); (ii) a
180 water trap (glass tube; 4 mm i.d.; 6 mm o.d.) with a NAFION™ membrane (Permatrace; Toms River, NJ;
181 0.3 mm i.d.; 0.6 mm o.d.; 20 cm length), being purged with counter-current stream of dry He at a flow
182 rate of 3–4 mL/min; (iii) and a second short GC column (Restek Rt®-Msieve PTL-5A column; 0.5 m ×
183 0.32 mm with 0.025 mm film; named column 2) (Figure 1). Both CO₂ and non-oxidised HCs were
184 detected by non-destructive TCD (Thermo Finnigan GC-combustion interface III) after an overall run
185 time of ~ 20 min and eventually trapped in the seven sampling loops of the fraction collector
186 (Brechtbühler AG, Schlieren, Switzerland) (Figure 1). The latter device consists of a collection valve,
187 seven loops (#2 to #8) and a purge valve controlled by a custom-made software. The collection valve
188 starts and stops the trapping of the analytes of interest in accordance with their retention time. The
189 loops #2 to #6 of the fraction collector have a volume of 25 mL, whereas the loops #7 and #8 have a
190 volume of 60 mL. It should be noted that the loop #1 serves as a by-pass. To avoid any contamination
191 with air, the purge valve was used to flush twice each loop before trapping (3 min and 1 min,
192 respectively). To trap all gaseous compounds in one single loop, the chromatographic Restek column
193 was replaced by a fused Si capillary (1 m × 0.32 mm) and the temperature programme of the GC oven
194 was adjusted. After an initial temperature of 150 °C (hold 4 min), the oven was heated up to 290 °C
195 (hold 5 min) at a rate of 40 °C/min (overall run time ~ 12.5 min). Once all the sampling loops were
196 filled, the collection valve was rotated to the by-pass (loop #1) to keep the other loops gas-tight.

197 The Thermo Xcalibur 3.0.63 software (Thermo Fisher Scientific Inc., Waltham, USA) operated the GC-
198 TCD system, while a custom-made software from Brechtbühler AG controlled the collection and purge
199 valves of the fraction collector. Two gases were used to run the set-up: He (Carbagas, AG, Basel,
200 Switzerland, grade 5.0) as carrier gas and N₂ (Carbagas, AG, Basel, Switzerland, grade 5.0) to switch
201 the injection valves of the GC. Moreover, fossil CH₄ (puriss.; 4.5 GC from Fluka Analytical, Sigma Aldrich
202 GmbH, Buchs, Switzerland), modern CH₄ (GPC Radiocarbon lab, University of Bern; $F^{14}\text{C} = 1.024 \pm$

0.003²⁹), C₂H₆ (Carbagas, AG, Basel, Switzerland, grade 5.0), C₃H₈ (puriss.; 2.5 GC from Westfalen Gas GmbH, Eiken, Switzerland) and C₄H₁₀ (puriss.; 2.5 GC from Westfalen Gas GmbH, Eiken, Switzerland) were used for calibration and optimisation of the method.

3.3. Quantification of ¹⁴C by AMS

At LARA, the fraction collector was connected to the GIS through a 1 m long 1/16" O.D. tubing (Figure 2). The ¹⁴CO₂/CO₂ trapped in the sampling loops of the fraction collector was flushed into the GIS one loop after the other with a flow of He at ~ 30 mL/min and then collected by the zeolite trap during a period set from 150 s to 300 s. Note that the trapping time was set according to the flow rate measured after each sampling loop and its respective volume. After collection, the zeolite trap was heated up to 450 °C and the ¹⁴CO₂/CO₂ mixture was released into a syringe whose plunger was controlled by a stepper motor (Figure 2). Helium was then added to the syringe to reach a pressure of ~ 0.16 MPa and obtain a final gas composition of ~ 5 % CO₂. Finally, the gas mixture was released into the 200 kV MICADAS gas ion source at a flow rate of ~ 40 µL/min. The total AMS measurement time was 10 min for each sample. Around 99 % of this time was required to count the ¹⁴C atoms and only 1 % to measure the stable isotopes (i.e. ¹²C + ¹³C). During the ¹⁴C measurements, the GIS system was flushed for 4 min to avoid any cross-contamination between samples. Transmission Control Protocol/Internet Protocol (TCP/IP) commands (generated by LabView) controlled the MICADAS and operated all the involved devices. To calibrate the MICADAS, ~ 5 % CO₂ from oxalic acid (International Atomic Energy Agency; SRM 4990C) in He, prepared by Hekal AMS Lab (Hungary) with ¹⁴C/¹²C ratios of 1.3407 ± 0.0005 and ~ 4.5 % fossil CO₂ in He (Messer AG, Switzerland) were used as standards.

In this study, original AMS measurements are reported in terms of fraction modern (F¹⁴C) and molarity of the sampled gas phase (mol ¹⁴C/L gas). The latter unit depends on the experimental conditions, in particular the volume of sampled gas and the addition of carrier (see section 4.2.2). The linear dynamic

range of the ^{14}C measurements with the MICADAS was previously determined and extends over three order of magnitude (i.e. 0.01 - 9.8 pmol $^{14}\text{C}/\text{L}$, which corresponds to 0.06 F ^{14}C - 50 F ^{14}C)¹⁶.

4. Results and discussion

Because CH_4 was anticipated to be the most important ^{14}C -carrying HC produced during alkaline anoxic corrosion of irradiated steel^{18,20}, fossil CH_4 was used as ^{14}C -free standard gas (^{12}C carrier) for the development of the CSRA method. Moreover, N_2 was used to prepare carbon-free gas samples, as it has been added in the reactor phase to maintain anoxic conditions. Preliminary tests were carried out by injecting simultaneously 40 μL fossil CH_4 (i.e. 20 μg stable carbon) via the carrier loop and 500 μL N_2 via the sample loop into the GC, trapping the CO_2 (corresponding to CH_4 oxidised in the oxidation oven) in the sampling loops of the fraction collector and releasing it into the AMS for ^{14}C measurements. Preliminary tests revealed non-reproducible AMS measurements because of too low stable carbon amounts (i.e. < 20 μg), indicating a loss of stable carbon between the GC injector and the gas ion source of the MICADAS. As a consequence, the main devices involved in the transport of the analyte stream were studied in detail with regards to their performance, in particular the degree of efficiency and gas-tightness. These devices comprise the GC-TCD set-up (i.e. injector, oxidation oven, reduction oven, water trap), the fraction collector (i.e. collection valve, sampling loops) and the GIS trap.

