Chemical characterization of particulate matter aircraft turbine engine exhaust using single particle mass spectrometry

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Outline

- **Motivation**
- **Campaign**
  - Experimental set-up
  - Single particle mass spectrometer (ATOFMS)
- **Results**
  - Chemical composition of individual particles
  - Average particle types
  - Metals found in the exhaust
- **Outlook**

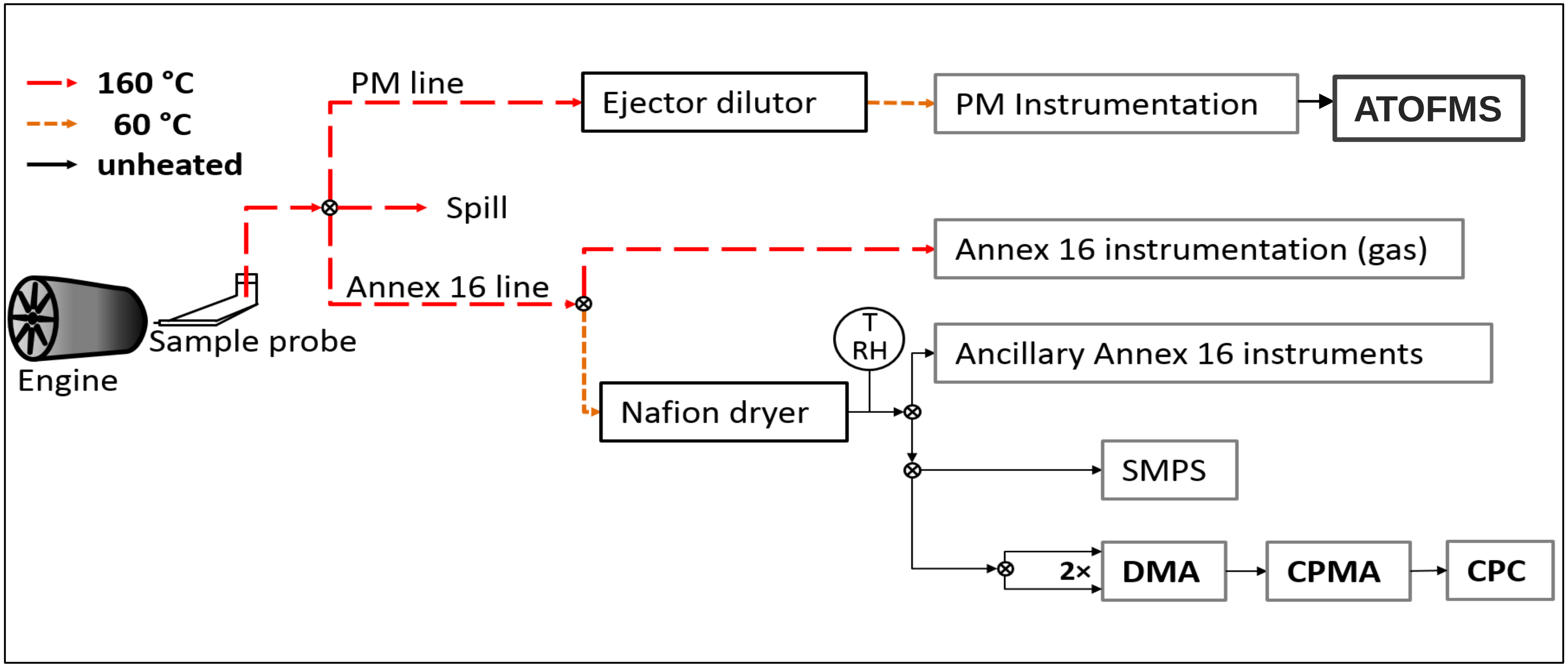
Motivation

- **Climate**
  - Air traffic increases ~5 % per year
  - Aircraft emission is a unique anthropogenic source of soot in the upper troposphere
    - Aerosol-radiation interactions
    - Aerosol-cloud interactions
  - Contrail and cirrus cloud formation due to exhaust particles
    - Contrail cirrus is reported as the largest aviation related net radiative effect (Burkhardt & Kärcher, 2011)
    - Role of exhaust particles in ice formation processes
    - Metallic containing particles represent a dominant fraction of ice crystal residuals in the atmosphere (Cziczo et al., 2014)

Aviation Particle Regulatory Instrumentation Demonstration Experiments - A-PRIDE5

- Conducted at the airport in Zurich in 2013 in a test cell run by SR-technics
- Dismounted engine was operated according to our research questions
- Engine under investigation: CFM56-7B26
  - Widely used in commercial aircraft (e.g. Boeing 737)
  - Single annular combustor
  - Core flow engine: exhaust is not mixed with bypass air
- Sample: collected ~0.7 m behind the engine

