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On the isolation of elemental carbon (EC) for micro-molar ^{14}C accelerator mass spectrometry: development of a hybrid reference material for ^{14}C-EC accuracy assurance, and a critical evaluation of the thermal optical kinetic (TOK) EC isolation procedure

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Abstract. The primary objective of the research reported here has been the development of a hybrid reference material (RM) to serve as a test of accuracy for elemental carbon (EC) isotopic (^{14}C) speciation measurements. Such measurements are vital for the quantitative apportionment of fossil and biomass sources of "soot" (EC), the tracer of fire that has profound effects on health, atmospheric visibility, and climate. Previous studies of ^{14}C-EC measurement quality, carried out with NIST SRM 1649a (Urban Dust), showed a range of results, but since the "truth" was not known for this natural matrix RM, one had to rely on isotopic-chemical consistency evidence (^{14}C in PAH, EC) of measurement validity (Currie et al., 2002). Components of the new Hybrid RM (DiesApple), however, have known ^{14}C and EC composition, and they are nearly orthogonal (isotopically and chemically). NIST SRM 2975 (Forklift Diesel Soot) has little or no ^{14}C, and its major compositional component is EC; SRM 1515 (Apple Leaves) has the ^{14}C content of biomass-C, and it has little or no EC. Thus, the Hybrid RM can serve as an absolute isotopic test for the absence of EC-mimicking pyrolysis-C (char) from SRM 1515 in the EC isolate of the Hybrid RM, as well as a test for conservation of its dominant soot fraction throughout the isolation procedure.

The secondary objective was to employ the Hybrid RM for the comparative evaluation of the thermal optical kinetic (TOK) and thermal optical transmission (TOT) methods for the isolation of EC for micro-molar carbon accelerator mass spectrometry (AMS). As part of this process, the relatively new TOK method was subjected to a critical evaluation and significant development. Key findings of our study are: (1) both methods exhibited biomass-C "leakage"; for TOT, the EC fraction isolated for AMS contained about 8% of the original biomass-C; for TOK, the refractory carbon (RC) isolated contained about 3% of the original biomass-C.; (2) the initial isothermal oxidation stage of the TOK method substantially reduced the transfer of artifact char to the RC fraction, improving isolation capabilities; (3) the Hybrid RM was not equal to the sum of its parts, with matrix interactions inducing premature loss of EC which, however, could be quantified and minimized; (4) the three-stage TOK method provided a superior capability for carbonate quantification at the sub-micromolar level, with "reagent-free" removal of carbonate-C from EC – essential for low-level EC-^{14}C AMS.

1 Background, objectives, and extant particulate carbon reference materials

Quantitative apportionment of fossil and biomass sources of carbonaceous particles is critically dependent on the capability to measure [14]C (and ^{13}C) in representative samples of such particles. When questions of long-range transport, or potential impacts on climate, or archival (ice core) records are involved, "low-level" (micro-molar) accelerator mass spectrometry (AMS) measurements may also be required (Currie et al., 2000). Low-level AMS, however, is particularly susceptible to chemical impurities; as a result, the "clean-chemistry" thermal and thermal optical processing techniques are especially attractive. Wet-chemistry carbonate removal, for example, proved disastrous in attempts to determine ^{14}C in non-carbonate particulate carbon in tiny samples of snow and firn from Greenland (Slater et al., 2002). (See also Sect. 4.2 of this manuscript.) Another critical issue is ^{14}C speciation – i.e., measurement of ^{14}C in

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individual chemical fractions of carbonaceous particles, especially "EC"[1]. ^{14}C speciation poses a special problem, in that the species of interest must be isolated prior to AMS target preparation, though, admittedly, on-line GC/AMS is on the horizon.

The main focus of the present work is to explore means to assure quality measurements of ^{14}C in the elemental carbon fraction of atmospheric particles. Isotopic-chemical particulate carbon Reference Materials (RMs) constitute a natural choice to accomplish this objective, but unless such RMs have known isotopic and chemical composition, they cannot be relied upon to guarantee "absolute" accuracy. NIST SRM 1649a (Urban Dust) is a case in point: Although it is a homogeneous, yet wonderfully complex RM, and comprises an excellent example of (^{14}C) isotopic heterogeneity, it does not have known EC-chemical or EC-isotopic (^{13}C, ^{14}C) composition. As a result, for measurements of EC and ^{14}C-EC, it is thus far limited to method-specific ("operational") QA. This was demonstrated in the international intercomparison of 2002, where results for EC in SRM 1649a spanned a factor of 7.5 among laboratories, and the very few data for ^{14}C in EC ranged over a factor of four (Currie et al., 2002). The median result for f_M(EC)=0.065 came from the work of Reddy et al. (2002), using the "thermal oxidation/residue" method (Gustafsson et al., 1997). More recently, a consistent result, 0.066±0.020, was obtained by Szidat et al. (2004), using a modification of that method; this supports the adoption of these results as the basis for an RM-Method specific "Reference Value."

To address the "isolation" problem, we must consider methods to uniquely separate the carbon fraction of interest (EC) for ^{14}C AMS, while avoiding the problem of attempting to sharply separate spurious char carbon from EC at the optical "split-point" of thermal optical analysis (TOA). Linked to this chemical isolation – split time problem is the assumption that the optical balance between char and EC accurately reflects isotopic-chemical balance at the same split time – i.e., the issue of char carbon and EC physical mixing or exchange. Another non-trivial issue related to the split time is the matter of uniformity, because the validity of the optical split point, and that of the measured attenuation function, per se, require a uniform deposit for meaningful transmittance (or reflectance) measurements. This represents a difficulty

for measurement of EC in bulk RMs (as SRM 1649a) and geochemical samples not processed to produce uniform deposits.

To overcome the uniformity problem, G. A. Klouda and coworkers prepared two series of uniformly deposited filter RMs, for quality control of thermal optical analysis in the atmospheric particulate science community. Both series represent progeny of SRM 1649a; that is, both series have been prepared by resuspension of the bulk SRM 1649a, for deposit on quartz fiber filters. The first, prototype series denoted "ACG" filter RMs, has been utilized both in the SRM 1649a intercomparison of 2002, and in our present study, as a calibration and uniformity check. The new reference material, RM 8785, represents a fine fraction ($<2.5\,\mu m$) of SRM 1649a, and it, too, has been subjected to an intercomparison. The EC/TC problem, observed with the results for the bulk SRM, is still present: Two widely-used TOA methods (as practiced by the "TOR laboratory" and the "TOT laboratories") had similar outcomes for the two reference materials, with TOR and TOT results differing in each case by roughly a factor of 1.8 (EC/TC≈0.49 and 0.28, respectively) (Klouda et al., 2005)[2].

"Black Carbon" (BC) reference materials have been made available also by the International Steering Committee for Black Carbon Reference Materials (BC-Steer, 2005). The Committee was formed during the 1999 Geochemical Society Meeting at Harvard University, in connection with the Symposium on Black Carbon (BC) in the Environment. The mission of the Committee is to address the need for developing BC reference materials for the broad environmental sciences community. Since its formation in 1999, BC-Steer has developed a suite of RMs, including: BC reference materials such as soot, charcoal, aerosol, soil, and sediment; and interfering materials, such as humics, kerogens, and coals. These materials served as the basis for perhaps the most extensive international comparison ("Ring Trial") to date involving BC reference materials. First results, available in April 2005, were a focus of the Committee's second BC Symposium, at the 2005 General Assembly of the European Geosciences Union (EGU, 2005). Detailed information concerning the Committee, background literature, and sources and descriptions of BC reference materials can be found on the website: http://www.geo.unizh.ch/phys/bc/, together with Ring Trial results, methods, and participants In August 2005, public discussion of the Ring Trial results was opened.

