Technical note: Intercomparison Study of the EC Radiocarbon Analysis Methods Using Synthetic Known Samples

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Abstract

The accurate identification of elemental carbon (EC) source in aerosol based on radiocarbon (^{14}C) depends on the method of EC isolation. The lack of aerosol EC reference materials with "true" ^{14}C values makes it impossible to evaluate the accuracy of various methods for the analysis of ^{14}C-EC in aerosols. In this study, EC isolation methods were evaluated by using samples of mixed biomass burning, vehicle exhaust and coal-combustion. The results show that ^{14}C-EC was not only related to the isolation method but also to the types and proportions of biomass sources in the sample. The hydropyrolysis (Hypy) method, which can be used to isolate a highly stable portion of EC$_{Hypy}$ and avoid charring, is a more effective and stable approach for the matrix-independent ^{14}C quantification of EC in aerosols. The ^{13}C-EC$_{Hypy}$ and non-fossil EC$_{Hypy}$ values of SRM1649b were -24.9‰ and 11%, respectively.

1. Introduction

The elemental carbon (EC) or black carbon (BC) fraction of carbonaceous aerosols (CAs) is derived from the incomplete combustion of fossil fuels or biomass and is responsible for an overall warming effect of the Earth by 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., 2004a; Szidat et al., 2009). The limited understanding of EC aerosol emissions results in poorly constrained estimates of their contribution to anthropogenic climate warming that globally may be second only to CO_2 and regionally, such as over East Asia, the dominant driver of climate change (Chen et al., 2013).Therefore, detailed knowledge of the sources of EC is necessary for the implementation of mitigation strategies for EC reduction. Carbon isotope (^{14}C and ^{13}C) analysis is a powerful tool for unambiguously distinguishing the carbon sources of EC (Currie, 2000; Szidat, 2009; Szidat et al., 2009; Gustafsson et al., 2009; Kirillova et al., 2013; Liu et al., 2013; Zencak et al., 2007; Zhang et al., 2019b). Carbon isotope source apportionment requires the physical isolation of organic carbon (OC) and EC, which is complicated by the fact that there is no sharp boundary between OC and EC in carbonaceous aerosols (Elmquist et al., 2006).Therefore, one of the large challenges of this method is the isolation of EC for ^{14}C and ^{13}C analysis.

Based on the thermal stability of EC, several methods for isolating OC and EC from aerosols have been developed. An intercomparison of 9 laboratories for ^{14}C analysis of carbonaceous aerosol samples was conducted in a previous study, and ^{14}C analysis of EC revealed a large deviation of 28-79% between the approaches as a consequence of the different isolation techniques (Szidat et al., 2013). Due to the application of the same principle as aerosol OC and EC measurement, thermo-optical isolation, also named oxygen-based OC-EC isolation, has gradually become the main method for EC isolation in recent years. Although the ^{14}C results of EC between three independent laboratory methods showed good agreement, the recovery of EC differed greatly (Zenker et al., 2017). Recently, hydropyrolysis (Hypy) has been introduced as an EC isolation method (Meredith et al., 2012; Zhang et al., 2019b). A comparison study of ^{14}C-EC in aerosol samples isolated using the two-step heating method (CTO-375), EC$_{He/O2-475}$ method and Hypy method was also conducted (Zhang et al.,

2019b). However, the ^{14}C intercomparisons of all studies were mainly restricted to ambient filter samples or urban dust (SRM 1649a/b), for which the "true" ^{14}C activity of EC is not known. As the literature emphasizes (Dasari et al., 2022), even when methods give similar results, it may still be unclear whether the methods give accurate results. In the worst case, if the methods give different results, then it is impossible to determine which method (if any) gives an accurate value (Zenker et al., 2017). Therefore, the key to evaluating the accuracy of different isolation methods is to obtain suitable EC reference materials for the ^{14}C analysis of aerosols.