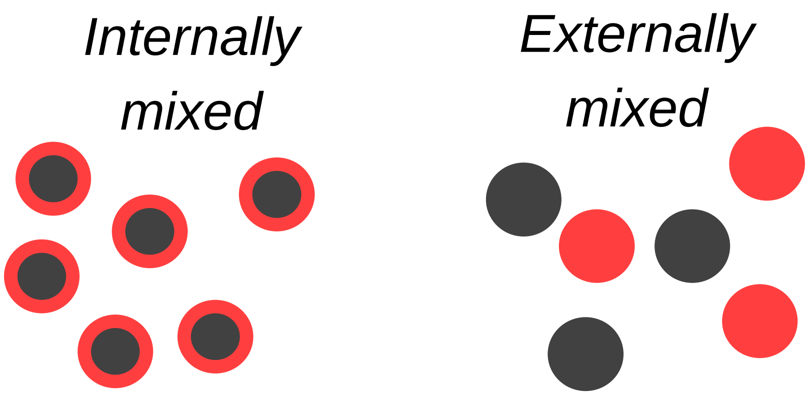
Experimental set-up at the airport



ATOFMS: Aerosol Time-of-Flight Mass Spectrometry
SMPS: Particle sizer system
DMA-CPMA-CPC: Particle mass system

ATOFMS – Aerosol Time-of-Flight Mass Spectrometry

- Single particle mass spectrometer
- Can determine if particles are internally or externally mixed
- Mass spectra of individual particles give insight into the mixing state
- Can also detect rare chemical species even if they are present only on very few particles



Particle characterization using the ATOFMS

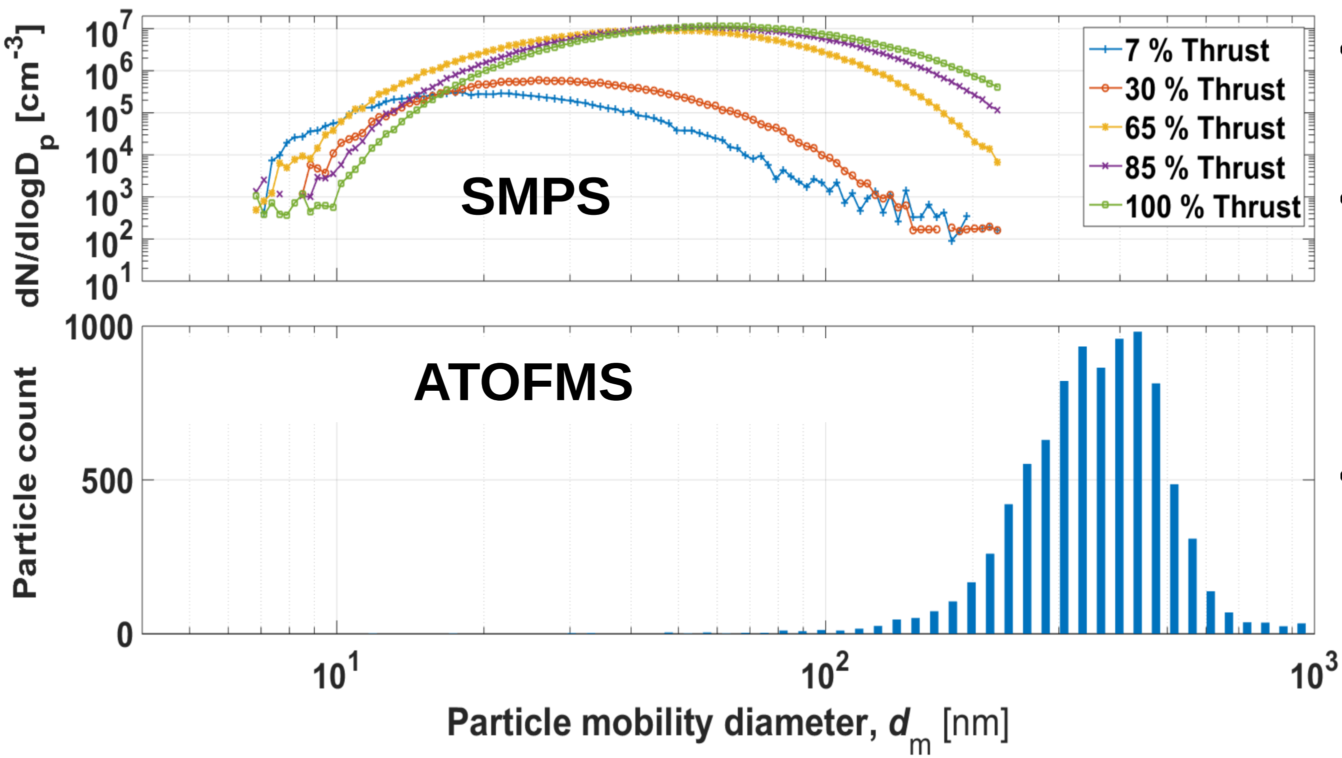
- Chemical properties
  - Information on refractory (metals, EC) as well as on non-refractory material (sulfate, organics …)
  - Chemical composition of individual particles
  - Particle mixing state
  - non-quantitative
- Physical property
  - Aerodynamic size

Total number of analyzed particles during A-PRIDE5:

Low thrust (3-7 %):	3’716
Medium thrust (20-65 %):	2’538
High thrust (85-120 %):	3’621

