Chemical Characterization of Freshly Emitted Particulate Matter from Aircraft Exhaust Using Single Particle Mass Spectrometry

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Motivation

- Aircraft exhaust is a unique anthropogenic source of soot inthe upper troposphere and near airports
- Aircraft exhaust interacts with radiation and clouds
- Contrail cirrus is the largest aviation related net radiative effect (Burkhardt & Kärcher, 2011)
- Role of soot in ice nucleation is not yet completely understood (Zhou & Penner, 2014)
- Metal containing particles are a dominant fractionof ice crystal residuals (Cziczo et al., 2014)
- Air traffic increases ~5 % per year (ICAO, 2013)

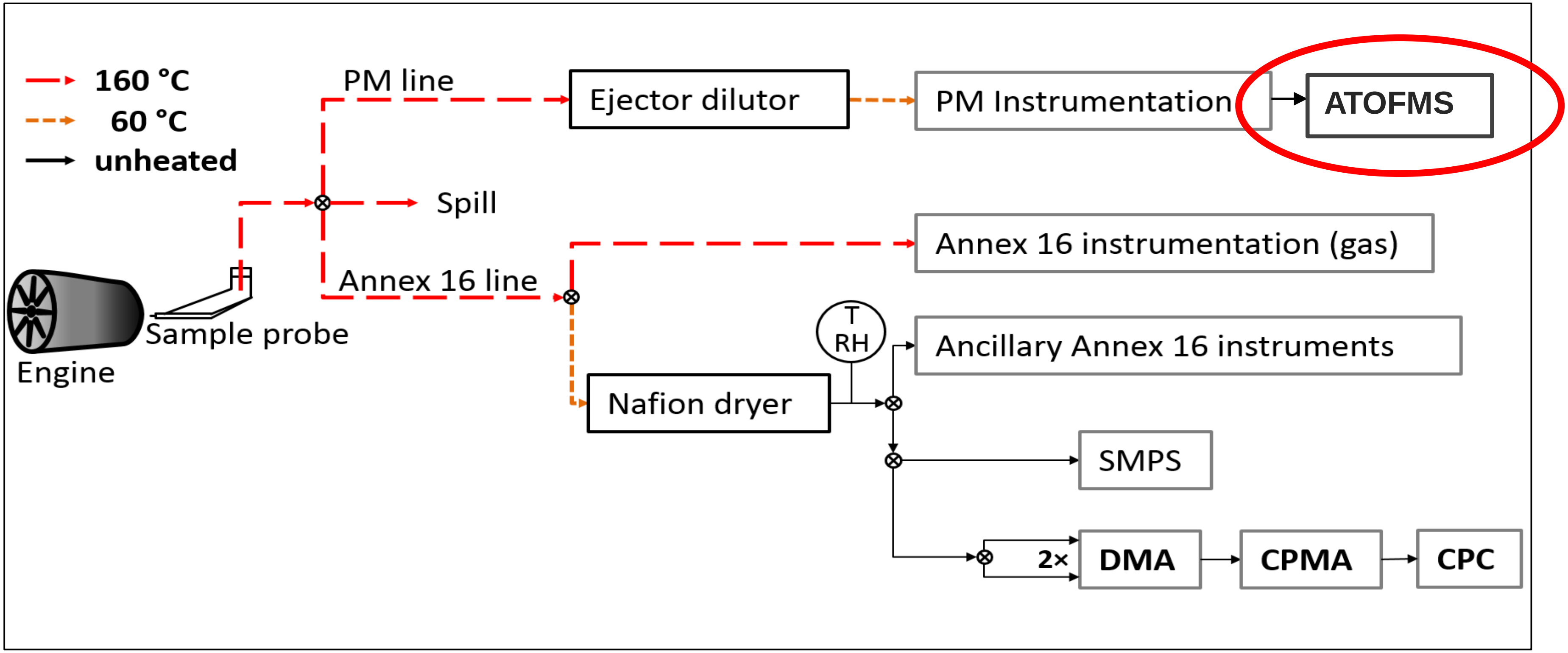
The A-PRIDE Campaigns (Aviation Particle Regulatory Instrumentation Demonstration Experiments)

- Took place at Zurich Airport in the SR Technics facilities
- Measurements during commercial test procedures using the aircraft engine test cell
- Sampling and non-volatile particulate matter (nvPM) measurements according to new aircraft engine nvPM standard
- The system allows the connection of ancillary instruments for the purpose of emission research

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Aircraft Engine in the Test Cell

