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### The new sample preparation line for radiocarbon measurements on atmospheric aerosol at LABEC

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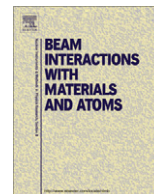
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## The new sample preparation line for radiocarbon measurements on atmospheric aerosol at LABEC

G. Calzolai<sup>a,b,\*</sup>, V. Bernardoni<sup>c</sup>, M. Chiari<sup>b</sup>, M.E. Fedi<sup>b</sup>, F. Lucarelli<sup>a,b</sup>, S. Nava<sup>b</sup>, F. Riccobono<sup>c</sup>, F. Taccetti<sup>b</sup>, G. Valli<sup>c</sup>, R. Vecchi<sup>c</sup>

<sup>a</sup> Department of Physics and Astronomy, Università degli Studi di Firenze, Florence, Italy

<sup>b</sup> INFN (Istituto Nazionale di Fisica Nucleare), Florence, Italy

<sup>c</sup> Department of Physics, Università degli Studi di Milano and INFN, Milan, Italy

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### ABSTRACT

Radiocarbon measurements on the carbonaceous aerosol fractions have been demonstrated as an effective tool for aerosol source apportionment. For these measurements, a new sample preparation facility was installed at the INFN-LABEC laboratory of Florence (Italy). The line was designed to allow the preparation of samples from different carbonaceous fractions: the combustion of the aerosol samples can be performed in helium or oxygen flows, according to thermal sequences. The evolved CO<sub>2</sub> is cryogenically trapped and reduced to graphite, which is the target material for following Accelerator Mass Spectrometry (AMS) <sup>14</sup>C measurements. This preparation line is described in detail in the paper. As a first step, the line was tested by means of AMS measurements performed on standards to check the reproducibility and the accuracy of the system; moreover, preliminary measurements on the total carbon fraction in aerosol samples were made. Results of these measurements are also reported.

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### 1. Introduction

In atmospheric aerosols, carbonaceous particles consist of soot and of a wide variety of organic compounds. Altogether they account for about 40% of the urban aerosol mass, and may be also more abundant depending on the location and the particle size fraction [1]; in Europe, carbon appears to be a major aerosol constituent [2]. Carbonaceous aerosols are thought to play a major role in both the health and the climatic effects of aerosols; however, due to their complexity, the level of understanding and the knowledge of the sources for this aerosol fraction are still very low.

Many organic molecular tracers have been proposed and employed to both identify and quantify carbonaceous aerosols sources but, unfortunately, their reliability often suffers from limited atmospheric lifetimes, due to chemical reactivity, and highly variable emission factors [3]. Radiocarbon, however, guarantees the opportunity of an unambiguous source apportionment of carbonaceous aerosol, as it is absent in fossil fuel combustion emissions.

Radiocarbon (<sup>14</sup>C) is formed in the stratosphere and in the troposphere by nuclear reaction of thermal neutrons (produced by cosmic rays) on atmospheric nitrogen and it decays with a half-life of 5730 years. Living organisms are in equilibrium with the atmo-

sphere and, as a good approximation, have the same radiocarbon concentration. After death, they behave as a closed system and radiocarbon is lost due to decay. Fossil fuels are so old they are radiocarbon-free. Biogenic and biomass burning sources are characterised by a similar radiocarbon concentration to the present atmosphere.

On these bases, a simple two-source model allows the assessment of the fossil and non-fossil contributions.

Radiocarbon measurements on the carbonaceous aerosol sub-fractions (EC, elemental carbon, and OC, organic carbon) allow an improvement in carbonaceous aerosol source apportionment since they permit an unambiguous distinction between the two non-fossil sources, namely the biomass burning and the biogenic source, when the OC/EC emission ratio for biomass burning is known. Therefore, radiocarbon measurements on the carbonaceous aerosol sub-fractions lead to the quantification of the contributions of all the three carbonaceous aerosol sources (i.e., fossil fuel combustion, biomass burning and biogenic source). Actually, the possibility of distinguishing between the contributions of the biomass burning and of the biogenic source leads also to the assessment of the contributions to the aerosol burden in atmosphere from the natural and the anthropogenic sources. This information is necessary to develop pollution abatement strategies and as an input for climate change models [4].