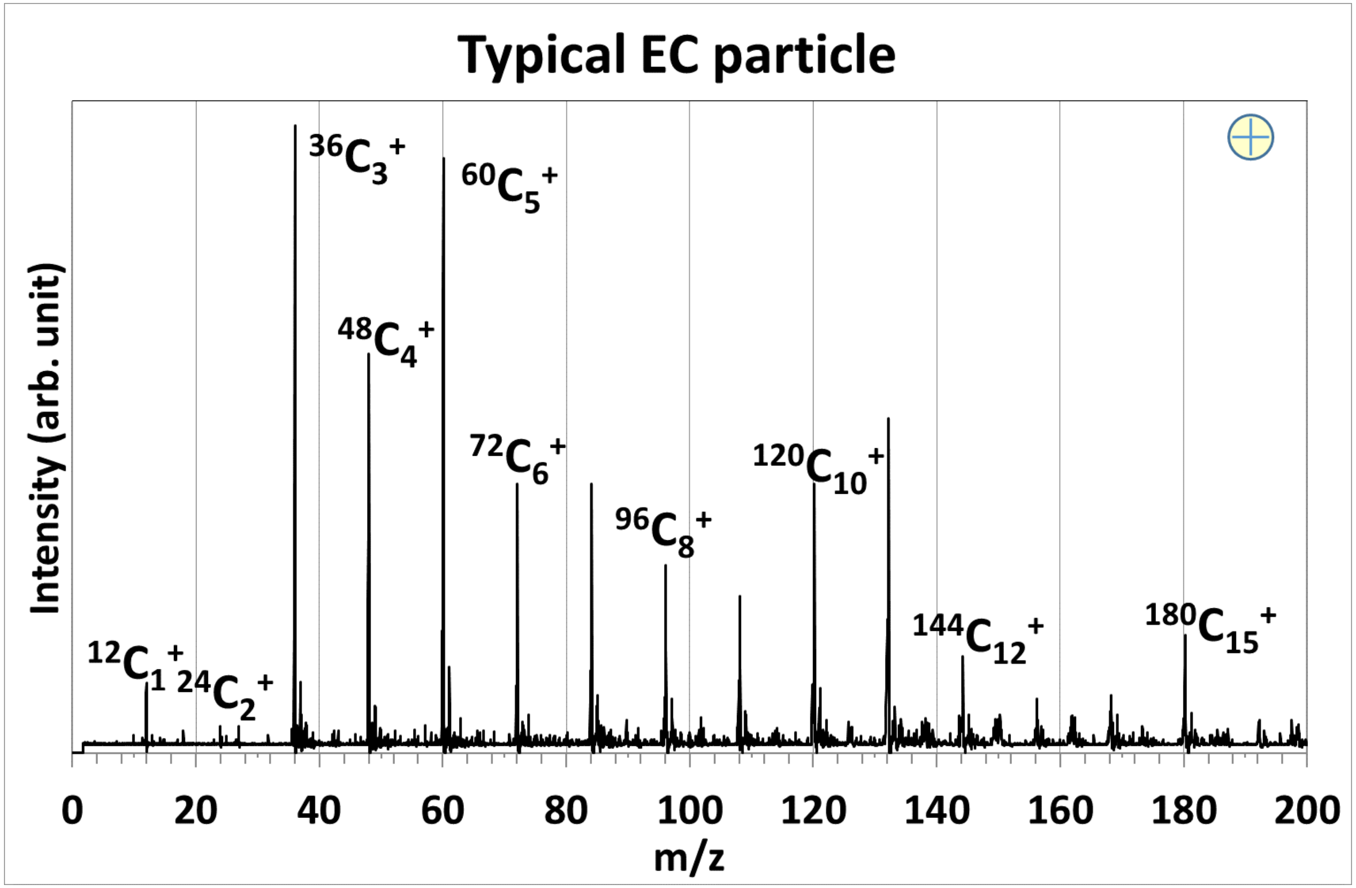
Only positive spectra were collected due to a broken detector.