In the following text, we present preliminary results of efforts: to develop a hybrid isotopic-chemical reference material having known EC-^{14}C composition; and to devise a "clean chemistry" process for carbonate carbon removal and

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[1] Terminology: In keeping with NIST usage, Elemental Carbon (EC) is used here as the generic term for carbonaceous material, resulting from incomplete combustion, that is optically absorbing and resistant to oxidation. Thus, EC could be taken as equivalent to black carbon. For the TOT and TOK thermal optical procedures, EC is quantified as the carbon that evolves beyond the optical split point. Refractory Carbon (RC) is used to denote the carbon that evolves in the last, high temperature oxidation stage of both procedures – stage II of TOT, which is identical to stage III of TOK. RC≥EC, since it may contain a pyrolytic char component, which is quantified before the optical split point. Where necessary for clarity, subscripts are applied, as in EC_{TOT}, RC_{TOK}.

[2] The TOT-TOR differences appear to derive primarily from differences in heating cycles ("temperature profiles") – in particular the difference in the first stage (helium) temperature maxima: 850°C to 900°C (TOT laboratories) vs. 550°C (TOR laboratory) (Klouda et al., 2005, Tables 1, 2).

Table 1. Carbon data[a,b].

	Forklift Diesel Soot SRM 2975 [D]	Apple Leaves SRM 1515 [A]	Hybrid RM (DiesApple) [DA][c]
Total Carbon	0.78 ± 0.06	0.45 ± 0.03	0.50 ± 0.04
TC/m: mass fraction	0.77 ± 0.06		0.53 ± 0.04
		<0.44>	<0.55>
Refractory Carbon	0.93 ± 0.04	0.29 ± 0.01^{d}	0.60 ± 0.02^{e}
X_{RC}: RC_{TOT} mole			
fraction (RC/TC)	<large>		<0.56>
(TOT procedure)			
Refractory Carbon	0.90 ± 0.04	0.005 ± 0.002	0.18 ± 0.01^{e}
X_{RC}: RC_{TOK} mole			
fraction (RC/TC)	<large>	<none>	<0.39>
(TOK procedure)			

[a] $\pm$ denotes estimated standard uncertainty; <...> denotes the expected (theoretical) result.
[b] Unless otherwise indicated, standard uncertainties of dimensionless quantities may be taken as ≤ 0.04.
[c] The mass fraction of SRM 2975 [D] in DiesApple [DA] is 0.303 ± 0.001; the carbon fraction is 0.427 ± 0.015. The respective mass and carbon fractions for SRM 1515 [A] in DiesApple [DA] complement those of SRM 2975.
[d] $\geq 99\%$ char-C
[e] n=2 (replicates)

elemental carbon isolation for micromolar ^{14}C speciation of carbonaceous particles. The Hybrid RM is then used to test the assumption that isolated EC fractions are free from certain artifacts – viz.: positive bias from char mixing/exchange, and negative bias from premature, matrix-dependent EC oxidation.

2 The hybrid reference material

As indicated above, a principal objective of our work was to prepare a reference material that could provide a direct test for ^{14}C measurement of elemental carbon. Valid ^{14}C-EC data can be extremely important not only for fossil/biomass apportionment of EC, per se, but also for demonstrating whether ^{14}C-EC data can serve as a surrogate for ^{14}C-PAH data, since PAH apportionment has vital implications for both health effects and combustion source identification. Such an isotopic-chemical link would be particularly interesting for investigations of time and space series of carbonaceous aerosols in remote atmospheres and ice cores, for example, where PAH abundances are far too low to permit direct ^{14}C assay. The reasonable assumption of such a direct, isotopic link gave weight to certain of the ^{14}C-EC data in the recent SRM 1649a intercomparison (Currie et al., 2002), but since the ^{14}C content of its elemental carbon fraction was unknown, this assumption and the question of possible measurement artifacts could not be tested rigorously.

To provide a material that could give a direct test of ^{14}C-EC measurement validity, we proposed to prepare a mixture of two of NIST's natural matrix standard reference materials – selected for their compositional relevance to atmospheric carbonaceous particles[3], and because of their complementary, nearly orthogonal isotopic-chemical properties. These are SRM 2975, Forklift Diesel Soot, and SRM 1515, Apple Leaves. The chemical relevance of the Diesel Soot is evident; that of the Apple Leaves follows: (1) from the significant occurrence of natural biopolymers[4], such as cellulose, in atmospheric particles (Kunit and Puxbaum, 1996), and (2) from the charring potential (hence artifact production) of such materials in the thermal and thermal-optical methods of EC analysis. Beyond that, these materials were selected because of their very special isotopic attributes: SRM 2975 is expected to be totally free of ^{14}C, while SRM 1515 should have the ^{14}C/^{12}C ratio of the living biosphere (at the time of photosynthesis). In effect, SRM 1515 can serve as an absolute isotopic tracer for artifact (pyrolysis) char in the EC or RC isolated for ^{14}C AMS.

[3] The expression "compositional relevance" is not intended to convey compositional identity. The aim was to prepare a reference material that could provide a means to explore quantitatively certain measurement artifacts, linked to EC isolation for ^{14}C AMS, and for isotopic particulate EC quality control in a variety of environmental disciplines.

