

# Mass Spectrometry of Soot From Six Different Sources: Carbon-Cluster and Refractory CO<sub>2</sub> Signals

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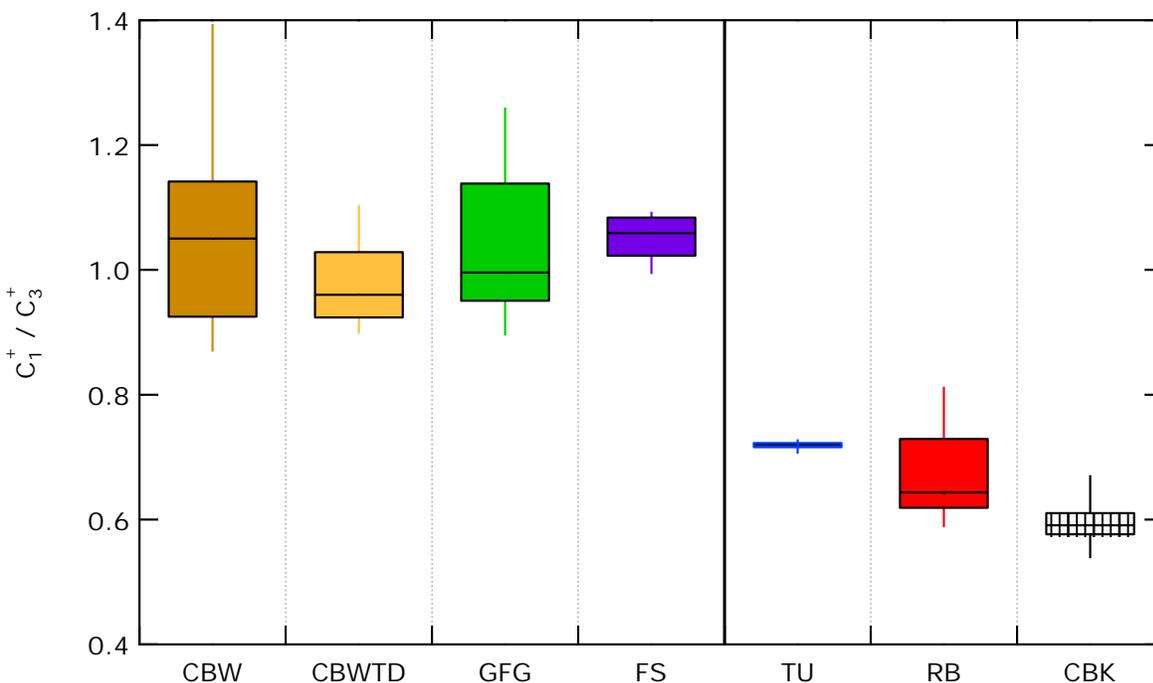
Combustion-generated particles represent the most absorbing particles in the atmosphere and are estimated to be the strongest anthropogenic climate warming agent after CO<sub>2</sub> (IPCC, 2007; Ramanathan and Carmichael, 2008; Bond et al., 2013). In addition to direct absorptive heating, such particles may enhance glacial melting, alter convection and precipitation, react with atmospheric trace gases, and serve as cloud condensation or ice nuclei (Bond et al., 2013). Their short atmospheric lifetime of days to weeks (Cape et al., 2012) makes them ideal candidates for near-term climate mitigation (Shindell et al., 2012; Bond et al., 2013). However, significant uncertainties in the atmospheric burden and mixing state of different combustion-generated particles lead to large uncertainties in current model predictions (Bond et al., 2013). Such uncertainties may be reduced by the new Aerodyne Soot-Particle Aerosol Mass Spectrometer (SP-AMS), a commercial instrument that can characterize both soot mixing state and chemical composition.

We presented the major SP-AMS mass spectral features of six soots, in terms of their relevance in atmospheric source identification. The soots were: fuel-rich and fuel-lean soot from a propane/air diffusion flame; graphite-spark-generator soot; fullerene-enriched soot; Regal Black, a commercial carbon black; and nascent aircraft-turbine soot. In general, these soots exhibited a refractory mass spectrum dominated by two components, carbon-

34 cluster ions  $C_x^{n+}$  and  $CO_2^+$ . ("Refractory" SP-AMS signals are those observed via laser-  
35 induced vapourization of the soot, but not observed via thermal-desorption vapourization  
36 at 600 °C.)

37  
38 We found that the ratio of  $C_1^+/C_3^+$  can be used to differentiate between  $C_x^{n+}$  spectra, and  
39 propose that it may be a useful marker for distinguishing soot sources in atmospheric SP-  
40 AMS measurements. The  $C_1^+/C_3^+$  ratios fell into two groups, with three soots (fuel-rich  
41 flame; spark-generated; fullerene-enriched) showing  $C_1^+/C_3^+ \approx 1$ , while three others (fuel-  
42 lean flame; aircraft turbine; Regal Black) showed  $C_1^+/C_3^+$  significantly less than 1.  
43 Furthermore, the ratio was related to the overall  $C_x^{n+}$  mass spectrum: ratios of 1  
44 corresponded to significant  $C_x^{n+}$  signal above mass-to-charge ratio 60 ( $C_{x>5}^+$ ), while ratios  
45 below 1 corresponded to the absence of high mass-to-charge  $C_x^{n+}$  ions.

