Short communication

Isolation and radiocarbon analysis of elemental carbon in atmospheric aerosols using hydropyrolysis

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GRAPHICAL ABSTRACT
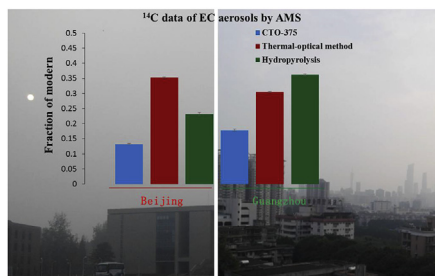
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ABSTRACT

Radiocarbon (^{14}C) analysis is a powerful tool that can unambiguously distinguish fossil and non-fossil sources of carbonaceous particles. However, one of the big challenges of this method is to isolate elemental carbon (EC) or black carbon (BC) for ^{14}C analysis. Hydropyrolysis (hypy) has proven to be an effective method for separating BC in environmental matrices. The potential of hypy for isolation of EC from atmospheric aerosols is evaluated using typical combustion products from non-fossil (biomass), fossil fuel (coal and petroleum), and ambient aerosol samples collected in Beijing and Guangzhou. Using solid state nuclear magnetic resonance (NMR) along with measurement of carbon content and ^{14}C, hypy conditions of 15 MPa hydrogen pressure and 550 °C temperature was confirmed to effectively separate EC from aerosol samples. Consequently, a comparison study of EC ^{14}C in aerosol samples separated using the two-step heating method (CTO-375), thermal-optical method and hypy was conducted. The results show that hypy is an effective and stable approach for matrix-independent ^{14}C quantification of EC in aerosols.

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1. Introduction

Elemental carbon (EC) or black carbon (BC) of carbonaceous aerosols (CAs) is derived from incomplete combustion of fossil fuels or biomass and is responsible for an overall warming effect due to either absorbing incoming solar radiation in the atmosphere or reducing the albedo of surface materials (i.e., snow and ice) (Fuzzi et al., 2006; Schwarz et al., 2015; Szidat, 2009; Szidat et al., 2004b, 2009). Therefore, detailed knowledge of the sources of EC is necessary for the implementation of mitigation strategies for their reduction.

Radiocarbon (^{14}C) analysis is a powerful tool for unambiguously distinguishing fossil and non-fossil sources of carbonaceous particles (Currie, 2000; Szidat, 2009; Szidat et al., 2006, 2009; Gustafsson et al., 2009; Kirillova et al., 2013; Liu et al., 2013; Pavuluri et al., 2013; Wang et al., 2013; Wozniak et al., 2012; Zencak et al., 2007a; Zhang et al., 2010). However, one of the big challenges of this method is to isolate elemental carbon (EC) for ^{14}C analysis. In 2013, a study showed the results from an intercomparison of 9 laboratories for ^{14}C analysis of carbonaceous aerosol samples. ^{14}C analysis of EC revealed a large deviation between the laboratories of 28–79% as a consequence of different separation techniques (Szidat et al., 2013). Results for the recovered EC mass concentration also showed poor agreement between two oxygen-based methods in the recent study (Zenker et al., 2017). Therefore, there is an urgent need to find an effective and stable approach to isolate EC for ^{14}C analysis, which approach is independent of laboratory, operator, and sample matrix.

Recently, hydropyrolysis (hypy) methods have been proposed to be an effective method for separating black carbon (BC$_{hypy}$) in environmental matrices (Ascough et al., 2009; Meredith et al., 2012). However, the chemical structure of CAs differs by source sample and combustion temperature, and the content and stability of EC produced from these CAs vary (Wurster et al., 2012, 2013). Whether these differences affect the separation of EC via hypy, and whether hypy can be used to separate EC from CAs for ^{14}C analysis, remains unverified.

