Atmos. Chem. Phys. Discuss., 5, 3341–3366, 2005
www.atmos-chem-phys.org/acpd/5/3341/
SRef-ID: 1680-7375/acpd/2005-5-3341
European Geosciences Union

Atmospheric
Chemistry
and Physics
Discussions

On the isolation of elemental carbon for micro-molar ^{14}C accelerator mass spectrometry; evaluation of alternative isolation procedures, and accuracy assurance using a hybrid isotopic particulate carbon reference material

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Received: 15 March 2005 – Accepted: 11 April 2005 – Published: 26 May 2005

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Abstract

The primary objective of the research reported here has been the development of an hybrid reference material (RM) to serve as a test of accuracy for elemental carbon (EC) isotopic (^{14}C) speciation measurements. Such measurements are critically important 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 from SRM 1515 in the EC isolate of the hybrid RM, together with testing for conservation of its dominant soot fraction through the isolation procedure.

A secondary objective was the use of the hybrid RM for the comparative evaluation of the thermal optical transmission (TOT) and thermal optical kinetic (TOK) methods for the isolation of EC for micro-molar carbon accelerator mass spectrometry (AMS). Key findings were: that both methods exhibited biomass-C “leakage” into the fossil EC fraction, with substantially more for the TOT method; that the initial isothermal oxidation stage of the TOK method substantially reduced charring, improving isolation capabilities; that the hybrid RM was not equal to the sum of its parts, with matrix interactions yielding premature loss of EC which, however, could be quantified and minimized; and that 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 individual chemical fractions of carbonaceous particles, especially "EC"[1]. ^{14}C speciation in C-particles poses a special problem, in that the species of interest must be isolated prior to AMS target preparation, though, admittedly, GC/AMS is on the horizon.

The main focus of the present work is to explore means to assure quality measurements for ^{14}C in selected chemical fractions of C-particles, especially EC (or SC). Isotopic-chemical C-particle 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

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[1] Terminology: For the purpose of the present discussion black carbon (BC) will be used as the generic term for carbonaceous material, commonly resulting from incomplete combustion, that is optically absorbing and resistant to oxidation. Elemental carbon (EC) is used to indicate the optically-absorbing carbonaceous fraction quantified by the thermal-optical-transmission (TOT) procedure. Soot carbon (SC) is used similarly, to denote that portion of the refractory carbon that is quantified by the thermal-optical-kinetic (TOK) procedure. We use the term refractory carbon (RC) specifically to describe the final carbon peak in TOK analysis, as this peak can be readily isolated for isotopic analysis.

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 C-particle 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 that method; this supports the adoption of these results as the basis for an RM-Method specific "Reference Value."

The other purpose of our research is to address the "isolation" problem – i.e., to consider means to uniquely isolate the C-fraction of interest (EC, SC) for ^{14}C AMS, while avoiding the problem of attempting to sharply separate char-C from EC-C 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-C and EC accurately reflects isotopic-chemical balance at the same split time – i.e., the issue of char-C and EC physical mixing or exchange. Another non-trivial issue related to the split time is the matter of uniformity: that is, the validity of the optical split point, and that of the measured absorption 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 carbonaceous particle filter RM, SRM 8785, represents a fine fraction (<2.5 μm) of SRM 1649a, and it, too, has been subjected to an intercomparison. The EC/TC problem, observed with the results for the bulk RM, is still present: Two widely-used TOA methods (as practiced by the "TOR laboratory" and the "TOT laboratories") had similar outcomes for the two RM's, 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).

"Black Carbon" (BC) reference materials have been made available also by the International Steering Committee for Black Carbon Reference Materials (BC-Steer). The committee was formed during the 1999 Geochemical Society Meeting at Harvard University, in connection with Symposia on Black Carbon (BC) in the Environment. Black Carbon, considered by the Committee to derive from the continuum of incomplete combustion products ranging from chars to soot (metaphorical "BC spectrum"), is "ubiquitous in the environment, including aerosols, sediments, and soil". The mission of the Committee thus relates to the need for developing BC reference materials for the broad environmental sciences community. The plan has been to identify existing and potential RMs that are: 1) BC RMs such as "soot, charcoal, aerosol, soil, and sediment;" and 2) interfering/artifactual materials, such as "humics, kerogens, and coals." Basic background information concerning the BC Committee, including its membership, activities, and references can be found on the website: http://www.geo.unizh.ch/phys/bc/. Reference Materials available include: 1) BC and matrices containing BC: soot-BC, lignocellulosic char, soils, marine sediments, and aerosol; 2) five materials potentially interfering with BC analysis: shale, natural organic matter, melanoidin, and two coals. BC-Steer held its second BC Symposium in April 2005, in connection with the meeting of the European Geosciences Union in Vienna. One focus of the Symposium was the consideration of results of a just-completed 22-team ring trial intercomparison of the above materials.

