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Factorial-based response-surface modeling with confidence intervals for optimizing thermal-optical transmission analysis of atmospheric black carbon

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ABSTRACT

Thermal-optical transmission (TOT) analysis measures black carbon (BC) in atmospheric aerosol on a fibrous filter. The method pyrolyzes organic carbon (OC) and employs laser light absorption to distinguish BC from the pyrolyzed OC; however, the instrument does not necessarily separate the two physically. In addition, a comprehensive temperature protocol for the analysis based on the Beer-Lambert Law remains elusive. Here, empirical response-surface modeling was used to show how the temperature protocol in TOT analysis can be modified to distinguish pyrolyzed OC from BC based on the Beer-Lambert Law. We determined the apparent specific absorption cross sections for pyrolyzed OC (σ_{char}) and BC (σ_{BC}), which accounted for individual absorption enhancement effects within the filter. Response-surface models of these cross sections were derived from a three-factor central-composite factorial experimental design: temperature and duration of the high-temperature step in the helium phase, and the heating increase in the helium-oxygen phase. The response surface for σ_{BC} , which varied with instrument conditions, revealed a ridge indicating the correct conditions for OC pyrolysis in helium. The intersection of the σ_{BC} and $\sigma_{\rm Char}$ surfaces indicated the conditions where the cross sections were equivalent, satisfying an important assumption upon which the method relies. 95% confidence interval surfaces defined a confidence region for a range of pyrolysis conditions. Analyses of wintertime samples from Seattle, WA revealed a temperature between 830 °C and 850 °C as most suitable for the helium high-temperature step lasting 150 s. However, a temperature as low as 750 °C could not be rejected statistically.

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1. Introduction

Atmospheric particulate matter (PM) adversely affects human health [1,2], visibility [3,4], and impacts Earth's radiative balance [5,6,7]. For measuring the mass of refractory carbon from combustion, i.e., elemental carbon (EC) in PM < 2.5 μ m, the U.S. EPA employs thermal-optical analysis (TOA) in its National Air Monitoring System. To quantify EC and distinguish it from organic carbon (OC), TOA combines a multiple temperature step protocol for removing carbonaceous PM on a quartz-fiber filter with laserlight detection to monitor the production of pyrolyzed OC on the filter during heating [8,9]. However, TOA is problematic, particularly the laser transmission technique, in that different temperature protocols produce different results for EC on the same sample material [10,11]. In addition, established protocols have been shown to produce EC measurements that disagree substantially with other methods [12,13,14]. As different temperature protocols are increasingly being used to generate EC datasets, it is increasingly difficult to interpret and intercompare those datasets. As a result, accuracy of EC by TOA has become paramount.

The optical part of TOA for the thermal-optical transmission (TOT) method, in particular, implies that what is measured is the mass of the light-absorbing refractory carbon in the sample, i.e., light-absorbing black carbon (BC). At present, EC is best defined operationally, i.e., by the measurement method. However, BC is defined by the Beer–Lambert Law. In this work, we focus on the validity of the TOT method for measuring BC and, thus, on optimizing TOT analysis optically. We refer to the TOT result in this work as BC rather than EC.

Fig. 1 is a schematic of the TOT instrument and an example of its output (thermogram). During the first stage of TOT analysis that typically employs four heating steps in an inert (helium) atmosphere within the front oven, thermally unstable OC is pyrolyzed, which causes the attenuation of laser light (670 nm) through the filter. Thermally stable OC is volatilized and removed from the filter at this stage and measured by flame ionization detection (FID). Some thermally unstable OC that does not attenuate the laser signal may also come off the filter at this stage. Later, in an oxidizing

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Fig. 1. Schematic diagram of the TOT instrument along with the thermogram showing front oven temperature profile, laser signal, and FID response to thermally evolved particulate carbon.

atmosphere of 1-2% O₂ in He in the front oven, pyrolyzed OC as well as the BC that is native to the sample (i.e., original BC in the sample) is removed from the filter and measured by FID. With the removal of light-absorbing carbon, the laser signal returns to the point prior to OC pyrolysis. All carbon measured beyond this point, the split point, is quantitatively assigned to BC, while all carbon measured prior to this point is quantitatively assigned to OC. In an ideal analysis, pyrolyzed OC would come off the filter before the split point and native BC would come off after the split point, and in some cases, this may occur. However, the pyrolyzed OC and native BC typically do not separate at the split point, in the context of a chromatographic separation [15,16].

The point in the laser signal prior to the onset of pyrolysis that is used to establish the split point is typically not the signal at the very start of the TOT run. Often, the laser signal increases to a plateau prior to pyrolysis. This plateau is typically used for determining the split point.

Selecting the laser signal plateau as the split point reference, likely corrects to some extent for a positive bias in the BC measurement due to light-absorbing OC in the sample such as humic-like substances [17]. Water-soluble organic compounds that appear humic-like may evolve at lower temperatures in the He phase [18]. Fig. 2 shows the first part of the thermogram from an analysis of one of the samples in this study. The increase in the laser signal occurs during the first temperature step (200 °C) and coincides with the first FID peak. The coincidence between the increase in the laser signal and the appearance of the FID peak suggests that the laser signal shift is caused by a loss of light-absorbing OC. Selecting the laser signal at the plateau rather than at the very start of the TOT run effectively decreases the BC determination, presumably by an amount of carbon equivalent to light-absorbing OC in the first FID peak. However, using the plateau as the split point reference likely does not fully correct for a bias from light-absorbing OC. Some lightabsorbing OC may come off the filter after pyrolysis has begun. In which case, any rise in the laser signal would be masked by the fall in the laser signal due to pyrolysis.

Several radiative-transfer models have been applied to methods that measure light-absorbing PM bound to a fibrous filter [19,20,21,22] including one to TOA [22]. Nevertheless, a reliable physical model for determining the TOT temperature protocol for measuring the Beer–Lambert mass remains elusive because of the complexity of pyrolysis product formation on quartz fibers [23] and differences in the optical behavior of pyrolyzed OC vs. BC for different types of samples. A statistically rigorous alternative to radiative-transfer modeling for optimizing the temperature protocol is afforded by empirical response-surface modeling in combination with composite factorial experimental designs.