Experimental Set-Up at the Zurich Airport



ATOFMS: Aerosol Time-of-Flight Mass Spectrometer

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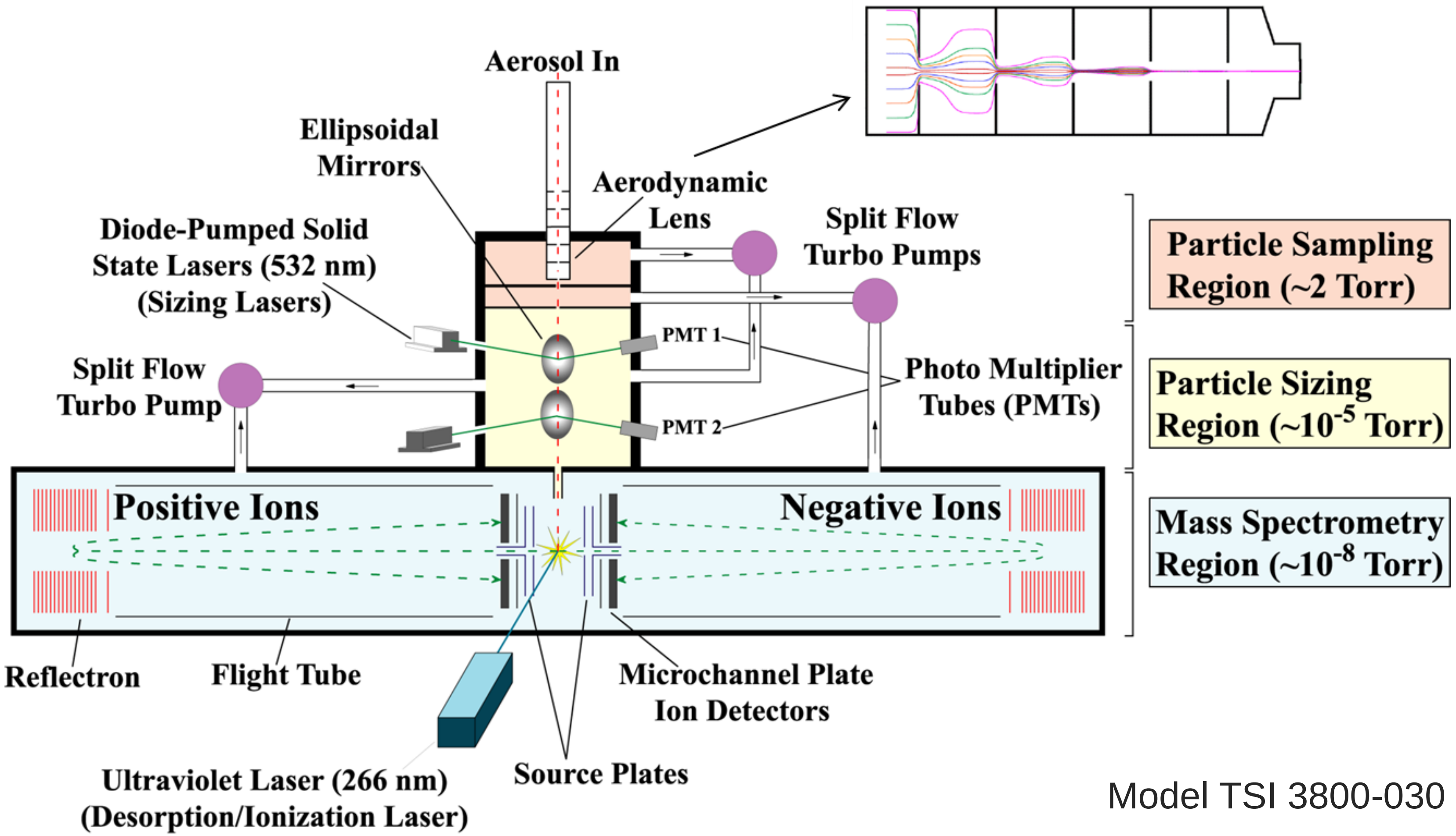


Model TSI 3800-030

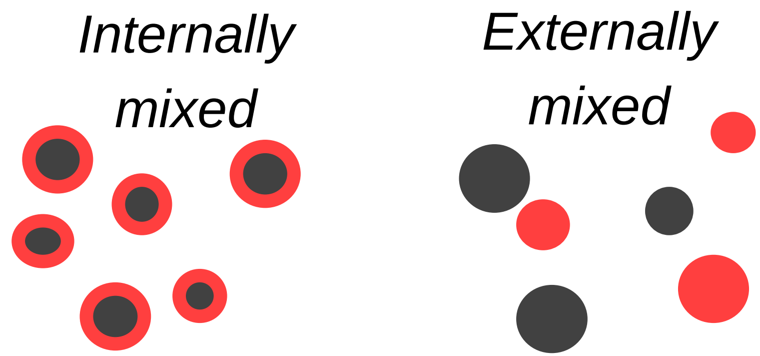
ATOFMS – Aerosol Time-of-Flight Mass Spectrometer

