



Title	The effects of accumulated refractory particles and the peak inert mode temperature on semi-continuous organic carbon and elemental carbon measurements during the CAREBeijing 2006 campaign
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1 The effects of accumulated refractory particles and the peak inert mode
2 temperature on semi-continuous organic carbon and elemental carbon
3 measurements during the CAREBeijing 2006 campaign

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23 **Abstract**

24 Two semi-continuous Sunset carbon analyzers, with different peak inert mode
25 temperatures (615 and 740°C), were simultaneously operated to measure fine
26 particulate organic carbon (OC) and elemental carbon (EC) using a thermal optical
27 transmittance method at an urban site in Beijing, China, from 16 August to 3
28 September 2006 during the CAREBeijing 2006 campaign. Excellent agreements were
29 obtained between the collocated semi-continuous carbon analyzers, with slopes of 1.02
30 ($R^2 = 0.91$) for OC and 1.06 ($R^2 = 0.93$) for EC, resulting in very similar average
31 EC/total carbon (TC) ratios of ~ 0.36 . These results imply that the different peak inert
32 mode (100% helium) temperatures did not cause significant biases on the semi-
33 continuous OC and EC measurements. However, it was found that the EC/TC ratio
34 was greatly influenced by the accumulated refractory particles remaining on a quartz
35 filter ($PM_{refractory}$). Fresh quartz filters, with low $PM_{refractory}$ loadings, which is
36 defined as a laser correction factor ≥ 0.94 , gave ~ 8 – 10% lower EC/TC ratios than aged
37 quartz filters with high $PM_{refractory}$ loadings. The linear regression slope between EC
38 and optically measured EC (OPT-EC) was much higher with fresh quartz filters (slope
39 = 1.03, $R^2 = 0.96$) than aged quartz filters (slope = 0.89, $R^2 = 0.95$), suggesting the
40 underestimation of EC on fresh quartz filters by $\sim 15\%$ compared to those measured on
41 aged quartz filters. Authentic standard humic-like substances (HULIS) on the clean
42 quartz filter showed the highest extent of pyrolyzed organic carbon (POC) formation
43 (47.4% in total detected carbon mass), followed by those on the Asian dust loaded
44 quartz filter (37%) and the refractory urban pollutant loaded quartz filter (34.1%),
45 indicating that the Asian dust and refractory urban pollutant reduced the POC

46 formation from the HULIS. Thus, this study suggested that the $PM_{refractory}$ loading
47 plays an important role in the semi-continuous OC and EC measurements by altering
48 the degree of POC formation in the inert atmosphere.

49 **1 Introduction**

50 Atmospheric particulate carbonaceous aerosols mainly comprises of organic (OC)
51 and elemental carbon (EC). The thermal-optical method is a conventional approach for
52 classifying carbonaceous aerosols into OC and EC (Huntzicker et al., 1982; Birch and
53 Cary, 1996). OC is usually defined as carbon evolved under a prescribed temperature
54 protocol in an inert atmosphere (100% He), while EC is defined as carbon evolved in an
55 oxidizing atmosphere (He/10% O₂ mixture). A fraction of OC is pyrolyzed during the
56 inert mode of the analysis. This fraction of OC is usually called pyrolyzed organic
57 carbon (POC), quantified as the carbon evolved in the oxidizing atmosphere, which is
58 necessary to return a laser transmittance or reflectance through a quartz filter to its
59 initial value.

60 There are many uncertainties in the measurements of OC and EC, which are mainly
61 caused by the denuder efficiency, different temperature protocols and POC correction
62 by laser reflectance or transmittance (Schauer et al., 2003; Chow et al., 2004;
63 Subramanian et al., 2006). Cheng et al (2010) reported that adsorbed gaseous organics
64 (positive sampling artifact) constituted 10 and 23% of the OC concentrations during
65 winter and summer, respectively, as determined from un-denuded quartz filter samples
66 collected at Beijing, China. Application of a very high peak inert mode temperature (the
67 temperature of the last step in the inert mode) may underestimate the EC concentration
68 due to the premature evolution of EC, while a very low peak inert mode temperature
69 may overestimate the EC concentration due to the incomplete evolution of OC in the
70 inert atmosphere (Chow et al., 2001; Sciare et al., 2003; Schauer et al., 2003;
71 Subramanian et al., 2006). Since POC simultaneously evolves with natural EC, as
72 indicated by a darker color (Yang and Yu, 2002; Chow et al., 2004; Subramanian et al.,

73 2006), the EC values determined using a thermal/optical transmittance (TOT) method
74 are usually lower than those using a thermal/optical reflectance (TOR) method (Chow et
75 al., 2004; Cheng et al., 2010). Chow et al (2004) reported that the EC values determined
76 using the TOT method were 30% lower than via the TOR method under the same
77 temperature protocol. In order to evaluate different peak inert mode temperatures on the
78 OC and EC measurements, previous studies have used aerosol sampling and an off-line
79 laboratory analysis (e.g., Chow et al., 2001; Schauer et al., 2003). Thus, it is necessary
80 to evaluate different peak inert mode temperatures on the *in-situ* on-line semi-
81 continuous carbon analysis.

82 Refractory metal oxides, such as iron oxide, can cause premature EC evolution in
83 the inert atmosphere at very high temperatures, resulting in underestimation of the EC
84 (Polidori et al., 2006). These refractory components in the particles also caused a
85 decrease of the laser transmittance at a high oven temperature (Huebert et al., 2004). It
86 has been reported that ammonium bisulfate enhanced the formation of POC from starch
87 and cellulose, but reduced their formation from levoglucosan (Yu et al., 2002). However,
88 there have been very few studies regarding the effect of the refractory particles on the
89 formation of POC and separation of OC and EC.

90 The Campaigns of Air Quality Research in Beijing and its Surrounding Regions
91 2006 (CAREBeijing 2006) was conducted in the summer of 2006 (e.g. Jung et al., 2009;
92 Takegawa et al., 2009). The CAREBeijing 2006 was designed to identify the sources of
93 ozone and aerosols in Beijing and its surrounding regions to achieve better air quality
94 during the Beijing Olympic Games in 2008. Many research groups from China,
95 Germany, Taiwan, Korea and Japan participated in the CAREBeijing campaign with
96 their own instruments. Thus, this campaign was a good opportunity to compare the

107 results from different instruments operated by different research groups, which will
108 contribute to improving data quality.

