

Particle mass spectrometry and laser diagnostics applied to iron oxide nanoparticle formation

Work in progress

Nanoscaled iron oxide particles are produced in a low pressure premixed H₂/O₂/Ar flame with iron pentacarbonyl as precursor. The experimental apparatus offers very variable flame synthesis conditions with respect to flame temperature, pressure and partial pressure of any gaseous specie of the system. For in situ studies optical access is given by quartz windows. Additionally a molecular probe sampling unit can be attached at various heights above the burner matrix. For ex situ studies EM substrates can be inserted in the molecular beam of the sampling unit and macroscopic powder quantities can be sampled on special filters. Primary particle formation and growth is studied in situ by means of particle mass spectrometry (PMS) and laser diagnostic methods.

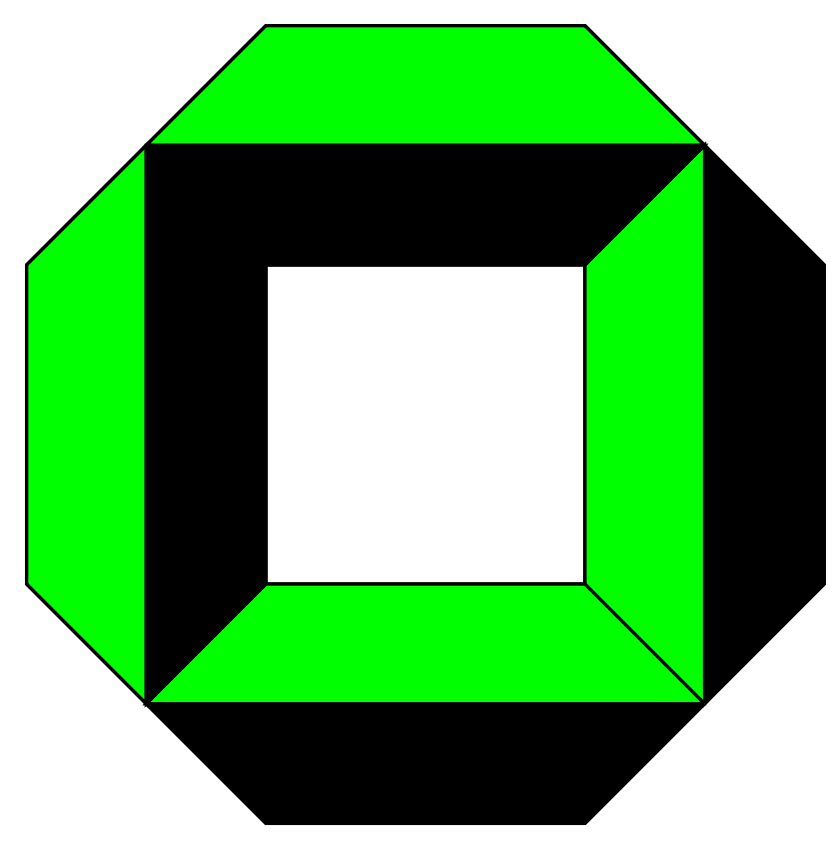
Flame generated particles are sampled as molecular beam out of the flame. The PMS detects the flame generated particle ions using Faraday cups with excellent S/N ratio. Particle mass and size distribution functions are determined by particle deflection and particle velocity measurement. PMS measurements are carried out pointwise, therefore subsequent measurements were carried out to study the particle size distribution evolution as function of height above burner.

The laser diagnostic method based on simultaneous detection of Rayleigh scattering, extinction and laser induced incandescence (RAYLIX) is capable of two dimensional detection of mean particle size, volume fraction and number densities by use of a laser sheet technique with high spatial (60-150 μm) and temporal resolution (20-100 ns). Because of the very small particle sizes in this study, the elastic scattering signals showed a very low S/N ratio, causing erroneous data for r_m and N_V .

Primary mean particle sizes determined by PMS measurements are in the range of 4-8 nm, number densities and volume fractions are variable by the widely variable iron pentacarbonyl feed. Ex situ XRD investigations showed the formation of mostly amorphous alpha hematite powders.

The results of both in situ diagnostic methods will be shown and compared with each other. Synergy effects of the complementary in situ methods are indicated, i.e. when ion generation or the knowledge of optical constants is lacking.

Advantages and disadvantages of either in situ particle diagnostic method will be discussed with respect to detection issues. Furthermore an outlook is presented for improving the applicability of both methods to deduce particle formation and growth kinetics.