Results: Size of particles analyzed by the ATOFMS



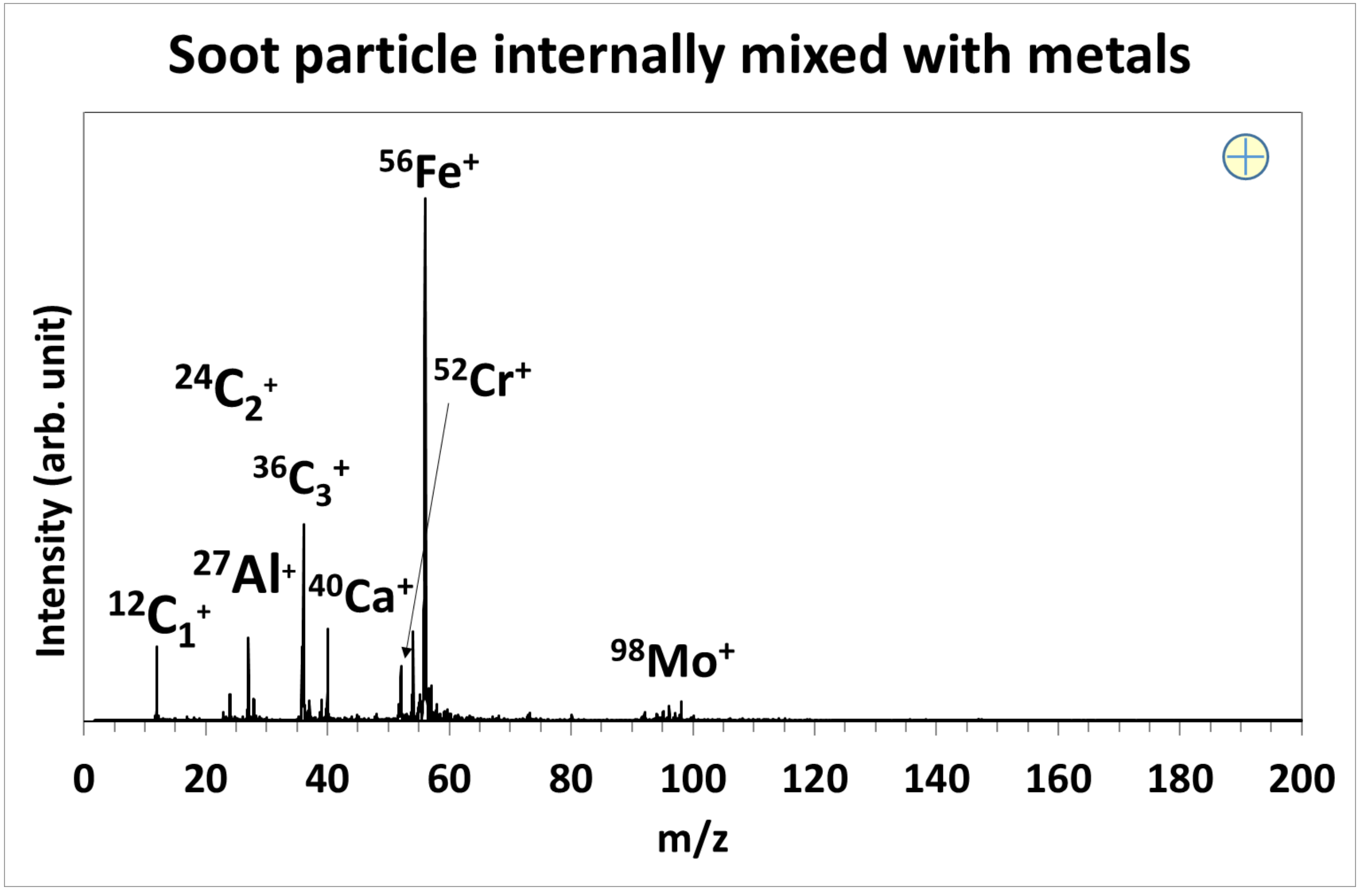
- d_{ae} (ATOFMS) was converted into d_m
- …using shape factors calculated from particle mass (Abegglen et al, 2015)
- → Only the largest particles could be analyzed

Results: Single particle spectra I



- C_n peaks: *(m/z = 12 * n)*
- Clear EC pattern from fresh soot
- Small amount of OC
- C_n-pattern also appear in the negative spectra

Results: Single particle spectra II



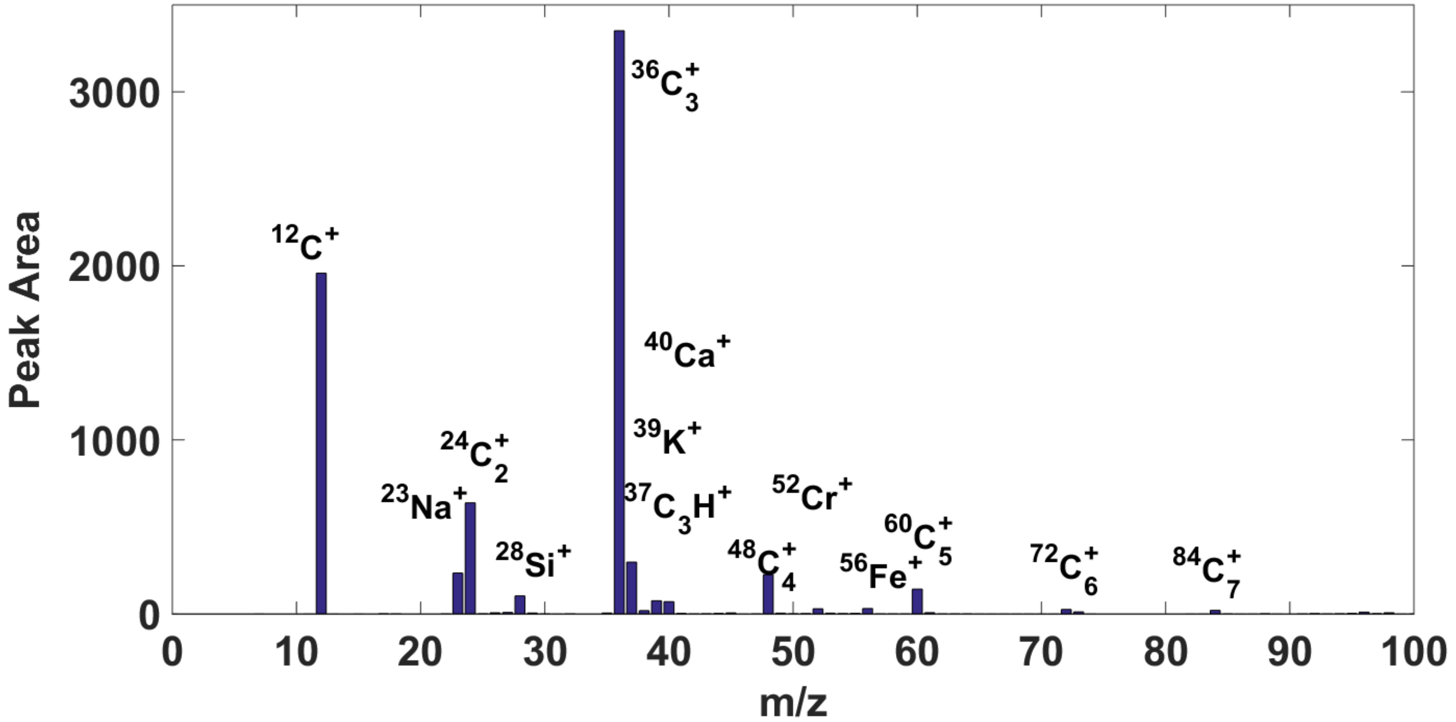
- Metals appear in the positive spectra
- Signature of EC/soot still obvious
- EC mixed with:
    - Aluminium
    - Chromium
    - Iron
    - Molybdenum