In the following text, we describe and present preliminary results of efforts: to develop an hybrid isotopic-chemical reference material having known EC (SC), ^{14}C composition; and to devise a “clean chemistry” inorganic carbon (IC) and soot carbon (SC) isolation technique for μ-molar ^{14}C speciation of C-particles. The former (hybrid RM) is then used to test the assumption that the isolated EC, SC fractions are free from certain artifacts – viz.: positive bias from char mixing/exchange, or negative bias from premature, matrix-dependent SC oxidation.

2. The hybrid reference material

As suggested above, a principal objective was to prepare a BC (EC) reference material that could provide a direct test for compound-specific ^{14}C measurement of soot carbon[2]. Valid ^{14}C-BC data may be extremely important in demonstrating whether fossil/biomass-C apportionment of BC 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 C-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 SRM 1649a intercomparison (Currie et al., 2002), but since its “compound-specific” ^{14}C value 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-BC 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, 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:

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[2] Although the expression “compound-specific” is popularly used for isotopic measurements in specific chemical fractions, such as individual PAH, it is a misnomer in the case of BC, which possesses a complex and varying physical and chemical composition.

from (1) the significant occurrence of natural biopolymers[3], 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 BC 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 artifactual char in the EC and SC isolated for ^{14}C AMS.

The relative portions of the two SRMs 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 soot-C 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 C-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 for Apple Leaves SRM.

The Hybrid RM was prepared by making an intimate mixture of the two SRMs: 204.1±0.5 mg of SRM 2975, plus 468.7±0.3 mg of SRM 1515. This gave an expected

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[3] 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 be responsible also for the nearly 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).

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 value for the Hybrid RM. Again, reasonable agreement is found (Table 2). The experimental replicates for TC and for f_M 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 BC 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 BC biomass carbon would also pose no difficulties. In light of the results of tests performed here, however, it would seem advisable to use BC components that are purer soot-C, without the complex polyaromatic hydrocarbon composition of the diesel soot SRM. (Hexane soot, as endorsed by BC-Steer, would be an interesting alternative for the BC end member of the hybrid RM.)

3. Analytical techniques

Although the development of an excellent BC ^{14}C isolation technique is an essential goal, that was not the primary objective for this report. Rather, our interest was in demonstrating the applicability of the hybrid RM, with known BC-^{14}C, for the testing of possible BC isotopic artifacts (as from isotope mixing from char) using existing procedures.

For this purpose, we applied two thermal oxidation procedures, one being the widely-used TOT procedure, described in Currie et al. (2002), the other being 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). 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 artifactual 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 (1997), and the wet chemical oxidation methods of Wolbach and Anders (1989) and Masiello et al. (2002). The thermal optical kinetic (TOK) procedure (Currie and Kessler, 1999) is similar, except that the initial isothermal oxidation stage (He, 1% O_2) is followed by the 2-stage TOT procedure discussed above. Also, it permits monitoring of sample absorbance 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 temperature program used for the refractory-C isolation and analysis is shown in the bottom right panel (Temp) of Fig. 1. The three regions reflect the differing processing conditions (thermal and chemical); and the results, depicted in the other three panels of the figure, suggest large gaps between the different C-classes, making for relatively facile isolation of RC for isotopic measurement. This contrasts with the TOT carbon 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 (for inorganic and/or intermediate carbon), where carbonates and surviving non-SC 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" carbonate destruction, of 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 and SC 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 C-contents of the EC and SC 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 (fossil-C) EC, SC 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. The observations are quite similar for the TOT procedure. Results for the hybrid (DiesApple (DA)), are not so straightforward, however. 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 analysis.