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Motivation

- Nanoscale iron oxides (Fe_xO_y) are versatile compounds for e.g.: pigments, catalysts, magnetic data storage and ferrofluids
- Iron oxides (Fe_xO_y) differ in structures and properties, objectives:
 - superparamagnetic maghemite and magnetite
 - high crystallinity and small particle sizes (≤ 20 nm)
- In situ diagnostics: detailed kinetics of particle formation and growth
- Tailoring nanoparticles by knowledge of governing flame parameters

Theory and implementation of in situ diagnostics

Particle Mass Spectrometry (Fig. 1, 2):

- Direct measurement of particle ion size distributions by molecular beam probing
- Requirement: particle ions generated by flame process
- Low current detection by use of Faraday cups
- Pointwise measurements at variable heights above burner (HAB)

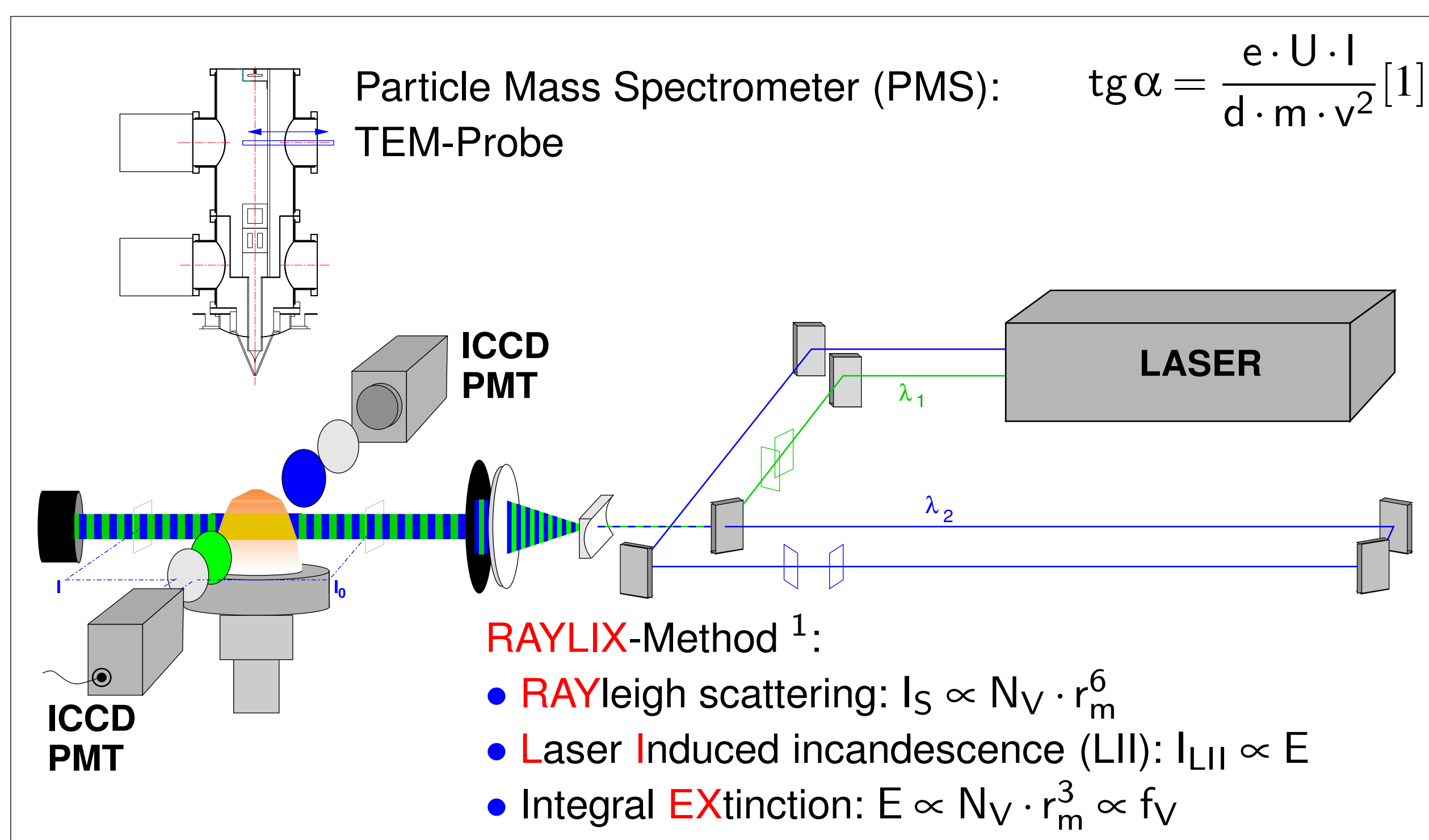


Fig. 1: In situ diagnostics setup

Laser Diagnostics¹ (Fig. 1):

- 2d maps of (depending on S/N ratio):
 - particle volume fractions f_V
 - particle mean radii r_m
 - particle number densities N_V
- High spatial ($< 200 \mu\text{m}$) and temporal resolution (≤ 500 ns, S/N ratio)
- Requires knowledge of optical constants.