Identification of average particle types using ENCHILADA

- ENCHILADA: a software used to analyze ATOFMS data
- Grouping of similar spectra into clusters using an algorithm
- Six reasonable clusters created
- Largest cluster covers 93 % of the analyzed particles
- Largest three clusters already cover 99 % of the analyzed particles

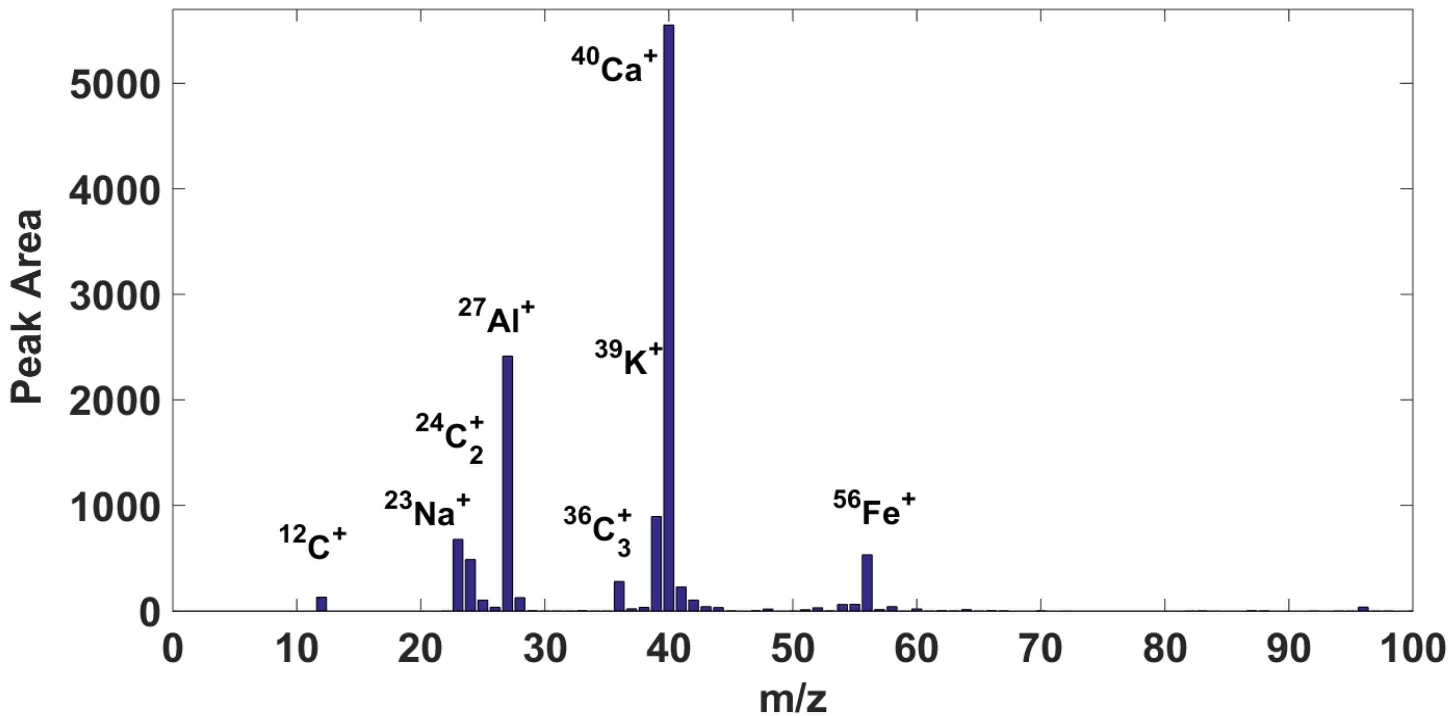
Cluster 1 (93,4 %): EC-Na-Si

- Typical ^{12}C pattern with a small peak of Sodium
- Other metals are present as well: Silicon, Chromium, Iron



Cluster 3 (1.8 %): Ca-Al-K-Fe-Na (metal type particle)

- Mainly inorganic compounds ^{40}Ca, ^{27}Al, ^{39}K, ^{56}Fe and ^{23}Na
- Weak EC signature



Analysis of metals found on exhaust particles

Metals (m/z, element) found in spectra:

- Vanadium (51, V^+)
- Chromium (52, Cr^+)
- Iron (56, Fe^+)
- Nickel (58, Ni^+)
- Cobalt (59, Co^+)
- Copper (63, Cu^+)
- Molybdenum (98, Mo^+)
- Lead (206, Pb^+)