Carbonaceous aerosols are mainly composed of primary emissions from fossil fuel and biomass combustion and secondary organic compounds (Huang et al., 2014; Zhang et al., 2015). In general, secondary organic aerosols are relatively easy to isolate from EC using methods such as water or organic solvent extraction. However, it is difficult to isolate insoluble OC from EC in primary combustion products. Biomass burning, coal combustion and traffic emissions are the main primary sources of EC in aerosols (Bond et al., 2013). In this study, six samples were synthesized artificially by using biomass combustion (corn straw or pine wood), coal combustion and motor vehicle exhaust samples according to the relative content of fossil carbon and modern carbon in actual aerosols in this study. The theoretical calculated values of the EC contents and EC carbon isotopes in six synthetic samples were determined based on the measured isotopes of each source sample and the elemental carbon/total carbon (EC/TC) measured by using the thermal-optical transmittance (TOT) method. And the calculated ^{14}C value of EC can be taken as the "true" ^{14}C-EC value. Consequently, four EC isolation methods, including Hypy (Zhang et al., 2019b), CTO-375 (Liu et al., 2013), EC$_{He/O2-475}$ (Liu et al., 2017) and EC$_{LARA}$ (Zenker et al., 2017), were selected for EC isolation, and then the EC contents and EC carbon isotopes were compared to the corresponding theoretical calculated value of each synthetic sample. The accuracy of each isolation method was evaluated based on the recovery of the EC contents and carbon isotopes. Finally, the EC contents and EC carbon isotopes (^{14}C and ^{13}C) of urban dust (SRM 1649b) were determined by the isolation method with the best accuracy.

2. Materials and Methods

2.1. Sample collection

Corn straw (*Zea mays*, C4 plant, with a carbon isotope composition that differs significantly from fossil fuels), pine wood (*Pinus tabulaeformis Carr.* woody plant), one type of raw coal in chunks sourced from Yanzhou (YZ) in Shandong Province, and one type of gasoline truck exhaust were selected as the representative sources for biomass burning, coal combustion and vehicle exhaust. Corn straw and pine wood combustion products were collected through a sampling system. Coal was combusted in a high-efficiency stove, and PM$_{2.5}$ emissions were collected using a dilution sampling system. Vehicle exhaust particles were collected using the on-board emission measurement system. A description of the detailed sampling information was provided in a previous report (Zhang et al., 2019b).

2.2. EC isolation method

CTO-375 method: To achieve the complete removal of the OC from the EC$_{CTO375}$

fraction, the samples were treated by vaporizing the OC at 375 °C in a muffle furnace in the presence of air using a shorter isolation time of 4 h (Liu et al., 2013).

EC$_{He/O2-475}$ method: The EC$_{He/O2-475}$ fractions in the samples were purified in the commercial OC-EC analyzer as follows: 120 s at 200 °C, 150 s at 300 °C, and 180 s at 475 °C in an oxidative atmosphere (10% oxygen, 90% helium), followed by 180 s at 650 °C in helium. Details of the handling methods were described in a previous report (Liu et al., 2017).

EC$_{LARA}$ method: A punch of the water-extracted filter was treated with a thermo-optical OC-EC analyzer using the first three steps of the "Swiss 4S protocol" to remove all remaining water-insoluble OC, giving a residue that constituted the EC$_{LARA}$ sample (Zenker et al., 2017; Zhang et al., 2015).

Hydropyrolysis: Each sample was mixed fully with ammonium dioxydithiomolybdate [(NH$_4$)$_2$MoO$_2$S$_2$] as a catalyst to reach a nominal molybdenum loading of more than 20% of sample carbon weight. 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 (550 °C) at 8 °C min^{-1}; samples were then held for 5 min under a hydrogen pressure of 15 MPa and a flow rate of 5.0 L/min. The resulting residue was the EC$_{Hypy}$ sample (Zhang et al., 2019b).