4.1. Carbon recovery in the GC-TCD system

4.1.1. Influence of the injection mode

As a result of the preliminary tests, the amount of ^{12}C carrier was increased from 20 μg to 30 μg stable carbon. Subsequent tests were carried out to determine the carbon recovery during GC injection of 30 μg stable carbon in the chemical form of CH_4 via the carrier loop (60 μL) and 500 μL N_2 via the

sample loop. GC injection was carried out in split mode with a splitless time of 1 min. During this time, the split line is closed and the CH_4/N_2 mixture, stored in the glass liner, reaches the GC column. After passing of the splitless time, the remaining gas present in the liner is flushed out through the vent and not subjected to analysis. The effect of the split mode was visible in the TCD signal, which showed cut peaks for both N_2 and CO_2 upon injection with the splitless time of 1 min (Figure 3). Using a splitless time of 2 min, a complete recovery of CO_2 and N_2 was observed and indicated by the presence of complete peaks (Figure 3). Nevertheless, this test showed that the retention time of the two peaks were very close to each other (Figure 3). By using a splitless time of 2 min, HCs could therefore co-elute and their peaks could overlap, making the collection of individual compounds in the sampling loops of the fraction collector impossible. As a consequence, we decided to retain a splitless time of 1 min. The carbon recovery for the chosen injection mode was quantified as 80 % based on the CO_2 peak areas recorded by the TCD with the two different splitless injection times (i.e. 1.62×10^7 a.u./min for the splitless time of 2 min and 1.29×10^7 a.u./min for the splitless time of 1 min).

Figure 3: N_2 and CO_2 peaks obtained at splitless injection times of 2 min (solid line; CO_2 peak area recorded by TCD = 1.62×10^7 a.u./min) and 1 min (broken line; CO_2 peak area registered by TCD = 1.29×10^7 a.u./min). The difference in the intensities of the N_2 and CO_2 peaks is due to the different concentrations injected and the different TCD sensitivities for the two molecules.

4.1.2. Efficiency of the oxidation oven

Injections of CH₄ were carried out with the oxidation oven switched off (T = 400 °C) and on (T = 1000 °C) to test the efficiency of the oxidation process (Figure 4a). For this purpose, injections of 30 µg C (as fossil CH₄) via the carrier loop (60 µL) and 500 µL N₂ via the sample loop were performed. With the oxidation oven set off, N₂ and CH₄ were detected by the TCD at almost the same retention time, i.e. N₂ between 3 and 3.5 min and CH₄ between 3.5 and 4.5 min, and co-eluted (Figure 4a). Note that the injection of 500 µL N₂ and 30 µg C did not allow us to verify if all the CH₄ was fully converted to CO₂ by the oxidation oven (Figure 4b). However, it was possible to distinguish the smaller peak of CH₄ from the bigger one of N₂ if a lower amount of N₂ was injected (i.e. 50 µL instead of 500 µL) (Figure 4a). As a consequence, He, which is not detected by the TCD, was used instead of N₂. Only one major peak was recorded by the TCD between 5.0 and 5.7 min after injection of 30 µg C and 500 µL He when the oxidation oven was operated in normal conditions (T = 1000 °C). This peak corresponds to CO₂. No other peak was present between 3.5 and 4.5 min, corresponding to the retention time of the non-oxidised CH₄ (Figure 4a). Thus, the entire amount of 30 µg C injected in the chemical form of fossil CH₄ into the GC was oxidised to CO₂ in the oxidation oven.

The efficiency of the oxidation oven was also checked at higher carbon loadings. To this end, 50 µg C as fossil CH₄ was injected via the carrier loop (100 µL) simultaneously with 500 µL He via the sample loop. Only one peak of CO₂ was observed at a retention time between 4.9 and 5.7 min, while the CH₄ peak was absent (3.5 to 4.5 min retention time) (Figure 4b), indicating complete oxidation of 50 µg C into CO₂. An additional injection was realised by loading 50 µg C as fossil CH₄ and 500 µL N₂ (instead of He) into the carrier and sample loops, respectively, to simulate oxidation of a gas sample from the corrosion experiment (N₂ atmosphere). The two CO₂ peak areas obtained between 4.9 and 5.7 min were identical for both injections with values of 2.220×10⁷ a.u./min and 2.223×10⁷ a.u./min, respectively (Figure 4b), thus proving 100 % efficiency of the oxidation oven under conditions representing a gas sample collected from the reactor.

Figure 4: Performance of the oxidation oven. a) TCD signal recorded by injecting 30 μg C as fossil CH_4 . Solid line: injection of 30 μg C (60 μL loop) and 50 μL N_2 with the oxidation oven switched off ($T = 400^\circ\text{C}$). Dashed line: injection of 30 μg C and 500 μL He with the oxidation oven switched on ($T = 1000^\circ\text{C}$). b) Test of the efficiency of the oxidation oven at 1000°C , by injecting 50 μg C (100 μL loop) as fossil CH_4 . Solid line: TCD signal due to injection of 50 μg C and 500 μL of He. Dashed line: injection of 50 μg C and 500 μL N_2 . c) TCD signal by injecting 60 μg C as fossil C_2H_6 . Dashed line: injection of 60 μg C and 500 μL He with the oxidation oven off. Broken line: injection of 60 μg C and 500 μL He with the oxidation oven operated at reduced temperature ($T = 700^\circ\text{C}$). Solid line: TCD signal after injection of

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304 60 μg C and 500 μL He with the oxidation oven on. d) Capacity of the oxidation oven at 1000 $^{\circ}\text{C}$. Black
305 full circles: CO_2 peak areas obtained by subsequently injecting 50 μg C as fossil CH_4 with 500 μL He.
306 Grey full circles: CO_2 peak areas obtained by subsequently injecting 60 μg C as fossil C_2H_6 with 500 μL
307 He. Black empty squares: CH_4 peak areas obtained by subsequently injecting 50 μg C as fossil CH_4 with
308 500 μL He with the oxidation oven switched off. e) CO_2 peak areas (oxidised CH_4) as a function of the
309 amount of C injected.