To verify the separation of EC from atmospheric aerosols for ^{14}C analysis via hypy, an experiment was conducted using typical combustion products and ambient aerosol samples under different hypy operating conditions. The objectives of this study were to evaluate the hypy method for separation and ^{14}C analysis of EC in aerosols, and to compare the ^{14}C results of aerosols separated using a two-step heating method (CTO-375), a thermal-optical method and hypy.

2. Materials and methods

2.1. Sample collection

Biomass burning, coal combustion and traffic emissions are the main sources of carbonaceous particles in China (Huang et al., 2014; Zhang et al., 2015b). Therefore, 7 smoke particle samples, including 3 typical biomass samples, 2 residential coal combustion samples and 2 vehicle exhaust particle samples were collected. Biomass burning emission samples, including wheat straw combustion (C4 plant), corn stem combustion (C3 plant) and pine wood combustion (woody plant), were collected through a sampling system (see details in the Supporting Information [SI], Fig. S1). Two different types of raw coal, chunks, sourced from Pingdingshan (PDS) in Henan province and Chongzhou (CZ) in Shandong province, were tested in this study. The characteristics of coal samples are summarized in Table S1 in the SI. Coal was combusted in a high-efficiency stove, and PM$_{2.5}$ emissions were collected using a dilution sampling system, which has been described in detail previously (Chen et al., 2015; Wang et al., 2016). One type of gasoline truck and one type of diesel truck were used in this study. Fine exhaust particles were collected using the on-board emission measurement system (Fig. S2). A description of the on-board emission test system was provided in a previous report (Cui et al., 2017). A detailed description and schematic diagram of this system are given in the SI.

Two urban aerosol samples were selected, which were collected in Beijing and Guangzhou in the winter. All the PM$_{2.5}$ samples were collected on pre-combusted quartz filters (8 × 10 inch; Pall) using a high-volume sampler equipped with a PM$_{2.5}$ impactor (Xintuo Analytical Instruments, Shanghai, China). After sampling, all filters were wrapped in aluminum foil and stored at −20 °C until analysis.

2.2. Hydropyrolysis

Particles captured on the surface of quartz filters were peeled off with stainless steel tweezers. The particles, along with remnants of the filters, were ground into powder. A fraction of the powder was mixed fully with ammonium dioxydithiomolybdate [(NH$_4$)$_2$MoO$_2$S$_2$] as a catalyst to reach a nominal molybdenum loading of 1% by weight. The mixture was vacuum dried and loaded into the quartz tube (5 mm inner diameter, 40 mm long) for hypy. The hypy method has been described in published studies (Bishop et al., 1998; Meredith et al., 2012). Briefly, the samples were first heated in the reactor tube from ambient temperature to 250 °C at a rate of 300 °C min^{-1}, and then from 300 °C to the final temperature (350 °C, 400 °C, 450 °C, 500 °C, 525 °C, 550 °C) at 8 °C min^{-1}, then held for 5 min, under hydrogen pressure of 15 MPa and a flow rate of 5.0 L/min. Blank experiments without samples were utilized to confirm that the hypy device (Meredith et al., 2012) (purchased from the University of Nottingham, Nottingham, UK) remained sufficiently clean throughout the experiment.

2.3. NMR analysis

All the ^{13}C solid state NMR experiments were performed using an AVANCE III 400-MHz NMR spectrometer (Bruker, Billerica, MA, USA). The selected samples were tested with direct-polarization/magic-angle-spinning (DP/MAS) ^{13}C solid state NMR experiments (Mao and Schmidt-Rohr, 2004) and details of the method was described in the SI.

2.4. ^{14}C analysis

The ^{14}C analysis experiments were determined using a compact AMS instrument (NEC, National Electrostatics Corporation, USA) at the Guangzhou Institute of Geochemistry, CAS. The method of the ^{14}C analysis (Liu et al., 2013, 2017; Zhu et al., 2015a,b) is also described in the SI.

