Combustion-generated particles represent the most absorbing particles in the atmosphere and are estimated to be the strongest anthropogenic climate warming agent after CO$_2$ (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-
cluster ions $\text{C}_x^+$ and $\text{CO}_x^+$. (“Refractory” SP-AMS signals are those observed via laser-induced vapourization of the soot, but not observed via thermal-desorption vapourization at 600 °C.)

We found that the ratio of $\text{C}_1^+ / \text{C}_3^+$ can be used to differentiate between $\text{C}_x^+$ spectra, and propose that it may be a useful marker for distinguishing soot sources in atmospheric SP-AMS measurements. The $\text{C}_1^+ / \text{C}_3^+$ ratios fell into two groups, with three soots (fuel-rich flame; spark-generated; fullerene-enriched) showing $\text{C}_1^+ / \text{C}_3^+ \approx 1$, while three others (fuel-lean flame; aircraft turbine; Regal Black) showed $\text{C}_1^+ / \text{C}_3^+$ significantly less than 1. Furthermore, the ratio was related to the overall $\text{C}_x^+$ mass spectrum: ratios of 1 corresponded to significant $\text{C}_x^+$ signal above mass-to-charge ratio 60 ($\text{C}_{x>5}^+$), while ratios below 1 corresponded to the absence of high mass-to-charge $\text{C}_x^+$ ions.

The second major component of the refractory soot mass spectrum, $\text{CO}_x^+$, was present in all six soot samples. A corresponding $\text{CO}^+$ signal was detected but not quantifiable. We showed that the SP-AMS mass spectrum (vapourization laser on) of Regal Black differs from the AMS spectrum (laser off) only in terms of $\text{C}_x^+$ and $\text{CO}_x^+ (= \text{CO}^+ + \text{CO}_2^+ )$, and propose that this $\text{CO}_x^+$ signal originates from oxygenated moieties incorporated into the refractory soot structure of Regal Black. Refractory $\text{C}_x^+$ and $\text{CO}_x^+$ may therefore be useful for identifying the source, composition and evolution of atmospheric combustion aerosols.
Figure 1. SP-AMS $C_1^- / C_3^+$ ratios for CAST “Brown” soot (CBW), thermodenuded CBW (CBWTD), spark-generated soot (GFG), Fullerene-enriched Soot (FS), aircraft-turbine soot (TU), Regal Black (RB), and CAST “Black” soot (CBK). All samples were monodisperse particles at multiple sizes, except TU, which represents a single engine thrust sampled at a point behind the engine.


Mass Spectrometry of Soot From Six Different Sources: Carbon-Cluster and Refractory CO₂ 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 agents after CO₂ [ref 1]. Their warming effects are enhanced with their atmospheric lifetime and mixing state. These two properties are influenced by soot sources, and during soot aging.¹,²

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)**

![Schematic of the SP-AMS](image)

### Fig. 1. Schematic of the SP-AMS

Sample aerosols are introduced and focused into a narrow beam via an aerodynamic lens. A rotating chopper rotates bursts of particles that become separated by time-of-flight through the chamber. Particles are vaporized by a metal surface (at 600°C) or a 1064 nm continuous-wave laser (absorbed by soot but not most inorganic material). The laser is switchable. For soot, particle diameters do not come into contact with the metal surface. After EI ionization, high-resolution mass spectrometry allows the elemental composition of ions below ~200 m/z to be determined.

**Experiment**

![Experimental setup](image)

### Fig. 2. Experimental setup.

Laboratory setup for all samples except turbine soot. Soot aerosols were diluted before passing through a 1 m² residence chamber with residence time ~30 min. Particles then flowed through two bipolar chargers before dividing the 4 L min⁻¹ sample flow equally between two DMA1s, each with 5 L min⁻¹ sheath flow.

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

![Schematic of the SP-AMS](image)

### Fig. 3. Experimental setup.

Timeseries of the two most intense carbon ions observed for Regal Black soot, μs 12 (C₁₀) and μs 36 (C₁₆), during two size-selected experiments. Green “AMS” data are with the soot vaporized using laser OFF—non-refractory organics or soot, at 600°C and also inorganic compounds are detected in AMS mode. Red “SP-AMS” data represent the same instrument, but with the laser vaporization 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), Tom Blaschke (Federal Office of Civil Aviation, Switzerland), S. E. U. S. (Zurich Airport, Switzerland), Paul Williams (University of Manchester, UK), and the鄱WMP-III team for their efforts and assistance in the aircraft surface measurements. We thank T. R. Glavaš for sharing his independent measurements for SP-AMS spectra of RB. This work was supported by the Swiss National Fund (Grant 200021_1, 12299 / 1).

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**Table 1. Soot samples and production methods.**

<table>
<thead>
<tr>
<th>Soot Type</th>
<th>Abbreviation</th>
<th>Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regal Black</td>
<td>RB</td>
<td>A commercial carbon black: used for SP-AMS calibration</td>
</tr>
<tr>
<td>Airplane-turbine soot</td>
<td>TU</td>
<td>Civil aviation gas turbine; Undiluted single-point measurement behind engine</td>
</tr>
<tr>
<td>CAST “Black”</td>
<td>CBK</td>
<td>Propane-flame soot (C/O 0.25); low organic (OC) content²</td>
</tr>
<tr>
<td>CAST “Brown”</td>
<td>CBW</td>
<td>Propane-flame soot (C/O 0.41); moderate PAH content²</td>
</tr>
<tr>
<td>Spark-generated soot</td>
<td>GFG</td>
<td>PALAS GIG 1000, arc discharge across graphite in argon</td>
</tr>
<tr>
<td>Fulleren-enriched soot</td>
<td>FS</td>
<td>Commercial C₇₀ and C₆₀(4% and 1%) enriched soot³</td>
</tr>
</tbody>
</table>

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**Carbon-Cluster Mass Spectrum**

![Carbon-Cluster Mass Spectrum](image)

### Fig. 4. Carbon-cluster fragmentation patterns.

The carbon-cluster mass spectrum for Regal Black (RB) and Fulleren Soot (FS). This spectrum represents C₇₀⁴⁻ based on the signal at integer multiples of 12. Carbon-13 isotopic peaks (|C⁷₀ - C₇₀|) 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 C₇₀⁴⁻ (RB). The colours in Table 1 show which patterns each soot fell into.

**Acknowledgements and References**

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