310 The conversion of a second HC (i.e. C_2H_6) into CO_2 by the oxidation oven was additionally tested. For
311 this purpose, 60 μg C as fossil C_2H_6 and 500 μL He were injected via the carrier and sample loops,
312 respectively, with the oxidation oven switched off ($T = 400\text{ }^{\circ}\text{C}$), operated at reduced temperature ($T =$
313 $700\text{ }^{\circ}\text{C}$) and switched on ($T = 1000\text{ }^{\circ}\text{C}$) (Figure 4c). The oxidised and un-oxidised forms of C_2H_6 obtained
314 with the oxidation oven on and off were separated by only 0.1 min retention time (Figure 4c). Co-
315 elution (i.e. double peak) of the two forms can be illustrated in case of partial oxidation at $700\text{ }^{\circ}\text{C}$. In
316 case of incomplete oxidation of C_2H_6 at $T = 1000\text{ }^{\circ}\text{C}$, we would expect a double peak, a shorter
317 retention time and a reduced peak height of the oxidised C_2H_6 . The absence of a double peak and a
318 high TCD signal at $T = 1000\text{ }^{\circ}\text{C}$ therefore suggests complete oxidation of 60 μg C as fossil C_2H_6 into CO_2 .

319 The capacity of the oxidation oven is limited and therefore regular regeneration of the catalysts was
320 required to ensure optimal conditions during oxidation. The limit of capacity was determined by a
321 series of consecutive injections with 50 μg stable carbon as fossil CH_4 and 500 μL He. We anticipated
322 that the appearance of a small peak of CH_4 between 3.5 and 4.5 min retention time in addition to the
323 one of CO_2 normally observed between 5.0 and 5.7 min retention time indicates the limit of capacity
324 of the oxidation oven. However, it was not possible to detect any CH_4 peak, even after injecting more
325 than 2500 μg C (data not shown). Nevertheless, a decrease of the CO_2 peak areas was observed after
326 the injection of 600 μg C into the GC, which corresponds to a capacity of 480 μg C by taking into
327 account the 80 % efficiency of the chosen injection mode (Figure 4d). As previously shown, a decrease
328 of the TCD signal and therefore the peak area might be an indication of incomplete C oxidation. This

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decrease in the peak area cannot be attributed to the TCD because 50 μg C (as fossil CH_4) injections were realised with the oxidation oven off ($T = 400^\circ\text{C}$) throughout this test and showed identical peak areas (Figure 4d). The capacity was further determined by conducting a series of consecutive injections with 60 μg C as fossil C_2H_6 and 500 μL He. The same trend in the CO_2 peak areas was observed as for CH_4 , confirming the limit of capacity of the oxidation oven at approximately 600 μg injected C (i.e. effective 480 μg C). For trapping a compound, typically seven injections were realised leading to a maximum loading of ~ 280 μg C. We therefore decided to regenerate the catalyst after trapping one single HC in the seven loops of the fraction collector.

By displaying the CO_2 peak area detected by the TCD as a function of the increasing amounts of injected C relevant to this study (i.e. 20, 30, 40, 50, 60 and 100 μg C), a linear increase is finally visible (Figure 4e) in accordance with complete oxidation of HCs at $T = 1000^\circ\text{C}$.

After the oxidation oven, the analyte stream passes through the reduction oven and the water trap, removing traces of O_2 , NO_x and residual water. Then, it reaches a second short GC column for a better separation of oxidised (i.e. CO_2) from non-oxidised compounds (i.e. N_2) (Figure 1). These parts of the GC-TCD set-up should not be responsible for any carbon loss, except in case of leakage. The efficiency of the reduction oven and the water trap was tested by connecting a non-dispersive infrared (NDIR) detector (detecting only CO_2) to the GC-system after the TCD and injecting 50 μg C as fossil CH_4 and 500 μL N_2 with the reduction oven switched off ($T = 50^\circ\text{C}$) and on ($T = 650^\circ\text{C}$). The two CO_2 peaks, resulting from the oxidation of CH_4 with the oxidation oven switched on, were similar in shape and size (data not shown). This indicates complete carbon recovery after these two devices.

Gas-tightness of the entire GC-TCD set-up was controlled before each run of analyses. Leakages at the injector and the GC column connections were checked with a He leak detector. In addition, the flow rate measured by means of a flowmeter should be equal to 13.5 mL/min at 50°C at the outlet of the GC column 1 during normal operation.

4.2. CO₂ trapping by the fraction collector

4.2.1. Test of the collection valves

Carbon loss could occur in the collection valve of the fraction collector, which needs to switch on/off correctly in order to allow/block the passage of CO₂ into/from the sampling loops. Gas-tightness of the collection valve was checked by loading the fraction collector loops with CO₂ and measuring the concentration (ppm) after release with a non-destructive infrared (NDIR) detector, making sure that the carrier flow conditions were the same for each test. The NDIR detector was connected to the outlet of the TCD and after the by-pass (loop #1) or one of the sampling loops (loops #2 to #8). The CO₂ peak areas obtained after the TCD and the by-pass of the fraction collector were almost identical with values of 1.11×10⁶ a.u./min and 1.10×10⁶ a.u./min, respectively (Figure 5a). A slightly lower area of the CO₂ peak was determined after loop #2 with a value of 1.06×10⁶ a.u./min, corresponding to 5 % reduction, which is within the uncertainty of the measurements. All the other loops showed a similar behaviour as observed for loop #2. For this reason, only the results for loop #2 are illustrated in Figure 5a. As the three CO₂ peaks areas were almost identical after TCD, by-pass and the loops, we infer that the collection valve is gas-tight.

4.2.2. Gas-tightness of the sampling loops

Gas-tightness of the fraction collector loops was a major requirement to avoid ingress of atmospheric ¹⁴CO₂ and allow for an artefact-free realisation of CSRA for the gaseous carbon compounds. The loops need to be completely gas-tight for at least one day, which was the time lag between sample preparation and injection into the AMS.

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Figure 5: a) CO₂ peak areas registered by the NDIR detector connected after the TCD (dashed line; peak area = 1.11×10^6 ppm/s), the by-pass (solid line; peak area = 1.10×10^6 ppm/s) and the loop #2 (broken line; peak area = 1.06×10^6 ppm/s). b) NDIR signal of released CO₂ after 1 h (dashed line; peak area = 1.34×10^5 ppm/s) and 3 days (solid line; peak area = 1.33×10^5 ppm/s) of storage in loop #2.

Gas-tightness of each loop was checked by loading them with CO₂ and measuring the concentration released after different storage times with the NDIR detector. For this purpose, 20 μ g C (40 μ L) in the chemical form of fossil CH₄ with 500 μ L N₂ was injected into the GC seven times in a row, trapped as CO₂ in the seven loops and released after 1 h of storage. This experiment was repeated by applying a storage time of 3 days. The CO₂ peak areas recorded by the NDIR were compared loop-by-loop for the two experiments (Table 2). The CO₂ peak areas determined after 1 h of storage corresponded to 100 % recovery and the areas obtained for the seven loops were almost identical (Figure 5b; Table 2). Hence, we infer from these results that all loops are gas-tight for a period of at least 3 days. In the loops #5, #7 and #8, the CO₂ recovery after 3 days of storage was slightly higher than 100 % (Table 2). This could be explained by a smaller flow rate of He applied during the release from the sampling loops. Note that the shape of the CO₂ peaks was wider after 1 h of storage than after directly passing through a loop due to gas dispersion (Figure 5 a/b).