[4] The substantial difficulties in EC measurements of SRM 1649a derive from the large degree of charring, which in turn may arise from the presence of natural biopolymers. Such components may contribute to the approximately 40% biomass carbon content of the SRM, greater than any of the component species thus far isotopically assayed in this material (Currie et al., 2002: Table 3).
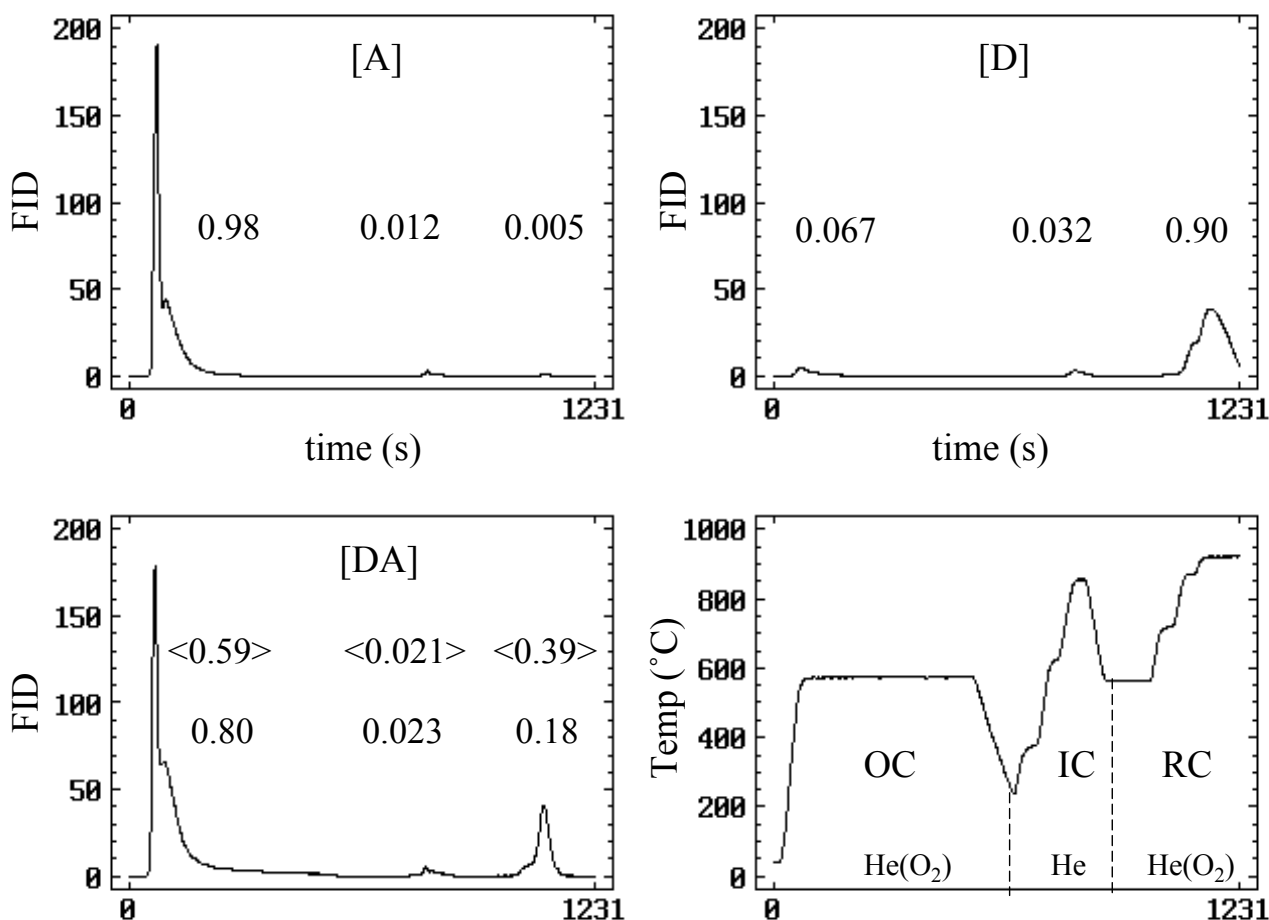
Fig. 1. Temperature profile and carbon evolution thermograms for thermal optical kinetic (TOK) analysis of NIST SRM 1515 (Apple Leaves) [A], SRM 2975 (Forklift Diesel Soot) [D], and the Hybrid, mixed RM "DiesApple" [DA]. The three stages of analysis include, I: isothermal oxidation (560°C; He+1% O_2) (OC); II: high temperature inert gas (He) decomposition of IC (inorganic and/or intermediate highly condensed, non-absorbing carbonaceous material); and III: stepped temperature oxidation (He+1% O_2) of refractory carbon (RC). Numerical triplets within each panel indicate the observed and, for the hybrid, the expected (< >) mole fractions of carbon evolution for each stage of the analysis. The thermograms [A] and [D] are scaled according to their mixing ratio in the Hybrid RM. The thermogram for the actual hybrid [DA] differs from the sum of those parts [D+A], however, showing matrix catalyzed carbon transfer from region-III (RC) to region-I (OC).

The relative portions of the two SRMs for this exploratory study were chosen for maximum artifact detection sensitivity – i.e., to yield a roughly equal mixture of biomass-C and fossil, soot-C in the hybrid (mixed) RM. Prior to this study no data existed on the ^{14}C content of the two SRMs. Reasonable assumptions, however, put the ^{14}C content of SRM 2975 as negligible, and that of SRM 1515 at 1.18 fraction of modern (f_M). This value for the Apple Leaves SRM is based on the presumed year of growth (1987) and the short-term (geochemical) decay curve of ^{14}C (Currie et al., 2002; Fig. 1). The EC fraction of SRM 2975 was expected to be "large," and that of SRM 1515, to be negligible. Also, if cellulose can be taken as a model for the carbon content of SRM 1515, its carbon mass fraction would be approximately 0.44. Experimental results for these two materials, as given in columns 2 and 3 of Table 1, are generally consistent with

expectations. Only the Diesel Soot SRM was tested for ^{14}C content (Table 2, column-2). A consistency check of the ^{14}C content (TC) of the Hybrid RM ("DiesApple") (Table 2, column 4) ruled out any major departure from the presumed ^{14}C value of the Apple Leaves SRM.

Prior data for SRM 2975 total carbon (TC) and "soot carbon" have been generated by W. P. Ball (personal communication, 2001) and by Ö. Gustafsson et al. (2001). For TC, Ball and Gustafsson report mass fractions of 0.817±0.048, and 0.872±0.003, respectively; our result is 0.774±0.049 (Table 1: average, taking into account covariance). For EC/TC by TOK analysis, we determined a ratio of 0.787±0.039; Ball's result for soot-C is 0.772±0.069; Gustafsson's, 0.782±0.011.

The Hybrid RM was prepared by making an intimate mixture of the two SRMs: 204.1±0.5 mg of SRM 2975, plus

Table 2. AMS (^{14}C) results[a].

	Diesel Soot SRM	Apple Leaves SRM	Hybrid RM (DiesApple)
f_M: Total Carbon	0.0026 ± 0.0002	–	0.656 ± 0.002
(TC – "large" AMS samples)			0.624 ± 0.003
	<0.00>	<1.18>	<0.68>
f_M: Elemental Carbon	–		0.190 ± 0.006
(EC$_{TOT}$ – "small" AMS samples)		<none>	0.152 ± 0.004
(TOT procedure)	<0.00>		<0.00>
f_M: Refractory Carbon[b]	–		0.123 ± 0.008
(RC$_{TOK}$ – "small" AMS samples)		<none>	0.093 ± 0.004
(TOK Procedure)	<0.00>		<0.00>

[a] <...> denotes a "theoretical" result; "–", not measured; ±, standard uncertainty

[b] The final, refractory carbon (RC) peak, which was isolated for AMS, was found by thermal optical analysis to contain a small amount of char-C (see Sect. 4.2).

468.7±0.3 mg of SRM 1515. This gave an expected total carbon (TC) mass fraction of about 0.55, which is consistent with the observed mass fraction (Table 1). Similarly, the C and ^{14}C contents of the individual SRMs can be used to determine the expected f_M(TC) value for the Hybrid RM. Again, reasonable agreement is found (Table 2). The replicates for TC and f_M(TC) for the Hybrid (Tables 1, 2) indicate that the material is relatively homogeneous, chemically (C) and isotopically (^{14}C), for the 0.5 mg to 1 mg portions used in this study.

Note that other complementary RM mixtures could be prepared, if, for example, one wished to test the hypothesis that a specific analytical technique accurately isolated EC that was entirely biomass-C. In that case soot from wood or biomethane could be used, together with a synthetic polymer having fossil fuel as feedstock. Preparation of mixtures giving various intermediate values for EC biomass carbon would also pose no difficulties. In light of the results of tests performed here, however, it would seem advisable to use EC components that are purer soot-C, without the complex polyaromatic hydrocarbon composition of the diesel soot SRM. (Hexane soot, as endorsed by BC-Steer, 2005, would be an interesting alternative for the BC (EC) end member of the Hybrid RM.)

3 Analytical techniques

Although the development of an excellent EC ^{14}C isolation technique was an essential goal, that was not the main driving force for this work. Rather, our prime objective was to demonstrate the applicability of a Hybrid RM, with known EC-^{14}C, for testing of possible EC isotopic artifacts (as from isotope mixing from char) using existing procedures.