Flame process setup and PMS adaption

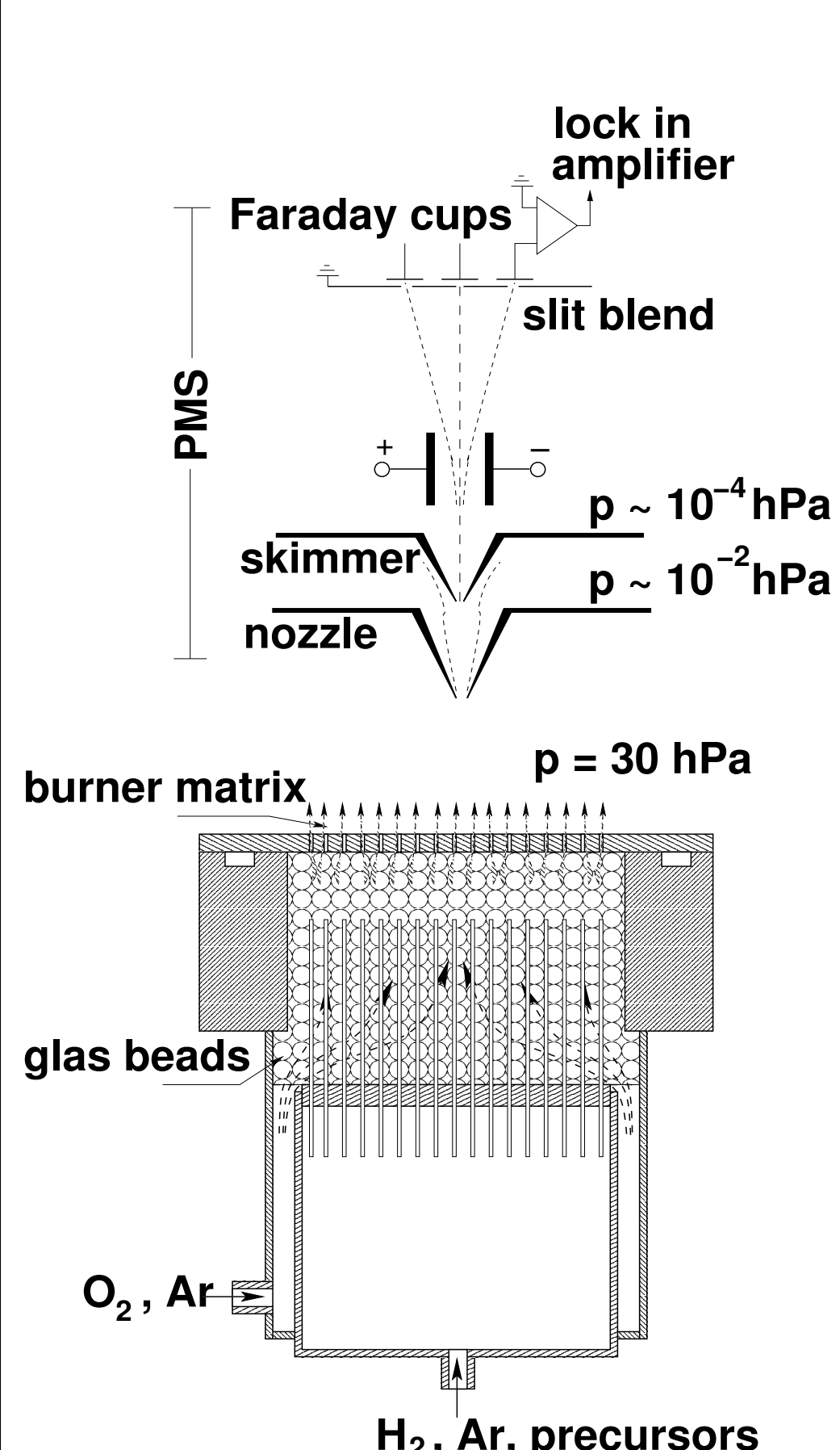


Fig. 2: PMS and burner setup

Flat premixed, low pressure $\text{H}_2/\text{O}_2/\text{Ar}$ -Flame doped with $\text{Fe}(\text{CO})_5$:

- Particle size, structure and properties tunable by synthesis conditions e.g. temperature, partial pressures of reactants, flame velocity
- Elongated reaction zones