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2
3 394 Table 2: CO₂ peak areas registered by the NDIR detector after 1 h and 3 days of storage in the loops. View Article Online
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5 395 The percentage of CO₂ recovery was calculated from the ratio of the CO₂ peak areas measured after 3
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7 396 days of storage to those registered after 1 h.

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Fraction collector loop	Peak area after 1 h storage (ppm/s)	Peak area after 3 days storage (ppm/s)	CO ₂ recovery (%)
#2	1.34×10 ⁵	1.33×10 ⁵	99
#3	1.71×10 ⁵	1.69×10 ⁵	99
#4	1.59×10 ⁵	1.58×10 ⁵	99
#5	1.64×10 ⁵	1.66×10 ⁵	101
#6	1.60×10 ⁵	1.58×10 ⁵	99
#7	1.36×10 ⁵	1.37×10 ⁵	101
#8	1.59×10 ⁵	1.71×10 ⁵	107

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28 398 After all the tests performed with the GC-TCD system, including the fraction collector, we conclude
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30 399 that carbon loss only occurs during injection and the overall recovery of fossil carbon injected via the
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32 400 carrier loop is equal to 80 %. This reduction in recovery is attributed to the splitless time set to 1 min
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34 401 during GC injection. As about 20 µg stable carbon is recommended for reliable ¹⁴C AMS measurements,
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36 402 we decided to use a 100 µL injection loop with a capacity of 50 µg C for the carrier. This should result
37
38 403 in the release of about 40 µg C as fossil CH₄ into the GIS and the AMS. A loop of 100 µL (50 µg C) was
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40 404 chosen in order to compromise on injecting a sufficient amount of ¹²C into the MICADAS and being
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42 405 able to perform the seven injections into the GC-TCD system that are necessary for the trapping of
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44 406 one single compound without exhausting the capacity of the oxidation oven.
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4.3. Validation of the CSRA method

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The CSRA method for HCs was validated by sequentially injecting 50 μg C as fossil CH_4 (100 μL loop) and 500 μL N_2 as sample into the GC, oxidising fossil CH_4 to CO_2 in the oxidation oven and trapping it in the fraction collector loops. The CO_2 was then released into the GIS and the MICADAS for ^{14}C AMS measurements.

The aforementioned recovery tests with the GC-TCD/fraction collector system (section 4.2) have shown that about 40 μg out of the 50 μg C injected should be released into the GIS and subsequently into the MICADAS. As the GIS manometrically measures the amount of CO_2 released into the syringe (Figure 2), it is possible to verify this statement. Only between 18 and 34 μg CO_2 were measured by the GIS, which corresponds to an overall carbon recovery ranging between 36 and 68 % from the GC injection to the AMS detection (Table 3; Run A). These lower values indicate that a portion of stable carbon was lost between CO_2 release from the fraction collector and its injection into the AMS ion source. An insufficient collection time during CO_2 release from the fraction collector loops and trapping by the GIS zeolite trap could explain this reduction in carbon recovery. Nevertheless, it should be noted that the trapping time was properly defined according to the geometry of each loop and the He flow rate applied to purge the CO_2 from the loops into the GIS (i.e. between 150 and 300 s). Another explanation might be the limited efficiency of the CO_2 trap of the GIS to quantitatively recover the CO_2 released from the sampling loops. In any case, by injecting between 18 and 34 μg stable carbon into the MICADAS source, the ^{12}C -related current detected by the Faraday cup was always $> 5 \mu\text{A}$ (Table 3; Run A), which is above the minimum current of $2 \mu\text{A}$ required for robust ^{14}C AMS measurements (LARA, University of Bern). The minimum ^{14}C total counts were 15000 and 150 for samples with $F^{14}\text{C}$ of 1.0 and 0.01, respectively. No further attempts were made to unravel the reason for the reduced carbon recovery in the GIS/AMS system because the ^{14}C measurements were highly reproducible and resulted in a mean value of the background of 0.012 $F^{14}\text{C}$ with a very low standard deviation of 0.008 $F^{14}\text{C}$ (Table 3; Run A).

Table 3: $F^{14}C$ records obtained when 50 μg stable carbon (as fossil CH_4) and 500 μL N_2 were injected into the GC, oxidised to CO_2 , trapped by the sampling loops of the fraction collector and released into the AMS through the GIS. The $F^{14}C$ values were corrected with the AMS blank (fossil $^{12}\text{CO}_2$) at the beginning of each sequence. The weight of carbon injected into the AMS was determined by the GIS manometric system and allowed the calculation of the overall total carbon recovery. The reference $F^{14}C$ value of the modern CH_4 is 1.024 ± 0.003^{29} .

Run	Fraction collector loop	Sample	^{12}C (μA)	$F^{14}\text{C}$	Uncertainties (%)	Carbon injected into the AMS (μg)	Overall carbon recovery (%)
A	-	AMS blank	5.91	0.010	8.3	-	-
B			6.81	0.011	7.6		
A	#2	fossil CH_4	5.72	0.021	8.0	21	42
B			5.15	0.038	7.3	26	52
A	#3	fossil CH_4	6.05	0.011	13.4	18	36
B		modern CH_4	4.76	1.005	1.1	39	78
A	#4	fossil CH_4	5.60	0.003	45.5	34	68
B		modern CH_4	5.67	1.017	1.1	32	64
A	#5	fossil CH_4	5.09	0.029	6.5	27	54
B			5.84	0.035	5.9	32	64
A	#6	fossil CH_4	5.47	0.007	20.3	28	56
B		modern CH_4	5.17	0.997	1.1	31	62
A	#7	fossil CH_4	5.65	0.010	17.4	23	46
B		modern CH_4	6.17	1.023	1.1	24	48
A	#8	fossil CH_4	5.81	0.007	22.1	33	66
B			6.32	0.024	8.9	22	44

To characterise the different $F^{14}C$ signatures of two gas sources and detect a potential cross-contamination during the successive release of samples having different ^{14}C contents, a second test was carried out by injecting 50 μg C as fossil CH_4 (100 μL) / 500 μL N_2 and 50 μg C as modern CH_4 (100 μL) / 500 μL N_2 (Table 3; Run B). Fossil and modern CH_4 were trapped one after the other in different

loops of the fraction collector and released into the AMS. As expected, fossil and modern CH_4 have a distinct F^{14}C signature with an average $0.032 \pm 0.007 \text{ F}^{14}\text{C}$ and $1.010 \pm 0.011 \text{ F}^{14}\text{C}$, respectively (Table 3; Run B). The low standard deviation shows a good reproducibility of the measurements and suggests that no cross-contamination occurred when different ^{14}C contents were successively injected into the AMS (Table 3; Run B). While similar conditions have been applied during sample preparation (i.e. GC separation and fraction collector sampling), the overall carbon recovery measured by the AMS tended to be better in Run B (from 44 to 78 %; Table 3) than Run A (from 42 to 68 %; Table 3). These slight differences could be explained by instabilities of the GIS/MICADAS system and/or by a slightly different He flow passing through the sampling loops while CO_2 was purged into the GIS.