3. Results and discussion

3.1. Purification of EC via hypy

The seven types of common combustion products were collected for hypy experiments. Based on previous studies, significant further loss of carbon occurs via hydrogasification, predominately yielding methane when the hypy temperature is above 575 °C; this indicates the decomposition of BC (Ascough et al., 2009; Rocha et al., 1999). Therefore, final temperatures of 350 °C, 400 °C, 450 °C, 500 °C, 525 °C and 550 °C were selected for hypy.

To monitor the stripping of non-elemental carbon, elemental analysis was used to determine the carbon content of hypy residue at each temperature and the measurement uncertainty of elemental analysis method was below 3%. Fig. 1 shows carbon loss for all typical combustion samples over the 350–550 °C range, corresponding to the loss of labile (i.e., non-EC$_{hypy}$) carbon from the aerosol organic matter. For all samples, a large proportion of the labile carbon was removed below 400 °C, indicating that a major portion of the labile organic carbon (OC) in fuel combustion emissions could be stripped under hypy conditions at 400 °C. However, the carbon contents of hypy residues from different fuel combustion aerosols showed differing results at temperatures above 400 °C. For the two motor vehicle emission samples, about 67% and 80% of carbon was removed at 400 °C, whereas less than 5% more
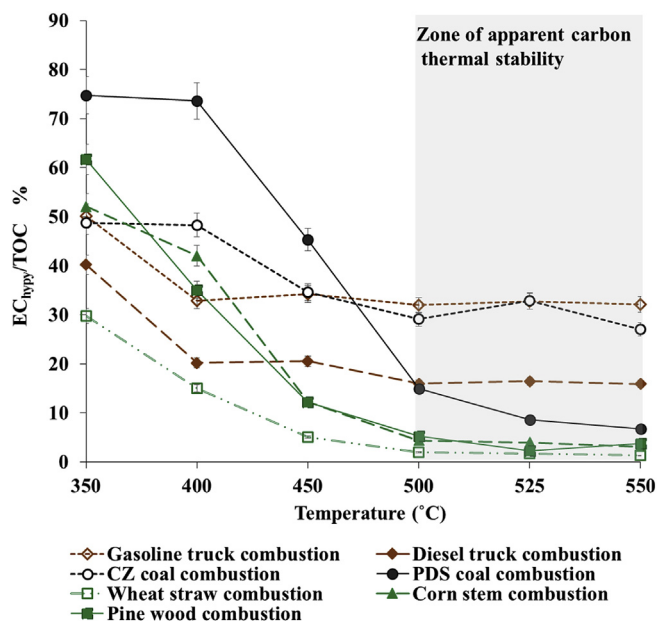
Fig. 1. Element carbon (EC_hypy) as a proportion of total organic carbon (TOC) measured for the residues of typical combustion products after hydropyrolysis (hypy) at different temperatures.

was stripped between 425 and 525 °C, and no further carbon loss was observed at 550 °C. The curve of carbon loss from vehicle emission aerosols at temperatures over 400 °C matched that of n-hexane soot (Meredith et al., 2012). This result implies that the refractory residue of vehicle emission aerosols has the same structure as that of n-hexane soot. Unlike vehicle emissions, the residual carbon from coal and biomass combustion aerosols decreased with increasing hypy temperature, with 9%–37% more carbon removed at 500 °C, and then a relatively stable state was reached from 500 °C to 550 °C. The subsequent plateau in remaining carbon content between 500 and 550 °C represents a zone of apparent thermal stability when non-EC_hypy organic matter (e.g., lignocellulosic material, humic acids, proteins and lipids) and relatively labile pyrogenic carbon have been removed, and thus the residual carbon represents the sample EC_hypy content, which is the portion of the EC continuum that is stable under hypy conditions. Differences in the carbon structures of the three types of typical combustion products may be responsible for their differing response to hypy conditions.