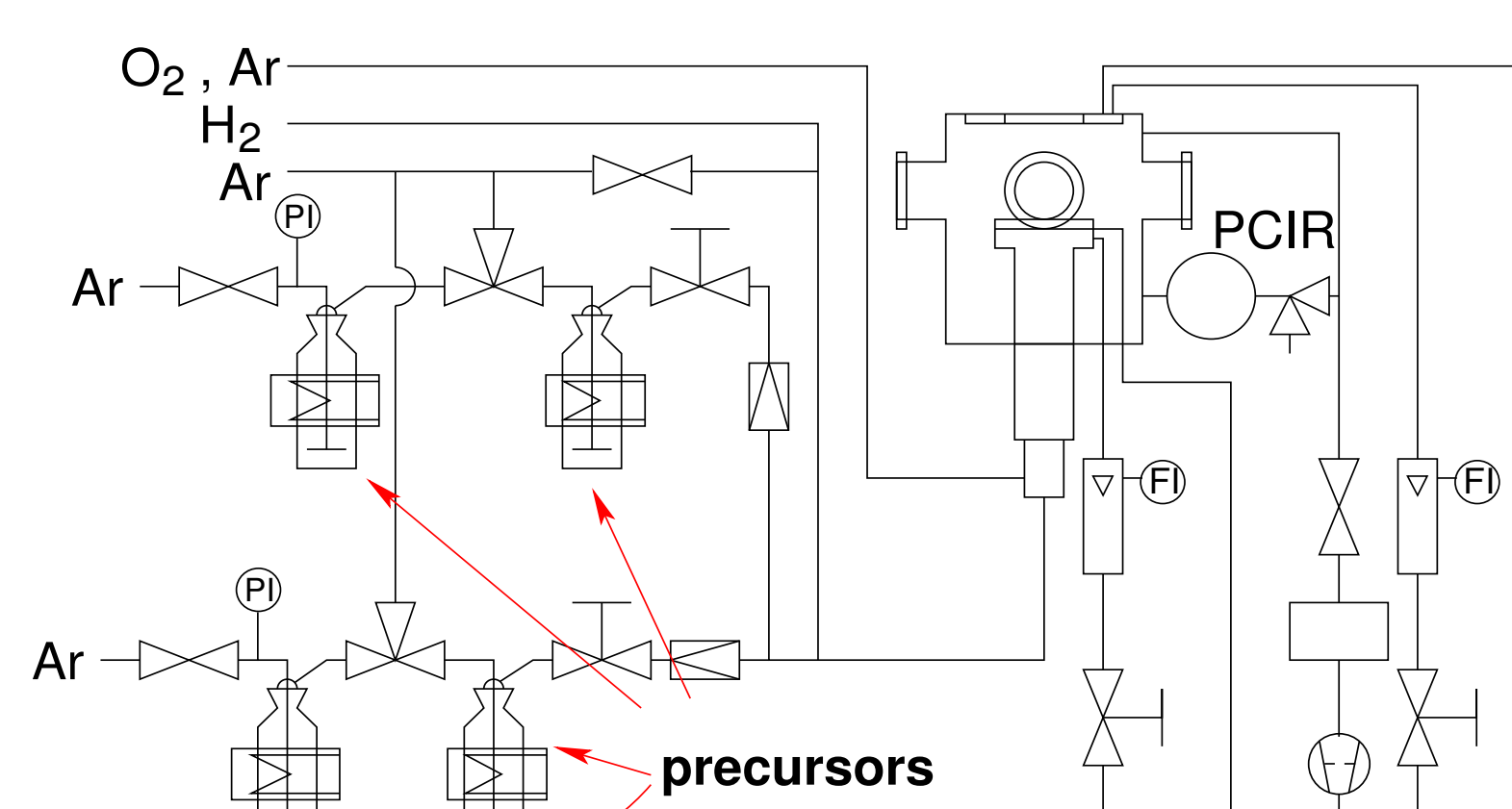


Fig. 3: Process scheme

Results

Particle Mass Spectrometry:

- High sensitivity of particle ion detection (≤ 8 fA)
- If particle ions are detectable, sum of non deflected particle ions $\neq 0$
Signal favoured in case of amorphous particles.