4.4. Analyses of the gas phase from the corrosion experiment

4.4.1. Identification of the HCs

After validation of the CSRA method, the gas phase from the reactor was sampled and analysed after 1114 days (Table 4) and 1252 days (Table 5) of corrosion of the irradiated steel nut specimens. A portion of the total volume of 50 mL gas collected was injected into the GC-MS to identify the stable carbon compounds. Carbon monoxide (CO) and small HCs containing from one (CH_4) to four (C_4H_{10}) carbon atoms were the only volatile carbon compounds formed at detectable concentrations during the alkaline anoxic corrosion of iron¹⁸. As we expected similar compounds to be formed during corrosion of irradiated steel, MS scans were carried out in accordance with the specific ion fragments and retention times of the compounds previously measured¹⁸. After 1114 days of reaction, only CH_4 and C_2H_6 were identified in the gas phase of the reactor. The concentrations of CO and the other HCs were below the LOD of GC-MS in agreement with earlier samplings⁸. Hence, CH_4 was the dominant HC present in the reactor after three years of alkaline anoxic corrosion, while C_2H_6 was only a minor species. We assumed that the concentrations of stable HCs could be an indication for the proportion of ^{14}C -carrying HCs released in the gas phase during the corrosion of irradiated steel.

4.4.2. ¹⁴C AMS measurements of single gaseous compounds

Prior to ¹⁴C analysis, scoping calculations were carried out to estimate the ¹⁴C concentrations in the gas phase of the reactor. In particular, the calculations enabled us to assess whether the expected ¹⁴C concentrations fall in the dynamic range of the AMS (i.e. from ~ 0.06 to ~ 50 F¹⁴C). They were based on the main parameters determining the amount of ¹⁴C released during the corrosion of irradiated steel, i.e. the corrosion rate of steel in alkaline conditions, the time period of corrosion, the surface area and the ¹⁴C content of the two irradiated steel specimens, as well as analytical parameters like the amount of fossil carbon injected in the GC. The corrosion rate was estimated based on the results from the first two years of the experiment⁸. During the first 92 days of reaction, the total organic ¹⁴C concentration in solution (TO¹⁴C) increased in line with a corrosion rate of 20 nm/a. After 92 days, the corrosion rate decelerated to ~ 2 nm/a. Based on these two corrosion rates, the ¹⁴C concentration in the gas phase was estimated to range between 5 and 10 F¹⁴C after 1114 days of reaction, taking into account the dilution of the gas phase by N₂ injection after each sampling. Hence, the ¹⁴C concentrations were expected to be in the dynamic range of the AMS.

The ¹⁴CH₄ samples for CSRA were prepared by injecting 40 µL gas phase of the reactor into the GC via the sample loop without further dilution, simultaneously with 50 µg ¹⁴C-free fossil CH₄ via the carrier loop (100 µL). CH₄ present in the sample plus the carrier were chromatographically separated from the other compounds, oxidised to CO₂ and finally trapped in loops #6 and #7. A fraction modern of ~ 0.45 – 0.50 F¹⁴C after blank correction was determined by AMS (Table 4). ¹⁴C-free fossil CH₄ was in parallel measured as blank by AMS and equal to 0.016 ± 0.005 F¹⁴C (Table 4). F¹⁴C can be converted into different units by using a conversion factor which is considering, among other parameters, the volume of injected gas phase, the amount of stable carbon carrier and the C recovery rate:

$$1 \text{ F}^{14}\text{C} = 1.70 \times 10^{-12} \text{ g } ^{14}\text{C/L} = 122.3 \text{ fmol } ^{14}\text{C/L} = 0.283 \text{ Bq/L} \quad (1)$$

This resulted in a ¹⁴CH₄ concentration of (5.77 ± 0.74) × 10⁻¹⁴ mol/L in the gas phase of the reactor.

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4 495 Interestingly, the ^{14}C AMS analyses resulted in $F^{14}\text{C}$ values that were around 10 to 20 times lower than
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6 496 expected from the scoping calculations (5 - 10 $F^{14}\text{C}$). This finding confirms that no further dilution of
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8 497 the gas was required for the ^{14}C AMS analysis and further that the corrosion rate estimated based on
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10 498 the time dependence of TO^{14}C was too high.

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13 499 In the gas phase, C_2H_6 was identified as stable carbon compound by GC-MS. As the MS chromatogram
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15 500 showed a peak five times smaller than the one of CH_4 , it was assumed that the concentration of $^{14}\text{C}_2\text{H}_6$
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17 501 was proportionally lower. For this reason, the gas sample for the measurement of $^{14}\text{C}_2\text{H}_6$ by AMS was
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19 502 not diluted either. For CSRA of $^{14}\text{C}_2\text{H}_6$, 40 μL gas sample was injected in parallel with 60 μL fossil C_2H_6
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21 503 which corresponds to a total of 60 μg C injected as carrier, taking into account the stoichiometry of
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23 504 C_2H_6 . $^{14}\text{C}_2\text{H}_6$ present in the sample was chromatographically separated from the other compounds,
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25 505 oxidised along with the carrier, and trapped in loops #4, #5 and #6. In addition to the gas sampled
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27 506 from the reactor, blanks with fossil C_2H_6 were also measured by AMS. Similar $F^{14}\text{C}$ values for the C_2H_6
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29 507 blanks (i.e. $0.19 \pm 0.07 F^{14}\text{C}$) and samples (i.e. $0.10 \pm 0.01 F^{14}\text{C}$) were recorded by the AMS (Table 4),
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31 508 indicating that the C_2H_6 carrier was not ^{14}C -free and that, if at all, $^{14}\text{C}_2\text{H}_6$ was only present at trace
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33 509 levels in the gas phase of the reactor. Thus, determination of the $^{14}\text{C}_2\text{H}_6$ was not possible due to the
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35 510 high background (Table 4).