Response surfaces are polynomial-based empirical models of predictable systems that are commonly interpreted graphically [24,25]. In chemical analysis, they are powerful tools for predicting how an instrument will perform when multiple adjustable parameters are involved in generating the instrument response [26]. In effect, response-surface models allow us to study the behavior of an instrument graphically from three-dimensional representations of the response as a function of variation in the instrument parameters.

OC in atmospheric aerosols typically consists of a myriad of organic compounds in varying concentrations [27]. In addition, different PM samples will likely have a different complement of



Fig. 2. Thermogram of the first two heating steps in the helium phase showing the plateau in the laser signal coinciding with the first FID peak.

compounds comprising the OC. We are not likely, however, to accurately predict the thermal behavior for those OC compounds that are thermally unstable in the TOT instrument. This dilemma, the fact that pyrolyzed OC and native BC typically do not physically separate in the instrument, and the need to employ a single comprehensive temperature protocol for different types of PM samples are the challenges in applying TOT analysis to accurately measure refractory light-absorbing carbon.

Faced with these challenges, faith in TOT as a true measure of BC relies critically on the assumption that for all samples the pyrolyzed OC which absorbs light (OC char) and the BC native to the sample have the same specific absorption cross sections (i.e., mass absorption coefficients). With this assumption, the fact that native BC does not physically separate from pyrolyzed OC in the instrument is inconsequential. It makes no difference where OC char and native BC come off the filter in the O_2 -He phase, relative the split point, or whether they co-evolve. If pyrolysis is optimal and the specific absorption cross sections are shown to be equivalent, then BC determination by TOT becomes a true measure of the native BC in the sample.

The equivalence of the absorption cross sections was assumed in the early days of the development of TOA [28]; however, the assumption has since been shown to be invalid [16,15]. There are two reasons for this. First, different PM samples with different types of thermally unstable OC would be expected to produced OC char with different absorption cross sections at a specified temperature. Second, OC char and native BC have been found to behave optically quite differently within the filter [29,16,15]. This is related to differences in light absorption by the particles containing the native BC, which are captured close to the surface of the filter, vs. the OC char, which penetrates through the filter [30,16] as what appears to be a condensate on the filter fibers [29]. From scanning electron microscopy we have observed no distinctive OC char particles in the quartz-fiber matrix. Differences in the optical behavior of native BC and OC char are related to differences in the enhancement of light absorption that is induced by the filter. Native BC contained in the particles undergoes absorption enhancement from multiple backscattering of light off of the filter fibers [31,32,33]. Since evidence suggests that OC char exists as a condensate on fibers rather than as separate particles, the filter-induced enhancement of OC char is fundamentally different from that of the native BC-containing particles.

In our approach, we do not attempt to determine the actual specific absorption cross sections for the OC char and native BC, nor do we attempt to determine the magnitudes of the filter-induced enhancement factors. Rather, we use the Beer–Lambert Law to calculate *apparent* specific absorption cross sections for OC char and native BC as they are determined by the instrument. These apparent cross sections wholly account for differences in the individual absorption enhancements for OC char and native BC. As we show in the Results and Discussion section, both apparent cross sections vary with the TOT temperature protocol. It is the sensitivity of the apparent cross sections to variation in the temperature protocol that allows us to establish equivalence in the cross sections and thereby establish the temperature protocol for determining the true Beer–Lambert mass of native BC in the sample.

Previously our NIST lab demonstrated the effects of two principal sources of bias in TOT analysis [10]. First, inadequate pyrolysis of OC due to insufficient heating during the critical step in He (step 4) results in a positive bias when residual unpyrolyzed or insufficiently pyrolyzed OC is measured beyond the split point as native BC. The sources of unpyrolyzed or insufficiently pyrolyzed OC may be higher molecular weight organic compounds such as humic materials and/or polycyclic aromatic hydrocarbons, the later which are commonly associated with soot but not with manufactured carbon blacks [34]. Among thermal oxidation methods, EC may be overestimated by as much as a factor of 50 if OC is carried into the fraction of refractory carbon [35]. Second, any loss of pyrolyzed OC or native BC during step 4 in He, which is not accounted for by the laser signal, results in a negative bias. The current study also considers these biases. However, from response-surface models of the apparent specific absorption cross sections of OC char and native BC, we show how the superposition of the response surfaces is used to adjust the temperature and duration of step 4 in He such that the apparent cross sections are equivalent. In addition, we show how the apparent cross section for native BC is used to identify thermal conditions in He that minimize the positive bias from insufficiently pyrolyzed OC. Finally, confidence intervals for the response surfaces reveal the range of optimal conditions in He.

2. Experimental methods

Models were based on PM2.5 samples collected on heatpurified $20 \text{ cm} \times 25 \text{ cm}$ quartz-fiber filters using an MSP Universal Air Sampler¹ during February 23, 2005 to March 10, 2005 in a residential section of Seattle, WA. Analyses suggest that the samples contained woodburning emissions, presumably from residential heating [36]. Details of the sampling operation are reported elsewhere [36]. All TOT measurements were made with Sunset Laboratory's Dual-Optics (transmission and reflection) Thermal Carbon Analyzer. Quality control samples were run using standards of sucrose or urea. Controls showed that within-day FID drift occurred (Suppl. Fig. 1); however, with one exception all recoveries were within 6% (the exception was 13%), and drift was independent of the standard or carbon level.

2.1. Apparent specific absorption cross sections

Laser transmission signals were log-transformed to an attenuation time series (ATN(t)) using the version of the Beer–Lambert Law that has been applied to the Aethalometer [37,38]:

$$ATN(t) = -100 \ln\left(\frac{I(t)}{I_0}\right)$$
(1)

Here, I(t) is the transmission signal time series. I_0 is taken at the end of the run after all carbon has been removed from the filter and then corrected to the TOT starting temperature (40–50 °C) based on laser signal differences at low and high temperatures for clean filters.

A follow-up TOT run after all carbon had been removed revealed a modest but consistent attenuation with increasing heat that was due to residual refractory non-carbonaceous material on the filter. Attenuation from the follow-up run was, therefore, used as a blank ($ATN(t)_B$) with the attenuation due to all labile and oxidizable (mainly carbon) material, $ATN(t)_L$, determined from:

$$ATN(t)_{L} = ATN_{(t)} - ATN(t)_{B}$$
⁽²⁾

Without the blank correction, split points tended to be around 3 s later in the thermogram and BC determinations tended to be around 5% lower.

