



Secondary aerosol measurement from vehicle exhaust with oxidation flow reactors

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Introduction & background

The particle emissions of automotive sources can be characterized to include fractions that are present in (1) hot exhaust aerosol, (2) in fresh exhaust aerosol after emission, and (3) components that are formed in the atmosphere due to oxidation processes. The hot exhaust aerosol contains only non-volatile primary particles, the fresh exhaust contains also delayed primary aerosol (semi-volatile), and the aged exhaust additionally contains secondary aerosol (Figure 1). The formation of secondary aerosol in the atmosphere takes place through oxidation processes that tend to lower the saturation vapor pressures of organic species. The more oxidized compounds are more likely found in the particle phase (Robinson et al., 2007). Most of the secondary aerosol work has been focused on the secondary organic aerosol (SOA), as the fresh exhaust contains numerous organic compounds (Gentner et al., 2017).

As discussed by Gentner et al., 2017, the studies of secondary aerosol formation can be divided by methodology into two groups: top-down and bottom-up. Much of the research work has used the top-down approach, based on ambient air quality measurements and estimation of the contributions of vehicles and vehicle types. This review, however, restricts to the studies applying the bottom-up approach where the exhaust of individual vehicles or engines is oxidized to simulate the atmospheric ageing process. To this end, both batch chambers (such as smog chambers) and flow-through chambers have been applied. A batch chamber is good for

detailed oxidation process studies, but cannot be used to differentiate rapidly changing driving conditions during the test driving cycle. Flow through reactors such as the **Potential Aerosol Mass (PAM)** reactor or **TUT Secondary Aerosol Reactor (TSAR)** reactor are designed to simulate secondary aerosol mass formation potential on a close to real-time basis (Kang et al., 2011; Lambe et al., 2011; Simonen et al., 2017).

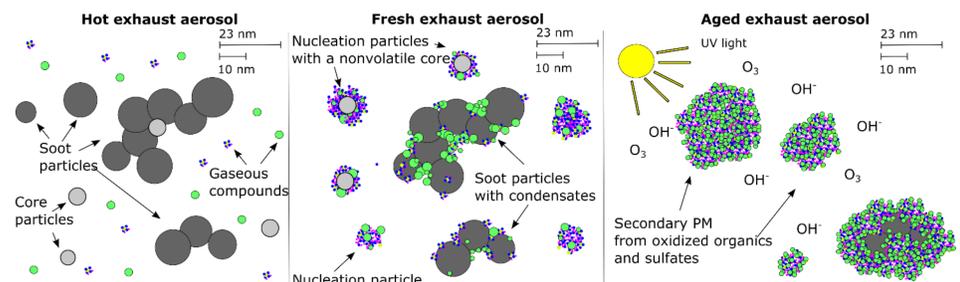


Figure 1. Types of exhaust related particulate material.

Potential Aerosol Mass (PAM) reactor



Figure 2. PAM reactor picture (above) and cross section (below) with information of reactants.

Method

- Flow-through type chamber (Figure 2)
- High oxidant concentrations of O₃, OH, HO₂ and UV lights used in chamber are shown to simulate SOA formation in the atmosphere
- Flow selectable, 4-10 l/min
- Represents 2–20 days of atmospheric oxidation
- Not laminar, continuously mixed flow (residence time 1.5-3 min)

Results

- Example of a result shown in Figure 3 (Timonen et al., 2017) for a gasoline passenger car with three fuels: E10, E85 and E100
- Due to continuous flow mixing, emissions “spikes” are broadened in the test cycle
- Enables in-cycle SOA formation analysis over different sections of the cycle (e.g. right after cold start or during extra-urban driving)

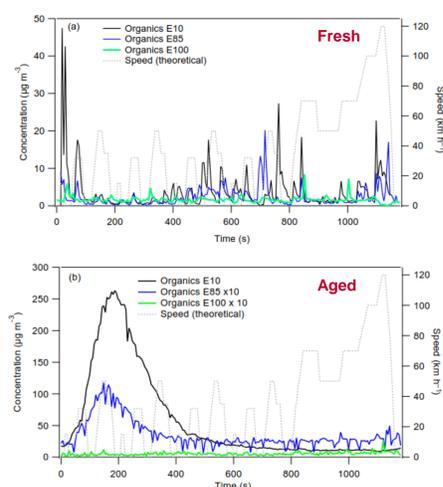


Figure 3. Time series of the organic compounds for the primary emissions (a) and for the emissions measured after the PAM chamber (b). The speed profile of the NEDC is also shown. The speed profile and the mass concentration in (b) do not correspond to each other directly due to the broad residence time distribution of the PAM chamber. (Timonen et al., 2017)

TUT Secondary Aerosol Reactor (TSAR)



Figure 4. TSAR layout: the residence time chamber (1), the expansion tube (2), the oxidation reactor (3) and the adjustable outlet (4) (modified from Simonen et al., 2017).

Method

- Flow-through type chamber (Figure 4) (Simonen et al., 2017)
- UV lights produce OH and HO₂ radicals from H₂O and O₃. The radicals together with O₃ simulate atmospheric oxidation.
- Recommended flow 5 l/min
- Represents 2-9 days of atmospheric oxidation
- Well-defined, near-laminar flow (residence time ~40 s)

Results

- Example of a result shown in Figure 5 for a gasoline passenger car during hot-start NEDC
- Faster response than in PAM reactor, thus enables more accurate analysis on SOA formation as a function of driving condition

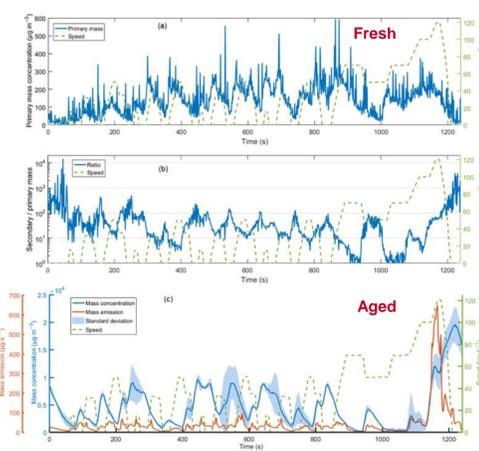


Figure 5. Time series of the vehicle speed and primary mass concentration (a), speed and the secondary-to-primary mass ratio (b), speed, the secondary mass concentration (μg m⁻³) and the secondary mass emission factor (μg s⁻¹) (c) during the NEDC. (Simonen et al., 2017)

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