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39 511 Generally, it should be noted that the ^{14}C AMS measurements were reproducible with low standard
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41 512 deviations, which corresponds to errors < 15 % (Table 4). Nevertheless, all measurements were close
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43 513 to the LOD of the AMS (Table 4). Consequently, a larger sample loop of 500 μL volume (corresponding
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45 514 to 250 μg C as CH_4) was tested during the analysis of a second gas sample collected at 1252 days of
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47 515 corrosion (Table 5). With this loop, 12.5 times more carbon was injected into the GC for the
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49 516 preparation of the AMS samples. In the case of $^{14}\text{CH}_4$, this resulted in an order of magnitude higher
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51 517 $F^{14}\text{C}$ values than the ones obtained with the smaller sample loop (i.e. $5.29 \pm 0.15 F^{14}\text{C}$ compared to
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53 518 $0.52 \pm 0.02 F^{14}\text{C}$). A different conversion factor for $^{14}\text{CH}_4$ was obtained by considering the larger volume
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55 519 of the gas phase injected (500 μL instead of 40 μL):
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520 $1 \text{ F}^{14}\text{C} = 1.37 \times 10^{-13} \text{ g }^{14}\text{C/L} = 9.78 \text{ fmol }^{14}\text{C/L} = 0.023 \text{ Bq/L}$

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521 After correction by the blanks, the fraction modern determined by AMS was converted into
522 concentrations which resulted in an average $^{14}\text{CH}_4$ concentration of $(5.10 \pm 0.26) \times 10^{-14} \text{ mol }^{14}\text{C/L}$
523 (Table 5).

524 The results for $^{14}\text{C}_2\text{H}_6$ were similar after injection with the two different sample loops (i.e. 0.13 ± 0.008
525 F^{14}C ; Tables 4 and 5), confirming the relatively high ^{14}C content of fossil C_2H_6 and the very low
526 concentration of $^{14}\text{C}_2\text{H}_6$ in the gas phase of the reactor. However, it was possible to correct the F^{14}C
527 value with the blank in order to calculate the average $^{14}\text{C}_2\text{H}_6$ concentration $(7.88 \pm 1.67) \times 10^{-16} \text{ mol/L}$
528 (Table 5). In this case, the conversion factor for $^{14}\text{C}_2\text{H}_6$ is based on the injected volume of 500 μL and
529 larger volume of the ^{12}C carrier loop (60 μL):

530 $1 \text{ F}^{14}\text{C} = 1.64 \times 10^{-13} \text{ g }^{14}\text{C/L} = 11.74 \text{ fmol }^{14}\text{C/L} = 0.027 \text{ Bq/L}$ (3).

531 During the analysis of the gas sampled at 1252 days of corrosion, two blanks were measured before
532 each sequence and one afterwards in order to determine possible cross-contamination occurring in
533 the GIS and/or MICADAS gas ion source. Blanks of fossil $^{14}\text{CH}_4$ and $^{14}\text{C}_2\text{H}_6$ had an average of $0.043 \pm$
534 $0.024 \text{ F}^{14}\text{C}$ and $0.020 \pm 0.004 \text{ F}^{14}\text{C}$, respectively, before analyses of $^{14}\text{CH}_4$, $^{14}\text{C}_2\text{H}_6$ and total gas. After
535 analyses, the F^{14}C values were only a factor ~ 2 higher (Table 5), suggesting that a very small aliquot
536 of the gas was not completely flushed out from the GIS/MICADAS.

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538 4.4.3. Determination of the total ^{14}C content in the gas phase

539 The total ^{14}C content in the reactor gas phase was determined in order to prove whether other ^{14}C
540 gaseous compounds than $^{14}\text{CH}_4$ and $^{14}\text{C}_2\text{H}_6$ were present at significant concentrations. To achieve this,
541 40 μL or 500 μL gas sampled from the reactor after 1114 and 1252 days of corrosion, respectively,
542 were directly injected into the GC via the sample loop simultaneously with 50 $\mu\text{g C}$ (fossil CH_4) via the
543 carrier loop. Instead of the GC column 1, the mixture passed through a fused silica capillary (Figure 1).

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3 544 All carbon compounds were therefore simultaneously oxidised to CO₂ in the oxidation oven and
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5 545 trapped in one single loop of the fraction collector (here in the loops #4, #5, #6). The average F¹⁴C
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7 546 value of the total gas amounted to 0.51 ± 0.007 F¹⁴C from injection of 40 µL gas collected after 1114
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9 547 days of corrosion, which corresponds to an average ¹⁴C concentration of (5.85 ± 0.15)×10⁻¹⁴ mol/L
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11 548 using the conversion factor (Eq. 1) previously developed for ¹⁴CH₄ (Table 4). F¹⁴C amounted to 5.80 ±
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13 549 0.11 F¹⁴C from injection of 500 µL gas collected after 1252 days of corrosion, equal to (5.61 ± 0.19)×10⁻¹⁴
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15 550 ¹⁴ mol/L using the conversion factor (Eq. 2) previously developed for ¹⁴CH₄ (Table 5). All ¹⁴C AMS
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17 551 measurements showed ¹²C currents above the required 2 µA, an overall carbon recovery > 35 % and
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19 552 low standard deviations of the replicates, revealing the reliability of these results (Tables 4 and 5).
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24 553 For both samplings, the total ¹⁴C concentration in the gas phase agrees within the expected
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26 554 uncertainty (< 15 %) with the ¹⁴CH₄ concentration, revealing that ¹⁴CH₄ is indeed the dominant ¹⁴C-
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28 555 carrying HC present in the gas phase of the reactor. Within a period of about six months, the total ¹⁴C
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30 556 content in the gas phase did not change, i.e. (5.85 ± 0.15)×10⁻¹⁴ mol/L and (5.61 ± 0.19)×10⁻¹⁴ mol/L
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32 557 (Tables 4 and 5), indicating that irradiated steel corrosion in alkaline anoxic conditions is a very slow
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34 558 process. The latter observation is in agreement with results from previous corrosion studies with steel
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36 559 in alkaline solution^{11,12,13,14}, measurements of ¹⁴C concentrations in the gas phase of corroding
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38 560 irradiated steel²⁰ and concentration of HCs observed in corrosion experiments with non-irradiated iron
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40 561 powders^{18,19}.
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Table 4: AMS measurements of the individual ^{14}C -carrying HCs and total ^{14}C in the gas phase of a reactor containing irradiated steel under alkaline anoxic conditions. The gas samples were withdrawn from the reactor after 1114 days of reaction.