It was assumed that by step 4 in He all light-scattering OC had been either volatilized or pyrolyzed to highly absorbing carbonaceous material (OC char) and from this point through the O_2 -He phase, $ATN(t)_L$ was largely due to attenuation by OC char or the native BC. Backscattering by refractory OC char and native BC at this point was assumed to be minimal because in a thinly

¹ Commercial products identified in this document specify the means by which experiments were conducted. Such identification is not intended to imply recommendation or endorsement by NIST or by EPA nor is it intended that the identified products are necessarily the best available for the purpose.

loaded diffusely reflective substrate, forward scattering largely cancels backscattering [31,19]. Any residual attenuation [39] by non-carbonaceous material was corrected by the blank. ATN_C is denoted as the value of $ATN(t)_L$ at maximum charring during step 4 in He. Following Petzold et al. [40], ATN_C is equal to the product of the carbon mass loading (S_C , μ gCcm⁻²) and the specific attenuation cross section due to carbon alone (σ_C , m²g⁻¹):

$$ATN_{\rm C} = \sigma_{\rm C}S_{\rm C} \tag{3}$$

Here, it is assumed that $ATN_{\rm C}$ is associated principally with absorption. At the point of maximum charring in the He phase, $ATN_{\rm C}$ is the sum of the attenuation due to charring ($ATN_{\rm Char}$) and the attenuation due to native BC in the sample ($ATN_{\rm BC}$):

$$ATN_{\rm C} = ATN_{\rm Char} + ATN_{\rm BC} \tag{4}$$

Here, ATN_{Char} is calculated as in Eqs. (1–3); however, I_0 in this case is taken at the *beginning* of the TOT run prior to the start of thermal desorption rather than at the end of the run after all carbon has been removed. I_0 in this case includes absorption due to native BC, which effectively factors out native BC from ATN_{Char} (Eq. (1)). ATN_{BC} is determined by difference in Eq. (4). Thus, the optical properties of OC char and the native BC are assessed at the same point: maximum charring in He. We now express ATN_{Char} and ATN_{BC} as the products of their respective specific absorption cross sections and carbon mass loadings (μ g C cm⁻²):

$$ATN_{\text{Char}} = \sigma_{\text{Char}} S_{\text{Char}}$$
(5)

$$ATN_{\rm BC} = \sigma_{\rm BC} S_{\rm BC} \tag{6}$$

Here, S_{BC} is the mass loading remaining at the split point, and S_{Char} is equal to S_C at the point of maximum charring less S_{BC} . As described in the Introduction, σ_{Char} and σ_{BC} are the apparent TOT specific absorption cross sections, which account for filter-induced differences in the optical behavior of OC char vs. native BC particles, respectively, Importantly, σ_{BC} is a method-dependent property (like σ_{Char}), rather than an absolute property of the original BC. σ_{BC} necessarily varies with the instrument's temperature protocol and can, thus, be modeled to establish the equivalence between σ_{Char} and σ_{BC} .

2.2. Response-surface modeling

In this study, response-surface functional models were constructed to relate three TOT responses (σ_{Char} , σ_{BC} , and BC/total carbon (TC) ratio) to the three factors under study: x_1 = He step-4 temperature, x_2 = He step-4 duration, and x_3 = temperature step ramp in the O₂-He phase. Experience and prior data [10] suggest that over the specified range of the three factors, the response function should accommodate (1) quadratic extremes in any of the three factors, and (2) interactive "twisting" between any of the three 2-factor pairings: ($x_1 + x_2$), ($x_1 + x_3$), and ($x_2 + x_3$). Given these assumptions, a simple but effective and useful functional model for each of the three TOT responses would be the fully generalized second-order polynomial [41,26,25] with 10 terms plus random error:

$$y_{1i} = \beta_0 + \beta_1 x_{1i} + \beta_2 x_{2i} + \beta_3 x_{3i} + \cdots$$
 main effects (7)

 $\beta_{11}x_{1i}^2 + \beta_{22}x_{2i}^2 + \beta_{33}x_{3i}^2 + \cdots$ curvature (quadratic extrema)

$$\beta_{12}x_{1i}x_{2i} + \beta_{13}x_{1i}x_{3i} + \beta_{23}x_{2i}x_{3i} + e_{1i}$$

between-factor interactions (twisting)

Here, y_{1i} is the modeled response (e.g., BC/TC, σ_{Char} , or σ_{BC}) for experiment *i*; β_0 , β_1 , β_2 ,... are the model parameters; x_{1i} , x_{2i} , x_{3i} are the factor values for experiment *i*.

Lease squares estimates of the model parameters (β) are calculated from matrix inversion in Eq. (8). Here, *b* is the vector of parameter estimates, *X* is the matrix of factor values associated with the factor levels in the experimental design (Section 2.3), and *y* is the vector of measured response values:

$$b = (X'X)^{-1}(X'y)$$
 (8)

Measured responses were assumed to be statistically uncorrelated and independent. The assumption is appropriate because the process of adjusting the TOT temperature protocol to establish factor levels did not affect the other factors. For example, establishing the He step-4 temperatures required no manipulation of the step-4 duration or the temperature ramps in the O_2 -He phase.

2.3. Factorial experimental design

The response-surface modeling in this study required a factorial experimental design that considered the various combinations of the factor levels. To estimate the 10 model parameters from the set of simultaneous equations represented in Eq. (7), the factorial design required at least 10 factor combinations at which *y* determinations were made. To efficiently satisfy this 10-parameter requirement, a three-factor, two-level central-composite design was employed [41]. As shown in Fig. 3, this design had eight runs at two levels for the full factorial and seven runs for the star design (solid and open circles, respectively, in Fig. 3).

This type of design has the following advantages:

- (1) The design easily accommodates the flexibility of the fully generalized second-order polynomial model with functional curvature and twisting across three factors.
- (2) The design is efficient because it requires only 15 runs, which is a mere surplus of 5 over the 10-run minimum dictated by the second-order polynomial model.
- (3) The design is orthogonal in that the inner products $x_1 \cdot x_2, x_1 \cdot x_3$, and $x_2 \cdot x_3$ are zero, which assures sequentially uncorrelated estimates of the 10 coefficients.