The ^{13}C solid state NMR spectroscopy can be used to illustrate carbon structural characteristics of the matrices, making it a good method for monitoring changes in carbonaceous functional groups caused by various hypy treatments (Ascough et al., 2010). The ^{13}C solid state NMR spectra of three typical combustion products (including gasoline truck combustion, coal combustion and corn stem combustion) subjected to various hypy temperatures are shown in Fig. S3. These NMR results show the content of aliphatic carbon decreases gradually with increasing hypy temperature. When the temperature reached 500 °C, aliphatic carbon was almost completely removed from vehicle exhaust aerosols (Fig. 2). At 525 °C, aliphatic carbon was also stripped from coal and corn stem combustion samples. In all the samples, probably only aromatic carbon remained when the hypy temperature was 550 °C (Fig. S3).

Two aerosol samples, collected in Beijing and Guangzhou, were also selected for hypy experiments. The carbon loss from both urban samples reached a plateau when the hypy temperature ranged from 500 to 550 °C (Fig. 3 and Table S3). To verify the effect of the hypy experiment on ^{14}C results, all hypy experiment products for the two urban aerosol samples were tested using ^{14}C-AMS. The ^{14}C contents of both urban aerosol samples remained stable over the range of 500–550 °C (Fig. 3). The differences of the highest and the lowest f_m values of the two urban

aerosols over the stable range were 0.0064 and 0.0111 with little difference in their measurement uncertainty, respectively. Combined with the carbon content results of EC residues obtained through hypy treatment (Fig. 3), these results illustrate that the source and composition of the two urban aerosol samples are stable over the range of 500–550 °C. This finding indicates that non-EC organic matter is effectively removed from the aerosol organic matter by hypy at 550 °C.

3.2. Radiocarbon comparison of EC via CTO-375, thermal-optical method and hypy

On the one hand, radiocarbon measurement provides a unique tracer that can directly apportion EC into fossil and non-fossil fractions, while on the other hand, the EC fraction is not a single compound and it is nearly impossible to separate these mixtures completely with current technologies. Therefore, isolation of the purest possible carbon fractions of interest is recommended for ^{14}C determination. Thermal treatment is the most common method currently used to separate EC, and the key technical difficulty is obtaining a sufficient mass of pure carbon to represent the ^{14}C signal of the entirety of EC (Szidat et al., 2004c). Previous studies have significantly improved our knowledge of the sources of EC, yet critical challenges remain in achieving complete separation of EC, and correlating radioisotope signals and mass recovery of EC. First, a portion of the EC fraction, in particular non-refractory EC (char-EC), will be stripped with some OC under an oxidative atmosphere, and thus the CTO-375 method may harvest only the most refractory portion of EC (soot-EC) (Hammes et al., 2007; Zencak et al., 2007b). Second, it has long been recognized that a fraction of OC (e.g., sucrose) in ambient aerosols heated in an O$_2$-free atmosphere will char to pyrolytic carbon (PyC) (Cadle et al., 1980), which has significantly different thermal and optical properties from OC that are similar to EC (Watson et al., 2005). When conducting the thermal-optical method, the formation of PyC is monitored via transmittance/reflectance of a visible laser during the He and He/O$_2$ heating phases, and the carbon evolved before the split line at which the laser signal returns to its initial level is defined as the OC fraction, while the carbon evolved after this line is considered the EC fraction (Birch and Cary, 1996; Chow et al., 1993). Therefore, the thermal-optical method has been widely used to separate OC from EC for radiocarbon analysis (Zhang et al., 2012, 2015a; Zotter et al., 2014; Liu et al., 2017). However, the ^{14}C results obtained by this method are affected by the thermodynamic heterogeneity, oxidability, and light-absorbing ability of the entire EC fraction in the ambient environment, as well as the fraction of EC isolated by the system (Liu et al., 2017; Zotter et al., 2014).