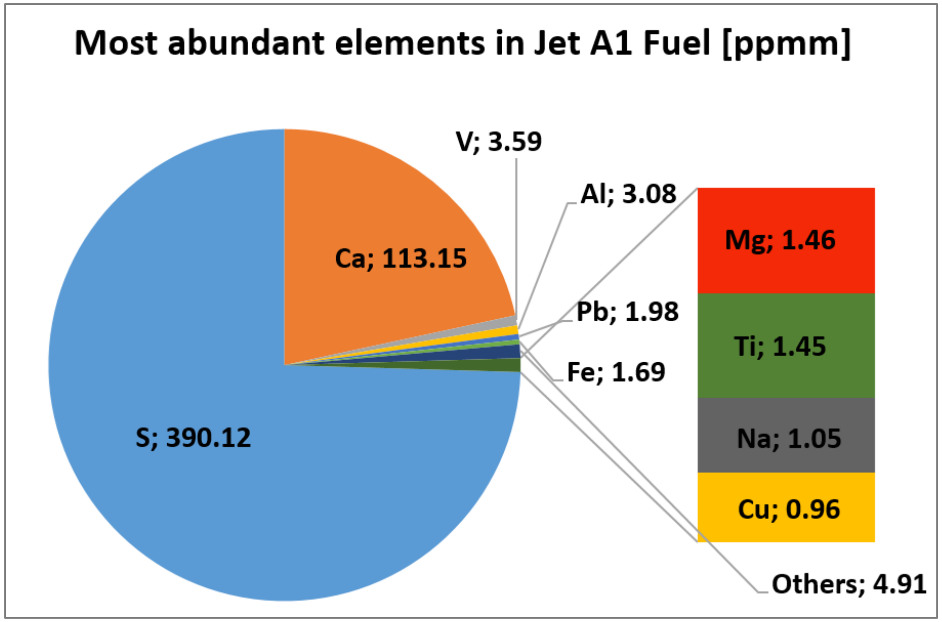
- Calcium (40, Ca^+)
- Barium (138, Ba^+)

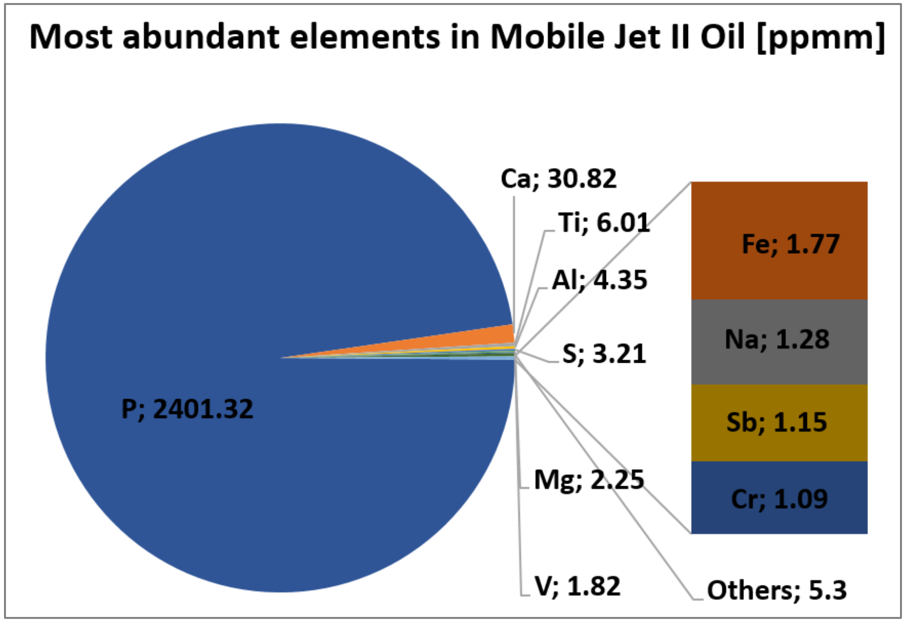
Can only be identified by searching for isotopes due to **overlapping peaks** with EC signature:

- Titanium (46+47+**48**, Ti^+)
- Magnesium (**24**+25+26, Mg^+)