2.3. OC/EC and carbon isotopes analysis

The OC and EC were analyzed by a laboratory OC/EC analyzer (Sunset Laboratory, USA) using the NIOSH2 thermal protocol (Maenhaut et al., 2005; Salma et al., 2004). Methods of ^{13}C and ^{14}C analysis for all samples were described in the SI (Liu et al., 2013; Liu et al., 2017).

2.4. Nuclear Magnetic Resonance (NMR) and Field Emission Scanning Electron Microscopy (FESEM) analysis

NMR experiments were performed with an AVANCE III 400-MHz NMR spectrometer (Bruker, Billerica, MA, USA). FESEM experiments were analyzed by the field emission scanning electron microscope (Hitachi su8010, Hitachi, Japan). Detailed experimental methods of NMR and FESEM analysis were described in the SI (Zhang et al., 2019b; Chen et al., 2020).

3. Results and discussion

3.1. Comparison of EC purified by different methods

The six synthetic known samples were made by biomass combustion (corn straw or pine wood), coal combustion and motor vehicle exhaust (Table S1). The hybrid samples were produced according to the proportioning principle, based on the approximate proportions (Figure S1 and Table S2). The average deviations of carbon content, ^{13}C$_{TC}$ and f_M(TC) of the hybrid samples between the theoretical values and the test values were 0.30%, -0.12‰ and 0.03, respectively (Table S3), and there was no significant difference (T-test, P=0.77, 0.96 and 0.49, respectively). These results show that the samples were well mixed and were therefore suitable for the method comparison experiments.

Before comparing EC recovery rates, it is necessary to obtain relatively accurate EC concentrations. The EC/TC ratios of the four combustion source samples were analyzed by the TOT method (Table S4). The EC/TC results of the four combustion source samples processed using the four isolation methods (CTO-375, $EC_{He/O2-475}$, EC_{LARA} and Hypy) are listed in Table S4. The amount of EC obtained by the CTO-375 method is obviously lower than the results of the other three methods. For example, due to the high content of soot in the vehicle exhaust, the amount of EC can reach about 20%, while the amount of EC in other source samples is less than 10% (Hammes et al., 2007). It indicates that the CTO-375 method has obvious defects in the quantitative analysis of EC content in aerosols. Therefore, this method is not suitable for isolating EC to isotopes analysis. The EC/TC ratios of the coal combustion and motor vehicle exhaust obtained by the other three methods are lower than those of the TOT method, and the EC/TC ratios of the pine burning samples are higher than those of the TOT method. Among the above four methods, the result obtained by the Hypy method is the closest to the result of the TOT method. For the corn straw combustion samples, the Hypy and EC_{LARA} methods are lower than the TOT method, but the results obtained by the $EC_{He/O2-475}$ are higher than the TOT method. On the one hand, this difference is the problem of the method itself. Each method only isolates a specific part of the EC continuum, rather than all the components of the EC continuum (Currie et al., 2002; de la Rosa et al., 2011; Schmidt et al., 2001). On the other hand, the different isolation effect of the method is due to the difference of the organic carbon structure in the source sample.

NMR spectroscopy is an essential tool for acquiring detailed structural characterization results of the complex natural organic matter. The four combustion source samples were characterized by using solid-state ^{13}C NMR (Figure S2 and Table S5). The ^{13}C NMR results show that the average lower limit estimate for organic oxygen (Kelemen et al., 2010) from biomass combustion is 37% higher than that for fossil combustion. This finding indicates that there are more oxygen-containing organic carbon components in biomass combustion samples. The more organic oxygen in the sample, the greater the sample's polarity, which contributes to the increased fraction of water-soluble components in biomass combustion compared to the fossil combustion samples. In the absence of oxygen, using an aromatization process based on the cleavage of O-alkylated carbons might overestimate the EC content analyzed by thermal-optical methods (Li et al., 2013). The fraction of methyls in the aliphatics (FMA) (Chen et al., 2020) and nonprotonated aromatics (Kelemen et al., 2010) in pine wood combustion are 22% and 12% higher, respectively, than those in corn straw. These findings indicate that the water solubility of pine wood combustion products is worse than that of corn straw, in addition to the fact that the aromatic structure of pine wood combustion materials is denser. The water-soluble components of the corn straw combustion products were high, such that OC charring has a greatly influenced EC isolation when using the $EC_{He/O2-475}$ method, while minimally impacting EC isolation following the water extraction EC_{LARA} methods (Zhang et al., 2012).