In this study, the modern EC fractions of two urban aerosol samples separated using the CTO-375 method, the thermal-optical method and hypy were compared (Fig. 4 and Table S4). There are many different heating methods used in conjunction with two-step heating system for EC/OC determination of radiocarbons (Calzolai et al., 2011; Lavanchy et al., 1999; Liu et al., 2013; Szidat et al., 2004c; Zhang et al., 2010). In this article, the two-step heating system (CTO-375) (Liu et al., 2013) and the thermo-optical method (Liu et al., 2017), were selected for separation of EC from aerosol samples, and details of these methods can be found in the literature (Liu et al., 2013, 2017). Fig. 4 shows the ^{14}C results of EC in the two urban aerosol samples. All ^{14}C values were reported as the f_m after correction for fractionation with δ^{13}C. In this study, f_m was converted into the fraction of contemporary carbon (f_c) to eliminate the effect of nuclear bomb tests using a conversion factor (Szidat et al., 2004a), which was 1.10 ± 0.05 for EC in 2013 (Liu et al., 2014).

The f_c results based on hypy show that the percentage of non-fossil-derived sources was significantly higher in Guangzhou (36%) than in Beijing (23%), and this pattern and spatial trend was also seen previously (Andersson et al., 2015; Huang et al., 2014). Compared to hypy, the f_c values of the CTO-375 method are much lower. As discussed above, a portion of the EC fraction, especially non-refractory EC (char-
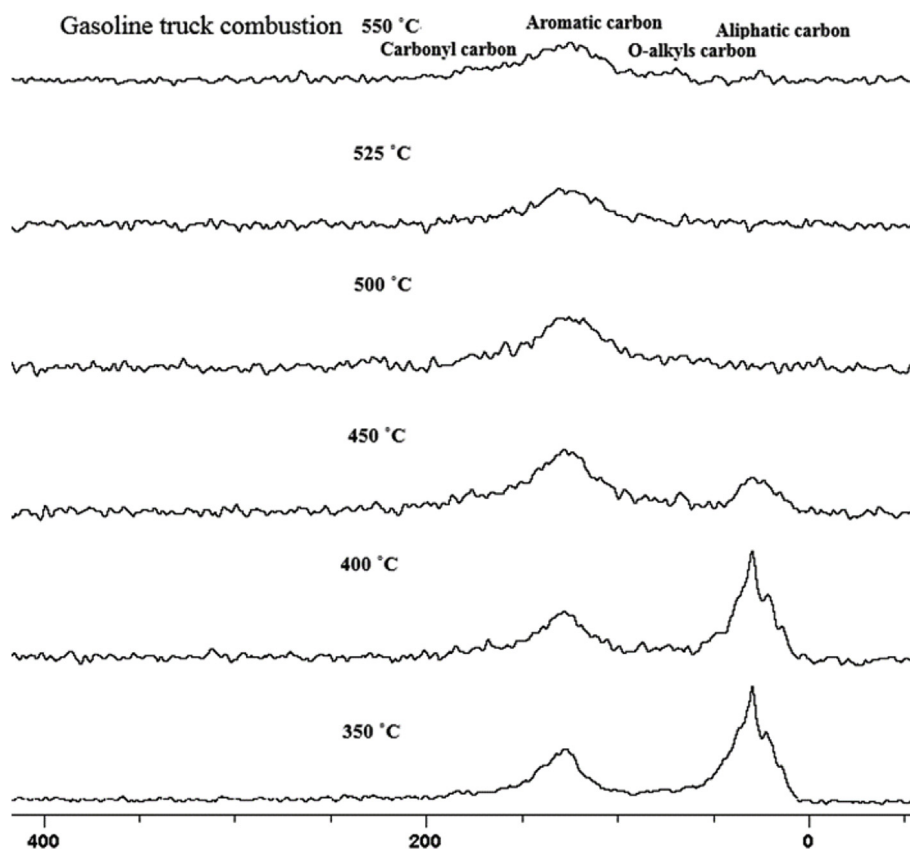
Fig. 2. ^{13}C solid state NMR spectra of the EC residues from the gasoline truck combustion samples following hypy treatment at 350 °C to 550 °C.
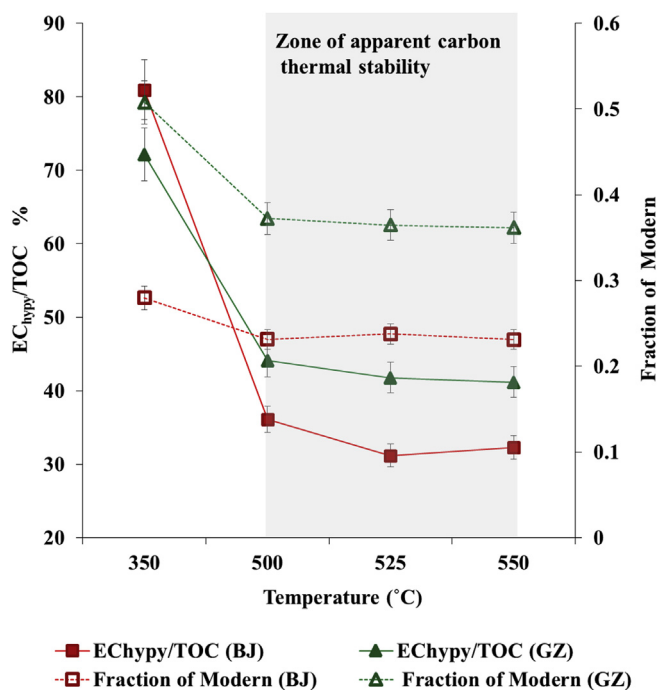

