Session 6: Nanoparticles: instrumentation, metrology, fundamentals, Talk

Characterization of a novel, mid-cost device for ambient monitoring of ultrafine particles

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Despite the potentially significant health impacts of ultrafine particles (UFP), they are not routinely measured at air quality monitoring stations. One barrier to routine monitoring of UFP is the relatively high cost and complexity of measuring solid and total particle number (sPN & tPN) down to 10 nm as is required by the new European Air Quality directive. Furthermore, ambient monitoring of the same metrics used for tailpipe emissions would allow stakeholders to better assess the effectiveness of emissions regulations and health impacts of such particles. To address this, a novel, mid-cost device for measuring UFPs down to 10 nm is characterized here.

The AirPN10 from nanoDUST GmbH measures particle number (PN) with a diffusion charging (DC) based particle counter, already approved for measuring particle number (PN) in diesel exhaust, adapted for ambient monitoring. The sample aerosol passes through a series of preconditioning steps before reaching the detector. This includes a stage with a high temperature zone to remove volatiles such that the sPN can be measured. A switch is used to by-pass the high temperature zone periodically such that sPN and tPN are monitored providing some information on particle composition. In addition, the two-stage DC sensor allows for the geometric mean mobility diameter (GMD_{mob}) of the particles to be estimated. The device was tested with polydisperse soot particles from a 5201 Type BC miniCAST soot generator. This generator produces particles with a very low volatile content, therefore, sPN and tPN were equal within the measurement variability. Various size distributions were used with GMD_{mob} of 10, 15, 23, 50, 80, 120 and 200 nm to span the operating range of the devices (10 to 200 nm). The counting efficiency (CE) of the AirPN10 was assessed by comparing the sPN and tPN values to that measured by a Condensation Particle Counter (CPC; TSI 3752). The results were in excellent agreement for aerosols with GMD_{mob} from 15 – 120 nm at concentrations above approximately 5000 cm^{-3}, with higher variability at very low concentrations (ca. 1000 cm^{-3}). At 10 and 200 nm, the CE was slightly reduced but the device was still able to detect these particles at CE of approximately 0.5 and 0.7, respectively. The GMD_{mob} was in excellent agreement with that measured by a Scanning Mobility Particle Spectrometer (SMPS; TSI 3752 and 3082) except at 200 nm where the size was slightly overestimated (ca. 10% overestimation).

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Ensuring the comparability of nanoparticle measurements by the international metrology community

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The international comparability of measurements is underpinned by the Mutual Recognition Arrangement of the International Committee for Weights and Measures (the CIPM MRA). This is the framework through which National Metrology Institutes (NMIs) demonstrate the global equivalence of their measurement standards at the highest metrological level. A crucial activity in supporting the CPIM MRA is the delivery of formal comparison exercises between NMIs and, where appropriate, Designated Institutes (DIs) and other reference laboratories.

In November 2024, ten laboratories participated in the experimental campaign for the CCQM-K185/P237 comparison at PTB-Braunschweig, Germany. The laboratories (which cannot all be named here to a limit on the number of co-authors) were: NPL (UK), PTB (Germany), KRISS (Korea), METAS (Switzerland), NIM (China), A*STAR (Singapore), NMIJ (Japan), NRC (Canada), UBA (Germany) and TROPOS (Germany). The comparison, which was coordinated by NPL, required the participating laboratories to measure all or some of:

- Particle number concentration of 30 and 50 nm monodisperse soot at six number concentrations from 1 000 to 100 000 cm^{-3} using condensation particle counters (CPCs).
- Particle charge concentration of 30 and 50 nm monodisperse soot at six charge concentrations between 0.16 and 16.0 fC cm^{-3} using aerosol electrometers.
- Particle number concentration of 80 nm polydisperse soot at four number concentrations from 1 000 to 100 000 cm^{-3} using CPCs.

Here, we briefly outline the role of the CIPM MRA in ensuring international comparability before presenting the results from the CCQM-K185/P237 comparison, which covered a much wider range of concentrations than previous such comparisons (most recently [1]). By comparing the results from CCQM-K185/P237 against those from these earlier comparisons, we highlight the strides that the NMI community has made in advancing nanoparticle measurements since the first nanoparticles comparison nearly 20 years ago. We also identify some key remaining challenges revealed by the results of the comparison, including the need to improve and harmonise the use of dilution devices, which if addressed will further improve comparability in the future.

Finally, we describe the ongoing activities of an international Aerosol Metrology Task Group, which was established in 2024 to bring the NMI/DI nanoparticle community closer together and deliver improved and coordinated engagement with the global aerosol science stakeholder community. In addition to delivering comparisons, the Task Group is harmonising the terminology and nomenclature used in aerosol metrology, undertaking stakeholder engagement activities and developing a research roadmap for aerosol metrology.