By using FESEM in this study (Figure S3), it was observed that the pine wood samples contained a coke structure that was more condensed than the structure of the corn straw samples. In addition, a large number of soot structures were observed in the fossil source samples, indicating that fossil source samples are more condensed

than biomass samples.

In general, due to the differences between the isolation technologies, the EC/TC ratios of the six synthetic known samples (Table S4) revealed a deviation of approximately -99%~+125% between the calculated EC/TC ratios and the EC/TC ratios isolated by the four methods. The deviations isolated by the Hypy, EC_{LARA}, $EC_{He/O2-475}$ and CTO-375 methods were approximately -8%~+31%, -39%~+121%, -62%~+125% and -93%~-99%, respectively. The result obtained by the Hypy method is closest to the TOT method, and the average value of the ratio is 1.1, which shows the advantages of stability and reliability in purifying EC.

3.2. Comparison of carbon isotopes in EC

The different EC recoveries of the source samples may lead to different carbon isotope results in the EC from the synthetic known samples. The theoretical EC/TC ratios and $^{13}C_{EC}$ values of each hybrid sample were calculated according to the EC/TC (TOT) ratios and $^{13}C_{TC}$ values in the combustion source and the relative proportion of each source, respectively (Table S3). In the calculation, it is assumed that the ^{13}C value in the EC is very close with that in the TC in each source sample. The ^{13}C results of the EC from the six synthetic known samples processed by the four isolation methods are shown in Table 1. No significant difference of ^{13}C was observed between the results of the four isolation methods and the corresponding theoretical calculation values of all samples (T-test, P>0.05), except for the samples (S1, S2 and S3) containing corn straw combustion material isolated using the $EC_{He/O2-475}$ method, which presented much higher ^{13}C values. This finding indicated that the EC isolated using the $EC_{He/O2-475}$ method contained more biomass carbon. The reason for this result may be that the organic carbon of combusted corn straw is charring during the EC isolation process. However, this phenomenon was not observed in the samples containing pine wood combustion, which may be the reason that the ^{13}C value of the pine wood combustion sample is close to that of coal combustion.

The ^{14}C results of the EC are shown in Table 1 and Figure 1. Fraction of Modern (f_M) is used to express the proportion of biomass burning. The theoretical values of $f_M(EC)$ in the hybrid samples were obtained according to the proportion of fossil carbon and modern carbon in each sample in accordance with the EC/TC (TOT) ratios (Figure 1). The results show that the f_M values obtained by different isolation methods are quite different, and are generally affected by the ratios of combustion source sample EC recovered by different methods. Due to the low recovery rate of EC by CTO-375 method, the $f_M(EC_{CTO-375})$ value is irregular. Generally, the $f_M(EC_{CTO-375})$ value obtained by this method is more than twice the theoretical value. For the $EC_{He/O2-475}$ method, due to the influence of biomass burning OC charring the $f_M(EC_{He/O2-475})$ value obtained by this method deviates greatly from the theoretical value. On the whole, f_M values obtained by the Hypy and EC_{LARA} methods are relatively close to the theoretical values, but the two methods have their own advantages in the two different sets of samples. For the combustion of herbaceous plants, the Hypy method has a low EC recovery rate for such source samples, resulting in a small f_M value. For the combustion of woody combustion, due to the higher EC recovery rate by the Hypy method, the $f_M(EC_{Hypy})$ value is slightly higher

than that of samples containing herbaceous plants. For the EC_{LARA} method, in the first group of samples with corn straw combustion, the EC recovery rate of each source sample is lower than the theoretical value, so that the $f_M(EC_{LARA})$ value obtained by this method is the closest to the theoretical value. However, in the second group of samples containing woody combustion, the $f_M(EC_{LARA})$ value obtained by this method was significantly higher than the theoretical value, due to the higher recovery rate of woody combustion EC by the EC_{LARA} method. The results show that the f_M value of EC was not only related to the isolation method but also to the types and proportions of biomass sources in the sample.