In the process of combining the full factorial design with the star factorial design, the 15-run experiment required five distinct symmetrical instrument settings for each of the three factors. In Fig. 3,



Fig. 3. Schematic of the three-factor, two-level central-composite design. The three axes represent three instrument control factors each with two levels. The design center (large circle) represents the level that is central to both the full factorial (cube, solid circles) and the partial factorial (star, open circles).

Table 1

The central-composite experimental design (k = 3, n = 15).

	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃
	-1	-1	-1
	+1	-1	-1
	-1	+1	-1
	+1	+1	-1
Full-factorial combinations	-1	-1	+1
	+1	-1	+1
	-1	+1	+1
	+1	+1	+1
	$-\sqrt{2}$	0	0
	+_2	0	0
	0	$-\sqrt{2}$	0
Star-factorial combinations	0	+\sqrt{2}	0
	0	0	$-\sqrt{2}$
	0	0	+\sqrt{2}
	0	0	0



Fig. 4. Ramps of the O₂-He step temperatures for factor 3. Ramp labels indicate their initial step temperatures.

this can be viewed as the number of points (settings) that a plane perpendicular to an axis would encounter if it is moved along that axis. These five settings were spaced relative to the central instrument setting for each factor, denoted 0, such that the remaining settings had levels spaced as follows: $-\sqrt{2}$, -1, 0, +1, $+\sqrt{2}$. Table 1 is the experimental design table for the orthogonal three-factor, two-level composite design.

Table 2 shows the instrument conditions for factors 1 and 2. For factor 1, the He step-4 temperature ranged from 630 to $890 \,^{\circ}$ C, with the design center point at 760 $^{\circ}$ C. For factor 2, the He step-4 duration ranged from 60 to 270 s, with the design center point at 165 s. Since we previously showed that variation in He steps 1–3 does not appreciably affect BC/TC in this type of study [10], these steps were fixed at 200, 400, and 600 $^{\circ}$ C, respectively, for 60 s.

For factor 3, variation in step temperatures in the O_2 -He phase was established as a series of five temperature step ramps as shown in Fig. 4. Factor 3 was designed such that the design center step ramp had 550 °C as its initial temperature. Step ramps are distinguished primarily (and designated throughout this paper) by their initial step temperature. The temperature of the final (6th) step was held

Table 2

Instrument conditions for factors 1 and 2 in the central-composite design.



Fig. 5. View through the x/y plane of the three-dimensional factorial design shown in Fig. 3. Open circles represent partial (star) factorial levels; solid circles represent full factorial levels.

constant at 900 °C, and steps 2–5 were adjusted accordingly so that the step-to-step rise was linear among the different factorial levels as shown in Fig. 4. Durations of the O_2 –He steps were fixed at 60, 60, 45, 45, 45, and 90 s, respectively.

2.4. Confidence intervals for response-surface models

Surface confidence intervals were important in this study for revealing the range of TOT temperatures and durations that were acceptable as optimal. Confidence intervals were calculated from Deming and Morgan [25] as follows:

$$\hat{y}_{\text{CI}} = \hat{y} \pm \sqrt{\{F_{(1,n-p)}s_{\text{r}}^2(1 + [X_0(X'X)^{-1}X'_0])\}}$$
(9)

Here, \hat{y} is the estimate of the response from the model, $F_{(1,n-p)}$ is the *F*-statistic based on *n* experiments and a model with *p* parameters, s_r^2 is the model variance based on model residuals determined from replicated measurements, *X* is a matrix of coefficients associated with the model parameters (Eq. (7)), and X_0 is a related matrix of coefficients associated with each factorial combination. *X* contains additional redundant coefficients to account for experiments that were replications in the design.

Response-surface confidence intervals reflect uncertainty associated with the spacing of the levels in the factorial design as well as the uncertainty in the response variable itself. For example, if factor levels of the star factorial extend far beyond the levels of the full factorial (Fig. 2), confidence interval surfaces will tend to exhibit excessive and distorted error at the edges of the response model space. To minimize this distortion, star factorial levels are adjusted such that their magnitudes are comparable with the full factorial levels. This is accomplished by making the design "rotatable", whereby the star factorial levels shown in Fig. 5 for the factor-1 and factor-2 axes, for example, can be rotated to coincide with the full factorial levels. The net effect is that the five points associated with each factor must have the spacing indicated earlier: $-\sqrt{2}$, -1, 0, +1, $+\sqrt{2}$.

	-				
	Star factorial lower level	Full factorial lower level	Star factorial middle level	Full factorial upper level	Star factorial upper level
Level spacings	-\sqrt{2}	-1	0	+1	+\sqrt{2}
x1: He step-4 temperature (°C)	630	668	760	852	890
x ₂ : He step-4 duration (s)	60	91	165	239	270

Fig. 5 also shows that the distance between the center point and its nearest neighbor is larger than the distance between all other points and their remaining neighbors. The result is that the response-surface tends to have more uncertainty at the center of the model space. This center-point uncertainty causes an anomalous "bulging" of the confidence surfaces at the center of the model space (Suppl. Fig. 2a). The uncertainty artifact is corrected (Suppl. Fig. 2b) by inserting replicate measurements for the center-point response in the matrix for estimating model parameters by least squares (Eq. (8)).

2.5. Three-day measurement protocol and the expanded experimental design

The experimental design was ultimately run for each of six samples, two each from Atlanta and Los Angeles, as well as two samples from Seattle that are modeled in this paper. In addition to measurements at the 15 sets of instrument conditions in the factorial design (Fig. 3), several replicate measurements were made, and each measurement run was followed up by a blank run. The 15 measurements from the factorial design were combined with nine replicate runs for a total of 24 measurement runs. Each run was also followed by a blank run for a grand a total of 48 runs. The 48 runs on each sample required 3 days to complete, which placed special demands on the design to avoid the effect of potential withinday and between-day systematic errors, i.e., drift. To meet these demands, a blocked, replicated, and randomized scheme for each day's runs was developed as shown in Fig. 6. The purpose was to distribute the sets of instrument conditions such that the whole factor space was adequately assessed each day and that day-to-day variation in instrument behavior would not impart systematic error in the response-surface models. Eight measurement runs (and eight blank runs) were made on each day as shown in Fig. 6. Replication of key points in the design insured that any confounding of the models by within-day variation or between-day variation could be tested.