4.1. AMS data

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

4.2. Thermal optical data

Table 1 showed 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 (hence SC) 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 SC, 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[4]. Additionally, a quantitative link between premature SC loss 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 effective isolation of the EC (SC) from the respective refractory carbon peak: i.e., the final isolated 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. For EC (TOT) the resulting ratio EC/RC is ≈0.6, whereas for SC (TOK) it is ≈0.9. (Standard uncertainties are large, ≈0.06 in each case, presumably as a result of non-uniform deposits.) Thus, some 40% of the refractory carbon peak is char-C for TOT, in contrast to about 8% for TOK. Failing to "split" the RC properly can be disastrous in the case of TOT, but introduces much smaller char contamination in the case of TOK[5].

The stage-II, high temperature decomposition of carbonaceous material that escapes destruction (oxidation) 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 SC in stage-III. (Otherwise that carbon fraction, which comprised a few % TC in our studies, might be co-emitted with SC, causing a positive artifact.) (2) It provides enhanced sensitivity for carbonate analysis, and contamination-free removal of carbonate carbon – the latter being crucial for valid SC ^{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 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

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[4] 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.

[5] 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.

carbonate-C peak to baseline ratio is but 0.42. 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. (No carbonate peak was visible for SRM 2975.)

4.3. Kinetic data

The isothermal oxidation stage of the TOK procedure lends itself to application of the kinetic approach to BC, or at least RC, assay, as pioneered by Wolbach and Anders (1989), and employed subsequently by Masiello et al. (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 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 from (A) is relatively rapid and nearly complete, while that from (D) is relatively slight and slow (ca. 2% over the 430 s time span of the isothermal oxidation stage). (D+A) is necessarily the weighted average of the end members. The hybrid RM (DA) however, is quite different, 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. (The residual-C curve, of course, follows the general pattern of the rate curve (thermogram) of which it is the integral.) The extended losses of carbon in the hybrid RM necessarily derive 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.)

Quantitative analysis of the f_{RC} data 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 is 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 time span of 430 s). The short-lived component has a time constant (34.3±0.8 s) which is similar to that of SRM 1515 (A). (Note that the standard uncertainties (u) reflect only the u's derived from fitting of the f_{RC} data.) A matrix-specific optimum time (or time-temperature combination) for the isothermal oxidation may be derived for each class of samples by balancing the need to exceed the time for practical elimination of the short-lived OC component ($\tau \approx 35$ s), and the desire to minimize loss of refractory components.

The initial values of the refractory components are interesting, in that the long-lived (intercept) component gives an estimated (TC normalized) value of 0.138±0.002 for its contribution to the refractory-C, to be compared to the observed SC value of 0.150 (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 0.211±0.001, large enough to account for most of the "missing" soot carbon. Finally, in Fig. 7 we give a comparison of the moderately refractory carbon component (τ=326 s) of the hybrid RM with the attenuation data from the isothermal region of the TOK procedure (Fig. 2d). The two sets of data are independently derived, yet they suggest a clear relationship, supporting the hypothesis that both the 326 s component and the "infinite" component 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.)

5. Summary and outlook

Mixed, natural matrix RMs of known and complementary isotopic composition show promise for revealing and quantifying unsuspected artifacts in EC and SC 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 quantitative QA materials, without which quantitative isotope carbon artifacts could not be assessed. An interesting first step might be the organization of a BC-isotope speciation intercomparison, using such materials.

The assessment of isotope peak BC abundance ((EC,SC)/RC) in isolated refractory carbon peaks can be a critical tool in the design of robust ^{14}C-BC isolation procedures. Recovery of BC fractions for such isotopic measurements could be optimized by investigation of matrix-specific BC loss functions, and selecting isothermal oxidation time-temperature combinations that lead to minimum loss while achieving adequate separation from non-BC. This is illustrated by Fig. 6 [DA], where the isothermal time span could be cut in half (reducing the premature BC oxidation by about a factor of two), while still avoiding any significant contamination from the more reactive 34 s component.

Acknowledgements. Special thanks go to A. P. McNichol and the NOSAMS staff for their out-

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standing cooperation in providing timely, high-quality data for ^{14}C in the bulk and speciated reference material samples. Thanks also to G. A. Klouda and J. M. Conny for important discussions, and to the latter for assistance with the transfer and rapid re-installation of the TOA apparatus during a critical laboratory move in the midst of the data acquisition. The assistance of A. M. James with some of the early laboratory experiments is gratefully acknowledged.

