

Development of a preparation system for the radiocarbon analysis of organic carbon in carbonaceous aerosols in China

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ABSTRACT

Carbonaceous aerosols comprising a large fraction of elemental carbon (EC) and organic carbon (OC) are considered to affect both global climate and human health. Radiocarbon measurements have been proved to be a useful isotopic tracer for distinguishing contemporary and fossil emissions. An optimized system of a two-step thermal preparation system for radiocarbon (¹⁴C) measurement of OC/TC is firstly established in China. In this system, OC/TC are converted into carbon dioxide under a pure oxygen flow at 340 °C/650 °C and then reduced to graphite for AMS target using the method of zinc reduction. Afterwards, radiocarbon measurements of the targets performed by the NEC Compact AMS System at the Institute of Heavy Ion Physics, Peking University. The measured results for estimated reference material including HOx I, HOx II and IAEA-C6 are consistent with internationally accepted values. The radiocarbon-based source appointment of carbonaceous aerosols in China would be much more convenient and faster with the preparation system developed in this work.

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1. Introduction

Carbonaceous aerosols are of worldwide concern due to effects on climate and air quality [1]. Carbonaceous particles mainly consist of weakly refractory and light polycyclic or polyacidic hydrocarbons (organic carbon, OC) and strongly refractory and highly polymerized (elemental carbon, EC), which is also designated as black carbon in urban, rural and remote areas [2,3]. Particulate EC derives from incomplete combustion of fossil fuels and biomass, whereas OC originates from either primary emissions or secondary organic (SOC) formation [4].

There is a large uncertainty about detailed apportionment and quantification of its sources due to the large number of sources and chemical compounds associated with the aerosols. Based on the amount of radiocarbon (¹⁴C) expressed in a unit of percent modern carbon (pMC) or fraction of modern (f_m), ¹⁴C has been proposed a unique and promising tracer to quantitative dissection between fossil and biomass origins, which may be used for source apportionment of biogenic and anthropogenic emissions [5]. It should be noted that ¹⁴C of total carbon (TC) from aerosols will

not provide complete or comprehensive information on the emission sources the formation process, since OC and EC do not originate from the same processes. Therefore, they often show very different ¹⁴C signatures [6,7]. The radiocarbon compositions in carbonaceous aerosols have been reported previously [8–10], including measurements for TC, as well as OC and EC. Due to the lower content of carbon in aerosol samples and complicated process of sample pre-treatment, little research has been done in China. For our knowledge, pMC or f_m values in TC have been reported for only few cities such as Beijing, Shanghai and Lhasa [11,12] in China; however, there has been no research on pMC for OC and/or EC in aerosols so far. For ¹⁴C determination in some fractions of aerosols, it is necessary to have a sophisticated preparation system including sample pre-treatment line and graphitization line. Until now there is no such a specialized pre-treatment system for ¹⁴C determination of OC/EC fractions in aerosols mainly due to technical problems.

The objective of the study described here was to establish a “clean-chemistry” thermal processing techniques and a preparation system for trapping CO₂ from OC fraction and/or TC for their ¹⁴C measurement in China. The system is similar to the THEODORE which originally developed at the University of Berne in Switzerland [13,14]. Due to various AMS systems, it was necessary to adjust some parameters in this preparation system to perform ¹⁴C analyses in AMS system at Peking University (PKUAMS).

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2. Experimental and methods

2.1. Combustion and separation

The presented method for the separation of OC from EC and other components of the carbonaceous particles bases on that OC and EC fractions can be thermally extracted at different temperatures [15] and under pure O₂ atmosphere [13,14,16]. Fig. 1 shows the instrument apparatus: two-step thermal separation and trapping system for OC used in this work, which is similar to that originally developed at the University of Bern, Switzerland [13]. To prevent any carbon contamination into the system due to the carbon containing atmosphere gas diffusion from outside [14,17], all units of instrument were made of stainless steel, quartz or glass.