For this purpose, we applied two thermal oxidation procedures, one being a particular version of the widely-used TOT procedure, used in both the 2002 intercomparison (Currie et al., 2002; Sect. 3.3.2 and footnote 4), and the RM 8785 intercomparison (Klouda et al., 2005, Table 1). The other was a modification of the TOK procedure (Currie and Kessler, 1999). The first (TOT) uses a 2-stage heating cycle of the sample, using multiple temperature steps – first in He, then in He (1% O$_2$). The heating cycle ("temperature profile") employed, shown in Fig. 2a, was based on the optimization study of J. M. Conny et al. (2003, Table 6). In this case the EC component is determined by optical balance – the split point (time) being given by the point at which the transmission (of a laser beam passing through the sample) returns to its initial value, signaling the removal of artifact EC (pyrolysis char-C). This procedure is not well suited for off-line isotopic measurement, however, since the char-C and the native EC form a composite peak, or are in close proximity We attempted isolation of the EC component by stopping the analysis at the split point, retrieving the residual material for AMS target preparation and analysis.

The second procedure (TOK) is better designed for isolation of a thermogram carbon peak. It is based on the refractory nature of soot carbon, and it begins with an isothermal oxidation stage, designed to oxidize more labile organic species, as well as their pyrolysis products (char). This approach was inspired by thermal oxidation studies of Cachier et al. (1989) and Gustafsson, et al. (1997), and the wet chemical oxidation method of Wolbach and Anders (1989) which was subsequently applied to RMs by Masiello et al. (2002). In addition to the thermal oxidation studies of Cachier et al. (1989), and Gustafsson et al. (1997), a method for OC elimination in an oxidizing environment to minimize artificial (pyrolytic) char was developed by Lavanchy et al. (1999) contemporaneously with the development of the TOK method.
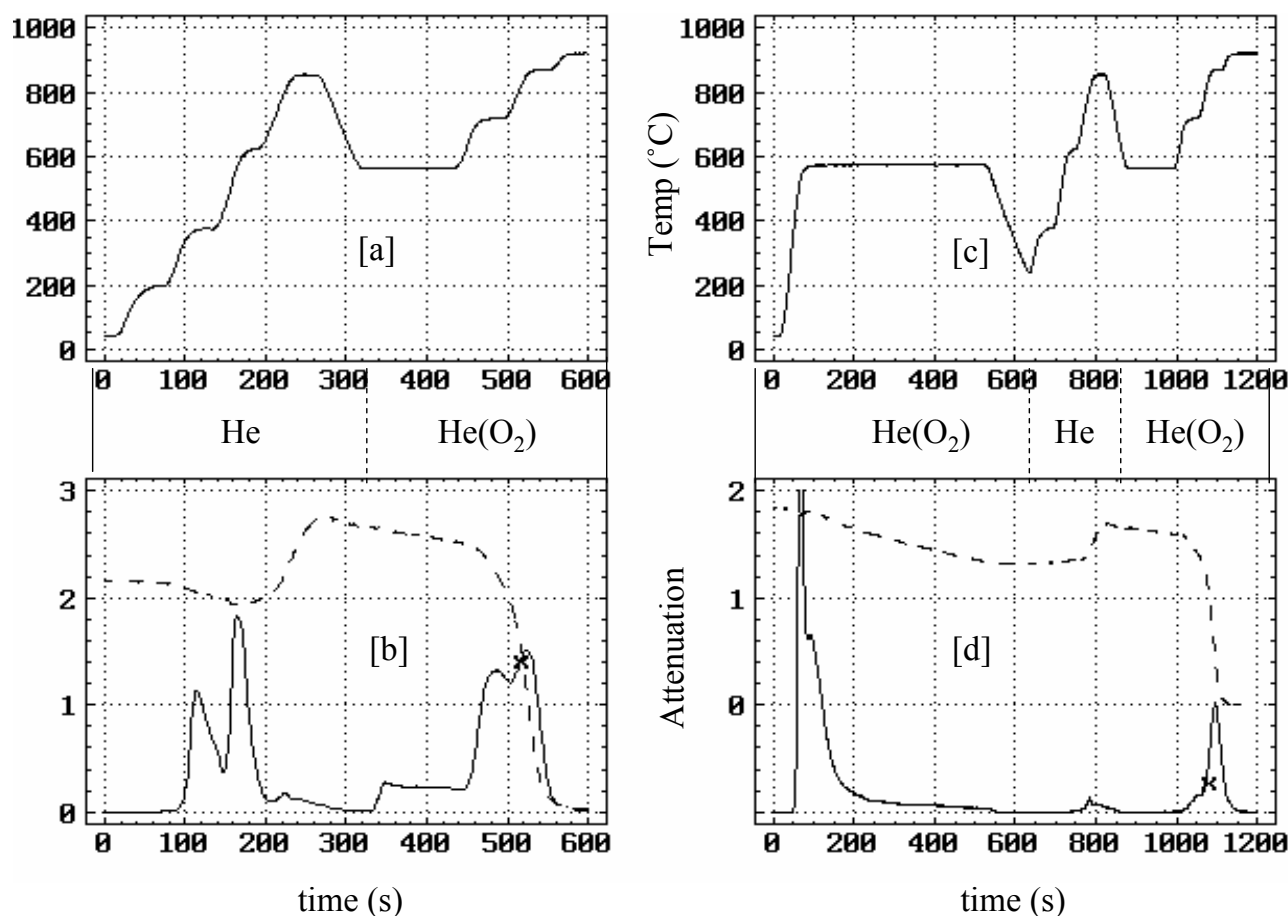
Fig. 2. Temperature profiles **(a, c)** and thermal optical carbon evolution thermograms (solid lines) for the hybrid RM, by thermal optical transmission analysis (TOT) **(b)**, and thermal optical kinetic analysis (TOK) **(d)**. Dashed lines represent the optical attenuation functions, with split points indicated by the symbol "x". (Note the monotonic decrease in attenuation during the isothermal oxidation stage of the Hybrid RM (d).)

The thermal optical kinetic (TOK) procedure (Currie and Kessler, 1999) is similar to the above thermal and chemical oxidation procedures, except that the initial isothermal oxidation stage (He, 1% O_2) is followed by the 2-stage TOT procedure discussed above. Also, the TOK method permits monitoring of sample attenuation during the entire 3-stage procedure. In this case the final carbon peak is well separated from other thermal carbon peaks, and it is selected as the refractory component (RC), for isotopic measurement.

Substantial isolation of a relatively char-free refractory component for isotopic assay has the merit of minimizing potential pitfalls linked to optical splitting. Besides the aforementioned assumptions of deposit uniformity and optical vs. isotopic balance (and a strictly sequential oxidation of char and EC), are significant questions regarding variations of apparent absorption coefficients with temperature, sample loading, and sample matrix, and even char vs. EC (Conny et al., 2003; Kirchstetter, T., personal communication, 2005).