Due to the extremely low <sup>14</sup>C isotopic abundance (the <sup>14</sup>C/<sup>12</sup>C ratio is of the order of 10<sup>-12</sup> in modern samples) and the small

\* Corresponding author at: Via Sansone 1, I-50019 Sesto Fiorentino (Firenze), Italy. Tel.: +39 055 4572273; fax: +39 055 4572641.

E-mail address: [calzolai@fi.infn.it](mailto:calzolai@fi.infn.it) (G. Calzolai).

quantities of carbon normally collected in aerosol samples, these measurements would not be possible without Accelerator Mass Spectrometry (AMS). Since 2004, the INFN-LABEC laboratory of Florence (Italy) has been involved in AMS measurements for radiocarbon dating. The main facility is a 3MV HVEE Tandemtron accelerator (a detailed description of the AMS system is given elsewhere [5]).

In order to be analysed by AMS, radiocarbon samples have to be properly prepared: in our case, they have to be inserted into the ion source of the accelerator as graphite pellets. At LABEC, a sample preparation laboratory for radiocarbon dating had been already developed for medium-size samples (about 600  $\mu\text{g}$  of carbon). However, a new preparation line was needed to fulfil specific requirements for aerosol samples: in particular, it was necessary to develop a system that allowed the separation of the EC and the OC during sample combustion and that was optimised for lower mass samples (down to about 100  $\mu\text{g}$  of carbon). Under the joint efforts of the research groups from Florence and Milan, the single components of this new sample preparation line were first designed and benchmark tested at the Physics Department of Milan and at LABEC, before the final assembly at LABEC. The sample preparation line was designed keeping in mind the final purpose of measuring the radiocarbon content on the separate EC and OC fractions. However, due to both the long time necessary for the sample preparation and the hard work necessary for the assessment of optimal OC/EC separation protocols, we set as a first milestone the test of the line for TC (total carbon) analysis.

Here we provide a comprehensive description of the final set-up of the sample preparation facility for the aerosol samples. Moreover, results are reported from the first TC measurements that were carried out on samples of about 450  $\mu\text{g}$  of carbon. These tests were aimed at fully characterising the line itself, controlling the suitability of the produced samples for AMS measurements and, finally, checking the reliability of the AMS results obtained for these samples.

## 2. Aerosol sample preparation laboratory

The new sample preparation line is designed to perform the four main steps: cleaning of the carrier gases, combustion of the sample, selection and collection of the evolved  $\text{CO}_2$  and finally the conversion of this gas into solid samples (graphitization) for insertion into the AMS source. A schematic representation is shown in Fig. 1.

In order to avoid any contamination, the line is built up with clean materials. In particular, quartz is used in all the “hot” parts of the line (temperatures ranging from 600  $^\circ\text{C}$  up to 900  $^\circ\text{C}$ ); all the other parts (tubes, valve bodies, fittings) are made of 316 stainless steel. The connections between stainless steel parts are made by means of fittings equipped with stainless steel ferrules. The connections to quartz parts are made with Swagelok Ultra-Torr Vacuum fittings whose Viton o-rings were replaced with Kalrez 8900 o-rings, since this elastomer is much more resistant to high temperatures (Kalrez 8900 is certified to have an outgassing rate less than  $2.7 \times 10^{-7}$  mbar l sec $^{-1}$  cm $^{-2}$  up to 290  $^\circ\text{C}$ ).