The method involves thermally controlled oxidation of carbonaceous particles to CO₂, cryogenically trapping, followed by manometrically quantification in a calibrated volume and sealing into the tubes. The combustion unit consist of two tube ovens (WATLOW®, USA) in series, through which passes an 18.2 mm ID quartz tube, where OC and TC are oxidized to CO₂ at temperatures of 340 °C and 650 °C in a pure oxygen stream, respectively, as several studies suggested [13,14,18]. The temperature inside the oven was calibrated against a thermocouple. Several punches of quartz filters can be placed on a moveable quartz boat (40 mm × 15 mm) with a thermal couple inside which was transported into the different temperature zones and to measure the actual reaction temperature.

In detail, OC is oxidized to CO₂ under a stream of pre-cleaned oxygen pure analytical grade O₂ (99.999%, 30 ml/min) during the pre-combustion step at 340 °C for 15 min. Before the OC is oxidized, the sample is first positioned in the 650 °C oven for about 45 s flash heating, as suggested by Lavanchy et al. [13]. This flash heating has the advantage of minimizing pre-combustion charring [19,20], since it reduces pyrolysis of OC [13]. A total conversion of incomplete combustion products (e.g., CO), is catalytically oxidized to CO₂ by a CuO₂ catalyst at 850 °C in a third oven. To obtain TC, the sample was combusted under a stream of oxygen at 650 °C for 20 min. The thereby resulting CO₂ was used for TC analysis. Evolving water vapor was removed by a dry liquid N₂ (LN₂)/ethanol trap (approximately -70 °C). The CO₂ formed by the combustion of OC or TC, respectively, was cryogenically trapped using an LN₂ trap (approximately -160 °C), whereas excess oxygen was exhausted by several expansions into a vacuum volume until a pressure of 10⁻³ bar was reached. The resulting CO₂ volume was finally quantified manometrically in a calibrated volume. Additionally a 2–5% aliquot of CO₂ was separated in an evacuated glass ampoule for subsequent IRMS analysis of δ¹³C (Section 2.2), before remaining CO₂ was finally sealed in a quartz ampoule for further reaction to the filamentous carbon and AMS analysis of ¹⁴C as described in Section 2.3.

2.2. Target preparation and AMS measurement

Preparation of graphite targets for AMS analysis from converting CO₂ was completed by the graphitization line at the Guangzhou Institute of Geochemistry, Chinese Academy of Science with the sealed tube zinc reduction method [21]. Briefly, the CO₂ was reduced to graphite at 600 °C using zinc with iron (200 mg, Alfa Aesar, 1.5–3 mm, 99.99%) catalyst. ¹⁴C analyses were carried out at the updated PKUAMS facility, which sensitivity was less than 6 × 10⁻¹⁵ and the precision and accuracy of ¹⁴C measurement for the samples was better than 0.5% [22,23]. δ¹³C were determined by mass spectrometer (DELTA plus XL, Finnigan Company), each sample was measured twice with the uncertainty less than 0.1‰. The ¹⁴C values are reported as fraction of modern (also as *f_m*) after correction by δ¹³C values with an average uncertainty of ±5‰.

2.3. Standards

For the preparation of blank and standard samples, quartz fiber filters (Whatman® Type GF/F QM-A Quartz Filters) were pre-baked in a furnace at 650 °C for 5 h and stored in a vessel coated with aluminum foil. Standards for the detection of OC were obtained by dissolution of analytical grade sucrose and oxalic acid in pure water (Millipore, Milli-Q, 18M), and by pipetting a known volume of these standards onto pre-heated quartz filter. For validation of the thermal separation, Chinese Sucrose Charcoal Standard which is stemming from pyrolyzation of sucrose [24] was mixed with organic compounds in filters. NBS oxalic acid I (HOx I), NBS oxalic acid II (HOx II) and ANU sucrose (IAEA-C6) were the radiocarbon standards for OC in this study.

3. Results

3.1. Separation and recovery

Several studies claimed 340 °C as optimum for the separation of OC in an oxygen flow [13]. The relationship between *f_m* and temperature for OC separation in the Theodore was investigated by Szidat et al., which showed that the *f_m* of OC was constant with temperatures from 340 to 440 °C, although OC/TC ratios continuously increased with increasing temperatures. As a result, 340 °C was chosen as separation temperature of OC in our protocol.