The TOK temperature program used for the refractory-C isolation and analysis is shown in the bottom right panel of Fig. 1. The three stages reflect the differing process-ing conditions (thermal and chemical): I, isothermal oxidation (560°C; He+1% O_2) (OC); II, high temperature inert gas (He) decomposition of IC (inorganic and/or intermediate highly condensed, non-absorbing carbonaceous material); and III, stepped temperature oxidation (He+1% O_2) of refractory carbon (RC). The other three panels in Fig. 1 show thermograms for SRM 1515 [A], SRM 2975 [D], and the hybrid RM [DA] – with [D] and [A] scaled according to their mixing ratio in the hybrid RM. (Numerical triplets within each panel indicate the observed and, for the hybrid, expected ($<$ $>$) mole fractions of carbon evolution for each stage of the analysis.)

With this method we find large gaps between the different C-classes, making for relatively facile isolation of RC for isotopic measurement. This contrasts with the TOT thermogram, which is compared in Fig. 2 to that of the TOK procedure, for the hybrid RM. Another important feature of the TOK procedure is represented by the second stage, labeled IC, where carbonates and surviving non-EC condensed carbonaceous material are decomposed at high temperature in an inert atmosphere. One advantage of this stage,

following isothermal oxidation for the minimization of char, is improved carbonate detection capability, and "clean chemistry" and loss-free carbonate destruction, of considerable importance for low-level AMS measurements.

Accelerator mass spectrometry measurements were performed at the National Ocean Sciences AMS (NOSAMS) facility at the Woods Hole Oceanographic Institution. Full replicate analyses were made on individual EC_{TOT} and RC_{TOK} preparations of the Hybrid RM, samples of which were prepared on $1.0\,cm^2$ Pallflex Quartz strips using the methods described below. Unlike the ^{14}C measurements (TC) made on the bulk SRM (2975) and Hybrid RM, the carbon contents of the isolated EC_{TOT} and RC_{TOK} fractions required the "small sample" (μ-molar-C) facility at NOSAMS. The goal in using these techniques was to test the applicability of the hybrid RM, and at the same time gain some quantitative assessment of isotopic-chemical artifacts – e.g., biomass-C "leakage" into the isolated fractions.

4 Experimental results

Results of the TOK experiments with the Apple Leaves SRM and the Diesel Soot SRM (Fig. 1, panels A and D, respectively) show that: (1) practically all of the Apple Leaf carbon (0.98 mole fraction) appears in the OC window, whereas 0.90 mole fraction of the Diesel Soot carbon appears in the RC window. For the DiesApple [DA] Hybrid, however, we find that the "whole" [DA] is not equal to the sum of its parts [D+A]. Qualitatively, by visual examination of Fig. 1, and quantitatively, from the C-mole fraction triplets, we see that evolved carbon has been transferred from stage-III (RC) (0.39 expected, 0.18 observed) to stage-I (OC) (0.59 expected, 0.80 observed). Also, for the preparation of AMS samples, it is clear from the thermograms in Fig. 2 that TOT and TOK offer quite different capabilities for clean isolation of EC from char. In this section, we consider these results from the perspectives of the ^{14}C data, the thermal optical data, and finally the kinetic data derived from the TOK thermogram.

4.1 AMS data

Since the hybrid RM derived virtually all of its EC from the Diesel Soot SRM 2975, and since that material was practically "dead" – ca. 0.3% modern carbon (Table 2), one would expect the EC fraction of the Hybrid to be essentially free of ^{14}C. The bottom rows of Table 2 show that that was not the case. Both the EC_{TOT} data and the RC_{TOK} data show significant contamination from modern carbon, hence, biomass carbon from the Apple Leaves (SRM 1515) component. This result demonstrates both the utility of an RM having known ^{14}C-EC, and the failure of both methods to isolate fractions free from isotopic exchange or contamination. This may be due, in part, to the fact that optical balance does not guar-

antee isotopic balance; and in part to the difficulty of batch-type fraction isolation from a continuous flow procedure, as discussed below. In the case of the TOK refractory carbon component, it is possible that exposure to biomass-C (from SRM 1515) may be slightly enhanced, because the isolated RC peak contains a small amount of char-C, as shown by the optical measurements. (See also Sect. 4.2 and footnote 6.) However, considering the total RC-char observed in the Diesel Soot [D] and Apple Leaves [A] end member SRMs – $\approx$11% and <0.01%, respectively, one would expect the RC_{TOK} char carbon to be essentially fossil. It would be very interesting indeed to apply the Hybrid RM to the testing of other methods that have been devised for the analysis of ^{14}C-EC. A quantitative assessment of the biomass-C contamination of the samples submitted for AMS follows.

The first step in estimating the fraction of biomass-C leakage into the (EC, RC) AMS samples is to consider the biomass-C contribution to each. The biomass-C fraction, ϕ_i, equals $f_M(obs_i)/f_M(bio)$, where $f_M(obs_i)$ is observed fraction of modern carbon in the material isolated for AMS (EC_{TOT}, RC_{TOK}), and $f_M(bio)=1.18$ is the f_M value for the carbon from the Apple Leaves SRM. The TC-normalized value for the biomass-C in the isolated material is then given by the product ($\phi_i r_i$), where $r_i=r_{TOT}$ equals EC/TC for the AMS samples isolated by TOT, and $r_i=r_{TOK}$ equals RC/TC for the AMS samples isolated by TOK. Finally, the fraction of the initial biomass-C (Apple Leaves-C) that contaminates the isolated material equals the ratio of ($\phi_i r_i$) to the fraction of Apple Leaves-C in the Hybrid reference material (0.573). Thus, for TOT, the average biomass-C fraction, ϕ_{TOT}, present in the isolated samples is (0.17±0.02)/1.18, or 14.4%. Given the observed value for r_{TOT} (i.e., EC/TC) of 0.31±0.02 for the Hybrid RM, we estimate the fraction of the original biomass-C that contaminates the isolated AMS sample to be [(0.144)(0.31)]/0.573 or (7.8±1.0)%. Since ideally the EC isolated should contain essentially no biomass-C, this result may be taken as a measure of EC-char mixing across the optical split point and/or imperfections in the batch isolation process when there is a composite peak, with a preponderance of (biomass-C) char (Fig. 2b).

Similar calculations follow for the isolated RC fraction from the TOK preparations. Here, the average value for the biomass-C fraction of the RC peak ϕ_{TOK} is (0.108±0.015)/1.18, or $\approx$9.2%, which is consistent with the observed percentage of char in the peak (7±4)% (Table 3), but not with the belief that that char should be primarily fossil. That discrepancy suggests the possibility of matrix-catalyzed carbon exchange between the fossil and biomass components of the Hybrid RM. Given the observed value for r_{TOK} (i.e., RC/TC) of 0.18±0.01 for the Hybrid RM, we estimate the fraction of the original biomass-C that was transferred to the RC isolate to be [(0.092)(0.18)]/0.573 or (2.9±0.4)%. Even this might have been eliminated, however, had the RC peak been split into EC, char components.

Table 3. Performance characteristics of TOT and TOK as a function of isothermal oxidation temperature[a].

	TOT	TOK (360°C)	TOK (460°C)	TOK (560°C)
[A]: RC/TC [b]	0.29±0.01	0.32±0.02	0.22±0.01	(0.005) [e]
[A]: peak/BL [c]	0.39±0.10	0.38±0.10	0.60±0.11	3.4±0.3
[DA]: char/RC [d]	0.47±0.03	0.49±0.03	0.31±0.03	0.07±0.04

[a] "±" denotes the standard uncertainty
[b] Apple Leaves SRM 1515 [A], RC /TC
[c] Apple Leaves SRM 1515 [A], carbonate peak/baseline
[d] DiesApple RM [DA]: RC char fraction (ratio: char/RC=1−(EC/RC))
[e] The ≈0.5% refractory-C (stage-III) is absent when an oven clean step is inserted after stage-II.