46  
47 The second major component of the refractory soot mass spectrum,  $CO_2^+$ , was present in all  
48 six soot samples. A corresponding  $CO^+$  signal was detected but not quantifiable. We showed  
49 that the SP-AMS mass spectrum (vapourization laser on) of Regal Black differs from the  
50 AMS spectrum (laser off) only in terms of  $C_x^{n+}$  and  $CO_x^+$  ( $= CO^+ + CO_2^+$ ), and propose that  
51 this  $CO_x^+$  signal originates from oxygenated moieties incorporated into the refractory soot  
52 structure of Regal Black. Refractory  $C_x^{n+}$  and  $CO_x^+$  may therefore be useful for identifying  
53 the source, composition and evolution of atmospheric combustion aerosols.



54  
 55 **Figure 1. SP-AMS  $C_1^+ / C_3^+$  ratios for CAST “Brown” soot (CBW), thermodenuded CBW (CBWTD), spark-**  
 56 **generated soot (GFG), Fullerene-enriched Soot (FS), aircraft-turbine soot (TU), Regal Black (RB), and**  
 57 **CAST “Black” soot (CBK), All samples were monodisperse particles at multiple sizes, except TU, which**  
 58 **represents a single engine thrust sampled at a point behind the engine.**

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# Mass Spectrometry of Soot From Six Different Sources Carbon-Cluster and Refractory CO<sub>2</sub> Signals

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## Background

Combustion-generated particles are the most absorbing in the atmosphere. They are estimated to be the strongest anthropogenic warming agent after CO<sub>2</sub> [ref. 1]. Their warming effects are entangled with their atmospheric lifetime and mixing state. These two properties vary between soot sources, and during soot aging.<sup>1,2</sup>

In order to improve our understanding of these processes, measurements of soot composition are required. Such measurements are useful for source apportionment and mechanistic insights. This poster discusses the composition of soot for use in future source apportionment and aging studies.

## Soot-Particle Aerosol Mass Spectrometer (SP-AMS)

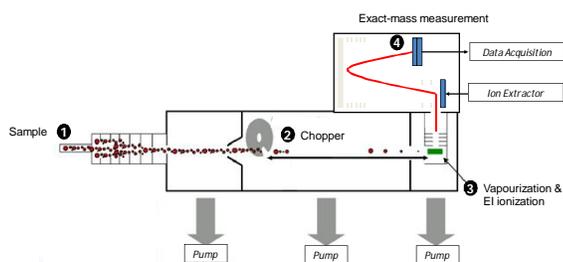


Fig. 1. Schematic of the SP-AMS.

1 Sample aerosols are introduced and focussed into a narrow beam via an aerodynamic lens. 2 A rotating chopper creates bursts of particles that become separated by time-of-flight through the chamber. 3 Particles are vapourized by a metal surface (at 600°C) or a 1064 nm continuous-wave laser (absorbed by soot but not most in/organic material). The laser is switchable: if on, soot particles do not come into contact with the metal surface. 4 After EI ionization, high-resolution mass spectrometry allows the elemental composition of ions below ~200 Th to be determined.

## Experiment

Fig. 2. Experimental setup.

Laboratory setup for all samples except turbine soot. Soot aerosols were diluted before passing through a 1 m<sup>3</sup> residence chamber with residence time ~30 min. Particles then flowed through two bipolar chargers before dividing the 4 L min<sup>-1</sup> sample flow equally between two DMAs, each with 5 L min<sup>-1</sup> sheath flow.

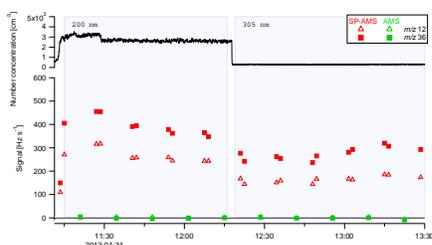
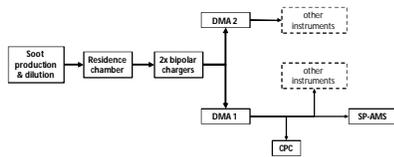


Fig. 3. Experimental setup.

Timeseries of the two most intense carbon ions observed for Regal Black soot, m/z 12 (C<sub>1</sub><sup>+</sup>) and m/z 36 (C<sub>3</sub><sup>+</sup>), during two size-selected experiments. Green 'AMS' data are with the soot vapourization laser OFF (non-refractory organics volatile at 600 °C and also inorganic compounds are detected in AMS mode). Red 'SP-AMS' data represent the same instrument, but with the soot vapourization laser ON. The mean AMS signal is not significantly different from zero.