109 This study investigated the semi-continuous measurements of carbonaceous aerosols
110 at two different peak inert mode temperatures (615 and 740°C). Possible reasons of the
111 disparity between the collocated semi-continuous carbon analyzers are discussed using
112 the peak inert mode temperatures and different loadings of refractory particulate matters
113 remaining on a quartz filter ($PM_{refractory}$). Clear biases in the EC/TC ratios were
114 obtained between the collocated semi-continuous carbon analyzers with respect to the
115 $PM_{refractory}$. The role of the $PM_{refractory}$ on the OC and EC measurements was
116 investigated based on the optically measured EC and the formation characteristics of
117 POC depending on the $PM_{refractory}$ loading.

108

109 **2 Experimental**

110 2.1 Description of the sampling site and campaign

111 Hourly carbonaceous particle measurements were conducted at an urban site (39.98°
112 N, 116.35° E) in Beijing from 16 August to 3 September 2006 during the CAREBeijing
113 campaign. Two Sunset semi-continuous carbon analyzers were installed on the rooftop
114 of a five-story building (~20 m above ground level) at Peking University, located in the
115 northwest of a Beijing urban area (Fig. 1). The measurement site was ~600 m north of
116 the 4th main ring road and ~220 m from the eastern main road.

117

118 2.2 Organic and elemental carbon analysis

119 Organic (OC) and elemental carbon (EC) were measured using a semi-continuous

120 Sunset carbon analyzer employing thermal-optical transmittance (TOT) protocol for
121 pyrolysis correction (Birch and Cary, 1996). The air samples were drawn at 8 L per
122 minute (LPM) through a PM_{2.5} sharp-cut cyclone. The sampled aerosols then passed
123 through a multichannel, parallel plate denuder with a carbon impregnated filter to
124 remove semi-volatile organic vapors, and then collected on a quartz-fiber filter. OC and
125 EC were quantified for a NDIR (non-dispersive infrared sensor) signal of CO₂ under a
126 prescribed temperature protocol in inert (100% He) and oxidizing atmospheres (He/10%
127 O₂ mixture), respectively. The correction of the pyrolyzed organic carbon (POC), which
128 was converted from OC in the inert mode of the analysis, was performed by monitoring
129 the transmittance of a pulsed He-Ne diode laser beam through the quartz fiber filter.
130 Internal calibration was automatically performed at the end of every analysis by
131 injecting a CH₄ internal standard mixture (5% CH₄ in He) via a fixed injection volume
132 loop. External calibration was also performed using known amounts of sucrose. The
133 uncertainty of the instrument was reported to be 5% (Polidori et al., 2006).

134 In addition to OC and EC, the semi-continuous carbon analyzer also measured the
135 optical EC (OPT-EC) in a similar, but not identical manner to that used by the
136 aethalometer (Jeong et al., 2004; Jung et al., 2011). The OPT-EC was calculated using a
137 second-degree polynomial fit of the attenuation measured from the laser transmittance.
138 The polynomial coefficients provided by the manufacturer were used in this study.
139 Thermally measured EC and optically measured EC are further denoted as EC and
140 OPT-EC, respectively. The total carbon (TC) was calculated by summing up OC and
141 EC.

142

143 2.3 Temperature protocol used for OC and EC analysis

144 Two Sunset carbon analyzers from Gwangju Institute of Science and Technology
145 (GIST) and Peking University together with University of Tokyo (PKU/UT) were
146 operated in parallel and run under similar conditions, except for the temperature
147 protocol, as shown in Table 1 (Jung et al., 2009; Han et al., 2009; Lin et al., 2009). The
148 PKU/UT carbon analyzer used a higher He4 temperature (740°C) than the GIST carbon
149 analyzer (615°C) (see Table 1). The PKU/UT carbon analyzer used four temperature
150 steps (300, 450, 600 and 740°C) in the inert atmosphere for the OC analysis. After the
151 sample had cooled, the oven temperature was increased to 870°C in the oxidizing
152 atmosphere for the analysis of the EC and POC. However, the GIST carbon analyzer
153 used a slightly different temperature protocol, with a lower peak temperature (615°C) in
154 the inert atmosphere. Since most EC and POC were initially oxidized to CO₂ in the
155 oxidizing atmosphere, an additional temperature step of 550°C was included with the
156 GIST carbon analyzer in the oxidizing atmosphere to obtain better separation.

157 The peak inert mode temperature substantially influenced the EC measurements.
158 Subramanian et al. (2006) reported that the NIOSH (National Institute for Occupational
159 Safety and Health) peak inert mode temperature (He4-870°C) protocol measured 20-
160 20% less EC in Pittsburgh atmospheric aerosol samples than the modified peak inert
161 temperature (He4-700°C) protocol, while the IMPROVE (Interagency Monitoring of
162 Protected Visual Environments) peak inert mode temperature (He4-550°C) protocol
163 measured 50% more EC than the He4-700°C protocol for wood smoke dominated
164 ambient samples. Schauer et al. (2003) also reported that the EC measured using the
165 He4-550°C protocol was 1.6–2.1 times greater than that measured using the He4-870°C
166 protocol for ambient and wood smoke samples. Polidori et al. (2006) found that the
167 effect of metal oxides on the TOT analysis was substantially reduced when the peak

168 inert mode temperature was decreased from 870 to 700°C. Subramanian et al. (2006)
169 suggested that the He4-700°C protocol provides the best estimate of the EC for the
170 Pittsburgh samples. Thus, slightly modified peak inert mode temperatures were used in
171 this study to minimize the measurement bias associated with the premature evolution of
172 EC and incomplete evolution of OC in the inert atmosphere.

173

174 2.4 Blank correction and detection limit

175 Since the denuder cannot remove all semi-volatile organic vapors, blank correction
176 is required for OC data. The dynamic OC blank level (positive artifact) was measured
177 by collecting particle-free ambient air through a Teflon filter placed upstream of the
178 denuder. The dynamic blank measurement was conducted fortnightly using the same
179 operational protocol used for the ambient aerosol measurement. The average OC
180 dynamic blanks were 0.94 ± 0.68 and $1.23 \pm 0.43 \mu\text{g C m}^{-3}$ for the PKU/UT and GIST
181 carbon analyzers, respectively. However, negligible EC dynamic blanks were obtained,
182 i.e. 0.007 ± 0.01 and $0.001 \pm 0.006 \mu\text{g C m}^{-3}$ for the PKU/UT and GIST carbon
183 analyzers, respectively. These OC and EC dynamic blanks were subtracted from the raw
184 OC and EC data.

185 The OC detection limits were 2.0 and $1.3 \mu\text{g C m}^{-3}$ for the PKU/UT and GIST
186 carbon analyzers, respectively, calculated as three times the standard deviation (3σ) of
187 the OC dynamic blank. The EC detection limits were also calculated as 3σ of the EC
188 dynamic blank, and found to be 0.03 and $0.02 \mu\text{g C m}^{-3}$ for the PKU/UT and GIST
189 carbon analyzers, respectively. However, these values were relatively small compared
190 to the instrument's minimum quantifiable level given by the manufacturer, i.e. $0.5 \mu\text{g C}$
191 m^{-3} . Therefore, $0.5 \mu\text{g C m}^{-3}$ was considered as the EC detection limits for both semi-

192 continuous carbon analyzers. Thus, OC and EC concentrations lower than 2.0 and 0.5
193 $\mu\text{g C m}^{-3}$, respectively, were screened out in this study.