Fig. 3. Initial, isothermal stage evolved carbon patterns (OC oxidation stage) for the virtual [D+A] RM (mixing ratio weighted average of [D] and [A]), and for the "real" mixed RM [DA]. Both curves are normalized to TC=100 µg. (The actual temperature profile is shown by the upper dashed curve.) The TC-normalized areas under the two curves show that this stage accounts for ≈60% of the [D+A] carbon, and ≈80% of the DiesApple [DA] carbon.

4.2 Thermal optical data

Table 1 shows consistency between the observed and expected refractory carbon fractions for the TOT procedure. For TOK, however, the "whole" [DA] was clearly not equal to the sum of its parts – i.e., as derived from the mixing ratio of SRMs 2975 and 1515. This is especially apparent in the relative areas of the OC and RC peaks of [DA] in Fig. 1, and numerical discrepancy shown in Table 1 (0.39 expected RC mole fraction, 0.18 observed). Some further insight into a cause for the apparent RC loss is given in Fig. 3. This figure presents an amplified view of the initial portion of the isothermal oxidation rates of the "ideal" (D+A curve) and real (DA curve) mixed reference material. What we observe is a greatly enhanced rate of loss of carbon in the hybrid RM, that continues through to the end of the isothermal stage. The increased loss is evidently EC$_{TOK}$, at least in part, given a

parallel decrease in attenuation. This is shown in Fig. 2d, where attenuation decreases (transmission increases) monotonically during the isothermal oxidation stage[5]. Additionally, a quantitative link between premature EC oxidation and the missing RC of Table 1, is given in Sect. 4.3.

A second important difference between the TOT and TOK procedures relates directly to the effective isolation of the EC from the respective refractory carbon peaks: i.e., the final RC peaks in Figs. 2b and d, respectively. The split points, as derived from the attenuation curves in Fig. 2, are indicated by the "x's" in the two panels. The corresponding EC/RC ratios for these samples, which had reasonably uniform deposits, were 0.53±0.03 (TOT) and 0.93±0.04 (TOK). (Errors in EC/RC estimates as large as 0.06 to 0.09 were observed when insufficient attention was given to sample uniformity and split-time validity.) Thus, roughly half of the refractory carbon peak is char-C for TOT, in contrast to about 10% for TOK. Failing to "split" the RC properly can be disastrous in the case of TOT, but it introduces much smaller char contamination in the case of TOK.[6]

The stage-II (IC), high temperature decomposition of carbonaceous material that fails to be oxidized in the isothermal stage (I) of the TOK procedure has two significant benefits: (1) It converts highly condensed organic matter to char that can be optically discriminated from EC in stage-III. (Otherwise that carbon fraction, which comprised a few % TC in our studies, will be co-emitted with EC, causing a positive artifact. This point has been made also by Novakov and Corrigan (1995), who observed that non-volatile organic carbon from biomass that escapes high temperature decomposition can mimic black carbon.) (2) It provides enhanced sensitivity

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[5]Attenuation, as used in this manuscript is equated to $\ln(I_f/I)$, where I is the transmitted laser signal, and I_f is the final laser signal following complete C-combustion. (Note the zero-offset for attenuation in Fig. 2d.)

[6] Splitting the TOK refractory-C peak for isotopic analysis merits further study. One drawback, however, is that such splitting would sacrifice the clean isolation characteristic of the TOK procedure; another is that the validity of the split point depends on the uniformity of the deposit.

for carbonate analysis, and contamination-free removal of carbonate carbon – the latter being crucial for valid EC ^{14}C data and the preparation of well-performing AMS targets. Improved carbonate measurement capability is depicted graphically in Fig. 4, which shows the IC-stage (II) of the TOK analysis of SRM 1515 (Apple Leaves). The (net) peak height to baseline ratio shown there is approximately 3.4, whereas for the same SRM analyzed by the TOT procedure, the carbonate-C peak to baseline ratio is but 0.39. The quantitative result for the carbonate carbon peak shown in Fig. 4 corresponds to 1.48±0.11 μg carbon in the sample taken for analysis, and a carbonate-C/TC ratio of 0.00544±0.00002 for this SRM. (The relative standard uncertainty of the estimated mass of carbonate-C [u_r=7.1%] is much larger than that of the estimated mole fraction [u_r=0.42%] because of the uncertainty of the absolute calibration factor for these analyses. The mole fraction uncertainty derives strictly from the uncertainty of estimating the net carbonate-C peak area.) An independent check on validity of so precise an estimate came from a comparison of the carbonate-C mole fraction of the Hybrid RM: observed, vs. calculated from the mixing ratio of SRMs 1515 and 2975 and the above carbonate-C value for SRM 1515. The observed value for the Hybrid RM was 0.00316±0.00007; the value calculated from the mixing ratio was 0.00312±0.00001. (For SRM 2975 no carbonate peak was visible – only a featureless, refractory organic carbon baseline that accounted for about 3% of the total carbon.)

4.2.1 Isothermal oxidation temperature (TOK)

To give a somewhat broader perspective to the performance of the TOK procedure for AMS sample isolation, we include here results of a brief study of the influence of the isothermal oxidation temperature. Temperatures selected covered the range from 360°C (just below the onset of biopolymer charring observed with the Apple Leaves SRM) to the default value 560°C (where just noticeable soot loss (≈0.8%) was observed with the Diesel Soot SRM). Charring, as evidenced by a local decrease in transmission, occurred with all three materials, though it was most noticeable with SRM 1515, because of the absence of EC-attenuation from the SRM 2975 end member The local attenuation maximum at ≈95 s for all three materials signaled the completion of charring, about 15 s after start of the 560°C isothermal phase. Following the transient phase of the analysis, relatively smooth char and EC combustion set in, where the decrease in the residual carbon function could be modeled as a sum of first order reactions (see Sect. 4.3.)

Performance criteria to assess the impact of oxidation temperature included: (1) the relative amounts of the Apple Leaves carbon appearing as char in stage-III; (2) the net peak height to baseline ratio for carbonate-C in stage-II; and (3) for the Hybrid RM, the fraction of char-C in the stage-III (RC) carbon. Results for isothermal temperatures of 360°C, 460°C, and 560°C were included, as well as for TOT, since it
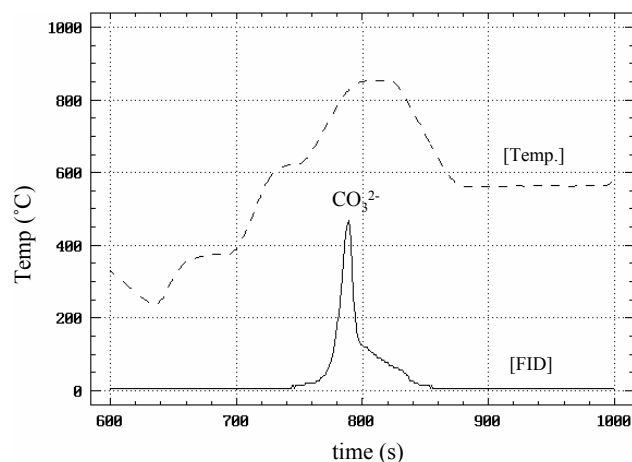