Table 3 is the complete 24-measurement experimental design table that includes the replicates for within-day and between-day variation tests. Here we may consider the within-day and between-day treatments as additional factors " x_4 " and " x_5 ", respectively. However, response-surface models were not generated for these factors. The 15 factorial combinations in the original central-composite design (Table 1) are in italics in Table 3.

3. Results and discussion

3.1. Drift assessment from experimental design

To test if significant measurement drift occurred during the three days of measurements for each sample, we compared the within-day variance and between-day variance in BC measurements using the thermal protocol associated with design center point (Table 2, Fig. 4). First, however, we verified that the measurements were normally distributed (Suppl. Fig. 3). This was accomplished using the six within-day duplicate measurements in the 3-day measurement protocol (points with concentric circles in Fig. 6 and factorial combinations pairs in Table 3 labeled AM and PM). In addition to the two Seattle samples which were the focus of this work, two ancillary samples each from Atlanta and Los Angeles were included. Differences in the duplicate BC measurements were used here because the differences were independent of the actual BC levels and, thus were expected to form a single distribution, which was indeed the case.

Table 4 shows results of the analysis of BC measurement variance for the two Seattle samples along with the ancillary Atlanta and Los Angeles samples. Within-day variation is used to test if any



Fig. 6. Three-day measurement collection scheme for the expanded centralcomposite factorial design consisting of 24 measurements. Circles indicate the eight factorial conditions employed on each analysis day. Concentric circles indicate duplicated measurements.

150

Table 3

Expanded central-composite experimental design^a (k = 3, n = 24).

Factor (k)	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	Within-day variation ("x4") ^b	Between-day variation $(*x_5")^c$
	-1	-1	-1		
	+1	-1	-1	AM	
	+1	-1	-1	PM	
	-1	+1	-1		
Full factorial combinations	+1	+1	-1		
Full-factorial combinations	-1	-1	+1		
	+1	-1	+1		
	-1	+1	+1	AM	
	-1	+1	+1	PM	
	+1	+1	+1		
	$-\sqrt{2}$	0	0		Day 1 ^d
	$-\sqrt{2}$	0	0		Day 3 ^d
	+√2	0	0	AM	
	+√2	0	0	PM	
	0	$-\sqrt{2}$	0		
	0	+_2	0		
Ctan fastanial combinations	0	0	$-\sqrt{2}$		
Stal-factorial combinations	0	0	+_2		
	0	0	0	AM	Day 1
	0	0	0	PM	Day 1
	0	0	0	AM	Day 2
	0	0	0	PM	Day 2
	0	0	0	AM	Day 3
	0	0	0	PM	Day 3

^a Italics show the factorial combinations from the base central-composite design in Table 1.

^b AM indicates morning run. PM indicates afternoon run.

^c Analysis day as indicated in Fig. 6.

^d Experiments were used in determining response-surface confidence intervals (see Eq. (9)), but not in the analysis of variance comparing within-day and between-day variation (see Table 4).

systematic error was related to the type of factorial combination in the design, i.e., center point vs. peripheral points. For all samples, the within-day *F*-value (column 5) is substantially smaller than the critical *F*-value with 95% confidence (9.28), indicating that no significant systematic error is associated with the type of factorial combination. Moreover, any instrument drift during an analysis day did not translate to a BC measurement bias.

The between-day variation in Table 4 was used to test if there was an overall shift in TOT behavior during the entire 3-day analysis period. For consistency, only the center points were used. Comparing within-day vs. between-day variance, the *F*-value is again substantially smaller than the critical *F*-value with 95% confidence (5.05), indicating no significant systematic measurement error associated with day-to-day TOT variation that might confound the models.

3.2. BC/TC measurements and models

Among the 10 samples collected at the Seattle site, two with low to moderate levels of total carbon were selected for modeling. Collected for different durations (24 and 48 h), the low carbon (level 1) sample had 7.52 μ g cm⁻² and the moderate carbon (level 2) sample

surements.

had $12.9 \,\mu g \, cm^{-2}$. BC/TC determinations for all factor combinations in the experimental design are plotted in Fig. 7 with respect to He step-4 temperature (factor 1) and He step-4 duration (factor 2). The figure shows a fairly large decrease in BC/TC from 630 to 890 °C: 19% for the level-1 sample and 24% for the level-2 sample (7% and 9% per 100 °C increase, respectively). This trend is consistent with a BC/TC decrease of 8% per 100 °C increase in the step-4 temperature reported earlier for forest fire emissions [10]. The trend is smaller, however, than the 17% decrease per 100 °C increase in that study for urban PM (NIST SRM 1649a). Tabulated BC/TC measurements for the Seattle level-1 and level-2 samples used in the matrix for estimating the model parameters (Eq. (8)) are shown in Supplementary Table 1.

Fig. 8 shows the modeled BC/TC response for the two samples as a function of the He step-4 temperature and duration. In this case, the 550 °C ramp (Fig. 3) was used for the O_2 -He step temperature rise (factor 3). At the low end of the temperature range, elevated BC/TC ratios are likely due to the positive artifact from the measurement of unpyrolyzed OC as native BC [10]. Over the upper half of the temperature range (760–890 °C), the BC/TC ratio for the level-2 sample clearly tends to level off while the ratio for the level-1 sample continues to exhibit a monotonic decrease. This contrast

Table 4					
Analysis	of variance	from	TOT	BC	mea

	Within-day variation	1	Between-day variation	Within-day vs.		
	Center; variance ^a (d.f. = 3) ^b	Periphery; variance (d.f.=3)	Center plus periphery; variance (d.f. = 5)	Center vs. periphery; F-test ($F_{0.95}$ = 9.28)	(center); variance (d.f.=5)	between-day (center); F -test ($F_{0.95} = 5.05$)
Atlanta #1	2.36E-04	4.32E-04	4.01E-04	1.83	2.47E-04	1.62
Atlanta #2	1.27E-02	1.29E-02	1.54E-02	1.02	8.83E-03	1.75
LA #1	3.56E-03	1.21E-03	2.86E-03	2.95	2.21E-03	1.3
LA #2	1.37E-02	1.53E-02	1.74E-02	1.12	9.40E-03	1.85
Seattle #1	3.22E-03	1.08E-03	2.58E-03	2.98	2.14E-03	1.21
Seattle #2	2.88E-03	1.00E-02	7.74E-03	3.48	1.73E-03	4.47

^a $(\mu g C cm^{-2})^2$.