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Table 1. Carbon data[a,b].

	Diesel Soot SRM	Apple Leaves SRM	Hybrid RM (DiesApple)
Total Carbon	0.77 ± 0.03	0.45 ± 0.03	0.50 ± 0.03
TC/m: C mass fraction	0.77 ± 0.03		0.53 ± 0.03
		< 0.44 >	< 0.55 >
Refractory Carbon	0.93 ± 0.04	0.01 ± 0.01[d]	0.48 ± 0.02[c]
X_{RC}: RC mole fraction			
(RC/TC)	< large >	< none >	< 0.50 >
(TOT procedure)			
Refractory Carbon	0.90 ± 0.04	0.005 ± 0.002	0.18 ± 0.01[c]
X_{RC}: RC mole fraction			
(RC/TC)	< large >	< none >	< 0.39 >
(TOK procedure)			

[a] ± denotes estimated standard uncertainty; < … > denotes the expected (theoretical) result.

[b] Unless otherwise indicated, standard uncertainties of dimensionless quantities may be taken as approximately 0.01

[c] n = 2 (replicates)

[d] EC/TC result

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

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

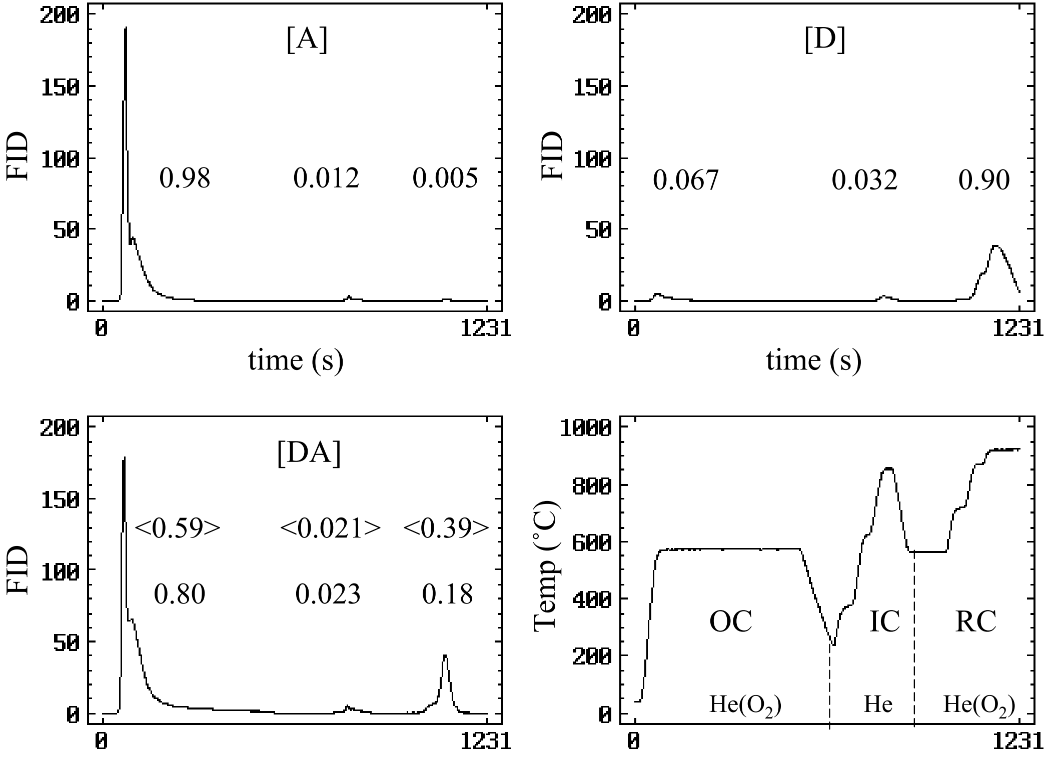

Fig. 1. Temperature profile (Temp) and carbon evolution thermograms for thermal optical kinetic (TOK) analysis of NIST SRM 1515 (apple leaves) (A), SRM 2975 (forklift diesel soot) (D), and the hybrid, mixed RM "DiesApple" (DA). Three stages of analysis are represented by isothermal combustion of organic carbon (OC) at 560°C, high temperature inert gas decomposition of IC (inorganic and/or intermediate highly condensed, non-absorbing carbonaceous material), and final high temperature oxidation of refractory carbon (RC). FID represents the response of the flame ionization detector. Numerical triplets within each panel indicate the observed and, for the hybrid, the expected (<>) mole fractions of carbon for each stage of the analysis.

