Using particle effective density to determine SMPS-based aerosol mass concentration: application to airborne carbon and titanium nanoparticles

Sébastien Bau, Benoît Oury, Virginie Matera and Xavier Simon

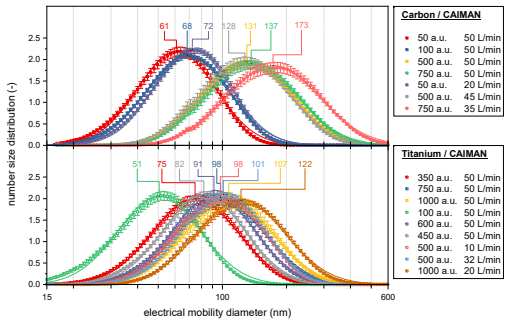
Institut National de Recherche et de Sécurité, Département Métrologie des Polluants, Vandœuvre les Nancy, France
*sebastien.bau@inrs.fr

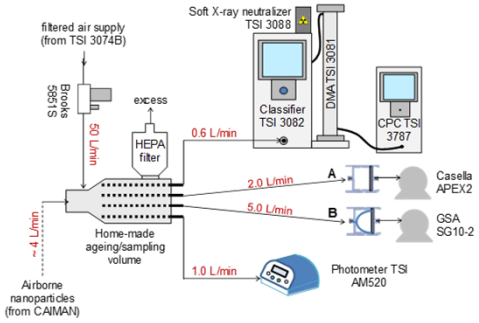
Motivation & Objectives

- ✓ Absence of consensus on the parameters to characterize occupational exposure to airborne nanoparticles
  - providing knowledge on the number size distribution and the number concentration of submicrometer aerosols is of interest [1]
  - mass concentration shall still be considered as a reference metric in OH&S
- ✓ Ideally, these parameters are intended to be measured in real-time
  - allowing a given task to be associated with a level of exposure / concentration or a specific size distribution
  - deploying multiple instruments in field measurement campaigns is to be avoided
- ✓ The Scanning Mobility Particle Sizer (SMPS) is capable of providing data relative to both the size distribution and total concentration according to the number metrics (raw data)
  - this work focuses on the determination of the mass concentration deduced from SMPS data by integrating airborne particle effective density

Materials & Methods

- ✓ Test aerosols
  - produced using the CAIMAN facility [2] equipped with carbon (n = 7) / titanium (n = 9) electrodes
  - range of modal diameters between ≈ 60 and 200 nm, with Geometric Standard Deviations (GSD) of ≈ 1.6



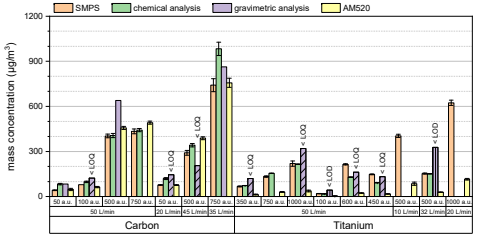


- ✓ Measurement and sampling strategy
  - number size distribution: SMPS (TSI DMA, model 3081 + CPC, model 3787)
  - sampling for further off-line analysis:
    - 2-pieces CFC (**A**) equipped with : 37-mm calcinated quartz fiber filter ⇨ thermo-optical C quantification (Sunset Carbon Analyzer – TOT)
      37-mm PVC filter (PALL, GLA5000) ⇨ ICP-AES Ti quantification (Agilent 5110 – filter & wall deposits)
    - 2-pieces CFC (**B**) equipped with 25-mm Gravi-Sert filter capsule (Zefon) ⇨ gravimetric analysis (Mettler, XP6U, 1µg resolution)
  - mass concentration: personal photometer (TSI, model AM520)
- ✓ Determination of the mass concentration from SMPS data
  - average number size distribution stemming from the SMPS fitted by a monomodal lognormal distribution law $C_N(d_m)$
  - fitted distribution converted into mass size distribution accounting for particle effective density $\rho_{eff}(d_m)$:

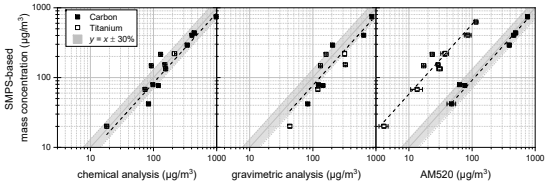
$$C_M = \sum_{d_m} C_N(d_m) \cdot \rho_{eff}(d_m) \cdot \frac{\pi d_m^3}{6}$$

Results & Discussion

- ✓ Determination of the mass concentration from SMPS data
  - particle effective density $\rho_{eff}(d_m)$ has been characterized earlier by tandem DMA-APM measurements [3]:
    - Carbon-based particles : $\rho_{eff}(d_m) = 20.135.\, d_m^{-1.020}$
    - Titanium-based particles : $\rho_{eff}(d_m) = 11.96.\, d_m^{-0.867}$
- ✓ Comparison of mass concentrations
  - Overall data



  - Pair plots
    - Linear fits ($y = a \cdot x$) described below



	chemical analysis	gravimetric analysis	AM520 (Carbon)	AM520 (Titanium)
slope (a)	0.84 ± 0.04	0.77 ± 0.06	0.91 ± 0.03	5.80 ± 0.58
R^2	0.93	0.88	0.98	0.88

  - Discussion
    - SMPS-based mass concentrations in line with chemical analysis (relative discrepancies by ≈ 15%) and gravimetric analysis (by ≈ 25%)
    - No effect of the modal diameter of the aerosol
    - Effect of particle composition in the correlation with AM520
  - Sources of uncertainty for the different approaches
    - SMPS ⇨ effective density from DMA-APM measurements reliable for PSL particles between 40 and 800 nm [4-6], deviations up to ≈ 20% reported for black carbon agglomerates in the range 100 – 500 nm [7]
    - ICP-AES ⇨ purity (only Ti was quantified, all samples above the LOQ of 40 ng/filter)
      ⇨ unknown state of oxidation (the sample was assumed to be 100% TiO_2)
    - C quantification ⇨ fraction of organic C (not considered), though pure graphite electrodes were used, might be due to the degradation of the polyamide chamber of the generator [8]
    - Gravimetry ⇨ 7 samples below the LOQ of GraviSert capsules (87 µg as determined according to ISO 15767:2009), 2 below the LOD
    - AM520 ⇨ photometric response dependent on particle physical and light scattering properties (including shape, density, size distribution and refractive index), which differ between the aerosols measured and the test dust used for factory calibration (ISO 12103-1 A1 Test Dust / ARD1 Arizona Road Dust) [9]

	ARD1	Carbon	Titanium
density (g/cm³)	2.65	~ 2.25	~ 4.00
refractive index @ λ ~ 650 nm	1.54 – 0,03i	2.0 – 0,63i	~ 2.5 – 2.9

- ✓ Outlook
  - This preliminary laboratory work is part of a larger project aimed at studying the performances of several optical direct-reading instruments regarding mass concentration of various aerosols, in both lab and workplaces
    - Photometers: DustTrak 8533, DustTrak 8534, AM510, AM520, MicroDust Pro, Nephelometer Sensidyne, Respicon II, DataRAM pDR-1500, Split 2, etc.
    - OPCs: OPS 3330, Grimm 11D, Palas Fidas Frog, LightHouse 3016, etc.

References

[1] Wang J. et al. – J. Nanopart. Res., 2011, 13, 1373-1387.
[2] Jacoby J. et al. – J. Phys.: Conf. Ser., 2011, 304, 012014.
[3] Charvet A. et al. – J. Nanopart. Res, 2014, 16, 2418.
[4] Liao et al. – Aerosol Sci. Technol., 2018, 52, 19-29.
[5] Tajima et al. – Environ. Sci. Technol., 2013, 47, 1152-1162.
[6] Tajima et al. – Aerosol Sci. Technol., 2011, 45, 196-214.
[7] Yao et al. – Aerosol Sci. Technol., 2020, in press.
[8] Roth et al. – Aerosol Sci. Technol., 2004, 38, 228-235.
[9] Görner P. et al. – J. Environ. Monit., 2012, 14, 420-428