### 2.1. Cleaning of carrier gases

Helium and oxygen can be used as carrier gases, alternately, to provide the proper atmosphere for the sample combustion, depending on the step of the preparation protocol. Two thermal mass-flow controllers, placed at the entrance of the line, set their flows (never exceeding 100 cc/min during the trapping phase). The carrier gases are supplied by gas cylinders of high-purity helium (99.998%) and oxygen (99.999%). To avoid any possible

contamination, the carrier gases are firstly cleaned by passing them through a CuO catalyst kept at 700  $^\circ\text{C}$ , in order to oxidise any carbonaceous gas to  $\text{CO}_2$ , and then through an irreversible soda lime trap, to adsorb any  $\text{CO}_2$ .

### 2.2. Combustion oven

The combustion oven was made in-house by but-welding two quartz tubes of different diameters and lengths. The wider tube is the so-called “main furnace”, which holds the sample boats consisting of two quartz semi-cylinders where several punches taken by an aerosol sample are suitably located. The second tube is filled with CuO grains in order to ensure a complete combustion. The two tubes are thermally insulated by means of ceramic fibre blankets, so that the catalyst can be kept at the working temperature of 700  $^\circ\text{C}$  while the main furnace is heated according to the chosen thermal program.

The heating of the two tubes is achieved by means of two stainless steel coils wrapped around the tubes themselves. Great care was put into optimising the temperature uniformity along the 11 cm-long zone of the main furnace holding the sample boats, so that differences between the temperatures measured along the tube with a 0.5 cm step and the selected temperature (at 400  $^\circ\text{C}$ ) were always below 3  $^\circ\text{C}$  (Fig. 2). This heating system, coupled with the low thermal inertia of the main furnace, assures that flash heating (about 200  $^\circ\text{C}/\text{min}$ ), necessary to minimise charring [6], can be performed.

Temperature monitoring of the furnace inside is achieved by a K-type (chromel–alumel) thermocouple inserted through the joint that closes the main furnace and is positioned along the main furnace axis, just in the middle of the two sample boats. The connection of the joint to the previous part of the line and to the thermocouple is by means of a Swagelok Ultra-Torr Tee connection.

As far as TC analysis is concerned, the adopted protocol includes a combustion of the sample at 800  $^\circ\text{C}$  for 20 min in a 100 cc/min oxygen flow. The thermal protocols for EC and OC separation have still to be validated.

### 2.3. Purification and collection of the evolved $\text{CO}_2$

In order to transfer only  $\text{CO}_2$  into the graphitization reactor, at the end of the line, the gas flow has to be purified removing all the “undesired” gases, and the  $\text{CO}_2$  has to be collected separating it from the carrier gas flow. To this purpose, the line includes some chemical and thermal traps in the following order: (1) chemical trap for halogens; (2) chemical trap for gaseous sulphur oxides; (3) thermal trap for water vapour and nitrogen dioxide; (4) thermal trap for carbon dioxide collection ( $\text{NO}_2$  and  $\text{CO}_2$  are expected after gases oxidation in the CuO catalyst).

The removal of gaseous sulphur oxides and halogens is achieved by means of two chemical reagents, namely silver vanadate ( $\text{AgV}$ ) and EA-1000 (Perkin–Elmer), respectively, both kept at the working temperature of about 800  $^\circ\text{C}$ . They are placed into the same furnace, separated from one another by quartz wool.

After the removal of halogens and gaseous sulphur oxides, the gas flow still contains not only the  $\text{CO}_2$  but also water vapour,  $\text{NO}_2$  and, obviously, the carrier gas (helium or oxygen). These gases can be separated by means of thermal traps on the basis of their different thermo-dynamical properties: in Table 1, phase change temperatures at 1 atm pressure are listed for water,  $\text{CO}_2$ ,  $\text{O}_2$ , He and  $\text{NO}_2$  (the thermal traps in the line work at slight over-pressure with respect to the ambient atmospheric pressure, so the quoted temperatures are indeed representative). Looking at the table, it is clear that the first thermal trap, working at a temperature of about 215 K, surely removes both water vapours and  $\text{NO}_2$  without