194

195 2.5 Laboratory experiments of an authentic organic standard

196 To investigate the effect of the refractory particles remaining on a quartz filter
197 ($PM_{refractory}$) on the thermal characteristics of OC and the formation of POC,
198 thermograms of an authentic organic standard were obtained in the laboratory under
199 three different sets of quartz filter conditions; baked clean quartz filter, refractory urban
200 pollutant loaded quartz filter, and Asian dust loaded quartz filter. For the filters loaded
201 with refractory urban pollutants and Asian dust, aliquots of the total suspended
202 particulate samples collected at the Gosan site, Korea (Fig. 1) during the severe long-
203 range transport pollution event (7 to 9 May 2007) and Asian dust event (30 March to 2
204 April 2007) periods, respectively, were used. Three types of the quartz filter were
205 prebaked in the Sunset carbon analyzer, using the GIST temperature protocol, to remove
206 volatile fractions from the aerosol samples, such as sulfate, nitrate, ammonium, OC and
207 EC. Thus, the term “refractory particles” in this study was defined as the particles that
208 did not vaporize under 850°C in the oxidizing atmosphere. Standard Suwannee River
209 Humic Acid (HULIS) (Cat. No: 2S101H) was obtained from the IHSS (International
210 Humic Substances Society). An aliquot (~15 $\mu\text{g C}$) of the HULIS was dissolved in ultra
211 pure organic free Milli-Q water and applied to the prebaked quartz filters using a micro
212 glass syringe and then dried over night inside a desiccator containing silica gel. The
213 prepared quartz filter samples were analyzed using the GIST temperature protocol.

214

215 **3 Results and Discussion**

216 3.1 Intercomparison of OC, EC, and TC between the collocated semi-continuous carbon
217 analyzers

218 The TC concentrations measured by the PKU/UT and GIST carbon analyzers ranged
219 from 2.5 to 49.5 $\mu\text{g C m}^{-3}$ (AVG $18.7 \pm 8.5 \mu\text{g C m}^{-3}$) and 3.3 to 49.8 $\mu\text{g C m}^{-3}$ (AVG
220 $19.0 \pm 9.2 \mu\text{g C m}^{-3}$), respectively (Table 2), and showed excellent agreement between
221 the two carbon analyzers, with a regression slope of 1.05 and R^2 of 0.95 (Fig. 2). The
222 OC and EC also showed excellent agreements between the two carbon analyzers, with
223 R^2 values > 0.92 (Fig 3a & b).

224 A similar intercomparison study was conducted at the Gosan site, Korea, using two
225 semi-continuous Sunset carbon analyzers, with slightly different peak inert mode
226 temperatures (870 and 840°C) during the Atmospheric Brown Clouds–East Asian
227 Regional Experiment 2005 (ABC-EAREX2005) campaign (Bae et al., 2007). Poor
228 correlation of the OC between the collocated carbon analyzers was reported, with a
229 slope of 0.97 ± 0.07 ($R^2 = 0.37$), while the EC showed good agreement, with a slope of
230 1.05 ± 0.15 ($R^2 = 0.98$) (Bae et al., 2007). Our comparative result for the OC showed
231 much better correlation, with a slope of 1.02 ($R^2 = 0.91$), indicating that the two
232 different peak inert mode temperatures used in this study caused no significant bias in
233 the OC measurement in Beijing, China. The EC also showed excellent agreement, with
234 a slope of 1.06 ($R^2 = 0.93$). Since an aerosol composition, both organic and inorganic,
235 can also influence the OC and EC measurements (Yu et al., 2002; Schauer et al., 2003),
236 different atmospheric aerosols chemical compositions at the Gosan and Beijing may
237 also have contributed to the difference in the OC regression results.

238

239 3.2 EC/TC ratio versus laser correction factor

240 The EC/TC ratios during the entire measurement period for the PKU/UT and GIST
241 carbon analyzers ranged from 0.15 to 0.62 (AVG 0.36 ± 0.07) and from 0.18 to 0.58
242 (AVG 0.36 ± 0.07), respectively. It is well known that very high peak inert mode
243 temperatures underestimate the EC and vice versa (Chow et al., 2001; Subramanian et
244 al., 2006). Schauer et al. (2003) and Cheng et al. (2010) reported gradual decreases in
245 the EC/TC ratios on increasing the peak inert mode temperature. Schauer et al. (2003)
246 obtained 1.07-1.19 times differences in the EC/TC ratios measured using two different
247 peak inert mode temperatures (650 and 750°C). The average EC/TC ratios in this study
248 were very similar between the two carbon analyzers, suggesting that the two different
249 peak inert mode temperatures caused no significant bias for the semi-continuous EC
250 measurement in Beijing.

251 A laser correction factor was used to account for the change in the laser
252 transmittance as a function of the temperature. This laser correction factor was
253 calculated for each run from the variation in the laser signal on cooling of the oven after
254 the analytical cycle had completed. The laser correction factor normally decreased as
255 the $PM_{refractory}$ increased (Huebert et al., 2004). Thus, the laser correction factor can be
256 used as an indicator of the aging of a quartz filter and $PM_{refractory}$ loading.

257 Although the average EC/TC ratios had very similar values between the two carbon
258 analyzers, relatively poor correlation of the EC/TC ratios was obtained, with an $R^2 =$
259 0.36 (Fig. 3 and Table 2). Bae et al. (2007) also reported a similar correlation ($R^2 = 0.4$)
260 between the two semi-continuous carbon analyzers at the Gosan site. Based on the
261 assumption that the $PM_{refractory}$ may influence the OC and EC measurements, the
262 quartz filter conditions were divided into fresh and aged quartz filters, with laser

263 correction factors ≥ 0.94 and < 0.94 , respectively. After omitting the EC/TC ratios with a
264 laser correction factor ≥ 0.94 , a better correlation of $R^2 = 0.59$ was obtained (Table 2),
265 suggesting that the $PM_{refractory}$ may play an important role in the EC measurement,
266 possibly by altering the OC/EC split point, the formation of POC, and the evolutions of
267 EC and POC. The effects of the $PM_{refractory}$ on the EC measurements are discussed in
268 detail in section 3.4.