Fig. 3. EC$_{hypy}$ as a proportion of TOC (left axis) and results of Radiocarbon (^{14}C) (right axis) measured for the residues from Beijing and Guangzhou after hypy at different temperatures.

EC), is over-burned with the CTO-375 method, and only the refractory part of EC (soot-EC) can be harvested (Hammes et al., 2007; Zencak et al., 2007b). This finding suggests that a large portion of EC from biomass burning was lost, along with some OC, in the oxidative

atmosphere. Furthermore, samples with higher proportions of biomass combustion had higher f_c loss; for example, the Guangzhou sample lost 54%, while the sample from Beijing lost 44%. Unlike the trend of f_c results for hypy and the CTO-375 method, f_c results measured with the thermo-optical method indicated a larger biomass burning component in Beijing (35%) than in Guangzhou (30%). The value measured from Beijing was higher than those based on the hypy and CTO-375 methods, while the value from Guangzhou was comparable to that of hypy, but higher than that of the CTO-375 method.

The cause of the above results as shown in Fig. 4 is not very clear. But according to previous studies which have indicated predominant contributions (more than 75%) of fossil fuel to EC in the Beijing winter (Zhang et al., 2015b), it could be speculated that this difference may arise from the analysis method itself. It is generally agreed that thermal conversion of biomass, and the resulting EC characteristics, are regulated primarily by the nature of the feedstock and heating temperature (Liu et al., 2015; Tripathi et al., 2016). In terms of heating temperature, the morphology of EC largely maintains the macrostructure of the feedstock during relatively low temperature pyrolysis, as lower treatment temperatures (usually < ∼300 °C) are not sufficient to break down the cross-linkage between carbon atoms in the raw materials. With increasing treatment temperature, removal of simple molecules from outer surfaces of the feedstock could gradually enhance the development of the pore structure and surface area of EC. However, a high treatment temperature may also induce deformation and collapse of some fine pore structures (Lian et al., 2011; Lian and Xing, 2017). The carbonaceous components produced from biomass combustion at high temperature are more stable, and more difficult to separate from EC, than low-temperature products (Wurster et al., 2013). Biomass combustion in Beijing originates from cooking and heating in winter, which involve high temperatures, while the biomass emissions from Guangzhou originate primarily from natural emissions at lower temperatures (Huang et al., 2014; Zhu et al., 2015a,b). The large