The above results show that the type of biomass combustion affects the efficiency of the isolation method to purify black carbon and the accuracy of the radiocarbon test results. Charcoal, harvest residues and wood materials are the most common biomass fuels used as energy sources (Anenberg et al., 2013). From a global perspective, the types of biomass fuels are complex, but generally can be divided into two categories, herbaceous burning and woody plant burning, the ratio of the two types of biomass is about 58:42 (Table S6). Different regions have different proportions. According to the literature (Bond et al., 2004; Stevens et al., 2017; Streets et al., 2003; Zhang et al., 2019a), developed countries, such as Europe and North America, have a relatively high proportion of woody plants, while developing countries, such as Africa and Asia, have a relatively high proportion of herbaceous plants (Table S6). According to the recovery rate of different types of biomass combustion EC by different methods, the deviations that may be caused by the results of testing ^{14}C in different regions are estimated. The results are listed in Table S6. It can be seen that on a global scale, the f_M value obtained by the Hypy method is the closest to the theoretical value. Therefore, the Hypy method is an effective and stable approach for matrix-independent ^{14}C quantification of EC avoiding charring in aerosols.

3.3. Carbon isotopes of EC in SRM 1649b

SRM 1649a/b, urban dust, was used to check the quality of EC or EC isotope measurement method (Currie et al., 2002; Liu et al., 2013; Szidat et al., 2004b; Reddy et al., 2002; Heal et al., 2011). SRM 1649b was prepared from the same particulate material that was issued in 1982 as SRM 1649 and re-issued in 1999 as SRM 1649a, and the only difference is that the bulk material was sieved to a smaller particle size fraction [47]. Therefore, the f_M and δ^{13}C of TC in SRM 1649b obtained in this study was consistent with SRM 1649a reported by Szidat et al (Szidat et al., 2004b). EC/TC ratios, f_M-EC and δ^{13}C-EC of SRM1649b isolated using Hypy method in this study and archived data from the literature using different isolation methods are listed in Table 2. The EC/TC ratios varied from 7.5% to 46% determined by the different analyzing methods. However, the value of about ~28% obtained in this study is in good agreement with that obtained by Hypy method (Meredith et al., 2012) and by TOT method (Currie et al., 2002). The f_M and δ^{13}C of EC in SRM 1649a ranged from 0.038 to 0.153 and from -26.55‰ to -24.8‰ respectively reported by the previous research using the different isolation methods except Hypy (Currie et al., 2002). The corresponding values of 0.11 and -24.9‰ treated by Hypy method in this study are just in the range of archived data. Therefore, the values of ^{13}C and ^{14}C of EC_{Hypy} in SRM 1649b provide a definite and comparable reference for the future research methods.

4. Conclusions

Carbon isotope (^{14}C and ^{13}C) analysis is a powerful tool for distinguishing the carbon sources in carbonaceous aerosols. As addressed in this work, one main challenge of this method is the isolation of EC or BC for carbon isotope analysis. In this study, six synthetic known samples were collected, including biomass combustion (corn straw or pine wood) and coal combustion products and motor vehicle exhaust. These samples were then used to evaluate four EC isolation methods, which included the Hypy, CTO-375, $EC_{He/O2-475}$ and EC_{LARA} methods. The results demonstrated the Hypy method was in good agreement with the thermo-optical (TOT) method for the quantification of EC. And the EC f_M values depended not only on the isolation method but also on the types and proportions of the biomass sources in the samples. The Hypy method is the most appropriate EC isolation method of the four methods reported here, followed by the EC_{LARA} method. The Hypy method, which can be used to isolate a highly stable portion of EC_{Hypy} and avoid charring, is a more effective and stable approach for the matrix-independent ^{14}C quantification of EC in aerosols. The EC_{Hypy} of SRM1649b sample was isolated by the Hypy method. The results indicated that the ^{13}C-EC_{Hypy} and non-fossil EC_{Hypy} values of SRM1649b were -24.9‰ and 11%, respectively. These two isotope values was able to provide a valuable reference for other EC isolation methods.