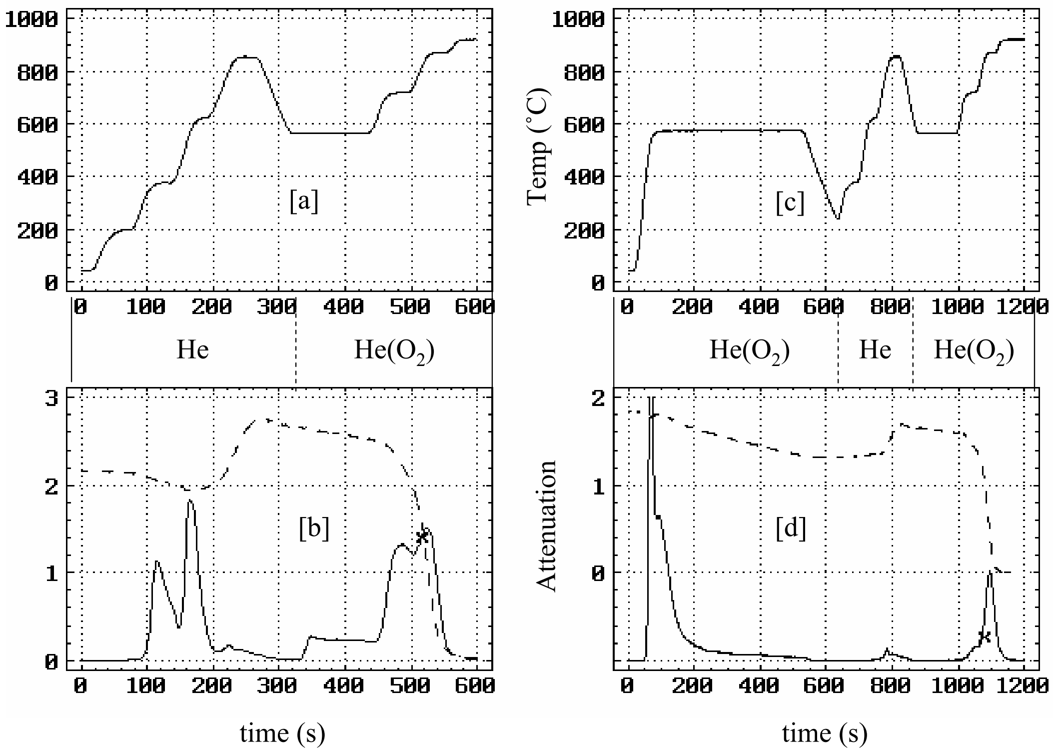

Fig. 2. Temperature profiles **(a, c)** and thermal optical carbon evolution thermograms (solid lines) for the hybrid RM, by thermal optical transmission analysis (TOT) **(b)**, and thermal optical kinetic analysis (TOK) **(d)**. Dashed lines represent the optical attenuation functions, with split points indicated by the symbol "x". (Note the monotonic decrease in attenuation during the isothermal oxidation stage of the Hybrid RM (d).)