^b d.f. = degrees of freedom.



Fig. 7. 3D scatter plots of BC/TC measurements vs. He step-4 temperature (factor x_1) and duration (factor x_2) for the level-1 sample (a) and level-2 sample (b) from Seattle. Shaded circles indicate measurements from the full factorial, open circles indicate measurements from the star factorial (Fig. 3). Arrows indicate standard deviation for replicate measurements.

between low-carbon and moderate-carbon samples has also been observed from the Los Angeles site [36].

The continued decrease in BC/TC at high temperatures in He for the Seattle level-1 sample may be due to the effect of an oxidative loss of refractory carbon [10,15], to which the laser signal failed to adequately respond. It was shown that for PM samples such as the NIST Standard Reference Material 1649a (Urban Dust), an increase in the He step-4 duration with temperature held constant resulted in a decrease in BC/TC [10]. At longer step-4 durations, there was a loss of refractory carbon (OC char and/or native BC) as indicated by an increase in the raw laser signal as well as the FID signal. The loss of refractory carbon in the He phase thus corresponded with the BC/TC decrease. If the laser signal had adequately responded to the carbon loss, there would have been no effect on BC/TC.

The cause for a possible refractory carbon loss in He is unclear. BC from biomass burning was shown to be oxidized by sodium and, in particular, potassium salts [35]. Others have speculated that the Hephase oxidative loss is due to the catalytic effect of various mineral oxides such as MnO₂, Fe₂O₃, SiO₂, and Al₂O₃ [29]. The cycling of



Fig. 8. BC/TC response surfaces as a function of He step-4 temperature (factor x_1) and duration (factor x_2) and using the central condition of factor x3 (550 °C step ramp). (a) Seattle level-1 sample; (b) Seattle level-2 sample. Gray-shaded 95% confidence interval surfaces bracket the BC/TC surfaces.

surface-bound CO and CO₂ involving Fe₂O₃ and refractory carbon has also been proposed [10].

For the Seattle samples in this study, we observed a slight rise in the raw laser signal when the step-4 temperature was $890 \,^{\circ}$ C, also at $852 \,^{\circ}$ C, but only over an extended duration (239 s). This indicated that if an unaccountable loss of refractory carbon did occur in the He phase, it was only at the highest step-4 temperatures.

3.3. Determinations of the apparent specific absorption cross sections

Determinations of the apparent specific absorption cross sections for OC char and native BC both increased with the He step-4 temperature. This is shown in Fig. 9 for the Seattle level-1 sample. Overall, the σ_{Char} increase over the temperature range is twice as large as the σ_{BC} increase. The Seattle level-2 sample exhibited a similar trend. Tabulated determinations of σ_{Char} and σ_{BC} for the level-1 and level-2 samples used in the matrix for estimating model parameters (Eq. (8)) are shown in Supplementary Table 1.

Values for σ_{Char} in Fig. 9a range from $21 \text{ m}^2 \text{ g}^{-1}$ at $630 \,^{\circ}\text{C}$ to $43 \text{ m}^2 \text{ g}^{-1}$ at $890 \,^{\circ}\text{C}$. We would expect σ_{Char} to increase with temperature because increased heat changes the absorptivity of



Fig. 9. 3D scatter plots of σ_{Char} (a) and σ_{BC} (b) vs. He step-4 temperature (factor x_1) and duration (factor x_2) for the Seattle level-1 sample. Shaded circles indicate measurements from the full factorial, open circles indicate measurements from the star factorial (Fig. 3). Arrows indicate standard deviation for replicate measurements.

the pyrolyzed material. Others have reported a similarly large magnitude for the absorption cross section of pyrolyzed OC: approximately 60 m² g⁻¹ by Yang and Yu [16], 48 to $53 \text{ m}^2 \text{ g}^{-1}$ by Chow et al. [29], and $35 \text{ m}^2 \text{ g}^{-1}$ by Subramanian et al. [15] The overall magnitudes of σ_{Char} in Fig. 9a and their dramatic increase over the temperature range reveal the absorption enhancement effect of the filter. This absorption cross section for filter-bound pyrolyzed OC contrasts sharply with what we might expect to see for the absorption cross section of BC particles residing on a fibrous filter. A consensus estimate of the actual (i.e., non-filter-enhanced) absorption cross section for BC is $7.5 \text{ m}^2 \text{ g}^{-1}$ [42,43]. In combination with this, the absorption enhancement factor from the filter has been reported as large as 3.5 [43]. Thus, we would expect the apparent specific absorption cross section for native BC to be no larger than 26 m² g⁻¹. In this study, σ_{Char} exceeds this value, for the most part, at He step-4 temperatures above 670 °C. This discrepancy between the reported absorption cross section for OC char and the expected filter-enhanced cross section for native BC was effectively demonstrated by Subramanian et al. [15].

A potentially confounding effect on the determination of $\sigma_{\rm Char}$ is the loss of either native BC or OC Char in the helium phase as dis-



Fig. 10. Overlay of the σ_{BC} and σ_{Char} surfaces for the level-1 sample (a) and level-2 sample (b) from Seattle. OC Char is pyrolyzed OC. Surfaces for the level-2 sample are bracketed by gray-shaded 95% confidence interval surfaces. Confidence intervals for the level-1 sample (omitted for clarity) are comparable to those for the level-2 sample.

cussed in Section 3.2. In this case, the σ_{Char} determination would be biased low, particularly at higher step-4 temperatures, and we would expect a more modest increase in the trend with step-4 temperature in Fig. 9a compared to σ_{Char} without bias.

3.4. Models of the apparent specific absorption cross sections

Fig. 10 shows how the response-surface models for σ_{Char} and σ_{BC} compare. The models are overlaid on the same plot to allows us to observe if an intersection exists between the σ_{Char} and σ_{BC} surfaces, and therefore, the conditions under which σ_{Char} and σ_{BC} are equivalent. The Seattle level-1 sample clearly exhibits the intersection while the level-2 sample does not. In this comparison, the σ_{Char} determinations (and the model) for the level-2 sample are problematic because, for the purpose of modeling, the sample is relatively



Fig. 11. Comparison of $\sigma_{\rm BC}$ surfaces for the level-1 and level-2 samples from Seattle.

heavily loaded with carbon. Among all samples (10) collected at the Seattle site, σ_{Char} determinations decrease dramatically, from 35 to 3.9 m² g⁻¹, with increasing carbon loading (Suppl. Fig. 4). The effect has been identified as the occluding of light, or shadowing, by an overabundance of particles in a fibrous matrix [44,39,45].