Fig. 4. Temperature profile and carbonate-C peak seen in the inert gas (He) IC stage of the TOK analysis of SRM 1515 (Apple Leaves).

represents the null case for TOK – i.e., the protocols for TOT and TOK are identical for the final IC- and RC-stages. From the experimental results (Table 3), it is clear that for this particular study the default temperature (560°C) yields the best performance. Kinetic analysis of the isothermal residual carbon function showed also that the residual organic carbon for the Apple Leaves was destroyed with a time constant of about 40 s, which is quite early in the isothermal stage of analysis (see also Fig. 3). "Tuning," or optimization of TOK parameters is a topic that is beyond the scope of this research, but one might consider adapting isothermal oxidation time-temperature selections to particular classes of samples. Premature EC loss from the Hybrid RM, for example, could be better controlled by reducing the overall isothermal time span to ≈150 s, given the 34 s time constant for OC oxidation in this material. Also, reducing the temperature for the Hybrid RM to 460°C proved effective in preventing most of the premature EC oxidation, but at the cost of increased char (≈30%) in the RC fraction An analogous temperature reduction strategy has been employed for the CTO procedure, to compensate for matrix catalyzed loss of soot BC in marine sediment (Elmquist et al., 2005).

4.3 Kinetic data

The isothermal oxidation stage of the TOK procedure lends itself to application of the kinetic approach to EC, or at least RC, assay, as pioneered by Wolbach and Anders (1989), and employed subsequently by Masiello and coworkers (1998, 2002). (Their "wet chemical" oxidation technique is described also in (Currie et al., 2002) under the label of "Ch(Cr)K".) By this approach, loss of carbon during isothermal oxidation is described by a sum of exponential terms, with the one having the largest time constant (slowest) being deemed the most refractory component. Input data for
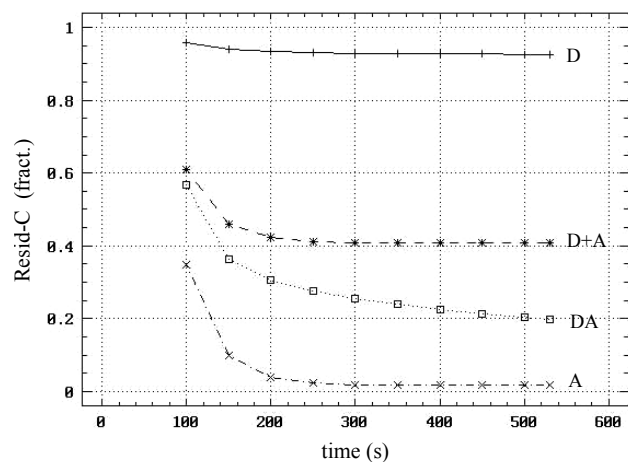
Fig. 5. Residual carbon functions for the isothermal oxidation stage of the TOK procedure. The curve for SRM 2975 [D] shows only a small decrease during the isothermal phase, including minimal (<1%) premature oxidation of EC. The curve for SRM 1515 [A] exhibits only a short-term "decay" resulting in nearly complete disappearance of its carbon during the first 100 s at 560°C. The virtual hybrid [D+A] shows the characteristics of both end members, while the real Hybrid RM [DA] exhibits premature loss of refractory carbon over the entire isothermal time span.

Fig. 6. Kinetic analysis (multicomponent exponential fitting) of the residual carbon data for [D+A] and [DA] as shown in Fig. 5. The 5-parameter model for the hybrid [DA] RM has long-lived components with time constants of 326 s and "large" (compared to the ≈430 s isothermal oxidation time span). The former gives an approximate match to the prematurely oxidized ("lost") refractory carbon. Both plots display a short-lived OC component.

such analysis comes from backward integration of the loss-rate data (thermogram) during the isothermal oxidation stage to determine the fraction of residual carbon (f_{rc}) as a function of time. Figure 5 shows the experimental f_{rc} curves for Apple Leaf [A] and Diesel Soot [D] end members of the DiesApple hybrid [DA], as well as the hypothetical curve [D+A] derived from the mixing ratio of [D] and [A]. The loss of carbon (organic carbon) from [A] is relatively rapid and nearly complete, while that from [D] is relatively slight and slow, with <1% loss of EC during isothermal oxidation at 560°C. [D+A] is necessarily the weighted average of the end members. The Hybrid RM [DA] is quite different, however, not being equivalent to a linear combination of the [D] and [A]. It exhibits premature loss of refractory carbon over the entire time span of the isothermal oxidation stage, illustrating the impact of composition-dependent matrix effects. (In the isothermal region, the residual-C curve follows the general pattern of the rate curve (thermogram), of which it is the integral)[7]. The partial, early loss of elemental carbon from the hybrid RM necessarily arises from thermochemical reactions made possible by interactions between the individual SRM components in the mixture. One hypothesis for

such mixture-induced enhanced oxidation is that oxygenated biomass carbon polymers may serve, perhaps indirectly, as supplementary oxidizing agents. (The "water gas" reaction, for example, comes to mind.) Matrix-catalyzed, premature oxidation of black carbon has been reported also by Novakov and Corrigan (1995), who investigated the catalytic effect of alkali metal ions on decreasing the combustion temperature of biomass smoke particles.

Quantitative analysis of the f_{rc} curves yields estimates of time constants and refractory-C component contributions. Up to 5-parameter non-linear least squares estimates were derived from the data shown in Fig. 5. Results are shown graphically in Fig. 6 for the (mathematically) synthetic TOK data [D+A] and for the real Hybrid RM [DA]. For the latter the best fit was represented by the 5-parameter model (a sum of 2 exponentials with unknown time constants, and an intercept), while for the former, only a 3-parameter model (one exponential function and an intercept) gave an acceptable fit. For the Hybrid, DiesApple, refractory carbon was modeled as moderate and very long-lived (slow reacting) components, having mean lives (time constants) of 326±6 s and "infinity" (i.e., much longer than the isothermal (560°C) time span of ≈430 s). The additional, short-lived component has a time constant (34±1 s) that is similar to that of SRM 1515 [A]. (The stated standard uncertainties (u) are based on the residual standard deviation from fitting the model to the f_{rc} data.) As noted earlier, one potential benefit from such kinetic analyses would be matrix-specific optimized times (or time-temperature combinations), for the isothermal oxidation stage for each class of samples, that balances the need to exceed the time for practical elimination of the

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[7] Figures 3 and 6 provide a direct, graphical comparison between the rate curves and the residual carbon curves, respectively. The latter can be modeled as a sum of exponential functions after about ≈100 s – i.e., some 20 s after the approach to temperature equilibrium (560°C). Figure 3 gives a clear indication of the shift from the transient state (during temperature rise) to the exponential state.
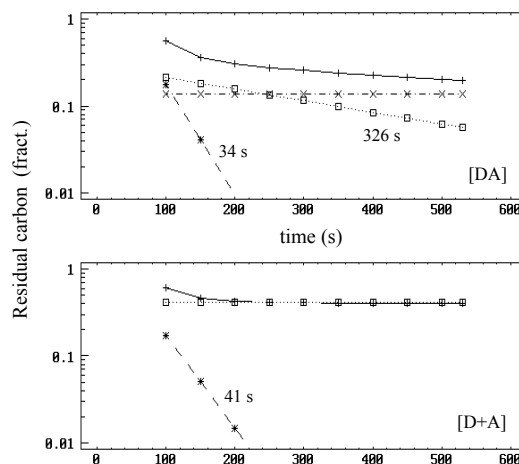
short-lived OC component and the desire to minimize loss of refractory components.