269 The average EC/TC ratios for the two carbon analyzers are summarized in Table 3
270 with respect to the different laser correction factors. Clear differences in the EC/TC
271 ratios were obtained depending on the $PM_{refractory}$ loading. The lowest EC/TC ratio of
272 ~ 0.30 was obtained when the laser correction factor for the two carbon analyzers was
273 ≥ 0.95 . The ratio increased with increasing $PM_{refractory}$ loading, and reached ~ 0.38
274 when the laser correction factor was < 0.94 . By comparing the EC/TC ratios between the
275 two carbon analyzers with different laser correction factors, it was found that fresh
276 quartz filters with low $PM_{refractory}$ loadings gave $\sim 8\text{--}10\%$ lower EC/TC ratios than
277 aged quartz filters with high $PM_{refractory}$ loadings.

278

279 3.3 Divergence of the EC measurement relative to OPT-EC

280 Overall, the EC and OPT-EC were well correlated, with a slope of 0.90 ($R^2 = 0.94$)
281 (Fig. 4a). A relatively high regression slope of EC to OPT-EC (slope = 1.03, $R^2 = 0.96$)
282 was obtained when the laser correction factor was ≥ 0.94 than for those under a laser
283 correction < 0.94 (slope = 0.89, $R^2 = 0.95$) (Table 2). A clear decreasing trend of the
284 OPT-EC/EC ratio was observed as the laser correction factor decreased to ~ 0.94 , and
285 then became invariant for further decreases in the laser correction factor. These results

286 can be explained by two possible reasons; the underestimation of the EC on the fresh
287 quartz filter or the underestimation of OPT-EC on the aged quartz filter.

288 The $PM_{refractory}$ caused underestimation of the light attenuation coefficient when
289 optical carbon measurement techniques, such as an aethalometer, were used, mainly due
290 to interference via light scattering by the $PM_{refractory}$ (Weingartner et al., 2003).
291 However, this kind of interference rarely impacts on the OPT-EC data measured by the
292 Sunset carbon analyzer for the following reasons: First, if the $PM_{refractory}$ interferes
293 with the OPT-EC measurement by reducing the light attenuation coefficient, the OPT-
294 EC/EC ratio should continuously decrease as the laser correction factor decreases.
295 However, the decrease of the OPT-EC/EC ratio was only observed when the laser
296 correction factor ≥ 0.94 , but then became invariant (Fig. 4b). Second, the Sunset carbon
297 analyzer uses a second order polynomial fit for the OPT-EC calculation from the light
298 attenuation measurement to compensate for the scattering effect due to the $PM_{refractory}$.
299 Thus, the possible underestimation of OPT-EC under high $PM_{refractory}$ loadings would
300 not be a reason for the much higher OPT-EC/EC ratios obtained for the fresh filter.
301 Rather, the underestimation of the EC for the fresh filter would more reasonably explain
302 this difference.

303 By assuming that EC on the fresh quartz filter was underestimated compared to that
304 measured from the aged quartz filter, the magnitude of the EC underestimation between
305 the fresh and aged quartz filters can be roughly estimated using the relative difference in
306 the OPT-EC/EC ratios. The OPT-EC/EC ratios were 1.09, 1.22 and 1.32 times higher
307 than those measured from the aged quartz filters when the laser correction factors were
308 0.94–0.96, 0.95–0.96 and 0.96–0.97, respectively. Thus, it was suggested that the EC

309 on the fresh quartz filter might be underestimated by ~15% compared that measured on
310 the aged quartz filter. These results indicate that the $PM_{refractory}$ may play an important
311 role in the EC measurement.

312

313 3.4 Effect of the accumulated refractory particles on the OC and EC separation

314 3.4.1 OC and EC split point and POC formation

315 The OC-EC split time is defined as the period when the laser transmittance reaches
316 its initial value to correct for the POC formed in the inert atmosphere. The POC
317 correction when using the thermal-optical method depends on one of the following
318 assumptions: (i) POC evolves before the natural EC in the oxidizing atmosphere, or (ii)
319 POC and natural EC have the same light attenuation coefficients (Yang and Yu, 2002).
320 However, both these assumptions have been demonstrated to be invalid (Yang and Yu,
321 2002; Yu et al., 2002; Chow et al., 2004; Subramanian et al., 2006), which results in a
322 systemic artifact for the split of OC and EC.

323 The OC-EC split times of the two carbon analyzers are shown in Fig. 5a as a
324 function of the laser correction factor. Interestingly, the OC-EC split times gradually
325 decreased as the laser correction factor decreased to ~0.94, and then became invariant,
326 implying that the OC-EC split time was highly influenced by the $PM_{refractory}$. It is well
327 known that the $PM_{refractory}$ lowers the laser transmittance through a quartz filter at high
328 oven temperatures (Huebert et al., 2004; Polidori et al., 2006). This phenomenon was
329 clearly observed in the CH₄ internal calibration mode, where the laser transmittance
330 increased as the oven temperature gradually decreased. To prevent the error associated
331 with the temperature dependent laser transmittance caused by the $PM_{refractory}$, the

332 Sunset manufacturer multiplies the laser correction factor by the initial laser
333 transmittance. Thus, the difference in the OC-EC split time between the fresh and aged
334 quartz filters cannot be explained by the temperature dependence of the laser
335 transmittance.

336 To examine the effect of shifting the OC-EC split time on the amount of POC
337 evolved in the oxidizing atmosphere, the POC/(POC+EC) ratios were plotted as a
338 function of the laser correction factor, as shown in Fig. 5b. The decreasing trend of the
339 POC/(POC+EC) ratios with decreasing laser correction factor was similar to that of the
340 OC-EC split time (Fig. 5a). The POC/(POC+EC) ratios sharply decreased from 0.46 to
341 0.11 as the laser correction factor decreased from 0.96–0.97 to 0.92–0.94 for the
342 PKU/UT carbon analyzer, and from 0.49 to 0.17 for the GIST carbon analyzers. The
343 ratios were then slightly decreased with laser correction factors between 0.94 and 0.84,
344 as shown in Fig. 5b. Much higher POC/(POC+EC) ratios with laser correction factors
345 ≥ 0.94 were observed than with those < 0.94 , suggested the enhanced formation of POC
346 on the fresh quartz filter. A decrease in the POC/(POC+EC) ratio with decreasing laser
347 correction factor may also be attributable to the premature evolution of EC in the inert
348 atmosphere due to mineral oxides, such as iron oxide, remaining on the quartz filter,
349 which promotes the catalytic oxidation of carbon on the filter in the inert atmosphere
350 (Polidori et al., 2006).