The ATOFMS allows the simultaneous measurement of size and chemical composition of single airborne particle

Chemical properties

- Information on refractory (metals, EC) and non-refractory material (e.g. sulfate, organics)
- Chemical composition of individual particles
- Mixing state
- Non-quantitative

Mixing state



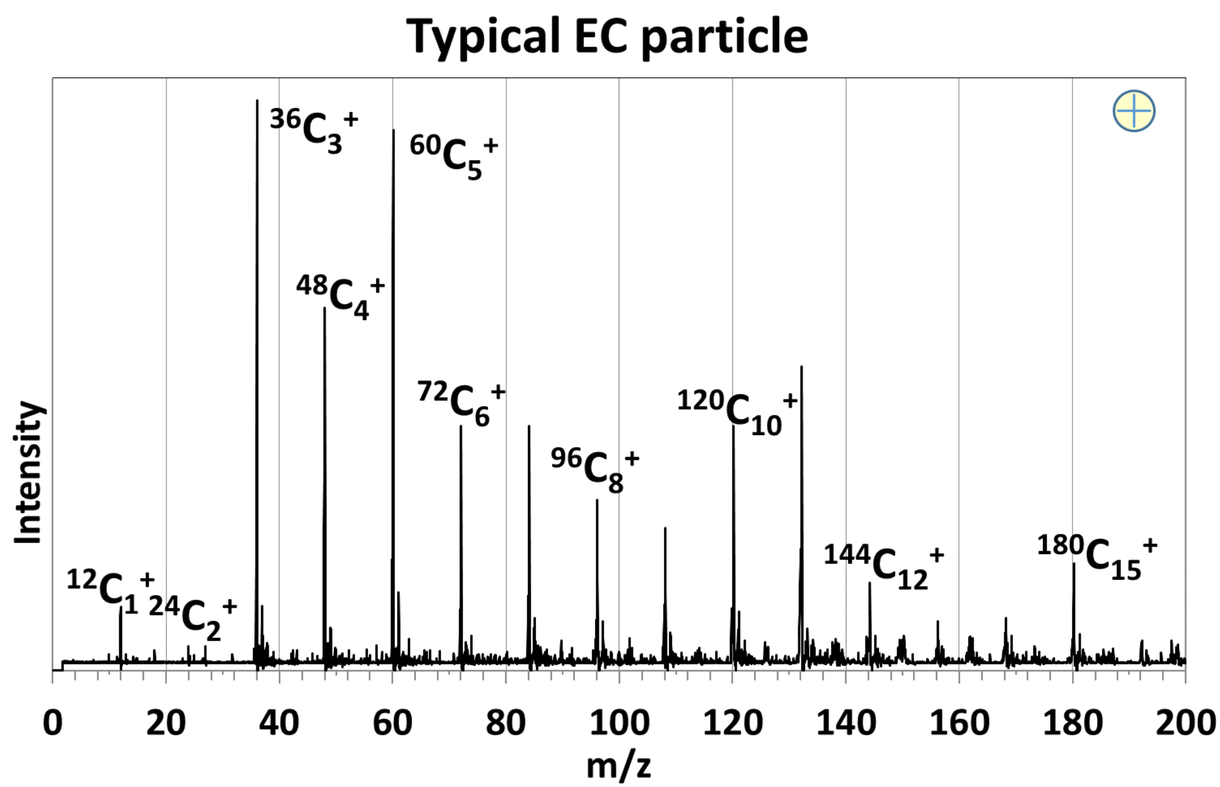
Physical property

- Aerodynamic size

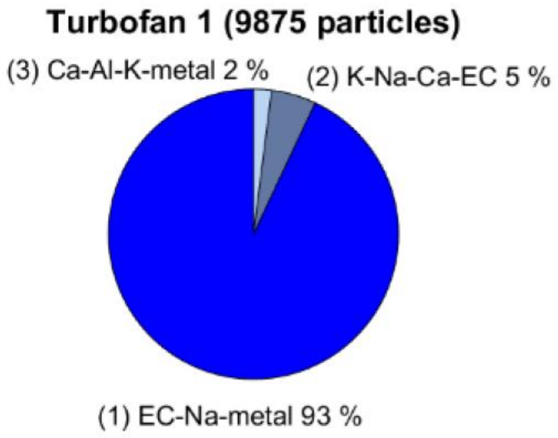
ATOFMS Results from a Turbofan engine

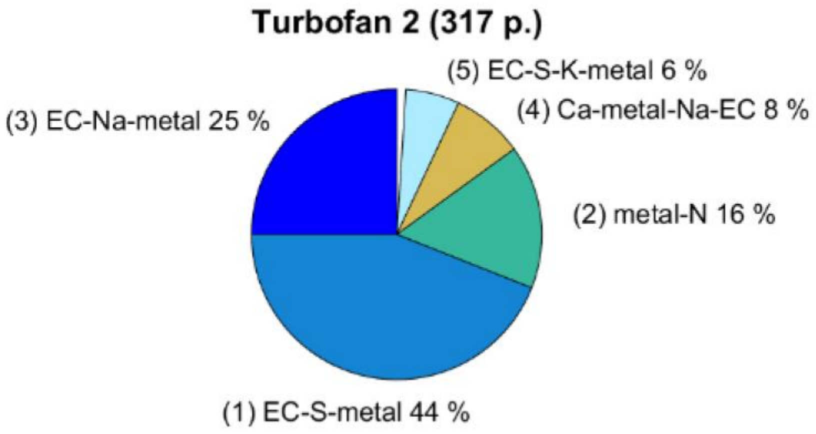
Mass spectra

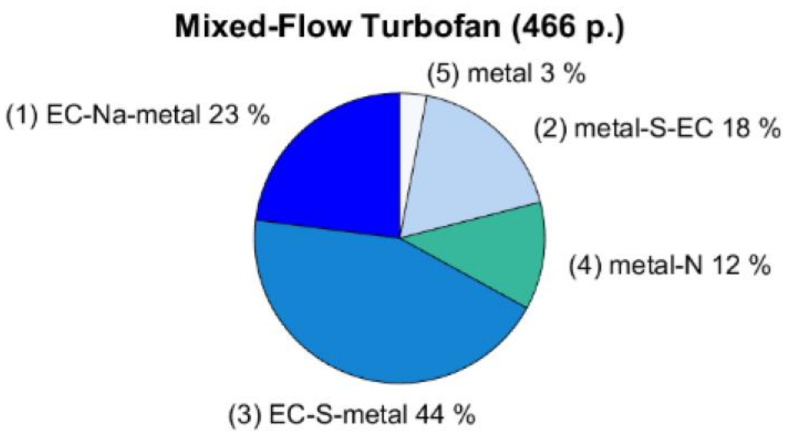
- Typical EC pattern, C_n peaks: *(m/z = 12 * n)*
- Only few negative spectra were recorded
- The analyzed particles represent the fraction of the largest exhaust particles