Run	Samples	Fossil carbon injected	Fraction collector loop	^{12}C	Carbon reaching the AMS	Overall C recovery	F^{14}C	Uncertainties on F^{14}C measurements	F^{14}C corrected from blanks	$n^{14}\text{C}$	Measured ^{14}C concentration	^{14}C concentration mean value
		(μg)		(μA)	(μg)	(%)		(%)			(mol/L)	(mol/L)
d1114	blank CH_4 -1	50	2	5.7	21	42	0.021	8.0	-	-	-	-
	blank CH_4 -2	50	3	6.1	18	36	0.011	13.4	-	-	-	-
	CH_4 -1	50	6	2.0	37	75	0.504	2.3	0.452	1.77×10^{-18}	5.53×10^{-14}	$(5.77 \pm 0.74) \times 10^{-14}$
	CH_4 -2	50	7	3.1	22	45	0.544	1.9	0.492	1.92×10^{-18}	6.02×10^{-14}	
	blank- C_2H_6 -1	60	2	5.3	21	35	0.267	2.8	-	-	-	-
	blank- C_2H_6 -2	60	3	4.2	26	43	0.130	3.9	-	-	-	-
	C_2H_6 -1	60	4	3.8	21	35	0.111	4.2	< 0	-	-	< LOD
	C_2H_6 -2	60	5	3.8	27	45	0.105	4.4	< 0	-	-	
	C_2H_6 -3	60	6	3.5	25	42	0.085	5.1	< 0	-	-	
	blank CH_4 -1	50	2	4.9	n. m.	n. m.	0.012	16.1	-	-	-	-
	blank CH_4 -2	50	3	4.0	n. m.	n. m.	0.014	14.9	-	-	-	-
	total gas-1	50	4	5.7	25	50	0.507	1.3	0.471	1.84×10^{-18}	5.76×10^{-14}	$(5.85 \pm 0.15) \times 10^{-14}$
	total gas-2	50	5	5.1	31	63	0.513	1.4	0.478	1.87×10^{-18}	5.84×10^{-14}	
	total gas-3	50	6	5.0	30	60	0.523	1.4	0.487	1.91×10^{-18}	5.96×10^{-14}	

"n.m." = not measured; "-" = not calculated. It should be noted that all the values for C_2H_6 are below the background values.

Table 5: AMS measurements of the individual ^{14}C -carrying HCs and total ^{14}C in the gas phase of a reactor containing irradiated steel under alkaline anoxic conditions. The gas samples were withdrawn from the reactor after 1252 days of reaction. “-” = not calculated.

Run	Samples	Fossil carbon injected	Fract. collect. loop	^{12}C	Carbon reaching into AMS	Overall C recovery	F^{14}C	Uncertainties on F^{14}C measurements	F^{14}C corrected from blanks	$n^{14}\text{C}$	Measured ^{14}C concentration	^{14}C concentration mean value
		(μg)		(μA)	(μg)	(%)		(%)			(mol/L)	(mol/L)
d1252	blank CH_4 -1	50	2	4.4	31	62	0.067	6.1	-	-	-	-
	blank CH_4 -2	50	3	3.8	47	94	0.068	6.9	-	-	-	-
	blank CH_4 -3	50	7	4.0	40	80	0.131	3.9	-	-	-	-
	CH_4 -1	50	4	3.8	29	58	5.391	0.9	5.318	2.08×10^{-17}	5.20×10^{-14}	$(5.10 \pm 0.26) \times 10^{-14}$
	CH_4 -2	50	5	4.5	31	62	5.391	0.9	5.322	2.08×10^{-17}	5.21×10^{-14}	
	CH_4 -3	50	6	4.3	31	62	5.085	0.9	5.012	1.96×10^{-17}	4.90×10^{-14}	
	blank- C_2H_6 -1	60	2	4.7	22	37	0.017	8.5	-	-	-	-
	blank- C_2H_6 -2	60	3	4.8	19	32	0.017	8.7	-	-	-	-
	blank- C_2H_6 -3	60	7	5.1	33	55	0.023	7.3	-	-	-	-
	C_2H_6 -1	60	4	4.1	33	55	0.136	2.8	0.070	2.74×10^{-19}	8.23×10^{-16}	$(7.88 \pm 1.67) \times 10^{-16}$
	C_2H_6 -2	60	5	4.9	34	57	0.141	2.6	0.075	2.93×10^{-19}	8.78×10^{-16}	
	C_2H_6 -3	60	6	4.7	34	57	0.123	2.8	0.056	2.21×10^{-19}	6.64×10^{-16}	
	blank CH_4 -1	50	2	5.6	43	86	0.016	16.4	-	-	-	-
	blank CH_4 -2	50	3	3.3	25	50	0.021	9.9	-	-	-	-
	blank- C_2H_6 -1	60	7	7.0	23	38	0.065	5.4	-	-	-	-
	blank- C_2H_6 -2	60	8	5.9	33	55	0.025	8.1	-	-	-	-
	total gas-1	50	4	3.7	31	62	5.681	0.8	5.616	2.20×10^{-17}	5.49×10^{-14}	$(5.61 \pm 0.19) \times 10^{-14}$
	total gas-2	50	5	5.8	34	68	5.787	0.8	5.723	2.24×10^{-17}	5.60×10^{-14}	
	total gas-3	50	6	5.5	33	66	5.939	0.8	5.875	2.30×10^{-17}	5.75×10^{-14}	

The two compounds released to the gas phase of the reactor during alkaline anoxic corrosion of irradiated steel (i.e. CH₄ and C₂H₆) can be perfectly separated by gas chromatography, trapped and released to AMS for ¹⁴C measurements (Figure 6). A comparison with the total ¹⁴C content of the gas phase shows that ¹⁴CH₄ is the major ¹⁴C-bearing compounds in the gas phase of the reactor whereas ¹⁴C₂H₆ is only present at trace level (Figure 6).

Figure 6: Chromatogram showing the two oxidised carbon compounds identified in the gas phase of the reactor and their ¹⁴C concentrations measured by AMS. It should be noted that each peak corresponds to the carbon compound oxidised to CO₂ (i.e. CH₄ at 5 min and C₂H₆ at 11 min retention time) both present in the sample and injected as ¹²C carrier for reliable ¹⁴C AMS measurements.