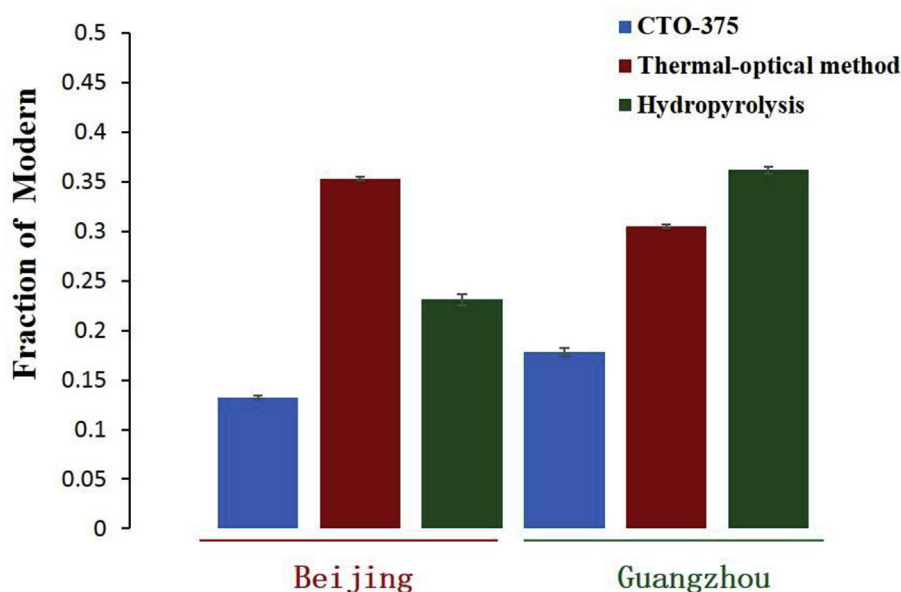
Fig. 4. Results of accelerator mass spectrometry (AMS) ^{14}C measurements of EC following treatment with the two-step heating system (CTO-375), the thermal-optical method and hydropyrolysis.

contributions from coal burning and biomass combustion in Beijing winter at high temperature may lead to a bias of EC separation determined through the thermal-optical method (Liu et al., 2017). Hypy, which is pyrolysis assisted by high hydrogen pressures (150 bar), facilitates the complete reductive removal of labile organic matter, thereby isolating a highly stable portion of EC_{hypy} and thus avoiding charring. This may lead to a different ^{14}C result of EC between thermal-optical method and the hypy. All the above causes may lead to the results as shown in Fig. 4.

4. Conclusion

To find an effective and stable approach to isolate EC from atmospheric aerosols for ^{14}C analysis, the potential of hypy was evaluated using typical combustion products and ambient aerosol samples. The ^{13}C solid state NMR spectra and carbon content results of three typical combustion products show that the content of aliphatic carbon decreases gradually with increasing hypy temperature. When the hypy temperature reached 550 °C, probably only aromatic carbon remained in the sample. The ^{14}C contents and carbon content results of both urban aerosol samples illustrate that the source and composition of the two urban aerosol samples are stable over the range of 500–550 °C through hypy treatment. This finding indicates that hypy conditions of 15 MPa hydrogen pressure and 550 °C temperature was confirmed to effectively separate EC from aerosol samples.

Consequently, a comparison study of EC ^{14}C in ambient aerosol samples separated using the CTO-375 method, thermal-optical method and hypy was conducted. The fc results based on hypy show that the percentage of non-fossil-derived sources was significantly higher in Guangzhou (36%) than in Beijing (23%). Compared to hypy, the fc values of the CTO-375 method are much lower and the trend of ^{14}C results measured with the thermo-optical method is the opposite. Hypy, which is pyrolysis assisted by high hydrogen pressures (150 bar), facilitates the probably complete reductive removal of labile organic matter, thereby isolating a highly stable portion of EC_{hypy} and thus avoiding charring. Therefore, hypy is an effective and stable approach for matrix-independent ^{14}C quantification of EC in aerosols.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2018.11.005.

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