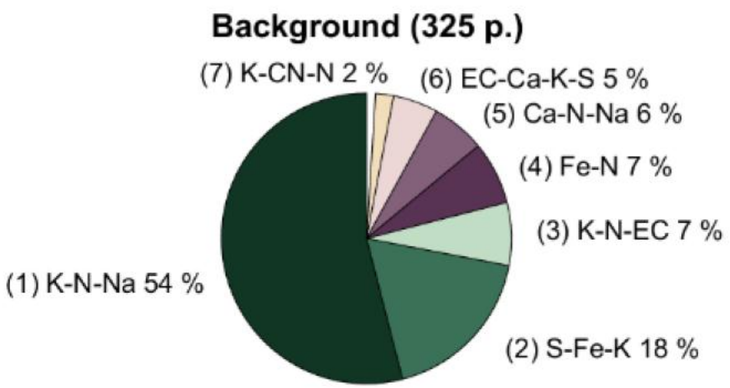


Identification of Major Average Particle Types

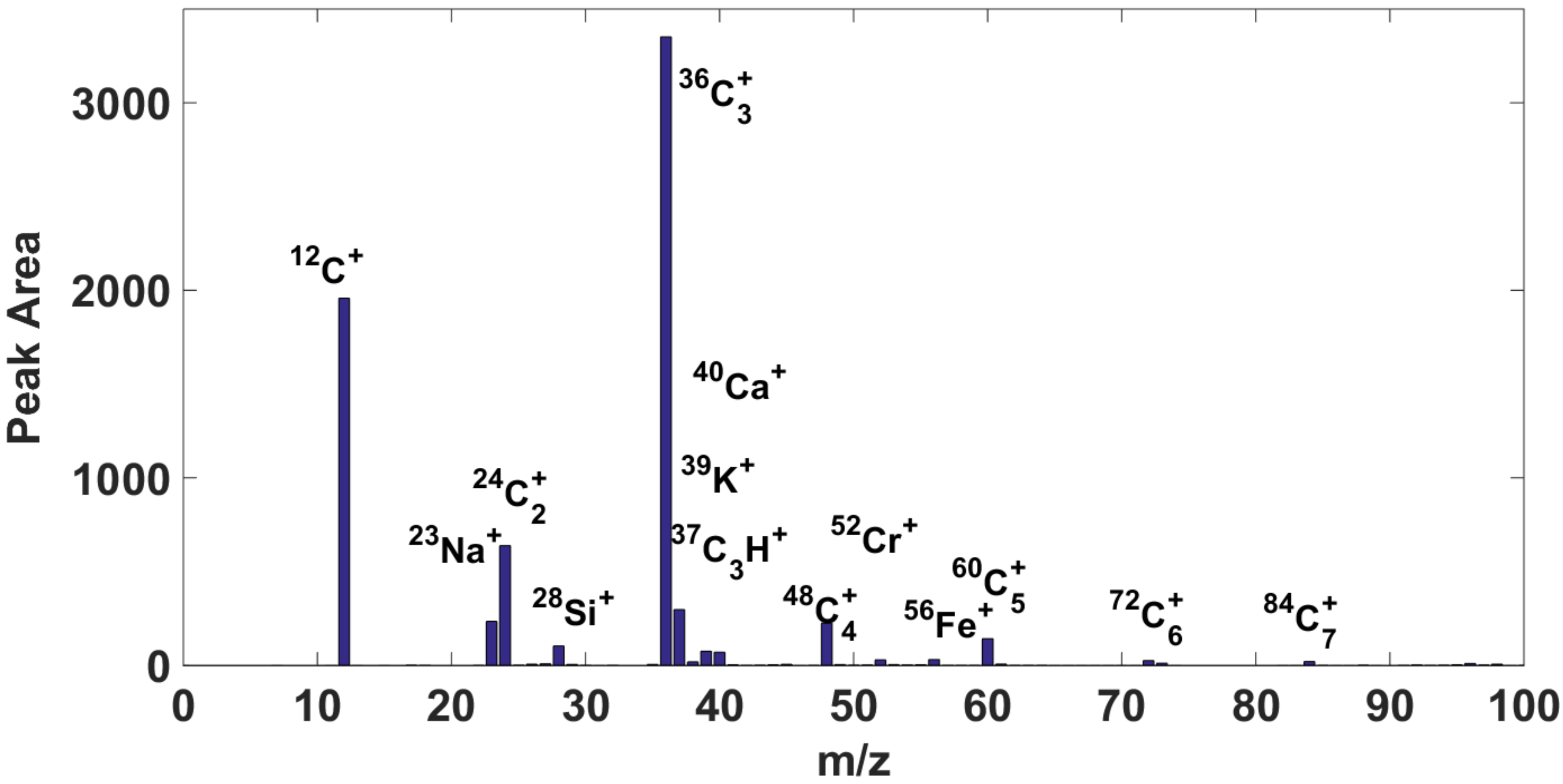