The blank contribution to OC and TC in the total procedure were 0.20 ± 0.02 (*n* = 5) μgC and 0.23 ± 0.03 (*n* = 4) μgC, respectively, which was mainly caused by impurities in the oxygen stream and the pre-cleaned filters. The blank value was too low to make graphite target for ¹⁴C measurement, and the contribution of *f_m* in blank was negligible for the real aerosol samples with

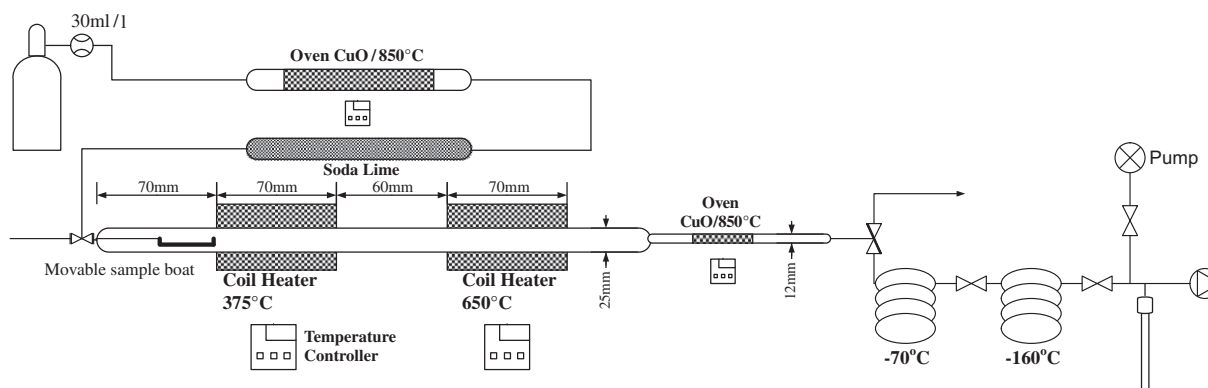


Fig. 1. Two-step thermal separation and trapping system for OC determination of ¹⁴C.

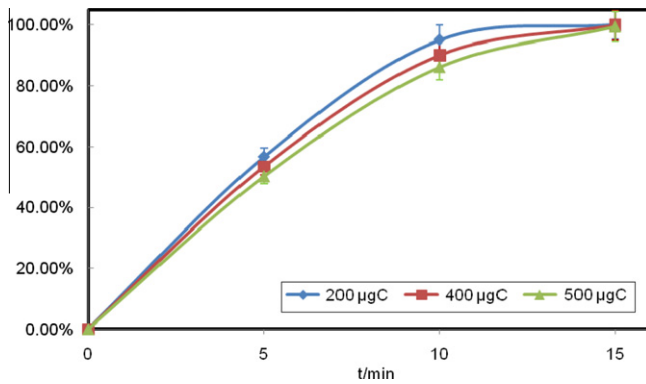


Fig. 2. The recovery of mixture standards within the different combustion time.

200–1000 μgC . But the exact determination for it should be addressed in future work.

Fig. 2 shows the recovery of OC after pre-combustion at 340 °C for 5, 10, and 15 min. Continuously increasing recovery of OC with increasing the combustion time are observed over the time range investigated. Fifteen minutes has been proven to be sufficient for separation of OC from mixture standards. The high recovery after combustion of the initial sample material on the filters allows to future work on OC in aerosol samples. The average recovery of EC was $1 \pm 2\%$ mainly due to the charring of OC or combustion of low-refractory fraction of EC at lower temperature with the pure O_2 inert. After combustion of EC standards alone at 340 °C for 15 min, the CO_2 trapped was below the limit of detection. The results showed that the artifact formation of EC was caused by charring in this case which was also a well-known problem [14,25]. As the suggestion by several other studies [13,14,19], the charring formation has already been minimized here after flash heating samples at 650 °C for 30 s.

For real aerosol samples, the charring problem could be reduced by extracting particulate matter collected on filters with water or organic solvents [25]. Furthermore, the main purpose in this study was to develop a method not for concentration determination but for ^{14}C determination. The charring problem arising here would not alter the results of AMS determination in OC which would be discussed in Section 3.2. In fact, artifact formation of EC would have influence on the ^{14}C analyses in EC which was also found in the THEODORE [14]. This is why we used this preparation line just for OC and TC but not for EC in aerosols.