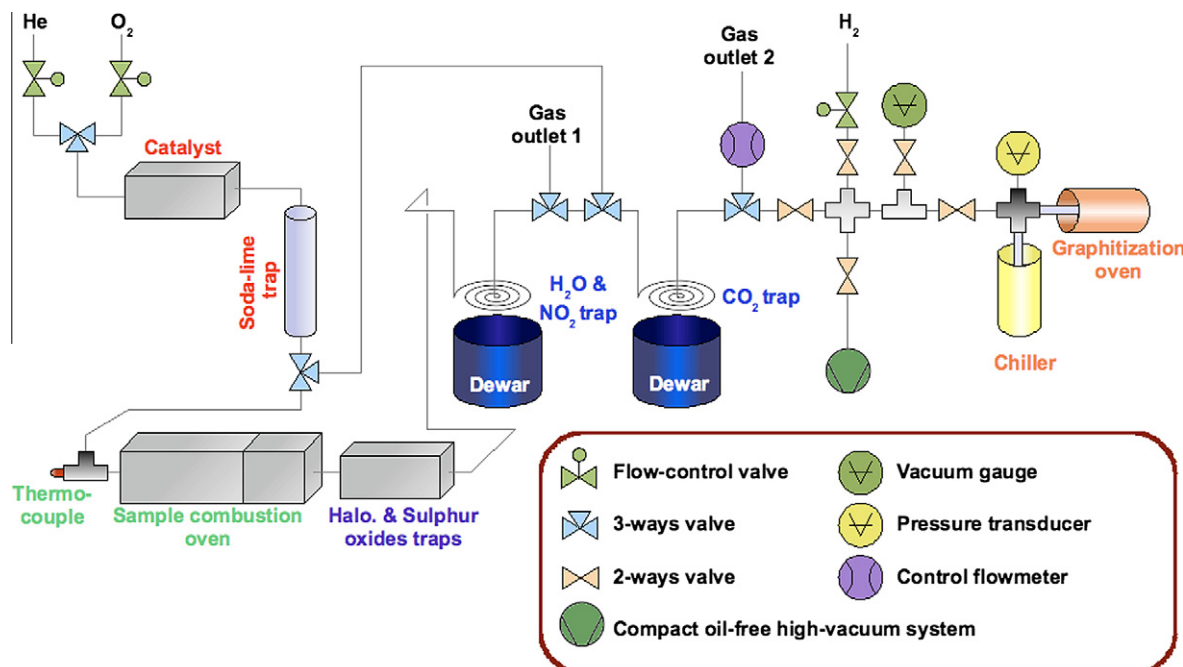


Fig. 1. Schematic diagram of the new sample preparation line for AMS measurements on aerosol samples installed at INFN-LABEC.

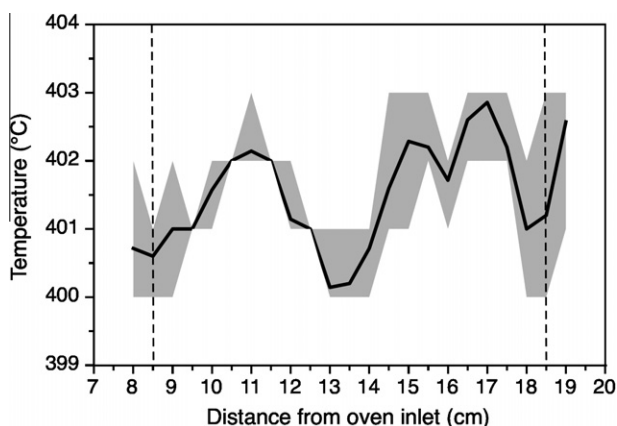


Fig. 2. Temperature uniformity in the combustion oven. The line represents the average value obtained during repeated tests, while the grey area spans minima-maxima temperatures measured. The vertical dashed lines mark the region where the punches taken from the aerosol sample are positioned.