Cluster 1 (93,4 %): EC-Na-metal



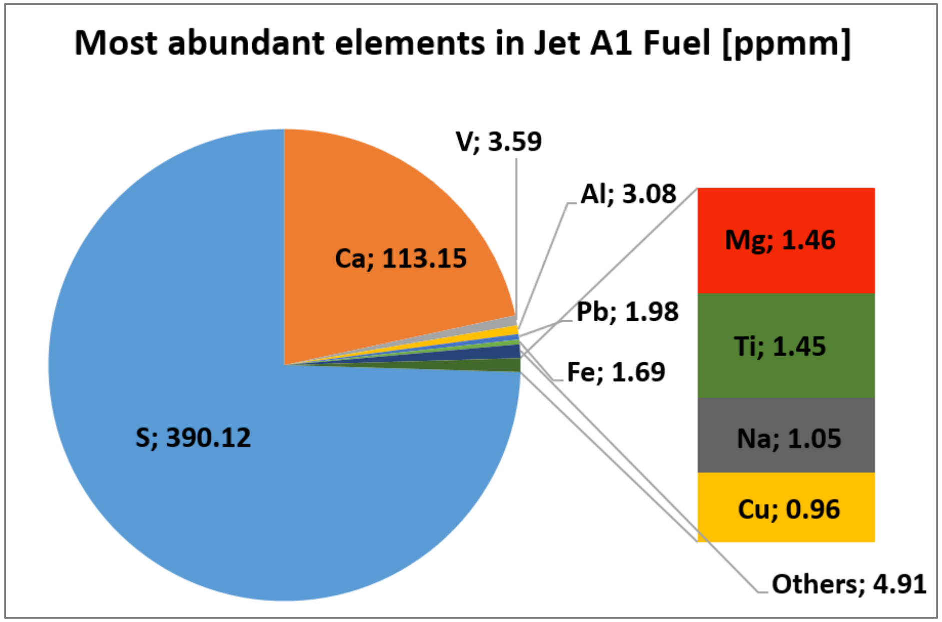
- Clear EC pattern from fresh soot plus some metals: Silicon, Chromium, Iron