351

352 3.4.2 Thermograms of the fresh quartz filter versus high loadings of refractory 353 particles

354 Figure 6 shows thermograms for selected samples (19 August 2006, 13:00 and 27
355 August 2006, 23:00) obtained by the PKU/UT and GIST carbon analyzers. The fresh

356 and aged quartz filters on 19 August 2006, 13:00 for the PKU/UT and GIST carbon
357 analyzers represent laser correction factors of 0.956 and 0.909, respectively. Those on
358 27 August 2006, 23:00 for the GIST and PKU/UT carbon analyzers represent correction
359 factors of 0.958 and 0.911, respectively. The thermograms showed that a dominant
360 fraction of OC evolved in the He1 temperature step for the two carbon analyzers,
361 followed by the He2 temperature step. As previously discussed for Fig. 5a, the OC-EC
362 split time with the aged quartz filter appeared earlier than that with the fresh quartz filter.

363 Increases in the laser transmittance at the peak inert mode temperature (He4) were
364 clearly observed with the aged quartz filters for the two carbon analyzers, indicating that
365 the earlier OC-EC split time with the aged quartz filter may be partially attributable to
366 the premature evolution of EC. However, no big difference in the CO₂ areas was
367 observed between the fresh and aged quartz filters in the He4 temperature step. Since
368 POC simultaneously evolves with natural EC, if the OC-EC split point does not occur in
369 the inert atmosphere, the premature evolution of EC would not affect the EC
370 measurement. However, clear differences in EC/TC ratios were reported for the
371 different peak inert mode temperatures used in previous studies (e.g. Schauer et al.,
372 2003; Subramanian et al., 2006). These differences can be explained by the different
373 vaporization rates of natural EC and POC between the peak inert mode and the
374 oxidizing atmosphere, as described by Subramanian et al. (2006). However, our results
375 showed very similar average EC/TC ratios for the aged quartz filters between the two
376 peak inert mode temperatures (Table 2), suggesting that the premature evolution of EC
377 did not significantly affect the semi-continuous EC measurement in Beijing. Thus, the
378 difference in EC/TC ratios between the fresh and aged quartz filters may have been
379 caused by the premature evolution of EC as well as other reasons.

380 Interestingly, it was clear that the POC formation able to be monitored by the
381 reduced laser transmittance was quite different between the fresh and aged filters. The
382 POC formation on the fresh quartz filter was quite noticeable in the He1 temperature
383 step for the two carbon analyzers, where the dominant fraction of OC evolved. However,
384 the enhanced formation of POC was observed in the He2 temperature step for the aged
385 quartz filter. These results imply that the $PM_{refractory}$ may alter the POC formation
386 mechanism.

387 Most of the EC and POC evolved at the beginning of the first step of the oxidizing
388 atmosphere (Fig. 6). Small uncertainties in the laser transmittance signal and transit
389 time correction (the time used to correct the differences in the laser signal and CO₂
390 response) can cause high uncertainties in the EC measurement. The intermediate
391 temperature step (550 °C) in the oxidizing atmosphere (Fig. 6a) gave better separation
392 than the one-step temperature (870°C) protocol (Fig. 6b), which would help to reduce
393 the uncertainties associated with the fluctuation in the laser signal and the error in the
394 transit time correction, which is the time required for CO₂ generated from a sample to
395 reach the NDIR.

396

397 3.4.3 Laboratory experiments on the formation of POC with and without refractory 398 particles

399 To investigate the relatively low EC/TC ratios on the fresh quartz filter compared to
400 those on the aged quartz filter (Figs. 3–4), the authentic standard HULIS was analyzed
401 under three different sets of quartz filter conditions; clean quartz filter, the refractory
402 urban pollutant loaded quartz filter and the Asian dust loaded quartz filter, to examine

403 the role of $PM_{refractory}$ on the OC and EC measurements (Fig. 7). Relatively low
404 evolutions of OC in the He2, He3 and He4 temperature steps were obtained in the range
405 of 11.5% – 22.1% (% of the evolved carbon mass in total detected carbon mass) with
406 the clean quartz filter compared to the quartz filters loaded with refractory urban
407 pollutants (16.7% – 28.1%) and the Asian dust (16.7% – 25.8%). Interestingly, the
408 HULIS on the clean quartz filter showed the highest degree of POC formation (47.4%),
409 followed by the Asian dust loaded filter (37%) and the refractory urban pollutant loaded
410 filter (34.1%). These results indicated that the Asian dust and refractory urban pollutants
411 reduced the POC formation from the HULIS. The HULIS on the refractory urban
412 pollutant loaded quartz filter and the Asian dust loaded filter showed similar evolution
413 patterns, with the exception of slight differences in the He1 and He2 temperature steps.

414 Since the attenuation coefficient of POC was ~2 times higher than that of natural EC,
415 as well as their simultaneous evolution (Yang and Yu, 2002; Chow et al., 2004;
416 Subramanian et al., 2006), a relatively high degree of POC formation on the clean
417 quartz filter would require the evolution of more EC in the oxidizing atmosphere until
418 the laser transmittance returned to its initial value, causing underestimation of the EC.
419 Thus, relatively low EC/TC ratios and high OPT-EC/EC ratios for the fresh quartz filter
420 were observed compared to those for the aged quartz filters, which were mainly
421 attributed to the variations in the POC formation caused by the $PM_{refractory}$.

422

423 4 Conclusion

424 Schauer et al. (2003) reported higher EC/TC ratios (~1.07 – 1.19 times) at the peak
425 inert mode temperature of 650°C than those at 750°C based on aerosol filter sampling

426 and off-line laboratory analyses using the thermal optical transmittance method.
427 However, the present study showed very similar average EC/TC ratios between the
428 collocated semi-continuous carbon analyzers with two different peak inert mode
429 temperatures (615 and 740°C), suggesting that the peak inert mode temperature did not
430 cause significant bias in the semi-continuous EC measurements. The standard humic-
431 like substance (HULIS) on the clean quartz filter showed the highest degree of
432 formation of pyrolyzed organic carbon (POC) (47.4% of the total detected carbon mass),
433 followed by the quartz filters loaded with Asian dust (37%) and the refractory urban
434 pollutants (34.1%). Relatively high POC formation on the clean quartz filter would
435 require to evolution of more EC in the oxidizing atmosphere until the laser
436 transmittance returned to its initial value, causing underestimation of the EC. Thus, the
437 relatively low EC/TC ratios and high OPT-EC/EC ratios for the fresh quartz filter (laser
438 correction factor ≥ 0.94) compared to those for the aged quartz filter (laser correction
439 factor < 0.94) were mainly attributed to variations in the formation of POC due to the
440 accumulated refractory particles remaining on the quartz filters. Since the effect of the
441 refractory particles on the formation of POC may also depend on the chemical
442 composition of organic aerosols, further studies are needed during different seasons and
443 at various locations.

444

445

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454

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528 Yu, J. Z., Xu, J. H., Yang, H., 2002. Charring characteristics of atmospheric organic
529 particulate matter in thermal analysis. Environmental Science & Technology 36,
530 754–761.