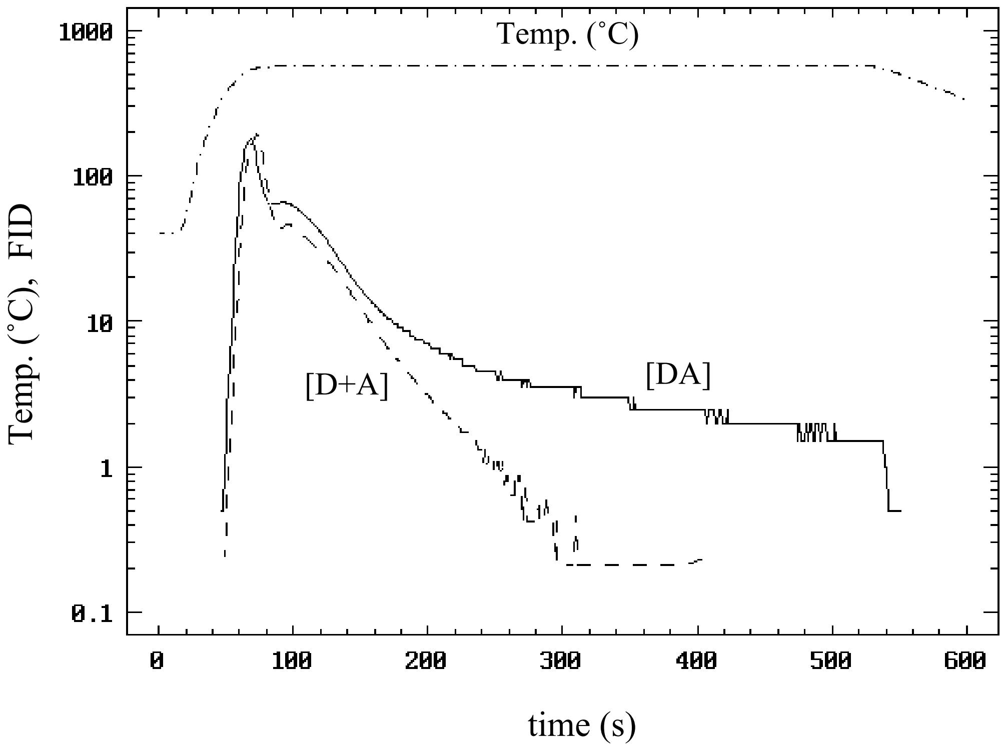

Fig. 3. Initial, isothermal stage evolved carbon patterns (OC oxidation stage) for the virtual (D+A) RM (mixing ratio weighted average of (D) and (A)), and for the "real" mixed RM (DA). Both curves are normalized to TC = 100 μg. (The actual temperature profile is shown by the upper dashed curve.) The 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.

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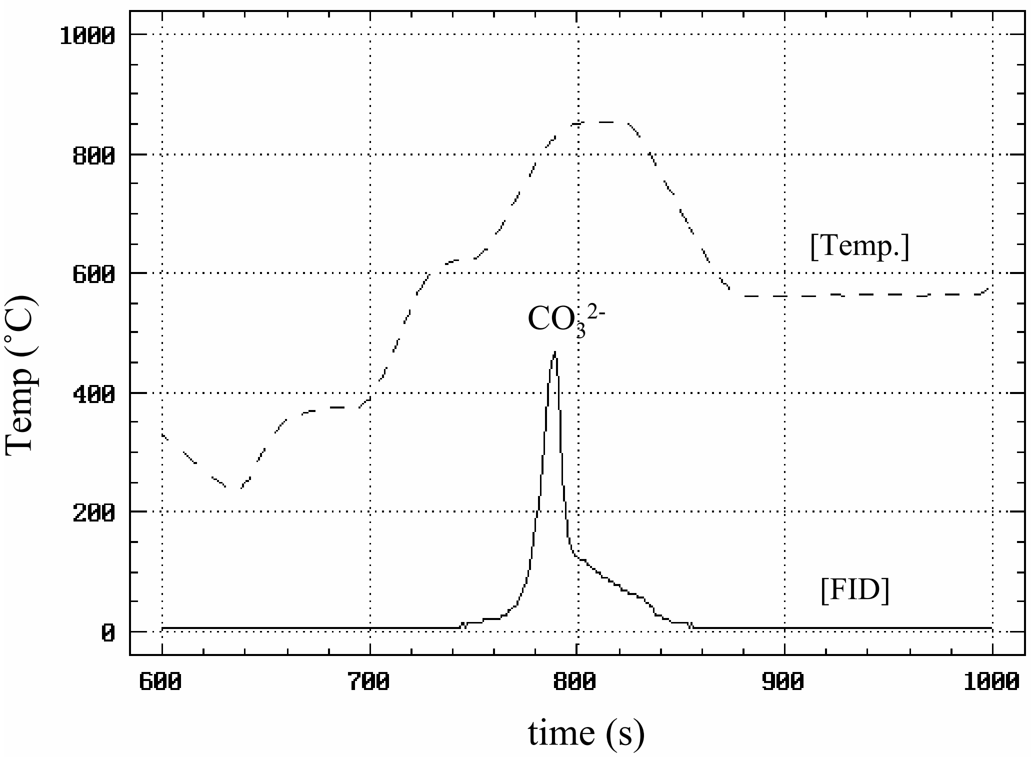

Fig. 4. Temperature profile and carbonate-C peak seen in the inert gas (He) IC stage of the TOK analysis of SRM 1515 (apple leaves).