Table 1

Phase change temperatures at 1 atm pressure for water, CO<sub>2</sub>, O<sub>2</sub>, He and NO<sub>2</sub>.

Gas	Melting temperature (K, at 1 atm)	Sublimation temperature (K, at 1 atm)	Boiling temperature (K, at 1 atm)
H <sub>2</sub> O	273.15	–	373.2
NO <sub>2</sub>	262.0	–	294.2
CO <sub>2</sub>	–	194.4	–
O <sub>2</sub>	54.8	–	90.2
He	–	–	4.2

trapping the CO<sub>2</sub>, while the second trap, working at about 115 K, meets the requirement of trapping the CO<sub>2</sub> but not the carrier gas (either He or O<sub>2</sub>).

These thermal traps, developed from a prototype devised at the Physics Department of Milan, utilise the temperature gradient in a

dewar between the LN<sub>2</sub> surface (at 77 K) and the top (at ambient temperature). Provided that the dewar is deep enough for the temperature gradient to be sufficiently low to allow a good temperature resolution, it is possible to make a thermal trap working at the desired temperature by positioning a coil at the proper depth into the dewar. In order to get a uniform temperature inside it, the coil was made bending a stainless tube to obtain a flat spiral; as the coil is connected to the line, the distance between the spiral and the liquid nitrogen can be regulated by lifting up and down the dewar with a properly controlled elevator. A resistive thermal device (PT100), connected to the spiral, allows us continuously monitoring the temperature: when a slight change with respect to the settled temperature is observed, the relative position of the dewar is adjusted in order to re-establish the desired temperature.

Before installing it in the sample preparation line, the CO<sub>2</sub> trap efficiency was verified using a Thermal Gravimetric-Infrared Analysis (TGA-IR) instrumentation by Perkin-Elmer, available at the Chemistry Department of the University of Milan. A known carbon quantity was combusted and cryogenically trapped, verifying by the IR system that, during the trapping phase, no CO<sub>2</sub> was detected. Then, the CO<sub>2</sub> trap was heated and the released CO<sub>2</sub> was measured by the IR detector (Fig. 3). The released CO<sub>2</sub> was 98 ± 3% of the expected value.

#### 2.4. Graphitization

The last part of the line (called “graphitization line”) is devoted to the conversion from gaseous CO<sub>2</sub> into solid graphite; unlike the upstream parts of the line working with a gas flow, this last section works at lower pressure (10<sup>−4</sup> mbar). The graphitization line is equipped with a compact oil-free high-vacuum system, to avoid possible pumping-oil contamination.

Before connecting the CO<sub>2</sub> trap to the graphitization line, the CO<sub>2</sub> trap is filled with He, cooled down to LN<sub>2</sub> temperature and then evacuated. LN<sub>2</sub> temperature ensures that no CO<sub>2</sub> sublimation occurs during evacuation (CO<sub>2</sub> sublimation temperature at 2 × 10<sup>−4</sup> mbar is 100 K [7], about 23 K higher than LN<sub>2</sub> temperature).

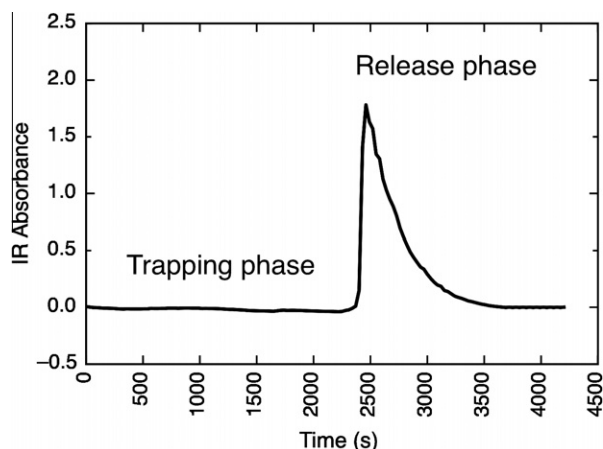
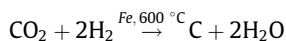


Fig. 3. IR CO<sub>2</sub> signal during trapping (no signal variation) and release (peak signal) phases.