## Acknowledgements and References

The authors are grateful to Mark Johnson (Rolls Royce, UK), Theo Rindlisbacher (Federal Office of Civil Aviation, Switzerland), SR Technics (Zurich Airport, Switzerland), Paul Williams (University of Manchester, UK), and the SAMPLE-III team for their efforts and assistance in the aircraft-turbine measurements. We thank Tim B. Onasch for sharing his independent measurements SP-AMS spectra of RB. This work was supported by the Swiss National Fund (Grant 200021\_132199 / 1).

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## Carbon-Cluster Mass Spectrum

Table 1. Soot samples and production methods.

Soot	Abbreviation	Production
Regal Black	RB	• A commercial carbon black; used for SP-AMS calibration
Airplane-turbine soot	TU	• Civil aviation gas turbine <sup>3</sup> ; Undiluted single-point measurement behind engine
CAST "Black"	CBK	• Propane-flame soot (C/O 0.25); low organic (OC) content <sup>4</sup>
CAST "Brown"	CBW	• Propane-flame soot (C/O 0.41); moderate PAH content <sup>5</sup>
Spark-generated soot	GFG	• PALAS GFG 1000; arc discharge across graphite in argon
Fullerene-enriched soot	FS	• Commercial C <sub>60</sub> and C <sub>70</sub> (~6% and 1%) enriched soot <sup>6</sup>

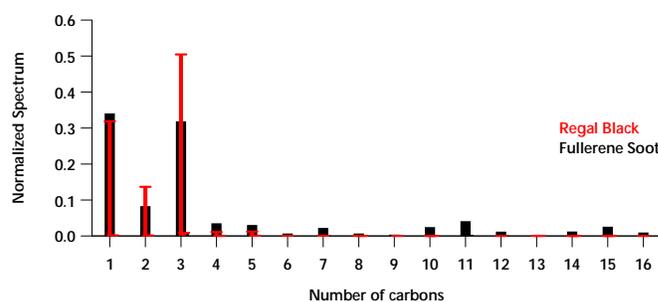


Fig. 4. Carbon-cluster fragmentation patterns.

The carbon-cluster mass spectrum for Regal Black (RB) and Fullerene Soot (FS). This spectrum represents C<sub>1-16</sub><sup>+</sup> based on the signal at integer multiples of 12. Carbon-13 isotopic peaks (<sup>13</sup>C<sub>1</sub>C<sub>x-1</sub><sup>+</sup>) are also shown. In general, two types of fragmentation patterns were observed, one extending up to large clusters (FS) and one with negligible signal above C<sub>3</sub><sup>+</sup> (RB). The colours in Table 1 show which pattern each soot fell into.

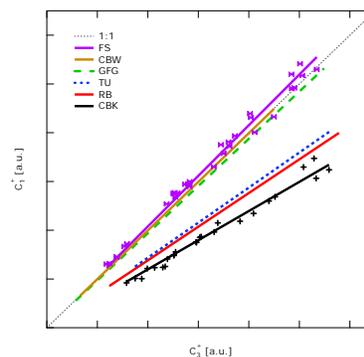


Fig. 5. Distinguishing soots based on the two major carbon-cluster ions.

The ratio of intensities at C<sub>1</sub><sup>+</sup> and C<sub>3</sub><sup>+</sup> was also sufficient to classify these six soot types. The figure shows this ratio as a linear fit through zero.

The carbon-cluster mass spectra in Fig. 4 show that different soots have different overall mass spectra, however, >30% of the total signal was at C<sub>1</sub><sup>+</sup> and C<sub>3</sub><sup>+</sup> for all six soot types.

In ambient samples, where total mass concentration may be low, using the most intense peaks may maximize signal-to-noise.

## Refractory CO<sub>2</sub> Signals

Fig. 5. SP-AMS vs AMS signals for RB differ by only C<sub>x</sub><sup>+</sup> and CO<sub>x</sub><sup>+</sup>.

SP-AMS data (red) and AMS data (green) were used to compare the non-refractory (volatile below 600 °C) and refractory (e.g. soot, volatile at ~4000 °C) components of RB soot.

The average hydrogen/carbon (H:C) and oxygen/carbon (O:C) ratios estimated from high-resolution mass spectrometry show that the SP-AMS and AMS differ only by C<sub>x</sub><sup>+</sup> and CO<sub>x</sub><sup>+</sup> = CO<sup>+</sup> + CO<sub>2</sub><sup>+</sup>.

It is well known that functional groups at the soot surface thermally decompose into CO and CO<sub>2</sub> at ~1000 K [ref 8-10]. We interpret our observations as originating from the decomposition of oxidized functional groups at the soot surface. These may play a major role in the CCN activity<sup>7</sup> of aged soot.