531 Table 1. Temperature protocols for the OC/EC instruments used during the
 532 CAREBeijing 2006 campaign.

Carrier gas	Carbon fraction	GIST ^{a)}		PKU/UT ^{b)}	
		Oven Temp (°C)	Holding time	Oven Temp (°C)	Holding time (sec)
He		-	10	-	300
He (He1)	OC1	310	60	300	75
He (He2)	OC2	480	60	450	60
He (He3)	OC3	550	60	600	60
He (He4)	OC4	615	90	740	90
He		cool down	35	cool down	30
10% O ₂ /He	EC1	550	35	870	120
10% O ₂ /He	EC2	850	105		

533 ^{a)}Thermal optical transmittance method, GIST: Gwangju Institute of Science and
 534 Technology, Korea.

535 ^{b)}Thermal optical reflectance method, PKU: Peking University, China, UT: University
 536 of Tokyo, Japan

537

538 Table 2. Regression analyses between the two semi-continuous carbon analyzers.

Parameter	X versus Y	R ²	Slope	Intercept	AVG X	AVG Y
					$\mu\text{g C m}^{-3}$	
TC	PKU/UT vs. GIST	0.95	1.05	-0.7	18.7 ± 8.5	19.0 ± 9.2
OC	PKU/UT vs. GIST	0.91	1.02	-0.2	12.0 ± 5.5	12.0 ± 5.9
EC	PKU/UT vs. GIST	0.93	1.06	-0.2	6.7 ± 3.3	6.9 ± 3.7
EC/TC ratio	PKU/UT vs. GIST	0.36	0.97	0 ^{a)}	0.36 ± 0.07	0.36 ± 0.07
	PKU/UT vs. GIST (laser corr ^{b)} < 0.94)	0.59	0.96	0 ^{a)}	0.37 ± 0.07	0.38 ± 0.07
GIST EC vs OPT-EC	EC vs. OPT-EC (laser corr < 0.94)	0.95	0.89	0.3	7.3 ± 3.7	6.8 ± 3.4
	EC vs. OPT-EC (laser corr ≥ 0.94)	0.96	1.03	0.2	5.3 ± 3.2	5.8 ± 3.3

539 ^{a)}Intercept was forced through zero.

540 ^{b)}laser corr: laser correction factor used to account for the change in a laser
541 transmittance as a function of the temperature.

542

543 Table 3. Average EC/TC ratios in the two carbon analyzers with respect to the laser
 544 correction factor.

Laser correction factor	Average EC/TC ratio	
	GIST	PKU/UT
All	0.36 ± 0.07	0.36 ± 0.07
$GIST \geq 0.94$ and $PKU/UT < 0.94$	0.34 ± 0.07	0.38 ± 0.07
$GIST < 0.94$ and $PKU/UT \geq 0.94$	0.38 ± 0.06	0.35 ± 0.08
$GIST \geq 0.95$	0.30 ± 0.07	
$PKU/UT \geq 0.95$		0.30 ± 0.08

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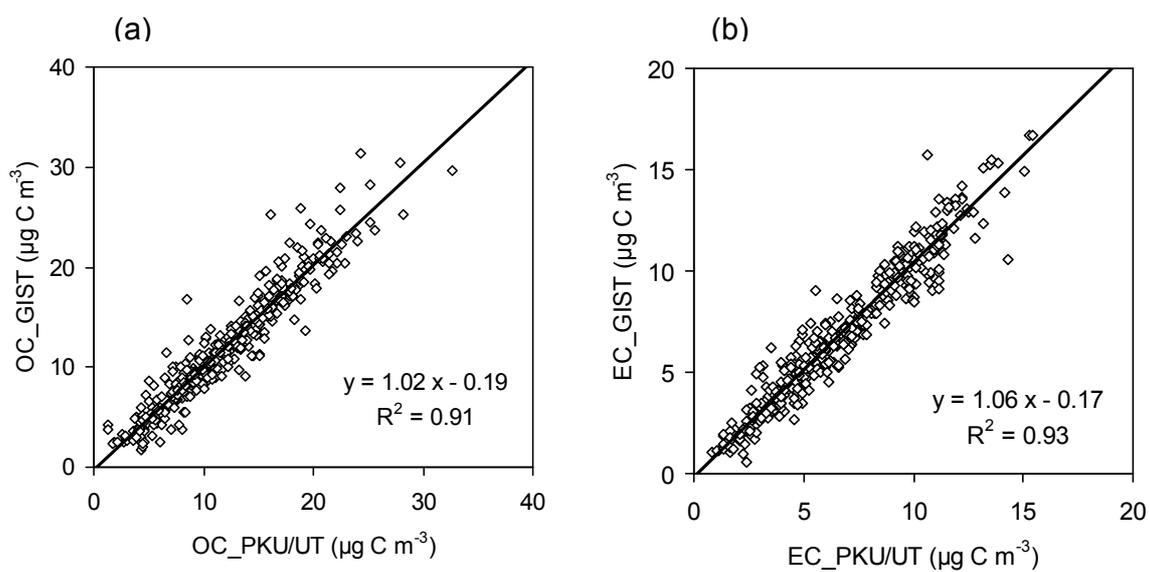
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Figure 1