The TC-normalized initial values for the short-lived isothermal kinetic components provide an opportunity to check for mass balance among the three RMs. For Apple Leaves, the initial value of the short-lived component ($\tau \approx 40$ s) was 0.286±0.003; for Diesel Soot ($\tau \approx 45$ s), it was 0.025±0.001. Combining these results with the mixing ratio of the two SRMs yields an estimated TC-normalized value in the Hybrid RM of [(0.286)(0.573)+(0.025)(0.427)] which equals 0.175. Five parameter kinetic analysis of the Hybrid RM gave an observed value of 0.177±0.003 ($\tau \approx 34$ s). (On average, the readily oxidizable (short-lived) pyrolysis carbon components represented about 30% of the OC present in these materials.) The fact that mass balance is achieved for the OC char, and the fact that it is oxidized nearly ten times as fast as the least refractory EC component, support the assumption that, under these particular circumstances, the thermal optical split point might be used for the physical separation of EC for isotopic measurement – i.e., that char oxidation and EC oxidation are approximately sequential (see footnote 8). Also, the reduced time constant for the OC char combustion in the Hybrid RM is consistent with the matrix catalyzed combustion enhancement observed with the EC.

Initial values for the refractory (EC) components are interesting also, in that the long-lived (intercept) component gives an estimated (TC normalized) value of 0.14±0.01 for its contribution to the refractory-C, whereas the observed EC$_{TOK}$ value is 0.16±0.01 (derived from the optical split point of the RC peak, Fig. 2d). The initial value of the 326 s component on the other hand equals 0.21±0.01, large enough to account for most of the "missing" soot carbon. (Uncertainties here are combined standard uncertainties, including the measurement-calibration uncertainties.) Finally, in Fig. 7 we give a comparison of the combined EC components of the hybrid RM with the attenuation data from the isothermal region of the TOK procedure, from ca. 100 s to 530 s (Fig. 2d). The two sets of data are independently derived, yet they suggest a clear relationship, supporting the hypothesis that the more refractory components (τ=326 s and τ=∞) represent absorbing (black) carbon. (Fig. 7, in effect, represents the projection of the 3-dimensional (attenuation, f$_{rc}$, time) data onto the (attenuation-f$_{rc}$) plane.) The figure shows also that roughly half of the total carbon is evolved by the onset of the isothermal period (5th point (+) from the top of the diagram) during the transient period, when the temperature increases linearly from ca. 40°C to 560°C.

4.4 Control material: SRM 1649a

Comparative data, obtained with the prototype 1649a ("ACG") thermal optical control RM, showed analogous premature EC oxidation during the isothermal phase of the TOK procedure. The residual-C plot for this material (not shown) was quite similar to the DiesApple [DA] curve in Fig. 5; and
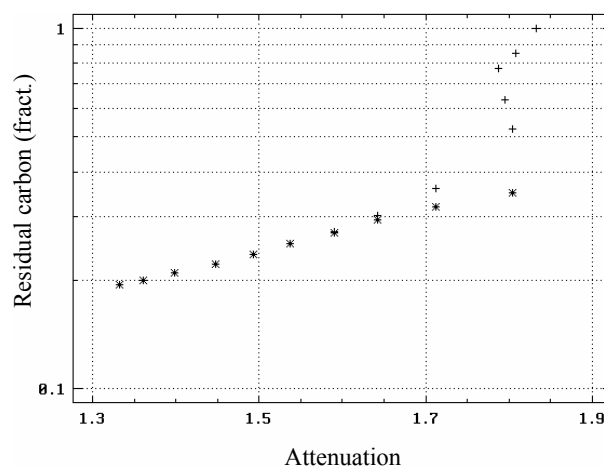

Fig. 7. Relation between the fitted longer-term exponential (refractory) components of the DiesApple RM and the parallel change in optical attenuation during isothermal oxidation, supporting the hypothesis that this refractory carbon is elemental carbon. Plus signs (+) represent total residual carbon; asterisks (*) represent the slowly oxidizing components [τ=326 s and τ=∞] during the isothermal period.

kinetic analysis, supported by a decrease in attenuation, gave an estimated EC/TC (stage-I) loss of 0.09±0.01. A tentative, temperature dependent decomposition of the final (stage-III) peak suggested greater and lesser refractory components of roughly 0.11 and 0.07, respectively. The total, 0.27, is consistent with cluster-2 data of the SRM 1649a intercomparison exercise (Currie et al., 2002), as well as the recent result (0.28) of Szidat et al. (2004) based on isotopic mass balance.

Additionally, the fact that the ACG controls had relatively uniform EC deposits increased the reliability of the estimated split times, compared to that of the bulk materials used in this study. This is reflected perhaps in the reduced magnitude and dispersion of the estimated char contribution to the RC (TOK) peak: (4.0±1.9)%, compared to (7±4)% for the Hybrid RM.

5 Summary and outlook

Mixed, natural matrix RMs of known and complementary isotopic composition show promise for revealing and quantifying unsuspected artifacts in EC analysis of complex carbonaceous particulate matter. A variety of known isotopic mixes could be generated, using for example, synthetic (fossil) fibers and wood-burning soot. For laboratories relying on carbon isotopes for source apportionment, such hybrid RMs could serve as essential QA materials, without which quantitative isotopic carbon artifacts could not be assessed. An interesting first step might be the organization of a EC-isotope speciation intercomparison, using such materials.

The assessment of EC abundance [EC/RC] in refractory carbon peaks isolated for AMS can be an essential step in

the design of robust ^{14}C-EC measurement procedures, reducing dependence on optical split times for char-free AMS fractions. In addition, the recovery of EC components for such isotopic measurements could be optimized by investigation of matrix-specific EC loss functions, and selecting isothermal oxidation time-temperature combinations that lead to minimum loss while achieving adequate separation from non-EC. This is illustrated by Fig. 6 [DA], where the isothermal time span could be cut in half (reducing the premature EC oxidation by about a factor of two), while still avoiding any significant contamination from the more reactive 34 s component.

A special opportunity for future research would be the development of thermal optical isotopic spectrometry (TOIS) for ^{13}C, ^{14}C characterization of different EC thermal oxidation kinetic components – i.e., "different parts of the BC spectrum" (BC-Steer, 2005). This would turn the seeming drawback of premature EC oxidation into an advantage: a powerful new tool to isotopically apportion individual EC kinetic components. Analogous to GC/AMS for ^{14}C characterization of individual chromatographic fractions, but with the addition of optical monitoring of attenuation, this approach would utilize samples of individual EC thermal fractions for carbon isotopic assay[8]. For materials such as the Diesel Soot, where the different EC fractions are in a degenerate state, an oxidation catalyzing matrix could be purposely added to bring about separation of the different components. Closely related to the TOIS concept is the work of Masiello and Druffel (1998) who pioneered the determination of isotopic-C (^{13}C, ^{14}C) functions (vs. oxidation time) in the application of the kinetic model to isotopic black carbon components in marine sediment, using an optimized version of the Wolbach-Anders (1989) wet oxidation (dichromate) technique.

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BC-Steer: International steering committee for black carbon reference materials, http://www.geo.unizh.ch/phys/bc/, 2005.

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[8] Unless the reaction time constants are dramatically different, pure component estimation would require a final mathematical step, since the sampled fractions would represent overlapping "decay curves".

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