[1] A. Brown *et al.*, NPL Report ENV 46, International Comparison CCQM-K150, Particle number concentration (100 to 20 000 cm^{-3}) and particle charge concentration (0.15 to 3 fC cm^{-3}).

Dynamic chemical evolution of incipient soot. An FT-IRC MS-based investigation

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In flame combustion, the inception of carbon nanoparticles is believed to be primarily driven by kinetics. However, experimental data on the concentration of species in the gas phase seem to challenge this view. While accurate knowledge of the chemical composition of incipient soot is essential for resolving this ongoing debate, measuring the properties of transient species in a reactive medium at high temperature remains extremely challenging.

The accurate determination of structure and concentration of transient species with minimum interference of the sampling process is possible by means of inline molecular beam synchrotron-based diagnostics. However, the complexity of this approach makes it feasible only for a few selected species. To capture the ensemble of the species generated during the nanoparticle inception process, ex situ mass spectrometry-based diagnostics are often employed. In this work, the chemical composition of incipient soot is investigated on a laminar premixed ethylene/air flame with unprecedented detail by means of a Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer having > 10 M nominal resolving power.

The advanced methodology proposed in this work reveals at least three distinct types of hydrocarbons in incipient nanoparticles, providing new molecular-level insights into the inception process. The findings indicate that, as the incipient nanoparticles evolve, dynamic interactions establish among oxygenated hydrocarbons, closed-shell polycyclic aromatic hydrocarbons, and hydrocarbons capable of undergoing easy dehydrogenation that may generate species such as resonance stabilized radicals. These findings will contribute to elucidate the fundamental mechanisms of carbon nanoparticles inception, and assist in the development of more accurate prediction models.

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Laboratory Intercomparison in Germany: Calibration of particle counters for the national periodical technical inspection

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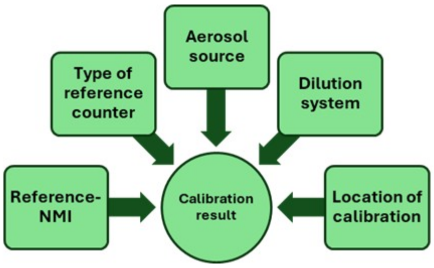
The measuring of the particle number concentration has been mandatory in Germany since 2023 for all diesel vehicles from emission class 6/VI as part of the national periodical technical inspection (PTI). The metrologically traceable calibration of these particle counters is a fundamental requirement for the comparability of PTI measurements on diesel vehicles and thus for the evaluation of the function of the installed diesel particulate filter.

The annual calibration of PTI particle counters is legally required in Germany and is carried out by independent calibration laboratories. The laboratories require accreditation from the German Accreditation Body (DAkkS) in accordance with ISO 17025 [1]. They must fulfil the German calibration guideline [2], which forms the framework and basic requirements for standardized calibration. More than 35 000 calibrations of particle counters are carried out in Germany per year.

Nevertheless, laboratories have freedom in the design of the calibration, such as in the selection of the calibration aerosol, the reference devices or the traceability chain. They may carry out calibrations both in the permanent or mobile laboratory and in the workshops on site. Some calibration laboratories form a further internal traceability level by calibrating other working standards with an externally calibrated reference standard (e.g. from an NMI). Depending on the procedure and traceability, the calibration laboratories calculate individual measurement uncertainties for their calibrations according to the Guide to the expression of uncertainty in measurement, GUM [3]. As part of the accreditation assessments, the achievable measurement uncertainties are confirmed by independent assessors.

The organization and responsibility for verification of particle counters in the field in Germany differs from that provided in the EU Recommendation [4]. It is mainly due to the large number of calibrations and is based on the established system of accreditation.

With the aim of evaluating the comparability of the different calibration procedures of AU particle counters, PTB has been carrying out a laboratory intercomparison in cooperation with the ASA Association (German Association of Manufacturers and Importers of Automotive Service Equipment) since October 2025. Twelve calibration laboratories and PTB as the pilot laboratory are taking part in the comparison measurement. Each laboratory calibrates a total of 5 measuring instruments of different manufacturers and types, according to their respective calibration procedures and with the individual accredited measurement uncertainty. The measurements will run from October 2025 to March 2026.



Ideally, the aim of the intercomparison is to confirm that the calibration results of the individual laboratories agree within the scope of their accredited measurement uncertainty. Potential systematic deviations will be identified from the results and recommendations for the further development of calibration procedures will be developed.

The first results of the intercomparison are expected in April / May 2026. They will be published in anonymized form. The comparative measurement will contribute to the harmonization of calibrations and to improving the traceability of the particle number concentration for the periodic emissions test on diesel vehicles in the second and third traceability stage.