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Figure 2

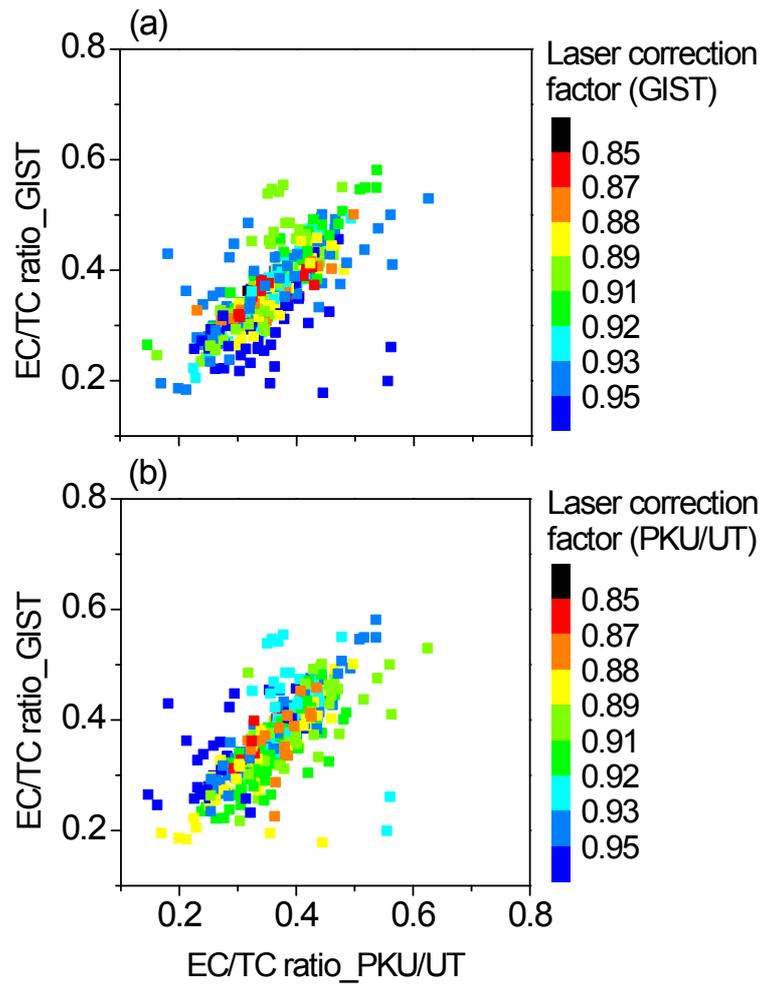


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Figure 3

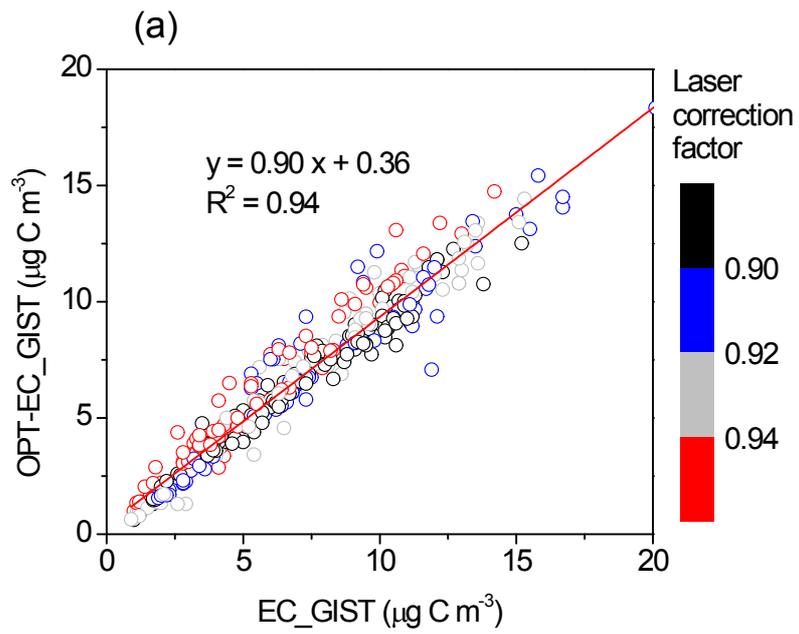


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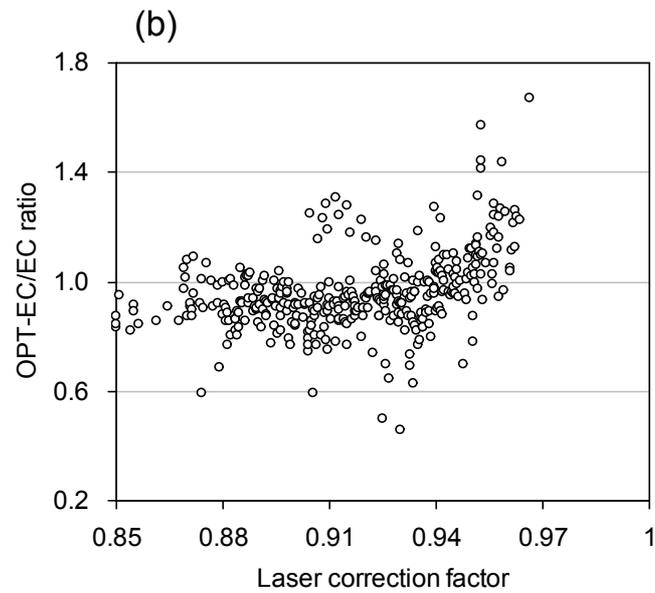
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Figure 4



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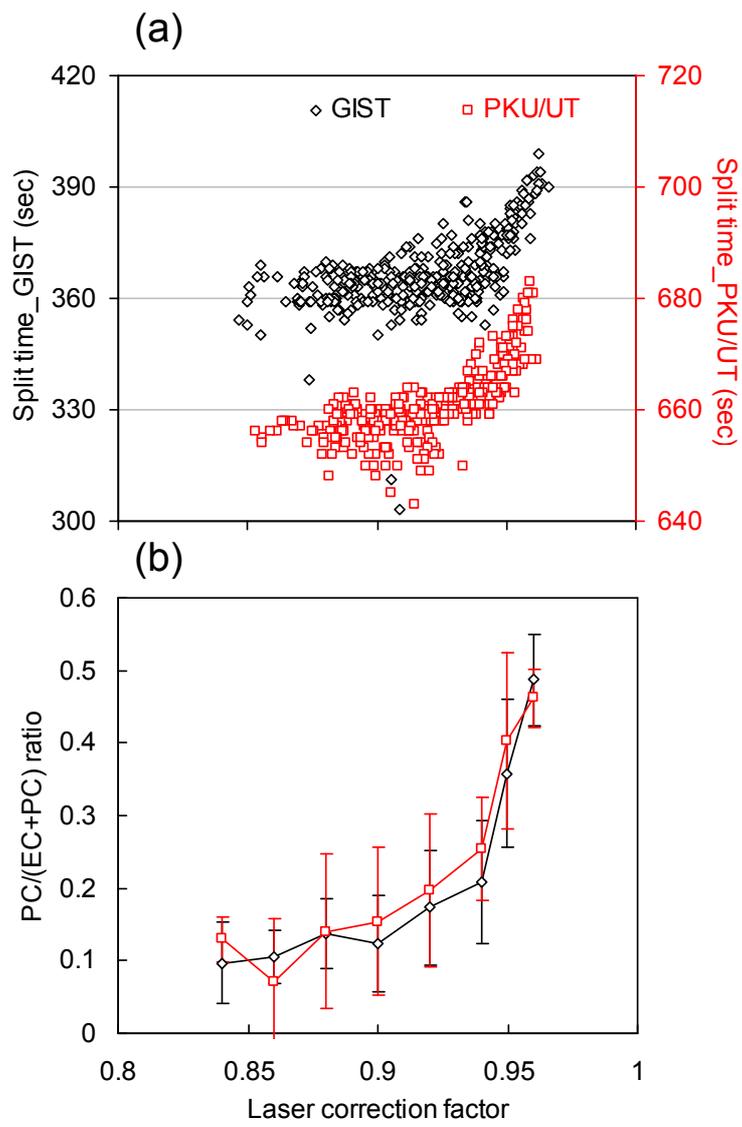
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Figure 5