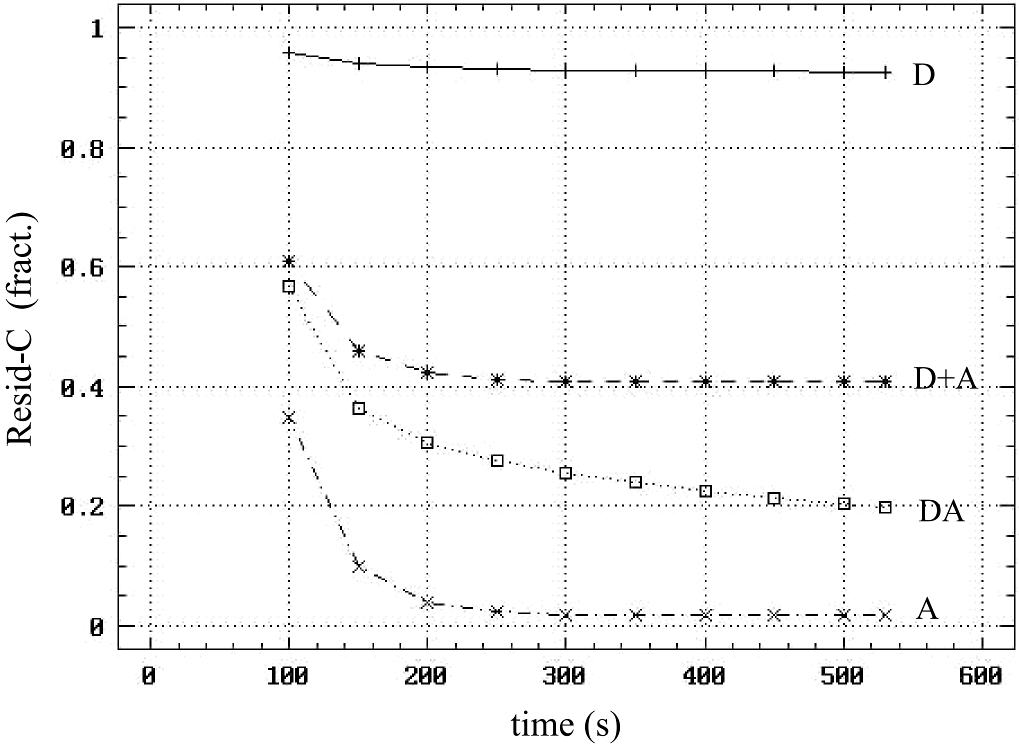

Fig. 5. Residual carbon functions for the isothermal oxidation stage of the TOK procedure. The curve for SRM 2975 (D) shows only a slight (ca. 2%) decrease over the 431 s time span; while that for SRM 1515 (A) exhibits only a short-term "decay" resulting in nearly complete disappearance during the first 100 s of the isothermal stage. 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 time span.