[1] DIN EN ISO/IEC 17025:2018-03 General requirements for the competence of testing and calibration laboratories

[2] Richtlinie zur Kalibrierung von Abgasmessgeräten, die für die Untersuchung der Abgase von Kraftfahrzeugen nach Nummer 6.8.2 der Anlage Vllla STVZO eingesetzt werden („AU-Geräte Kalibrierrichtlinie"), Verkehrsblatt 2021 Heft 11, Nr. 133, geändert durch Verkehrsblatt 2024 Heft 17, Nr. 118

[3] JCGM GUM-1:2023, Guide to the expression of uncertainty in measurement

[4] Commission Recommendation (EU) 2023/688 of 20 March 2023 on particle number measurement for the periodic technical inspection of vehicles equipped with compression ignition engines, (OJ L 90, 28.3.2023, p. 46)

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NO-Triggered RO-Mediated Propagation in the OH Oxidation of a Saturated Cyclic Alkane

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Highly oxygenated organic molecules (HOMs) formed during gas-phase oxidation of volatile organic compounds play a key role in secondary organic aerosol (SOA) formation and particle growth. While HOM formation is commonly attributed to rapid unimolecular autoxidation of peroxy radicals (RO_2), this mechanism is often kinetically constrained in saturated hydrocarbons, particularly on short atmospheric timescales. In this work, we investigate the early-stage OH-initiated oxidation of cis-decalin, a representative bicyclic anthropogenic alkane, under controlled laboratory conditions to elucidate how radical propagation proceeds when unimolecular RO_2 isomerization is slow.

Experiments were conducted in a quartz flow-tube reactor at ambient temperature and pressure with residence times between 0.9 and 2.9 seconds. Oxidation products were characterized using a high-resolution Orbitrap mass spectrometer coupled to a multi-scheme chemical ionization inlet employing bromide and nitrate reagent ions. This dual-ionization approach enabled simultaneous detection of early-generation oxidation products and highly oxygenated species, including accretion products.

In the absence of NO, cis-decalin oxidation produced only minimal levels of oxygenated products within the studied timescale, indicating that OH initiation alone is insufficient to sustain multigenerational oxidation. In contrast, the introduction of NO led to a pronounced enhancement in oxidation, marked by the rapid appearance of highly oxygenated monomers containing up to ten oxygen atoms as well as C_{20} accretion products at longer residence times. Product distributions exhibited a strong, non-linear dependence on NO concentration, with maximum oxidation observed at moderate NO levels and suppression under high-NO conditions.

These observations demonstrate that NO promotes oxidation not merely through termination but by converting RO_2 to alkoxy radicals (RO), thereby enabling RO-mediated structural rearrangement, ring opening, and subsequent O□ addition. This bimolecular radical cycling bypasses kinetic limitations associated with slow RO_2 H-shifts and allows efficient propagation of oxidation on second timescales. The results reveal that saturated cyclic alkanes can rapidly form low-volatility, multifunctional products under polluted conditions when RO-mediated propagation is active.

Overall, this study highlights the critical role of bimolecular radical chemistry in controlling HOM formation from anthropogenic hydrocarbons and provides new mechanistic insight into SOA formation pathways in combustion-influenced and urban atmospheres.

[1] Barua, S.; Kumar, A.; Seal, P.; Bezaatpour, M.; Jha, S.; Myllys, N.; Iyer, S.; Rissanen, M. Rapid Formation of Aerosol Precursors from the Autoxidation of Aromatic Carbonyls and the Remarkable Enhancing Influence of NO Addition. In Review August 29, 2025. https://doi.org/10.21203/rs.3.rs-7332278/v1

[2] Rissanen, M. P.; Mikkilä, J.; Iyer, S.; Hakala, J. Multi-Scheme Chemical Ionization Inlet (MION) for Fast Switching of Reagent Ion Chemistry in Atmospheric Pressure Chemical Ionization Mass Spectrometry (CIMS) Applications. *Atmos. Meas. Tech.* **2019**, *12* (12), 6635–6646. https://doi.org/10.5194/amt-12-6635-2019.

[3] Smith Lewin, C.; Kumar, A.; Herbinet, O.; Arnoux, P.; Asgher, R.; Barua, S.; Battin-Leclerc, F.; Farhoudian, S.; Garcia, G. A.; Tran, L.-S.; Vanhove, G.; Nahon, L.; Rissanen, M.; Bourgalais, J.

[4] Barua, S.; Kumar, A.; Seal, P.; Iyer, S.; Rissanen, M. Rapid Formation of Secondary Aerosol Precursors from the Autoxidation of C_5 –C_8 n-Aldehydes. Gases/Laboratory Studies/Troposphere/Chemistry (chemical composition and reactions) October 24, 2025. https://doi.org/10.5194/egusphere-2025-5207.

[5] Riva, M.; Da Silva Barbosa, T.; Lin, Y.-H.; Stone, E. A.; Gold, A.; Surratt, J. D. Chemical Characterization of Organosulfates in Secondary Organic Aerosolderived from the Photooxidation of Alkanes. *Atmos. Chem. Phys.* **2016**, *16* (17), 11001–11018. https://doi.org/10.5194/acp-16-11001-2016.