3.2. AMS performance

In order to evaluate the accuracy of these protocols, four samples each of IAEA-C6 [26], HOx I and HOx II RM (reference material) with amounts between $\sim 150 \mu\text{g}$ and $\sim 1500 \mu\text{g}$ were produced according to the description in Section 2.3 and were subsequently measured by the described method above in Section 2.2. Results of the corrected f_m was illustrated in Fig. 3 68% of the ^{14}C signatures lie within the 1σ interval and 95% within the 2σ interval, which demonstrates a good agreement with normal distribution. For IAEA-C6, the mean value of f_m with the uncertainty of the mean (1σ) was 1.502 ± 0.015 (consensus value: 1.506 ± 0.001). For HOx I, the resulting f_m was 1.050 ± 0.007 (consensus value: 1.0526). For HOx II, the resulting f_m was 1.3381 ± 0.0072 (consensus value: 1.3407). Our results were in agreement with the consensus values of the examined RM on a 95% confidence level (2σ). The difference between reality and normal values for fraction of modern (f_m) would be denoted as δf_m in the following, according to the definition in Eq. (1):

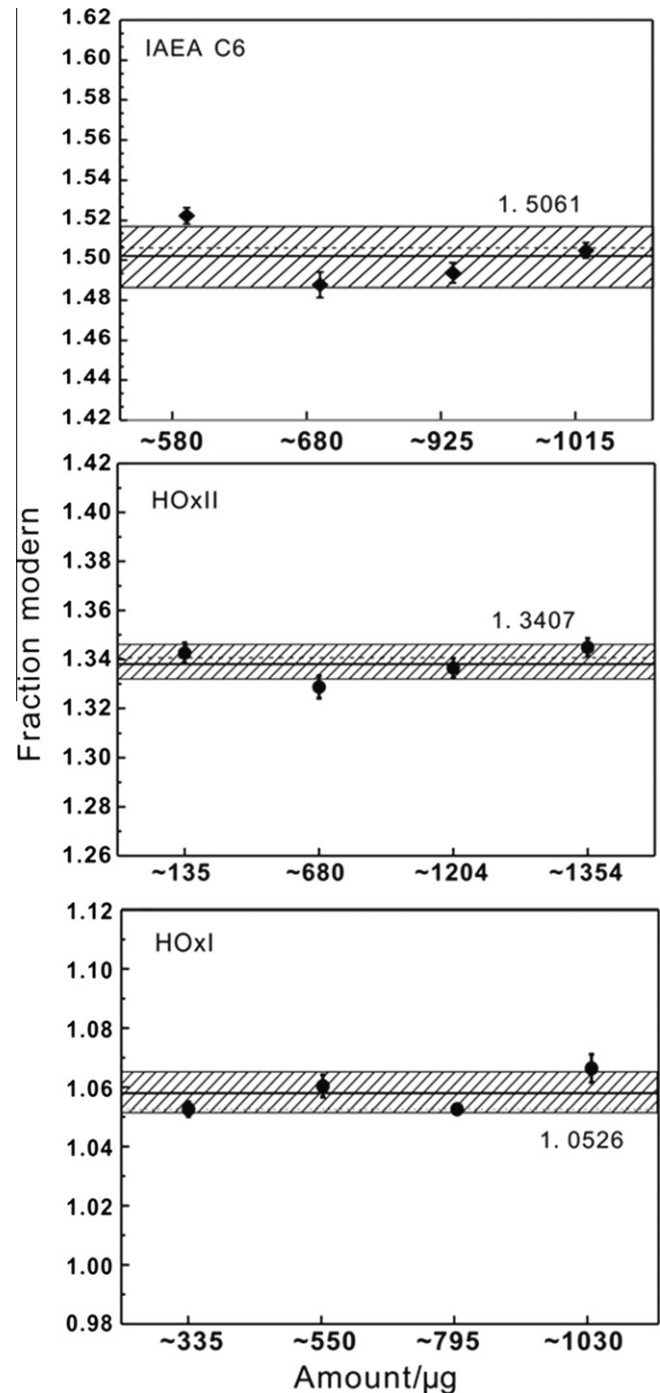


Fig. 3. Values of f_m for HOx I, HOxII and IAEA-C6 RM. Solid lines and shaded areas represent mean values with the uncertainty of the mean (1σ). Dashed lines mark the consensus values of the RM.