Once the trap is evacuated, the CO<sub>2</sub> is cryogenically moved from the trap to the graphitization line.

CO<sub>2</sub> is reduced to graphite according to the well-known Bosch reaction (e.g., [8,9]):



The core of this part of the line is the graphitization reactor, which is based on a Swagelok Ultra-Torr ¼ Tee union, modified to connect a pressure transducer. It is connected to the upstream line at one side and houses two quartz vials into the other two connections.

The reaction vial is heated to 600 °C in an oven; the second vial is cooled to –30 °C by a Peltier chiller and acts as a “cold-finger”, where the water produced during the reaction is cryogenically trapped.

The H<sub>2</sub> for the reaction is supplied by a gas generator, producing 99.999% pure H<sub>2</sub> by hydrolysis of ultra-pure water. Iron powder (Alfa Aesar®, 99.9+%, <10 μm) is used as catalyst; it is pre-treated by heating for 30 min at 600 °C in vacuum and subsequently at 350 °C in H<sub>2</sub> at 800 mbar for 30 min.

A low-vacuum capacitive pressure transducer placed on the upper part of the reactor allows the monitoring of the pressure trend during reaction: pressure settling on a constant value gives the indication that gases inside the graphitization chamber will not react further.

Finally, the iron powder coated by graphite is pressed into aluminium capsules to be inserted into the accelerator ion source for radiocarbon measurements.

### 3. Efficiency of the sample preparation line

Before working with real aerosol samples, a full characterisation of the line was carried out, including an evaluation of the efficiency of the sample preparation line and a check of the reliability of the sample preparation procedure (see Section 4).

The efficiency of the sample preparation line can be evaluated as the ratio between the produced graphite mass and the carbon quantity introduced into the combustion oven.

This efficiency obviously includes the efficiencies for every single process, such as combustion, trapping, transfer and graphitization.

In order to exclude any possible dependence from the sample material, the topic of the efficiency was investigated not only by the combustion of a standard reference material, namely NIST 4990C (hereinafter HOxII), but also taking some data for samples

from “dead” graphite (Alfa Aesar graphite powder, 200 mesh, 99.9999%) and from aerosol loaded quartz-fibre filters. The carbon content of aerosol samples and HOxII had been previously estimated by means of thermal–optical analysis [10].

Samples were converted to graphite according to the protocol developed for TC analysis (see Section 2.2). The mass of the produced graphite was obtained by the difference between the final mass of the vial containing the graphite coated iron powder and the initially measured masses of the vial and the iron powder, using an analytical balance with a precision of 0.02 mg.

We prepared 12 HOxII, four dead graphite and five aerosol samples. The overall efficiency (as obtained averaging the efficiencies measured for all samples) resulted to be  $1.00 \pm 0.09$  for the preparation of HOxII samples,  $1.04 \pm 0.06$  for the graphite samples and  $1.05 \pm 0.07$  for the aerosol samples. All these data are consistent with a 100% efficiency within their uncertainties.

## 4. First tests at the LABEC AMS facility

In order to verify the reliability of the sample preparation procedure with the new sample preparation line, several cathodes (i.e., graphite samples pressed inside capsules to be inserted into the AMS ion source), all having the same size (about 450 μgC), were produced and analysed by AMS. Samples were prepared by matching the samples and standards size: using this method, it is possible to compensate effectively for machine and chemistry induced isotopic fractionation [11,12].

In total 20 cathodes were prepared according to the protocol for TC analysis: 13 samples from HOxII, which were used to check the reproducibility of the results; three cathodes from “dead graphite” samples (Alfa Aesar graphite), which were analysed to investigate the background of our measurements; four cathodes from the C7 reference material by IAEA (International Atomic Energy Agency), which were employed to check the accuracy of the attained results.