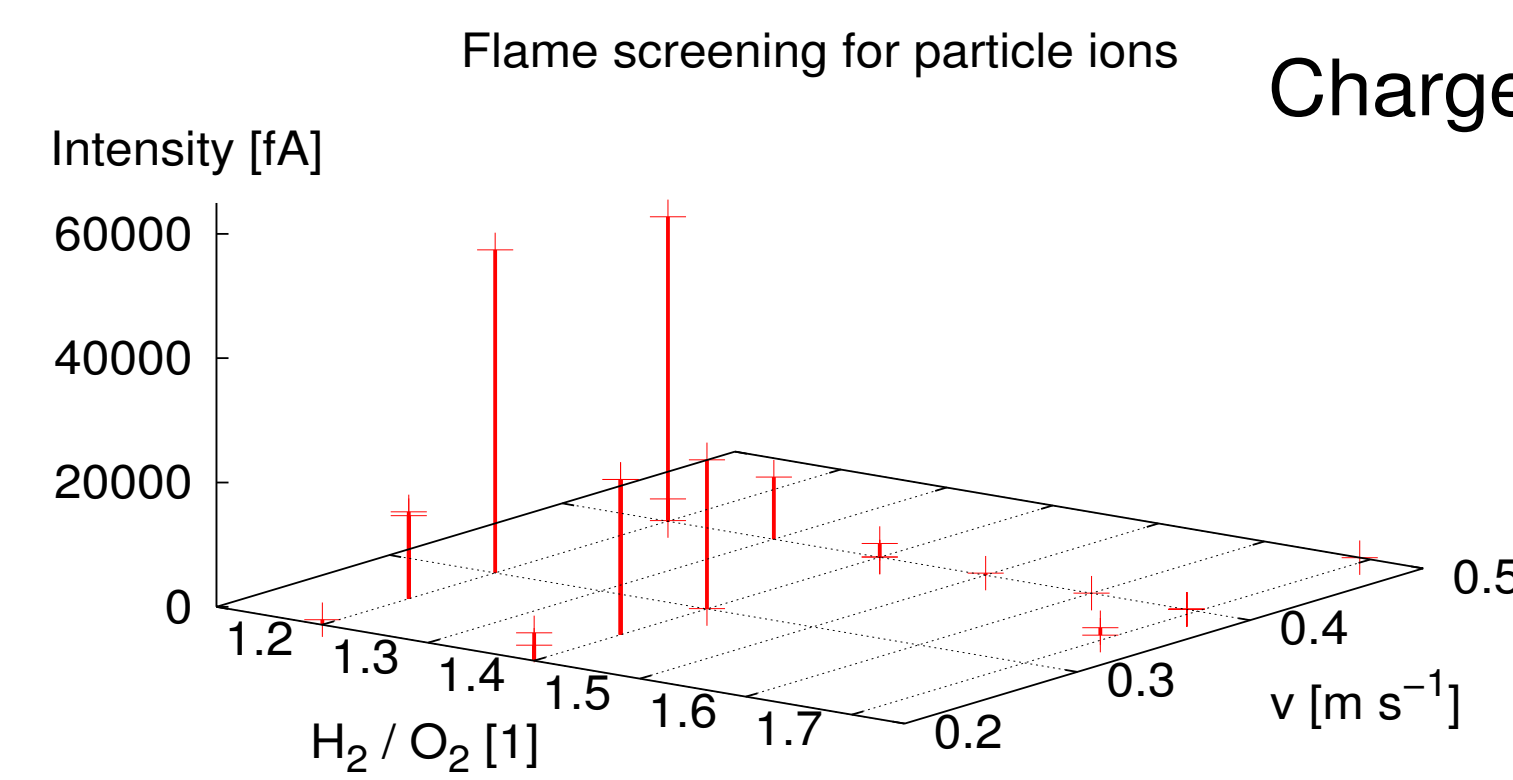


Fig. 4: Ion generation issue

Charge balance: gas \leftrightarrow particle phase

- Effects on particle ions generation rate:
 - ⇒ stoichiometry (H_2/O_2)
 - ⇒ gas velocity v
 - $c(\text{Fe}(\text{CO})_5)$ or dilution by Ar