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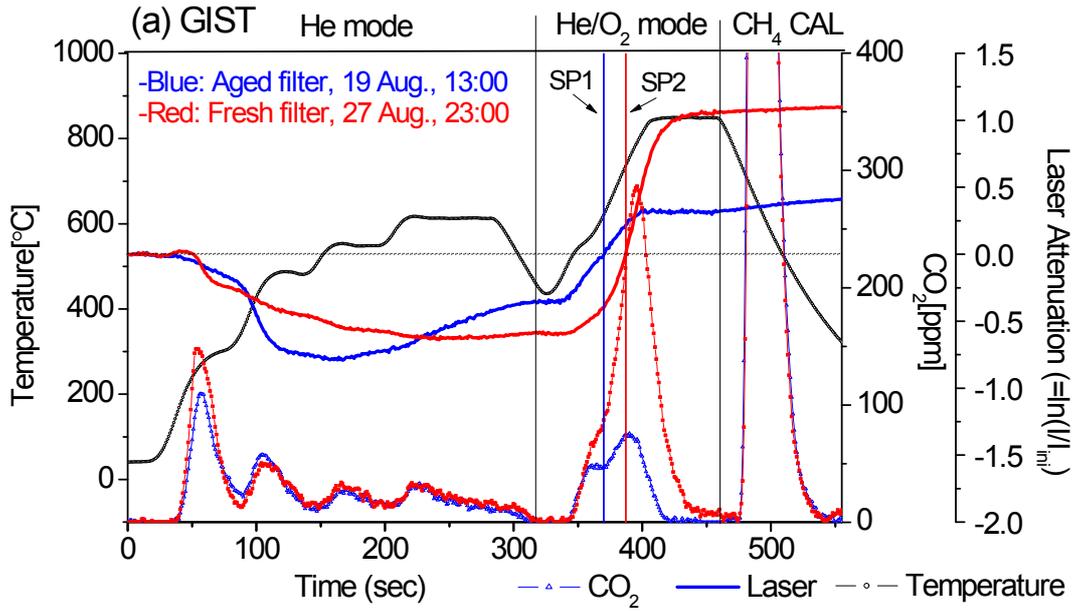
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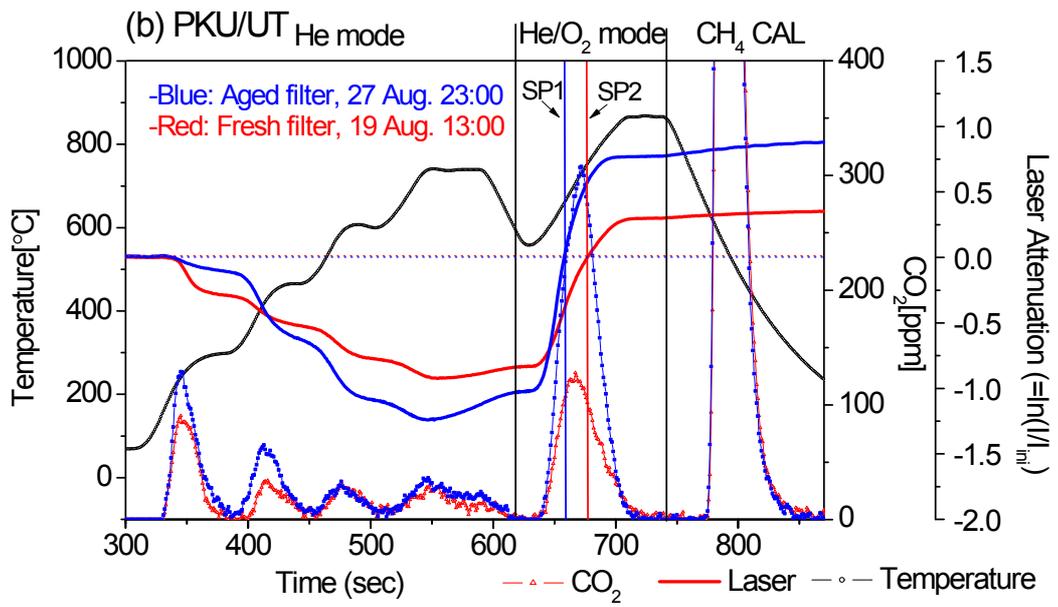
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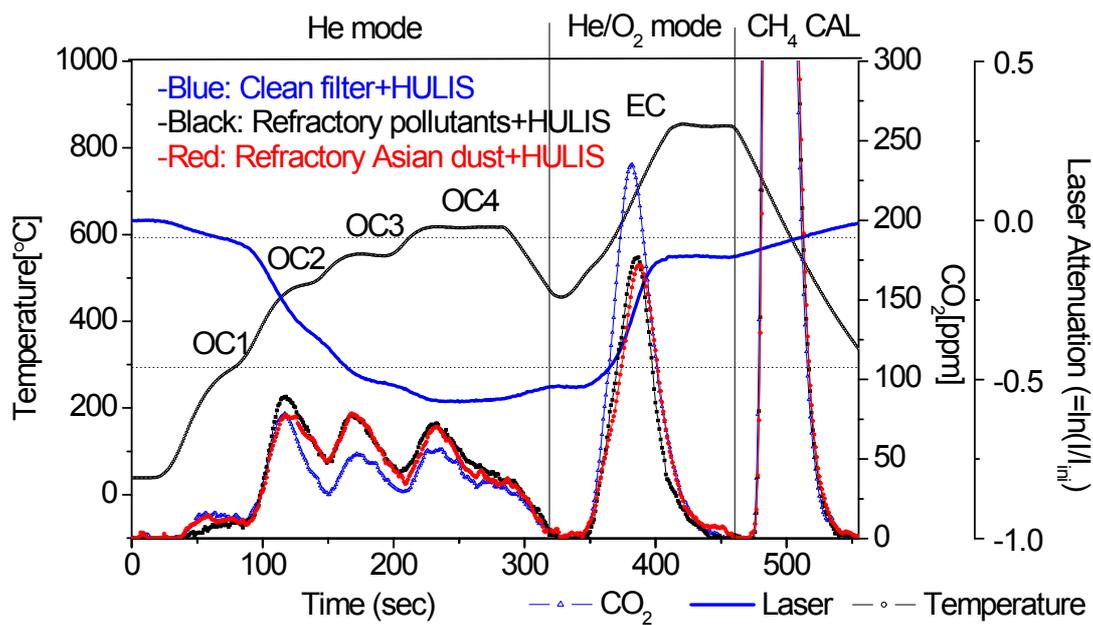
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Figure 7

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