Measurements lasted until collecting at least 40000 <sup>14</sup>C counts on each HOxII cathode; all the samples were measured for the same time.

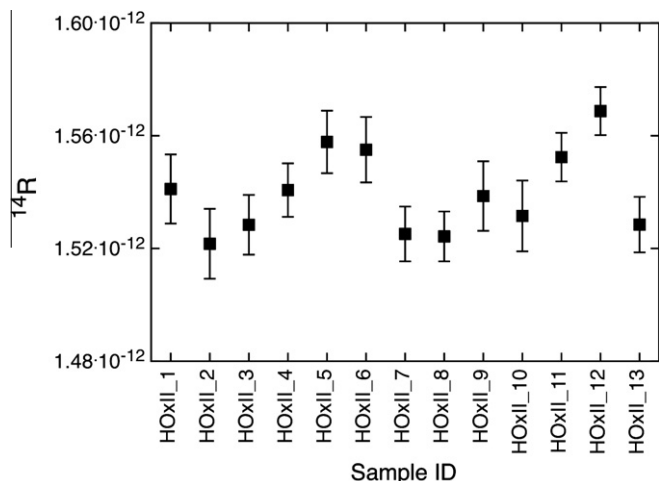
### 4.1. Reproducibility

The reproducibility was tested on the HOxII standards. The average <sup>14</sup>R ratios (i.e., the measured <sup>14</sup>C/<sup>12</sup>C ratios) of all standard samples, calculated over all the measured batches, are shown in Fig. 4. The reproducibility is evaluated as the ratio between the standard deviation of the mean ( $\sigma^{\text{mean}}$ ) and the averaged isotopic ratio ( $R_{\text{av}}$ ) over all the measured standards. As far as the <sup>14</sup>R is concerned, the measured  $^{14}R_{\text{av}}$  and  $\sigma_{14}^{\text{mean}}$  were  $1.5395 \times 10^{-12}$  and  $0.0041 \times 10^{-12}$ , respectively; thus, the evaluated reproducibility ( $\sigma_{14}^{\text{mean}}/^{14}R_{\text{av}}$ ) was 2.7‰. Analogously, for <sup>13</sup>R (i.e., the measured <sup>13</sup>C/<sup>12</sup>C ratio) we measured a  $^{13}R_{\text{av}}$  of  $1.1832 \times 10^{-2}$  and a  $\sigma_{13}^{\text{mean}}$  of  $0.0023 \times 10^{-2}$ , and, thus, a reproducibility ( $\sigma_{13}^{\text{mean}}/^{13}R_{\text{av}}$ ) of 2.0‰. In conclusion, the overall reproducibility of sample preparation and sample AMS measurement is very satisfactory, being better than 3‰ for both <sup>13</sup>R and <sup>14</sup>R.

### 4.2. Background

Although the background contribution in aerosol source apportionment is much less critical than in radiocarbon dating, it is important to keep this aspect under control. Therefore, three cathodes from Alfa Aesar graphite were prepared and analysed.

The measured average background level is  $(0.43 \pm 0.03)$  pMC (percent of Modern Carbon) and it does not represent a limitation for our measurements. In fact, the expected minimum radiocarbon concentration values are the ones that can be measured in the EC

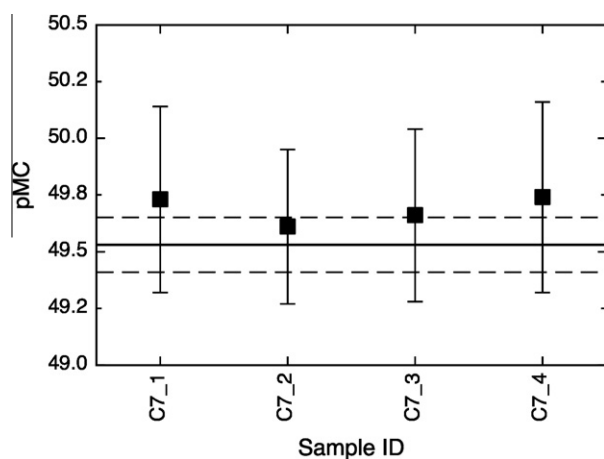


**Fig. 4.** Average  $^{14}\text{R}$  ratios (i.e., the average of the raw measured  $^{14}\text{C}/^{12}\text{C}$  isotopic ratios) measured for all the HOxII standards; error bars represent the standard deviation of the mean over the performed batches.