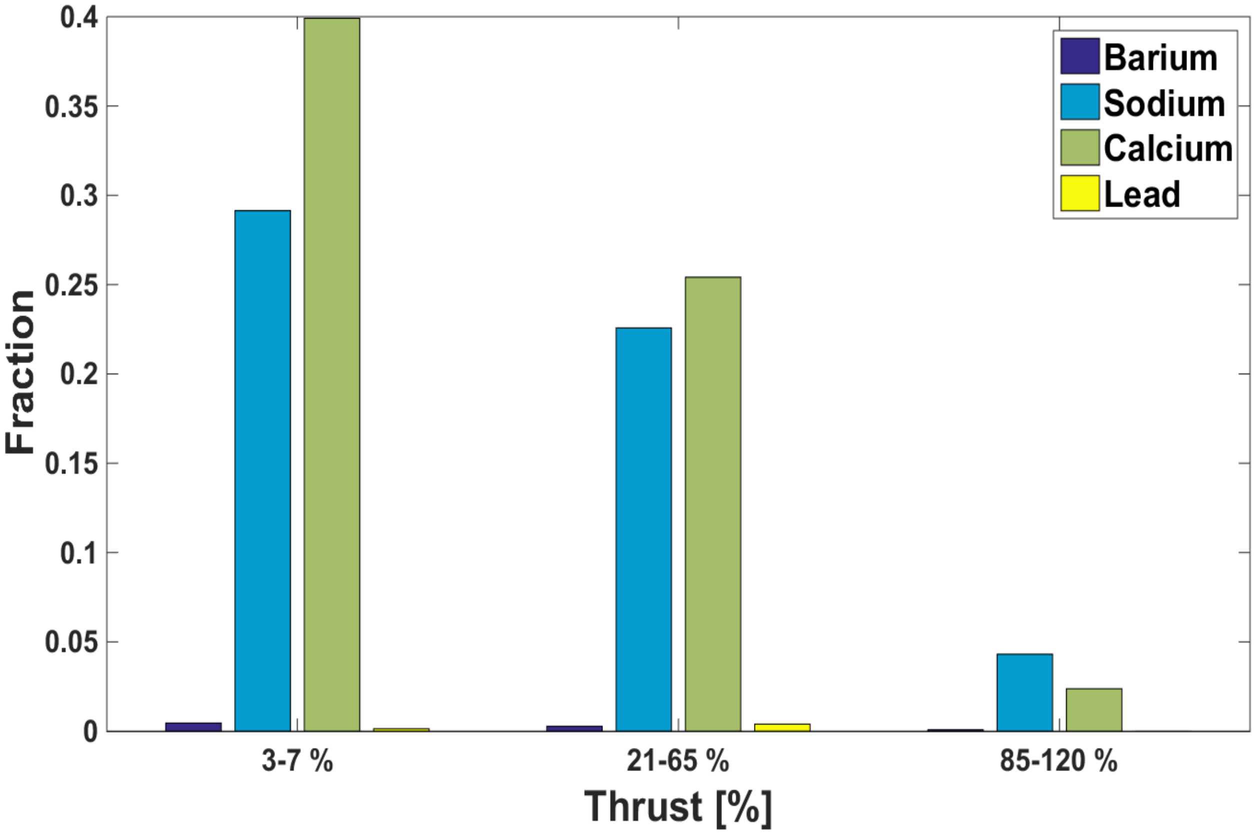
Results – Trace elements found in fuel and oil

- Inductively coupled plasma mass spectrometry results from jet fuel and lubricant oil samples (EMPA)
- Obtained with inductively coupled plasma mass spectrometry
  - Quantitative bulk analysis



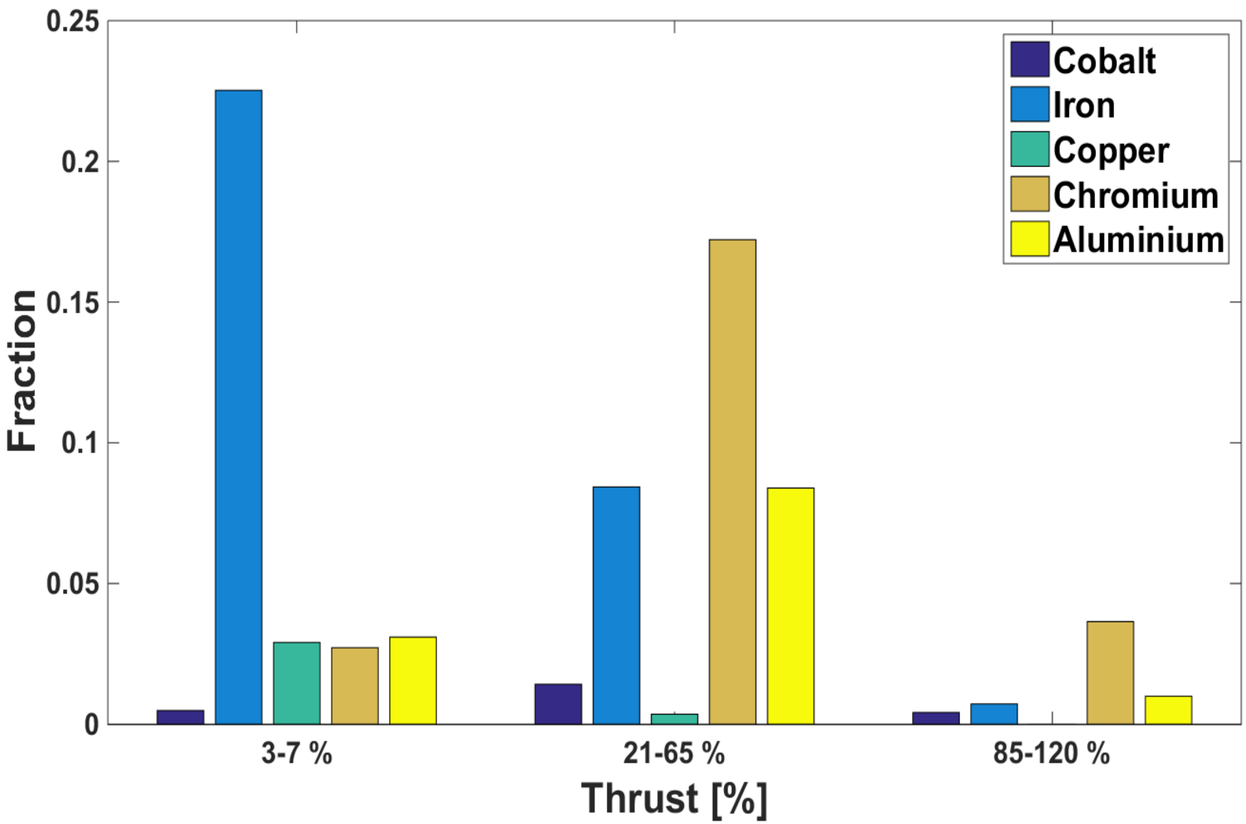


Results – Thrust dependent occurrence of metals from fuel and oil



- Ba, Na and Ca: probable decrease due to higher particle concentration
- Na and Ca also show a decrease in rel. peak area as well → amount on these particles is likely to decrease
- Pb: probably from fuel (only very small amount found in oil)