5. Conclusions

A ¹⁴C AMS-based methodology has been developed and allows the quantification of single ¹⁴C-carrying HCs and the total ¹⁴C content in the gas phase at ultra-low concentrations (femto to pico molar range). The CSRA approach combines chromatographic separation of the ¹⁴C-carrying HCs, their oxidation to ¹⁴CO₂ and ¹⁴CO₂ trapping in the sampling loops of a custom-made fraction collector. The total ¹⁴C content was determined in the same manner while replacing the chromatographic GC column by a

587 fused silica capillary. A 20 % loss of carbon was identified between injection into the GC and trapping
588 by the fraction collector loops due to the relatively short splitless time used. By contrast, the
589 conversion of the HCs (e.g. CH_4 , C_2H_6) into CO_2 by the oxidation oven was quantitative at $T = 1000^\circ\text{C}$
590 (100 % efficiency). The limit of capacity of the oven was reached after oxidation of about 480 $\mu\text{g C}$.
591 Furthermore, the fraction collector loops were found to be gas-tight for a period of at least 3 days.
592 During injection of the gas samples into the GIS and subsequently into the AMS, the overall recovery
593 rate of carbon determined by a syringe of known volume was not always equal to $\sim 80\%$ but varied
594 between $\sim 40\%$ and $\sim 80\%$. This is presumably caused by small variations in the He flow applied
595 during sample transfer or due to partial trapping/release of CO_2 in/from the GIS trap into the AMS.
596 After the method development and implementation, we decided to inject 50 μg stable carbon as
597 carrier via the GC carrier loop in order to be above the AMS threshold of 20 $\mu\text{g }^{12}\text{C}$ for reproducible ^{14}C
598 measurements.

599 The analysis of the carbon compounds in the gas phase produced during the alkaline anoxic corrosion
600 of irradiated steel revealed the presence of two compounds. Methane ($^{14}\text{CH}_4$) is the dominant ^{14}C -
601 carrying carbon compound (on average 5.4×10^{-14} mol/L gas) and ethane ($^{14}\text{C}_2\text{H}_6$) is present at much
602 lower concentration (7.9×10^{-16} mol/L gas). As the total ^{14}C content in the gas phase corresponds to the
603 concentration of $^{14}\text{CH}_4$, it was confirmed as the main ^{14}C -carrying carbon compound in the gas phase
604 of the reactor. The analytical approach reported in this study substantially improves the current
605 knowledge on the ^{14}C speciation during the anoxic corrosion of irradiated metallic waste in a deep
606 geological repository for radioactive waste.

607

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Figure captions

Figure 1: Schematic representation of the chromatographic system and the fraction collector used for sample preparation for CSRA of the ¹⁴C-carrying HCs. The inset on the right shows a picture of the fraction collector.

Figure 2: Scheme of the connection of the fraction collector to the ion source of the AMS via the GIS.

Figure 3: N₂ and CO₂ peaks obtained at splitless injection times of 2 min (solid line; CO₂ peak area recorded by TCD = 1.62×10⁷ a.u./min) and 1 min (broken line; CO₂ peak area registered by TCD = 1.29×10⁷ a.u./min). The difference in the intensities of the N₂ and CO₂ peaks is due to the different concentrations injected and the different TCD sensitivities for the two molecules.

Figure 4: Performance of the oxidation oven. a) TCD signal recorded by injecting 30 μg C as fossil CH_4 . Solid line: injection of 30 μg C (60 μL loop) and 50 μL N_2 with the oxidation oven switched off ($T = 400^\circ\text{C}$). Dashed line: injection of 30 μg C and 500 μL He with the oxidation oven switched on ($T = 1000^\circ\text{C}$). b) Test of the efficiency of the oxidation oven at 1000°C , by injecting 50 μg C (100 μL loop) as fossil CH_4 . Solid line: TCD signal due to injection of 50 μg C and 500 μL of He. Dashed line: injection of 50 μg C and 500 μL N_2 . c) TCD signal by injecting 60 μg C as fossil C_2H_6 . Dashed line: injection of 60 μg C and 500 μL He with the oxidation oven off. Broken line: injection of 60 μg C and 500 μL He with the oxidation oven operated at reduced temperature ($T = 700^\circ\text{C}$). Solid line: TCD signal after injection of 60 μg C and 500 μL He with the oxidation oven on. d) Capacity of the oxidation oven at 1000°C . Black full circles: CO_2 peak areas obtained by subsequently injecting 50 μg C as fossil CH_4 with 500 μL He. Grey full circles: CO_2 peak areas obtained by subsequently injecting 60 μg C as fossil C_2H_6 with 500 μL He. Black empty squares: CH_4 peak areas obtained by subsequently injecting 50 μg C as fossil CH_4 with 500 μL He with the oxidation oven switched off. e) CO_2 peak areas (oxidised CH_4) as a function of the amount of C injected.

Figure 5: a) CO_2 peak areas registered by the NDIR detector connected after the TCD (dashed line; peak area = 1.11×10^6 ppm/s), the by-pass (solid line; peak area = 1.10×10^6 ppm/s) and the loop #2 (broken line; peak area = 1.06×10^6 ppm/s). b) NDIR signal of released CO_2 after 1 h (dashed line; peak area = 1.34×10^5 ppm/s) and 3 days (solid line; peak area = 1.33×10^5 ppm/s) of storage in loop #2.

Figure 6: Chromatogram showing the two oxidised carbon compounds identified in the gas phase of the reactor and their ^{14}C concentrations measured by AMS. It should be noted that each peak corresponds to the carbon compound oxidised to CO_2 (i.e. CH_4 at 5 min and C_2H_6 at 11 min retention time) both present in the sample and injected as ^{12}C carrier for reliable ^{14}C AMS measurements.

Table captions

Table 1: Limits of detection (LOD) and quantification (LOQ) of the GC-MS analysis.

Table 2: CO₂ peak areas registered by the NDIR detector after 1 h and 3 days of storage in the loops.

The percentage of CO₂ recovery was calculated from the ratio of the CO₂ peak areas measured after 3 days of storage to those registered after 1 h.

Table 3: F¹⁴C records obtained when 50 µg stable carbon (as fossil CH₄) and 500 µL N₂ were injected into the GC, oxidised to CO₂, trapped by the sampling loops of the fraction collector and released into the AMS through the GIS. The F¹⁴C values were corrected with the AMS blank (fossil ¹²CO₂) at the beginning of each sequence. The weight of carbon injected into the AMS was determined by the GIS manometric system and allowed the calculation of the overall total carbon recovery. The reference F¹⁴C value of the modern CH₄ is 1.024 ± 0.003²⁹.

Table 4: AMS measurements of the individual ¹⁴C-carrying HCs and total ¹⁴C in the gas phase of a reactor containing irradiated steel under alkaline anoxic conditions. The gas samples were withdrawn from the reactor after 1114 days of reaction.

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