fraction of an aerosol sample collected at an urban site (i.e., with fossil sources dominating). In this case, radiocarbon values are expected to be about one order of magnitude higher than the background value reported above. For example, a study on particulate matter collected in Göteborg reported radiocarbon concentrations in the range 5–17 pMC for the EC fraction at an urban site, rising up to 35 pMC for a rural site, while radiocarbon concentrations in the OC fraction were always higher than 50 pMC [13].

#### 4.3. Accuracy test

The attainable accuracy of both sample preparation and measurement was tested by means of some cathodes prepared from the C7 reference material provided by IAEA, i.e., oxalic acid with  $\text{pMC} = 49.53 \pm 0.12$  [14]. After background subtraction, the measured  $^{14}\text{C}/^{12}\text{C}$  ratios were corrected for isotopic fractionation according to the  $^{13}\text{C}/^{12}\text{C}$  ratios also measured in the accelerator and were normalised to the isotopic ratio measured for the HOxII standards (see for example [15]). Results are summarised in Fig. 5, where the certified concentration is also reported for comparison. As can be seen, our results are fully consistent with the reference value.



**Fig. 5.** Measured radiocarbon concentrations for samples from IAEA C7; certified concentration and  $\pm 1$  sigma uncertainty are shown with continuous and dashed lines, respectively.

#### 4.4. First tests on aerosol samples

Preliminary TC measurements on atmospheric aerosol samples were also carried out. Aerosol samples were collected at an urban background monitoring station of the Environmental Protection Agency of Lombardy Region (Milano-Pascal) in Milan. The sampling period (5–16 July 2008) was meteorologically variable as stable-sunny days and rainy days alternated. However, typical summer temperatures were registered, with daily maximum temperatures in the range 26–30 °C and minima in the range 15–19 °C. PM10 was sampled on Munktell quartz-fibre filters (15 cm diameter) with 24–48 h resolution using a sequential Digital high volume sampler. PM10 levels were in the range 11–37  $\mu\text{g m}^{-3}$  during the sampling period.

The carbon load on the filters was evaluated by thermal–optical measurements; 12  $\div$  15  $\text{cm}^2$  of loaded filter, containing about 450  $\mu\text{g}$  of carbon, were burnt for each sample. Samples were prepared according to the protocol developed for TC analysis (see Section 2.2). The results obtained on three samples were  $67.3 \pm 0.6$ ,  $53.7 \pm 0.4$ ,  $52.2 \pm 0.7$  pMC. These preliminary results are scarcely significant as far as aerosol monitoring is concerned but are important as first tests on aerosol samples since they are comparable to the fraction of contemporary carbon found in other studies [16,17].

#### 5. Summary and perspectives

The new aerosol sample preparation facility, including new technical solutions for sample combustion and  $\text{CO}_2$  separation, was installed and tested. In the light of the reported results, we can state that the system is now reliable for TC measurements.

First tests indicated that the graphitization of samples down to about 110  $\mu\text{g}$  of carbon is possible with the new graphitization line. AMS measurements on these samples were very encouraging in terms of reproducibility and accuracy of the results. However, these results have to be regarded as very preliminary. Further efforts are needed to analyse smaller samples.

It is worth recalling that the sample preparation line is already optimised for the future EC/OC separation. Studies on thermal protocols for fraction separation are in progress and, obviously, the next step of this work will consist in testing and validating of such protocols.

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