$$\delta f_m = (f_m (\text{sample}) - f_m (\text{normal})) / f_m (\text{normal}). \quad (1)$$

In the equation, f_m (sample) and f_m (normal) represent the measured value of the RMs for the fraction of modern, and the consensus values of the RMs for the fraction of modern, respectively. As Fig. 4 showed, there was no dependence between δf_m and sample size. In actuality, OC could be yield more than 95% in 15 min for less than $\sim 500 \mu\text{g}$ samples. But for some high loading filters, 15 min might not be still adequate for separate all the OC. Therefore, we investigated the relationship between the ^{14}C value and recovery in large amount of OC together with EC. The ^{14}C value

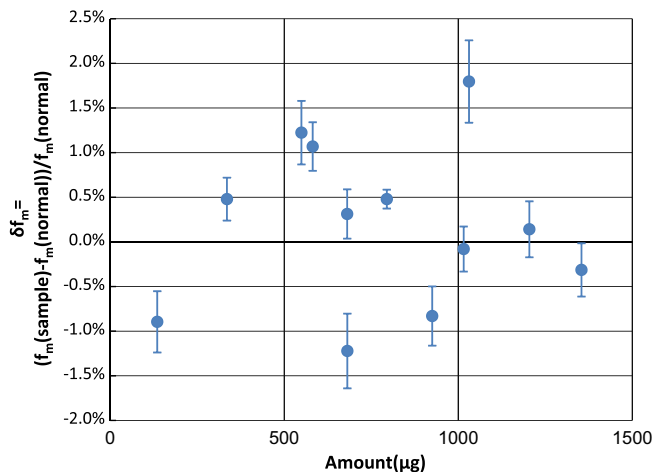


Fig. 4. The relationship between δf_m values (see Eq. (1)) and sample size.

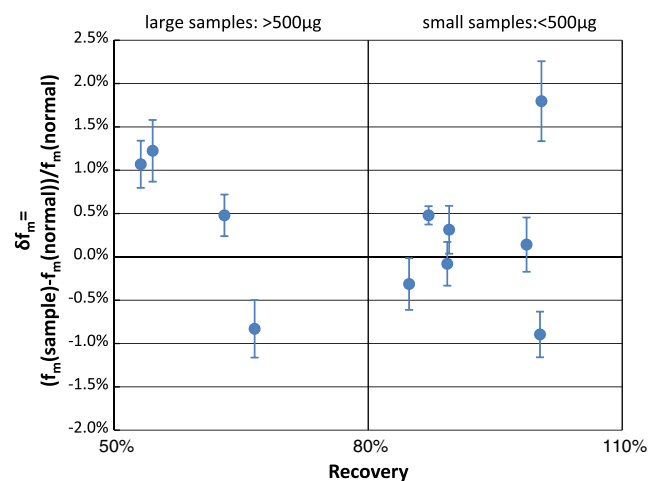


Fig. 5. The relationship between δf_m values (see Eq. (1)) and recovery.

was not dependent on the recovery of OC as displayed in Fig. 5. This conclusion could allow ^{14}C determination for OC in aerosols on the assumption that OC on filters is homogenous.

4. Summary

A preparation system for the determination of ^{14}C in the organic carbon (OC) fraction of aerosol samples was firstly established in China. CO_2 evolved in the preparation system was reduced to graphite for AMS target using the method of zinc reduction. And then radiocarbon measurements performed by NEC Compact AMS System at the Institute of Heavy Ion Physics, Peking University. The measured results for estimated RMs are consistent with internationally accepted values that are widely known in the ^{14}C community. Future investigation will focus on adapting the thermal method to separate EC from atmospheric aerosols together with OC in order to achieve ^{14}C measurements of OC/EC/TC in real atmospheric filters. The radiocarbon-based source appointment of carbonaceous aerosols in China would be much more convenient and faster with the preparation system developed in this work.

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