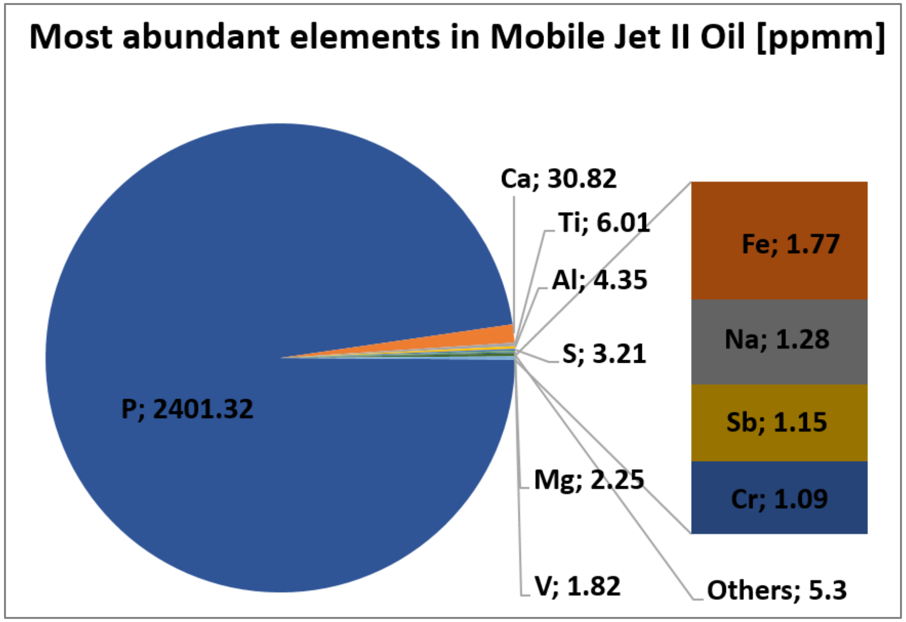
Metal Detected in Exhaust Particles

- Determination of the particle fraction containing the individual metals
- Metals detected (abundance, max. value)
  - >10 %: Sodium, Iron, Calcium and Chromium
  - 1 % – 10 %: Silicon, Aluminium, Cobalt, Copper, Molybdenum and Magnesium
  - <1 %: Vanadium, Manganese, Nickel, Barium, Titanium and Lead (and Zirconium)

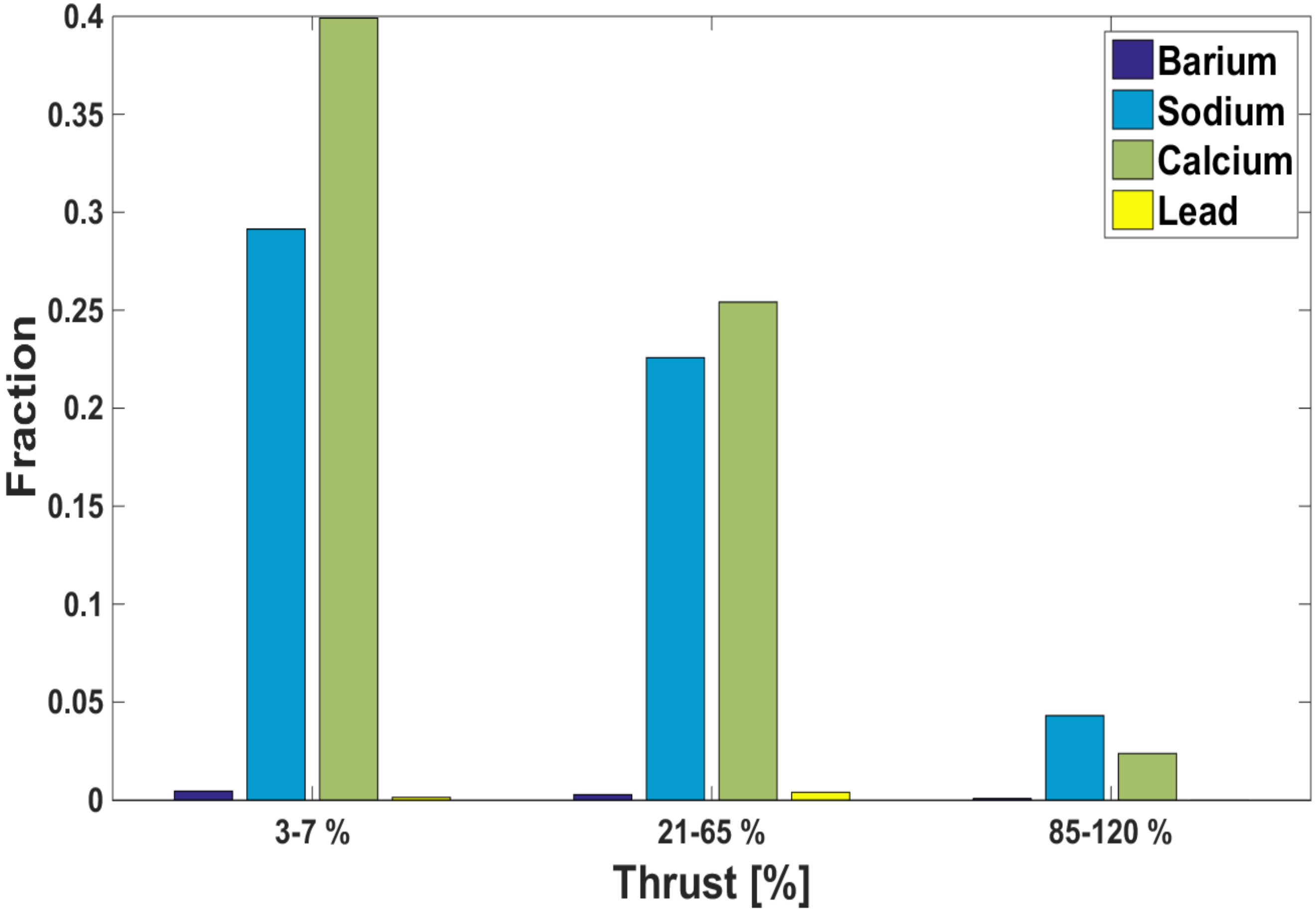
Results – Trace elements found in fuel and oil