Even though modeling of σ_{Char} for the level-2 sample is problematic, shadowing of the laser light by OC char should not adversely affect the actual BC determination. The O₂–He phase is usually long enough for a controlled release of oxidized carbon from the filter whether char or native BC. By time the split point is reached, any shadowing effect will be on the order of shadowing at the split point reference prior to pyrolysis. Therefore, an optimized protocol would be suitable for samples that exhibit shadowing by OC char in the He phase as well as lightly loaded samples that do not. We now focus on modeling the lightly loaded level-1 sample.

With the level-1 sample, we first note the difference in the magnitudes of σ_{Char} and σ_{BC} surfaces in Fig. 10a, particularly at the low end of the temperature range (630 °C). At the 165 s duration, the σ_{BC} value (33.4 m² g⁻¹) is larger than what would be expected for the native BC in particles on the filter (at most 26 m² g⁻¹). It is also larger than the σ_{Char} value (21.8 m² g⁻¹). While σ_{BC} is associated with the mass of carbon assigned as native BC at the split point, it is also associated with the attenuation of native BC at maximum charring in He. The magnitudes of σ_{BC} over the temperature range reveal that it is affected by the same filter enhancement effects as OC char. This is important because we are able to compare the optical properties of OC char and native BC under the same filter conditions that cause absorption enhancement.

The σ_{Char} surface in Fig. 10 is, for the most part, monotonic with temperature. In contrast, the $\sigma_{\rm BC}$ surface for the level-1 sample in Fig. 10a is parabolic with temperature, i.e., it levels off and forms a ridge at higher He step-4 temperatures. This is shown from a different angle in Fig. 11. For example, the value on the $\sigma_{\rm BC}$ ridge at 165 s is 38.7 m² g⁻¹ for the level-1 sample and occurs around 850 $^{\circ}$ C. In contrast, the σ_{BC} value at 630 °C is 33.4 m² g⁻¹. Taking the difference between these σ_{BC} values allows us to observe the optical properties of the instrument-determined BC without "interference" from the absorption enhancement effect of the filter. The difference, $6 \text{ m}^2 \text{ g}^{-1}$, is close to what is expected for the actual specific absorption cross section of native BC (7.5 m² g⁻¹). If we extrapolate σ_{BC} to an even lower He step-4 temperature (550 °C), the difference from the ridge $\sigma_{\rm BC}$ value is larger necessarily (9.8 m² g⁻¹), but still close to the expected actual cross section for native BC. These results show that at the He step-4 temperatures where the σ_{BC} ridge appears, the amount of carbon which the instrument has determined is the mass of BC exhibits optical behavior that resembles the actual BC absorption cross section.

The σ_{BC} surface also indicates the conditions where OC pyrolysis is sufficient. Some heavier organic compounds such long-chain aliphatics or soot-associated PAHs may contribute to a positive BC/TC bias if they do not change optically at the pyrolysis temperatures. If these compounds are removed in oxygen before the split point, then they will be correctly assigned as OC. If instead they are removed after the split point, then they will bias the BC measurement. However, their effect on σ_{BC} would be to lower it. Therefore, the largest σ_{BC} values indicated by the response-surface ridge reveal the He step-4 conditions where the potential bias from inadequately charred OC is minimized.

Fig. 11 shows that the σ_{BC} surfaces for the Seattle level-1 and level-2 samples are remarkably similar. In fact, at temperatures above 760 °C the level-2 σ_{BC} surface is within the 95% confidence intervals for the level-1 σ_{BC} surface. In addition, the σ_{BC} ridges for the two samples are remarkably close (see also Fig. 13b). Thus, the conditions for sufficient OC pyrolysis are independent of the carbon level in the sample, at least for samples that are not overloaded such as those in this study. This is important because ideally the TOT temperature protocol should be independent of carbon loading.

3.5. Effect of factor 3

Adjusting the temperatures in the O₂-He phase may have the effect of shifting the relative positions at which pyrolyzed OC and native BC evolve in the thermogram. Fig. 12 shows how $\sigma_{\rm Char}$ and $\sigma_{\rm BC}$ change with variation in the O₂-He temperature step ramp (factor 3) for the Seattle level-1 sample. Little variation in σ_{Char} is seen; however, it appears that by changing the ramp from 550 to 630 °C (Fig. 3), σ_{BC} is substantially lowered at higher He step-4 temperatures. Nevertheless, the σ_{BC} surface ridge does not appear to change much with the O₂-He temperature ramp. Since the σ_{BC} surface shifts to lower values as the $\sigma_{\rm Char}$ surface remains relatively constant, we might expect the σ_{Char} , σ_{BC} intersection to occur at lower He step-4 temperatures if, for example, we use the 630 °C O₂-He ramp rather than the 550 °C ramp. Nevertheless, Fig. 12 clearly shows that any shift in σ_{BC} caused by the O₂-He ramp is within the boundaries of the 95% confidence intervals for the central 550 °C ramp. Therefore, σ_{BC} variation with the O₂–He ramp does not appear to be statistically significant in our models, and from this sample alone we cannot determine with certainty how the σ_{Char} and σ_{BC} intersection might be affected by variation in the O₂-He ramp. Further study of the effects of varying the O₂-He steps in the temperature protocol is necessary.

3.6. Establishing optimal TOT step-4 conditions

An overhead view of superimposed σ_{Char} and σ_{BC} surfaces for the Seattle level-1 sample in Fig. 10a is shown in Fig. 13a. The figure clearly displays the functional nature of the surface intersection and, therefore, the points where σ_{Char} and σ_{BC} are equivalent. We identify the optimal He step-4 conditions for this sample by projecting the surface intersection onto the time vs. temperature plane (Fig. 13b). The shaded area displays a confidence region bounded by the intersections of the σ_{Char} 95% confidence intervals with the σ_{BC} surface. The σ_{BC} ridge for this sample is well within the confidence region. Fig. 13b also shows the σ_{BC} ridge for the level-2 sample and the BC/TC "trough" for this sample (Fig. 8b). Both the ridge and trough are well within the 95% confidence region.