Results – Thrust dependent occurrence of metals probably from engine wear (used as alloys)



- Co: (**not** in fuel or oil)
- Fe (fuel and oil) and Cu (oil):
  - Cu occurs always together with Fe → probably from engine wear
  - Decrease with increasing thrust
- Cr (also in oil)
- Al (also in fuel and oil)

Conclusion and Outlook

- Almost all particles show EC pattern
- All metals internally mixed with soot
- Only the largest particles emitted could be analyzed
- About 20 % of the spectra show metal tracers
- Sources of metallic compounds are fuel, lubricant oil and engine wear

- Investigation of additional aircraft engine types
- Is the occurence of the shown metals size dependent?
- Further investigation of possible sources
- Interprete the results with respect to ice nucleation measurements performed in our group

Thank you for your attention!

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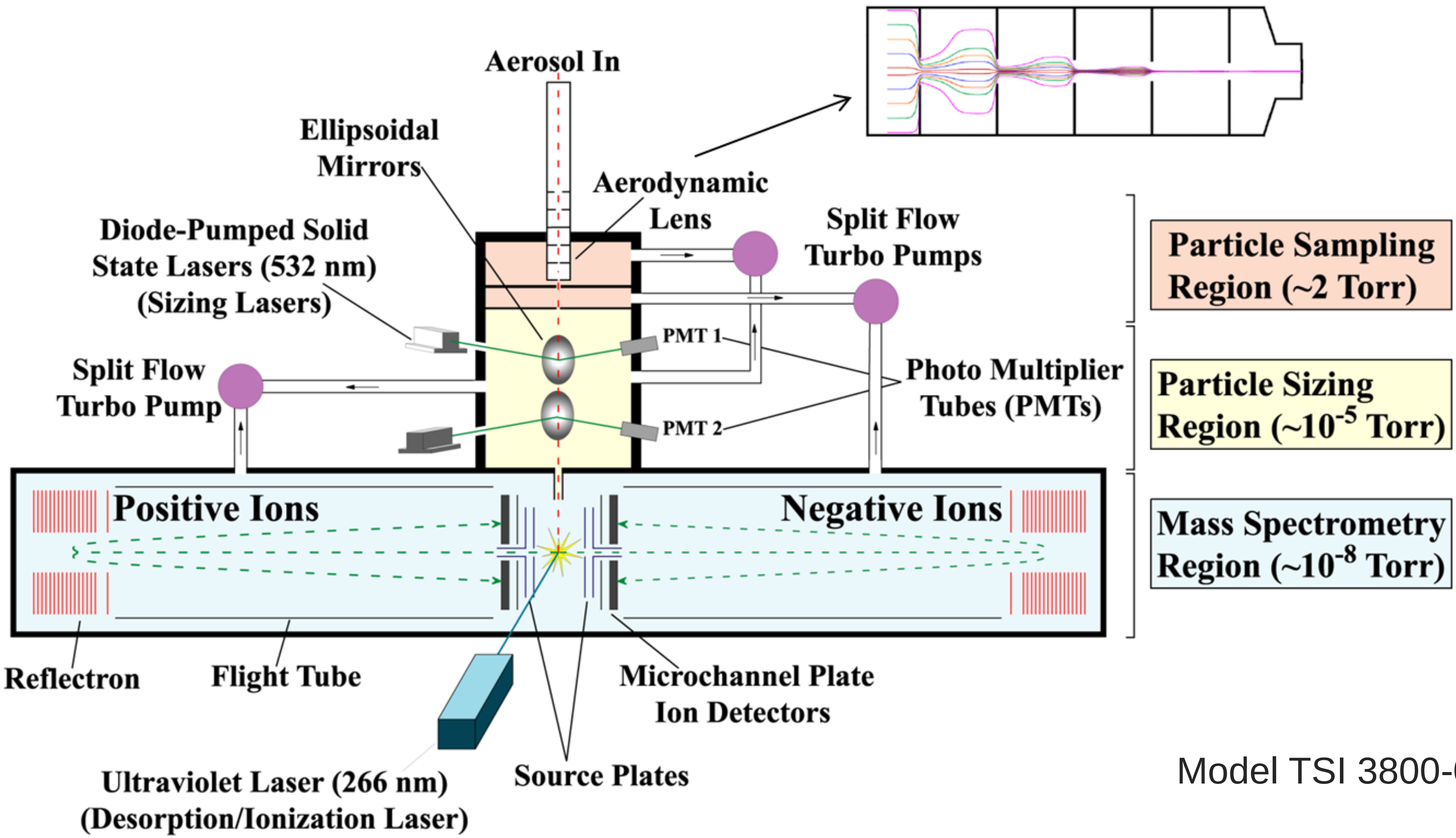
ATOFMS - Aerosol Time-of-Flight Mass Spectrometer



Model TSI 3800-030