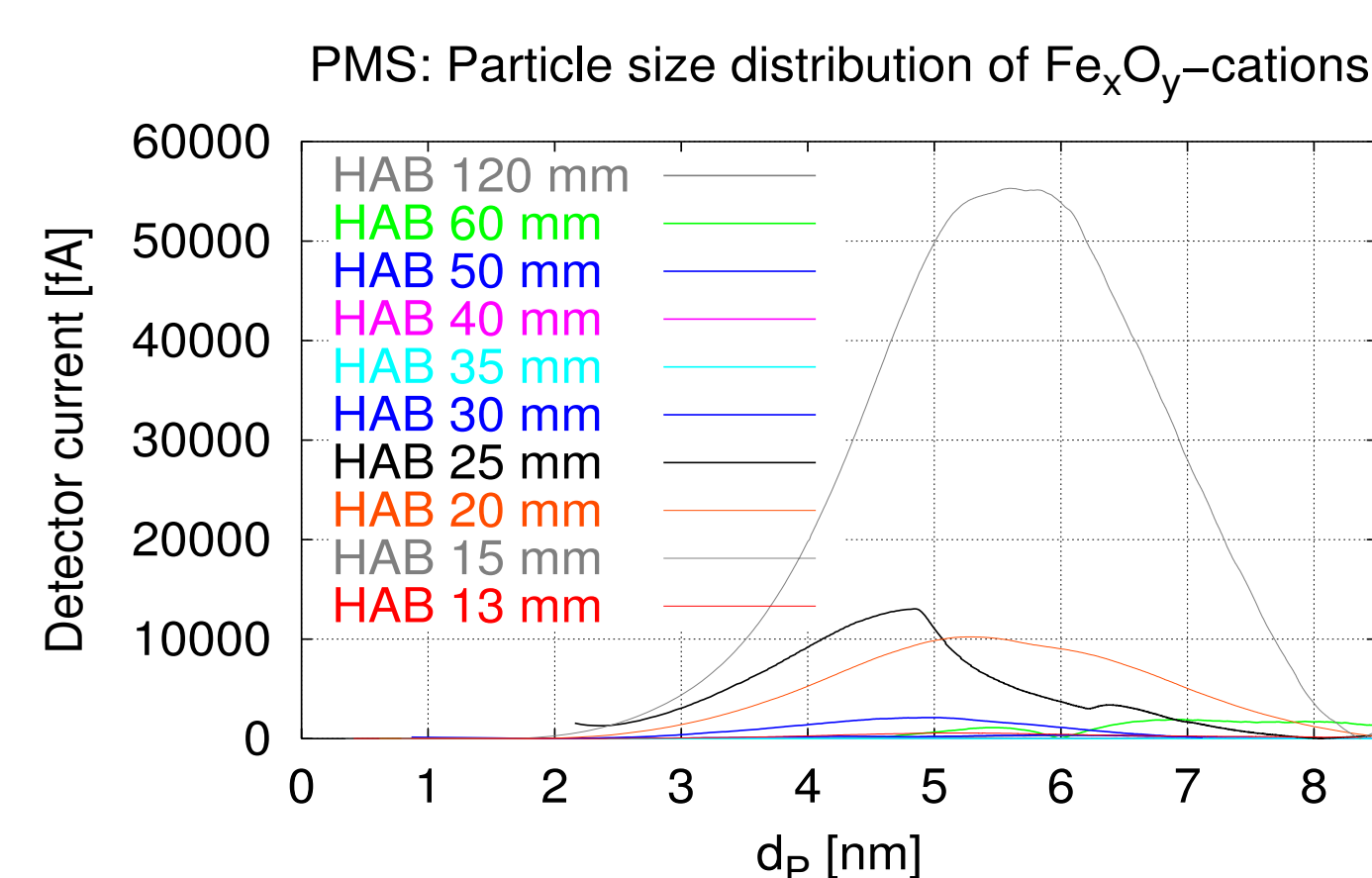


Fig. 5: PMS-spectra

PMS: Mean particle size of Fe_xO_y -nanoparticles

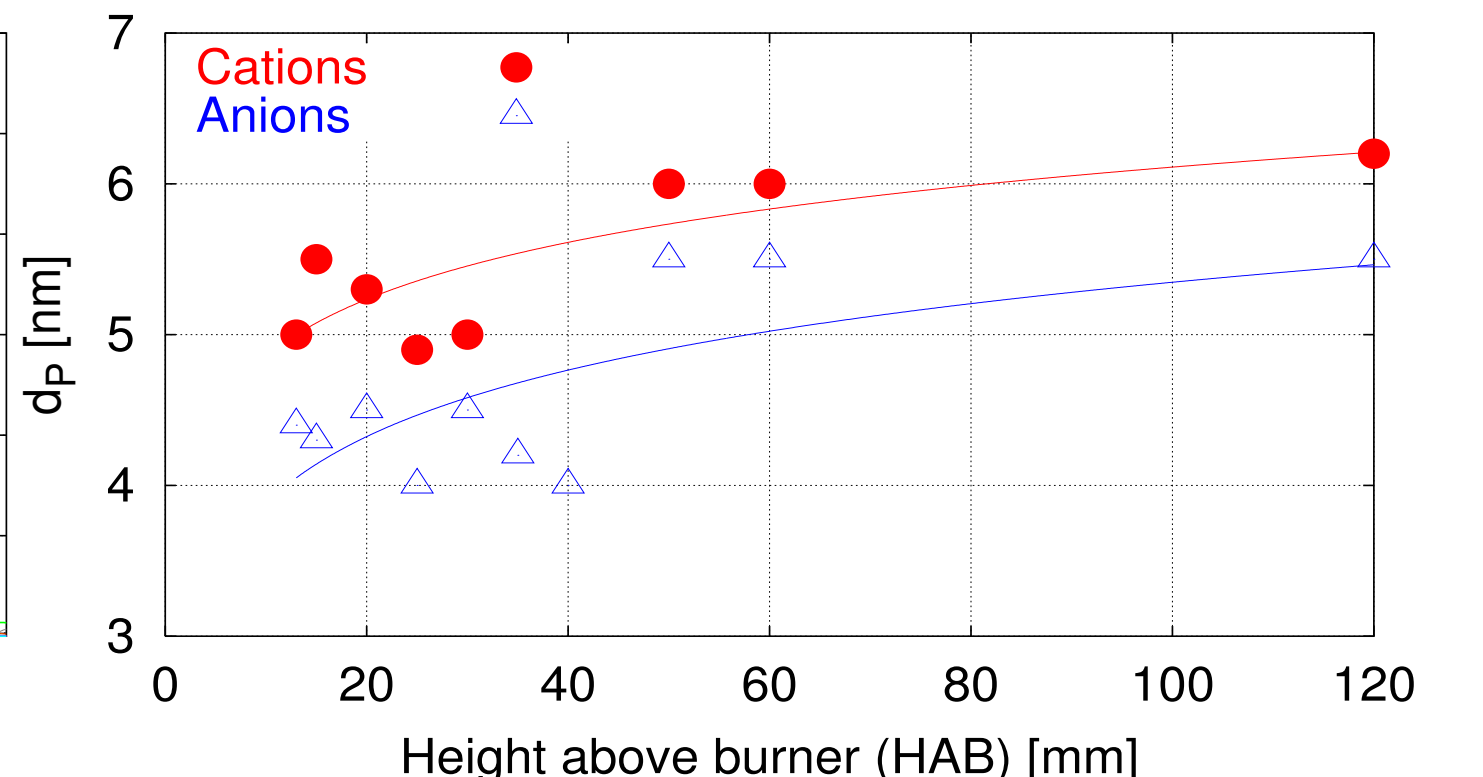


Fig. 6: Mean particle size f(HAB)

Flame: $v = 0.28$ m/s, 340 ppm $\text{Fe}(\text{CO})_5$, $\dot{V}_{\text{H}_2}/\dot{V}_{\text{O}_2} = 1.32$, $\dot{V}_{\text{Ar}}/(\dot{V}_{\text{H}_2} + \dot{V}_{\text{O}_2}) = 0.41$

- Fig. 5, 6: PM Spectra recordable with good S/N ratio
- Particle size distributions differ for anions and cations!
- Recorded size distributions are nonuniform (lognorm-, Gauss-type)

Laser Diagnostics:

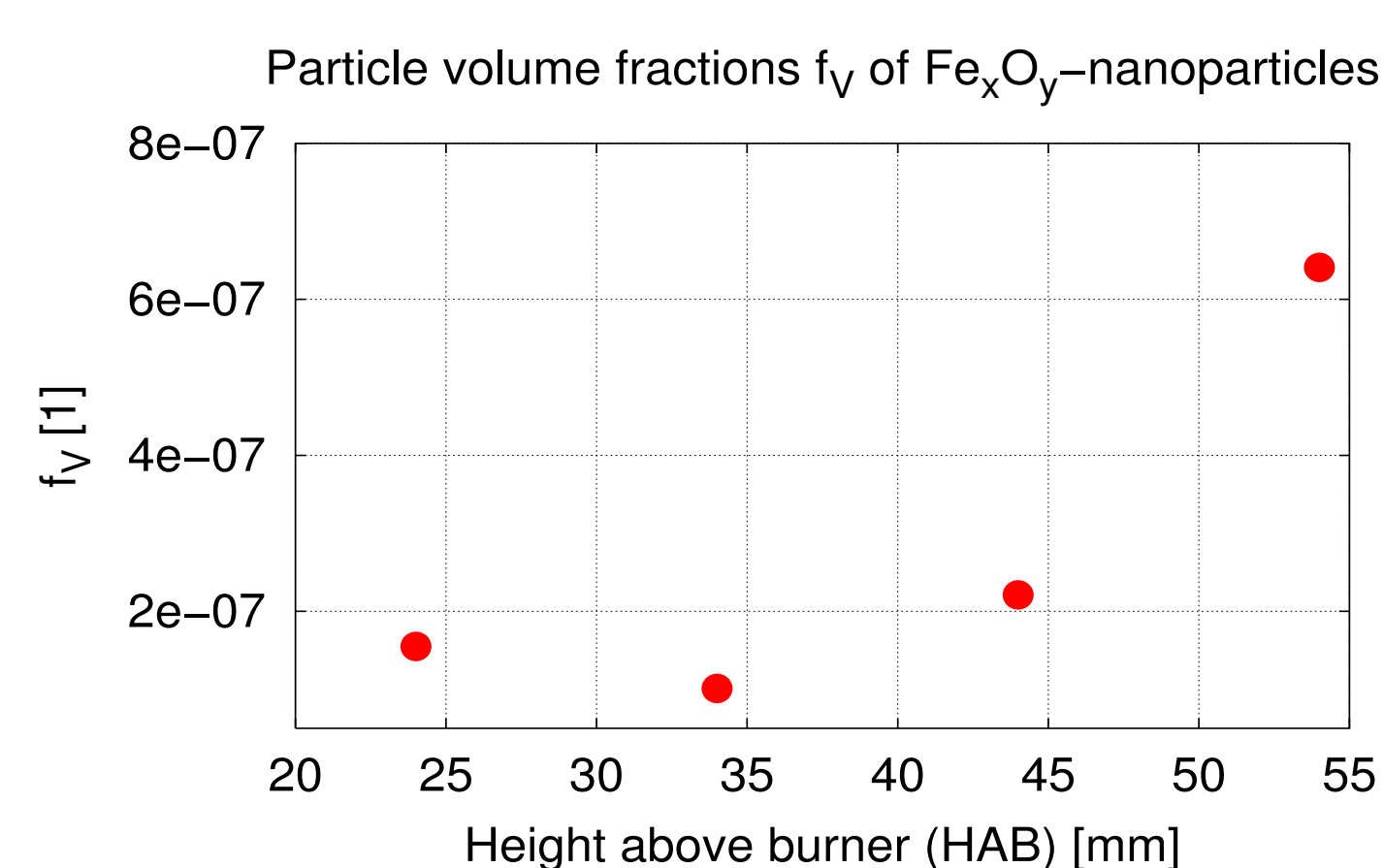


Fig. 7: f_V as f(HAB)

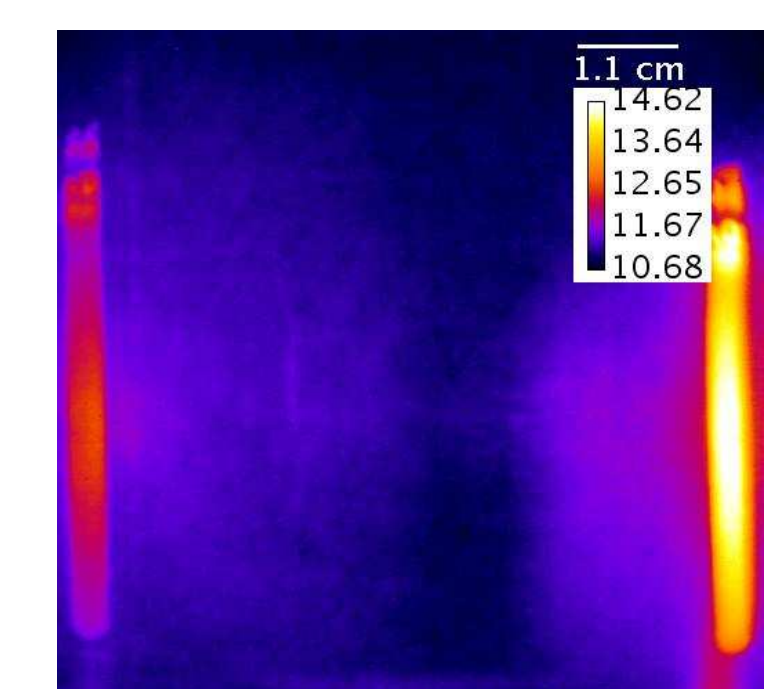


Fig. 8: Logarithmic intensities

Flame: $v = 0.30$ m/s, 500 ppm $\text{Fe}(\text{CO})_5$, $\dot{V}_{\text{H}_2}/\dot{V}_{\text{O}_2} = 1.4$, $\dot{V}_{\text{Ar}}/(\dot{V}_{\text{H}_2} + \dot{V}_{\text{O}_2}) = 0.70$

Fig. 8: Stripes left (I_1), right (I_0): fluorescence signals for extinction measurements, central area elastic scattering signal

- Good agreement for f_V with mass balance: LII, extinction ✓
- Elastic scattering $\propto r_m^6$, $r_m \approx 7.5$ nm (PMS): low S/N ratio
- Erroneous data for r_m and N_V in this study

Conclusions & Outlook

Both in situ characterisation methods should be capable to study nanoparticle formation and growth kinetics in a flame.

- ✓ PMS: Direct access to particle ion size distributions, selfvalidating principle and high sensitivity
- ✓ Non-intrusive laser diagnostics
- ✓ Laser diagnostics and PMS are complementary methods.
 - ⇒ Synergies (optical constants / ionisation)
- Ionisation issue: necessity for further ionisation source?
- Laser diagnostics: S/N-ratio improvement by e.g. change of excitation wavelength, detection optic

Acknowledgements

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Literature: [1] H. Bockhorn et al., *Phys. Chem. Chem. Phys.*, **2002**, 4, 3780