Supporting Information
Supporting Information may be found in the online version of this article.

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Author contributions
GZ led the study. JL and XZ designed the study, developed the analysis protocols, and wrote the initial manuscript. XZ, SZ, JL, PD, SG, CT, YC and PP provided data, provided comments on the analysis, and contributed and reviewed the final manuscript.

Competing interests
The authors declare that they have no conflict of interest.

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536 **Table 1.** The $\delta^{13}C$ and ^{14}C results of EC from the six synthetic known samples by four isolation methods.

Sample	$\delta^{13}C$‰(EC) (calculated)	f_M(EC) (calculated)	$\delta^{13}C$‰(EC_{Hypy}) (±0.5 ‰)	f_M (EC_{Hypy})	$\delta^{13}C$‰($EC_{CTO-375}$) (±0.5 ‰)	f_M ($EC_{CTO-375}$)	$\delta^{13}C$‰($EC_{He/O2-475}$) (±0.5 ‰)	f_M ($EC_{He/O2-475}$)	$\delta^{13}C$‰(EC_{LARA}) (±0.5 ‰)	f_M (EC_{LARA})
S1	-22.98	0.2192	-23.40	0.0946±0.0013	-22.26	0.4027±0.0145	-19.69	0.3378±0.0025	-23.55	0.2140±0.0023
S2	-22.77	0.2795	-23.42	0.1375±0.0015	-22.42	0.5332±0.0172	-17.00	0.3809±0.0038	-23.77	0.2437±0.0024
S3	-22.43	0.3201	-23.31	0.1694±0.0016	-22.60	0.7368±0.0169	-18.69	0.4547±0.0029	-24.11	0.2590±0.0025
S4	-25.16	0.2403	-24.33	0.3145±0.0045	-25.83	0.4019±0.0076	-24.36	0.5005±0.0036	-24.28	0.5101±0.0030
S5	-25.52	0.3053	-24.55	0.3382±0.0049	-25.85	0.4779±0.0119	-24.57	0.6487±0.0036	-24.54	0.6655±0.0041
S6	-25.59	0.3483	-24.57	0.3707±0.0063	-25.76	0.5966±0.0098	-24.84	0.7226±0.0033	-24.68	0.7315±0.0034

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559 **Table 2.** [14]C and ^{13}C analysis results in SRM 1649 a/b.