Even though the amount of carbon in the Seattle level-2 sample precludes us from establishing an intersection between σ_{Char} and σ_{BC} , Fig. 13b shows excellent agreement between the σ intersection for the level-1 sample and the σ_{BC} ridges for the two samples. A disparity between the σ intersection and the σ_{BC} ridges could



Fig. 12. Variation in the σ_{Char} (a) and σ_{BC} (b) surfaces for the Seattle level-1 sample at five temperature ramps in the O₂–He phase (factor x_3), which correspond to factor levels in the factorial design. Gray-shaded 95% confidence interval surfaces are for the 550 °C ramp.

be a symptom of a bias in the σ_{Char} determinations due to a loss refractory carbon in the He phase as mentioned earlier. In this case, the σ intersection in the response surfaces would occur at lower step-4 temperatures from the σ_{BC} ridge. Nevertheless, the agreement between the intersection and the ridge exhibited in Fig. 13b and the fact that we observed a only a slight rise in the laser signal at the highest step-4 temperatures indicate that the models were not significantly confounded by bias in the σ_{Char} determinations.

The σ intersection and σ_{BC} ridges in Fig. 13b also show that TOT optimization depends on the duration of step-4 in helium as well as the temperature, as reported by others [46]. Higher temperatures allow for a shorter duration. If we select 150 s for the step-4



Fig. 13. (a) Overhead view of the overlay of σ_{Char} (light) and σ_{BC} (dark) surfaces for the Seattle level-1 sample from Fig. 10a. (b) Two-dimensional projection of the 95% confidence region (see text) and the σ intersection for the level-1 sample, ridges of σ_{BC} maxima for both samples, and the BC/TC minimum for the Seattle level-2 sample.

duration, a suitable temperature for the Seattle samples is around 830–850 °C. However, from the limits of the confidence region, we do not have sufficient reason to reject a temperature as low as 750 °C or as high as 890 °C. If we select a temperature below the confidence region in Fig. 12b, say 700 °C for 150 s, then BC/TC would be 11% greater for both samples than if 840 °C for 150 s were used.

A desirable improvement in this optimization approach would be a reduction in the size of the confidence region. However, this would necessarily require additional replication of measurements at key points in the central-composite design, which would compromise the efficiency of the design. Key points to replicate would include the extremes of the star design shown in Fig. 3, particularly the helium step-4 temperature at 630 and 890 °C (Table 2). It is instructive to note also the sensitivity of the response-surface models to replication of the center point in the design mentioned in Section 2.4. Additional center-point replication serves to reduce the size of the surface confidence intervals overall (Suppl. Fig. 2) and, therefore, the confidence region defined by the σ intersection (Fig. 13b). Moreover, the lack of sufficient center-point replication causes a distortion of the confidence surfaces (Suppl. Fig. 2) such that the σ intersection and σ_{BC} ridge shift to higher temperatures (Suppl. Fig. 5). As a result of this distortion, selection of a suitable He step-4 temperature would have been erroneously high.

Our results are consistent with a relatively high step-4 temperature in protocols reported previously [10,47,48]. Our results are also consistent with the step-4 temperature and duration in the UST-3 protocol reported by Yang and Yu [16]. Others, however, have employed or suggested a much lower step-4 temperature for TOT analysis [15,49]. The purpose of this study was to demonstrate the use of empirical modeling in TOT optimization. The treatment is based primarily on the analysis of samples from a single site. It is likely that for samples that exhibit a greater oxidative loss of refractory carbon in the He phase (negative bias), response-surface models would result in lower optimized step-4 temperatures [36]. A recommended comprehensive temperature protocol should be the product of a comparison of models and confidence regions for multiple sample types. In addition, the confidence region as shown in Fig. 13b appears large enough to accommodate overlap of confidence regions from models of other sample types. However, reducing the size of the confidence region by improving the experimental design could have the undesirable effect of restricting this overlap and, therefore, hinder our ability to converge on a comprehensive temperature protocol. Nevertheless, this study has shown that the best conditions for the critical pyrolysis step in TOT analysis are revealed graphically from the intersection between σ_{Char} and $\sigma_{\rm BC}$ response-surface models and the $\sigma_{\rm BC}$ surface ridges.

4. Conclusion

We have demonstrated the use of empirical response-surface models with confidence intervals for optimizing the TOT temperature protocol based on the analysis of PM2.5 samples collected in Seattle, WA. An efficient central-composite factorial experimental design focusing on the temperature and duration of the critical high-temperature step in the helium phase (factors 1 and 2) and the temperature step ramp in the O_2 -He phase (factor 3) was used for acquiring measurement data for the models. Models were full second-order polynomial surfaces exhibiting between-factor interaction as well as within-factor variation to reveal the optical absorption behavior of the TOT instrument. Since the number of measurements for the models required three analysis days and quality controls revealed drift in the FID response, bias in the models was critically avoided by randomizing the run order of the factorial conditions and strategically using replicates in the experimental design. Adequate replication of the design center point was necessary to avoid distortion particularly in the surface confidence intervals.

Our optimization approach satisfied two criteria. First, sufficient pyrolysis of OC must occur so that insufficiently pyrolyzed OC is not measured as native BC after the split point. Second, equivalence must be established between the apparent specific absorption cross sections of OC char and that which the instrument determines is the native BC. Temperature conditions in the helium phase that satisfied the first criterion were revealed from a σ_{BC} ridge at higher temperatures. The intersection of the response surfaces for σ_{Char} and σ_{BC} revealed the temperature conditions in the helium phase that allowed for the cross sections to be equivalent, thus satisfying the second optimization criterion. Excellent agreement was found between the σ_{BC} ridge and the intersection between σ_{Char} and σ_{BC} . Moreover, the σ_{BC} ridge fell well within the 95% confidence region defined by the intersection of the $\sigma_{\rm BC}$ surface with the 95% confidence interval surfaces for σ_{Char} . The confidence region revealed a range of acceptable temperatures and durations for the high-temperature step (4) in helium. For a duration of 150 s, 830–850 °C was suitable for the samples from our Seattle

site. However, different ambient PM sample types likely require different step-4 conditions. If we apply the overlap of confidence regions from response-surface models of different sample types, then the empirical modeling approach presented here should lead to a comprehensive TOT temperature protocol. A manuscript on the comprehensive protocol based on this approach is in preparation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.aca.2008.12.046.

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