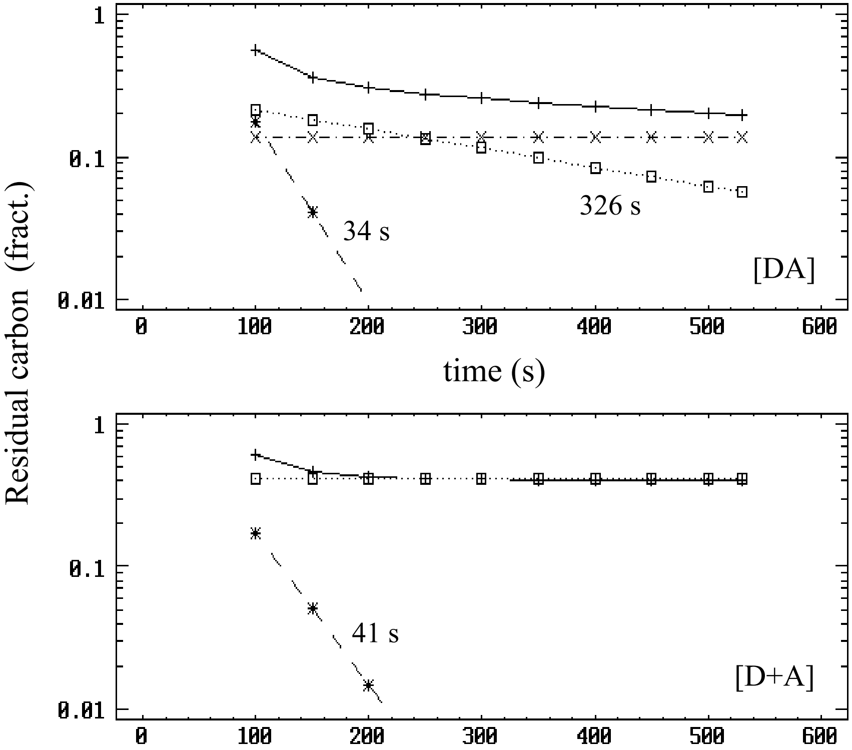

Fig. 6. Kinetic analysis (multicomponent exponential fitting) of the residual carbon data for (D+A) and (DA) as shown in Fig. 5. The 5-parameter model for the hybrid (DA) RM has long-lived components with time constants of 326 s and "large" (compared to the 431 s isothermal oxidation time span). The former gives an approximate match to the prematurely oxidized ("lost") refractory carbon. Both plots display a short-lived OC component.

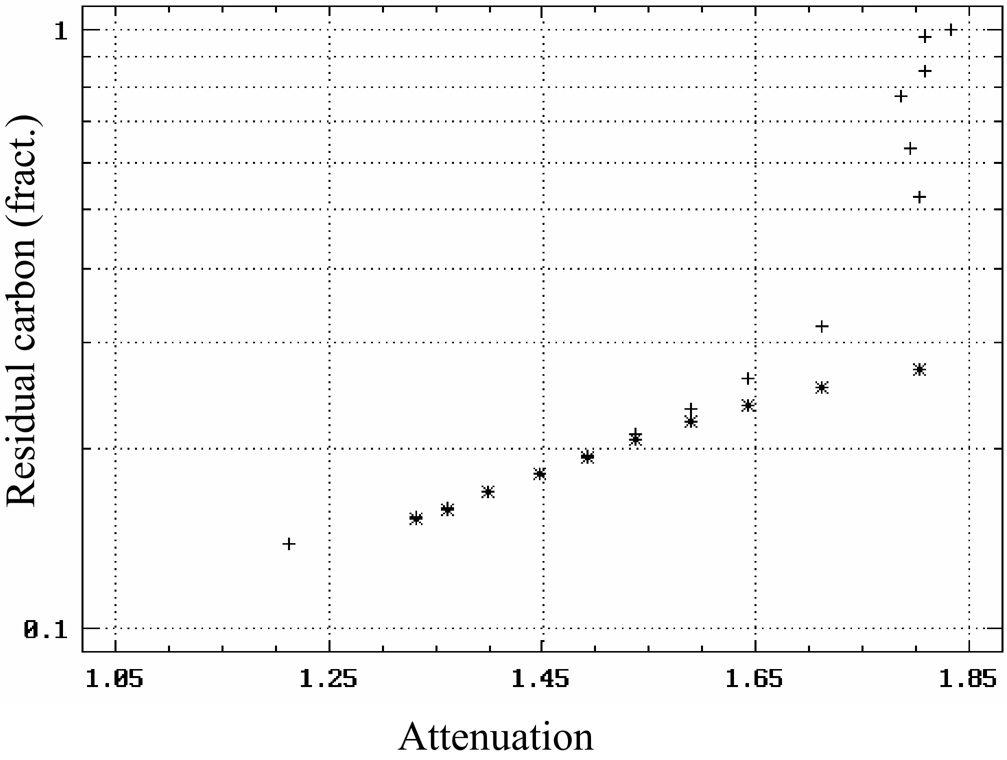

Fig. 7. Relation between the fitted longer-term exponential component of the DiesApple RM ($\tau \approx 326$ s) and the parallel change in optical attenuation during isothermal oxidation, supporting the hypothesis that this refractory-C component is also a BC component. (Plus signs represent total residual carbon; asterisks represent the slowly oxidizing component.)