Sample	f_M	M_C (μg)	δ^{13}C (‰ vs VPDB)	EC/TC	reference
1649b TC	0.525±0.002 (n = 1)	220	-25.6±0.5 (n =2)	0.275± 0.050	this work
1649a TC	0.522±0.018 (n = 5)	12–87	-25.5±0.6 (n = 2)	0.280 ± 0.080	ref (Szidat et al., 2004)
1649a TC	0.510±0.011 (n = 3)	not given	-25.3±0.3 (n =2)	0.080±0.010	ref (Reddy et al., 2002)
1649a TC	0.610±0.040	not given	not given	not given	ref (Currie et al., 2002)
1649a TC	0.505±0.003	not given	not given	0.458± 0.025	ref (Currie et al., 2002)
1649a TC	0.517±0.004	not given	not given	not given	ref (Currie et al., 2002)
1649b EC	0.108 ± 0.002 (n = 1)	270	-24.9±0.5 (n = 2)	0.275±0.050	this work
1649b EC	0.112±0.080* (n = 1)	~460	-24.9±0.5 (n = 2)	0.275±0.050	this work
1649a EC	0.066±0.020 (n = 4)	37–70	-24.8±0.5 (n = 4)	0.280 ±0.080	ref (Szidat et al., 2004)
1649a EC	0.065±0.014 (n = 3)	~2800	-26.55± 0.04	0.080±0.010	ref (Reddy et al., 2002)
1649a EC	0.140±0.050 (n = 1)	459	not given	~0.280	ref (Liu et al., 2013)
1649a EC	0.150±0.080	not given	not given	not given	ref (Heal et al., 2011)
1649a EC	0.065±0.003 (n = 1)	not given	not given	0.077±0.002	ref (Currie et al., 2002)
1649a EC	0.153±0.002	not given	not given	0.458± 0.025	ref (Currie et al., 2002)
1649a EC	0.038±0.012	not given	not given	0.109± 0.005	ref (Currie et al., 2002)

560   * The same 1649b EC obtained by the Hypy method was sent to BETA for ^{14}C analysis.

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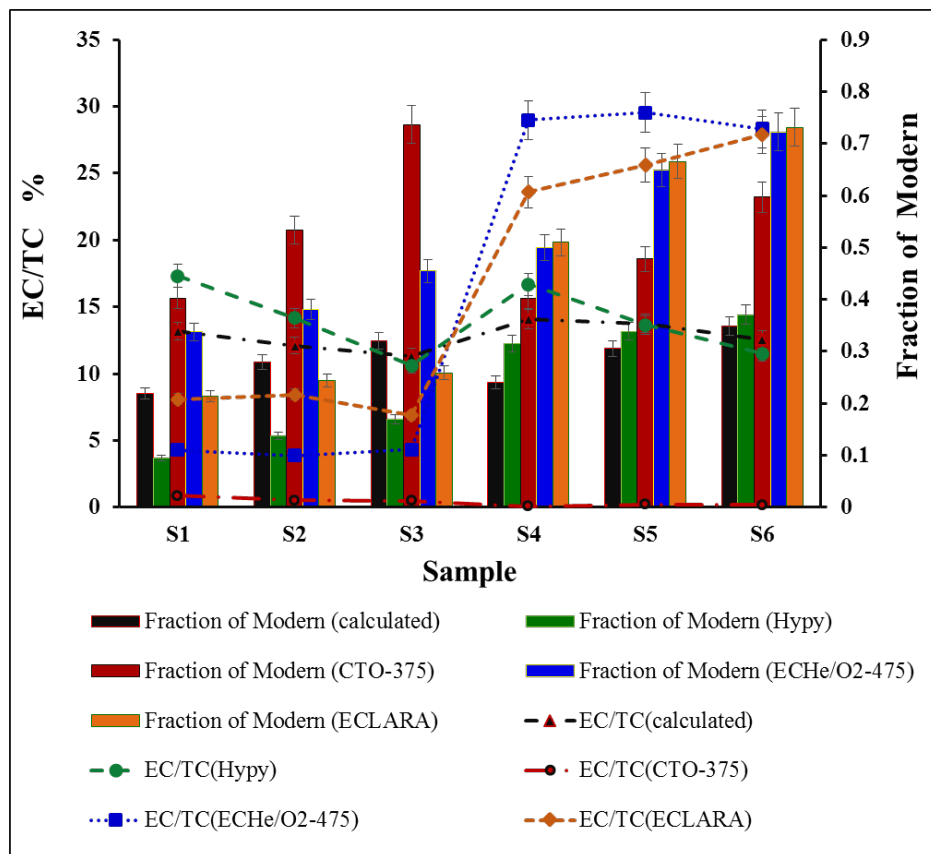
Figure 1. The EC/TC% and ^{14}C results of EC from the six synthetic known samples by four isolation methods.