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



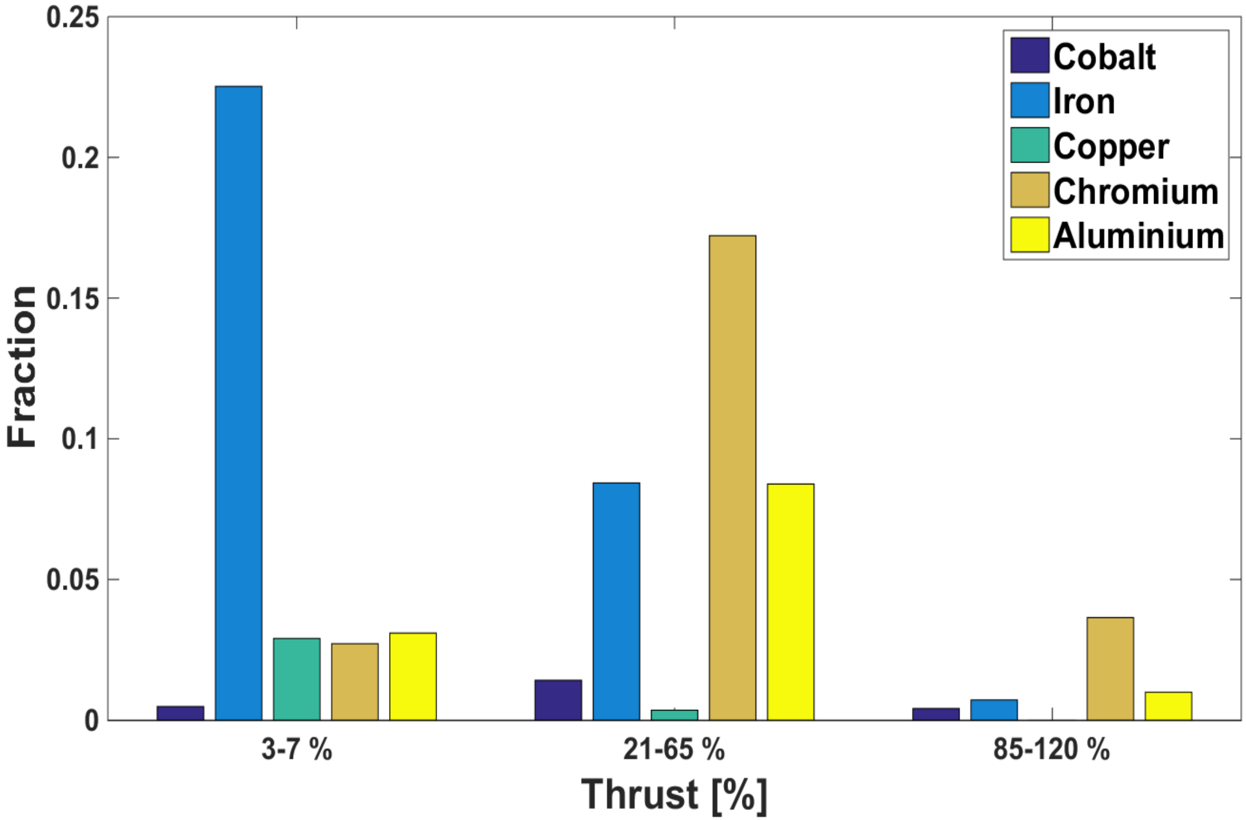


Thrust dependent occurrence of metals from fuel and oil



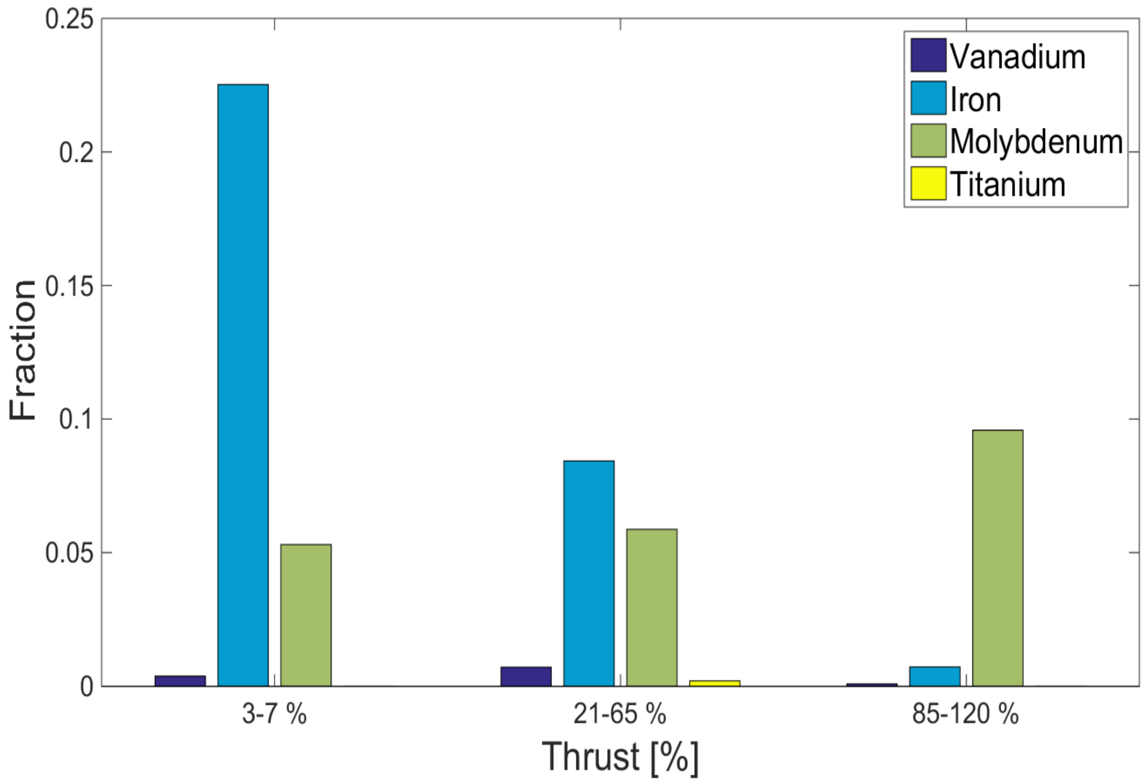
- Ba, Na and Ca: probably decrease due to higher particle concentration
- Na and Ca also show a decrease in relative peak area
- Pb: probably stems from contamination of the fuel tank (only tiny amount found in oil)

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
  - Conc. decreases with increasing thrust
- Cr (also in oil)
- Al (also in fuel and oil)

Metals found in fuel, oil and used as alloys in aircraft engines



Vanadium

Iron: *occurs mainly with copper → probably from engine wear*

Molybdenum: *occurs at highest thrust*

Titanium: *probably underestimated*

Summary and conclusions

- Measurements were conducted on individual, freshly emitted aircraft exhaust particles considering the entire engine operating range
- First in-line measurements of chemical composition of single particles show
  - Almost all particles showed EC pattern
  - All detected metals were internally mixed with soot
  - 36% of the analyzed particles contained a metallic compound
  - Most metals are detected in more than one source (fuel, oil, engine wear)
  - Cobalt and Zirconium result only from engine wear

Thank you for your attention!

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Motivation

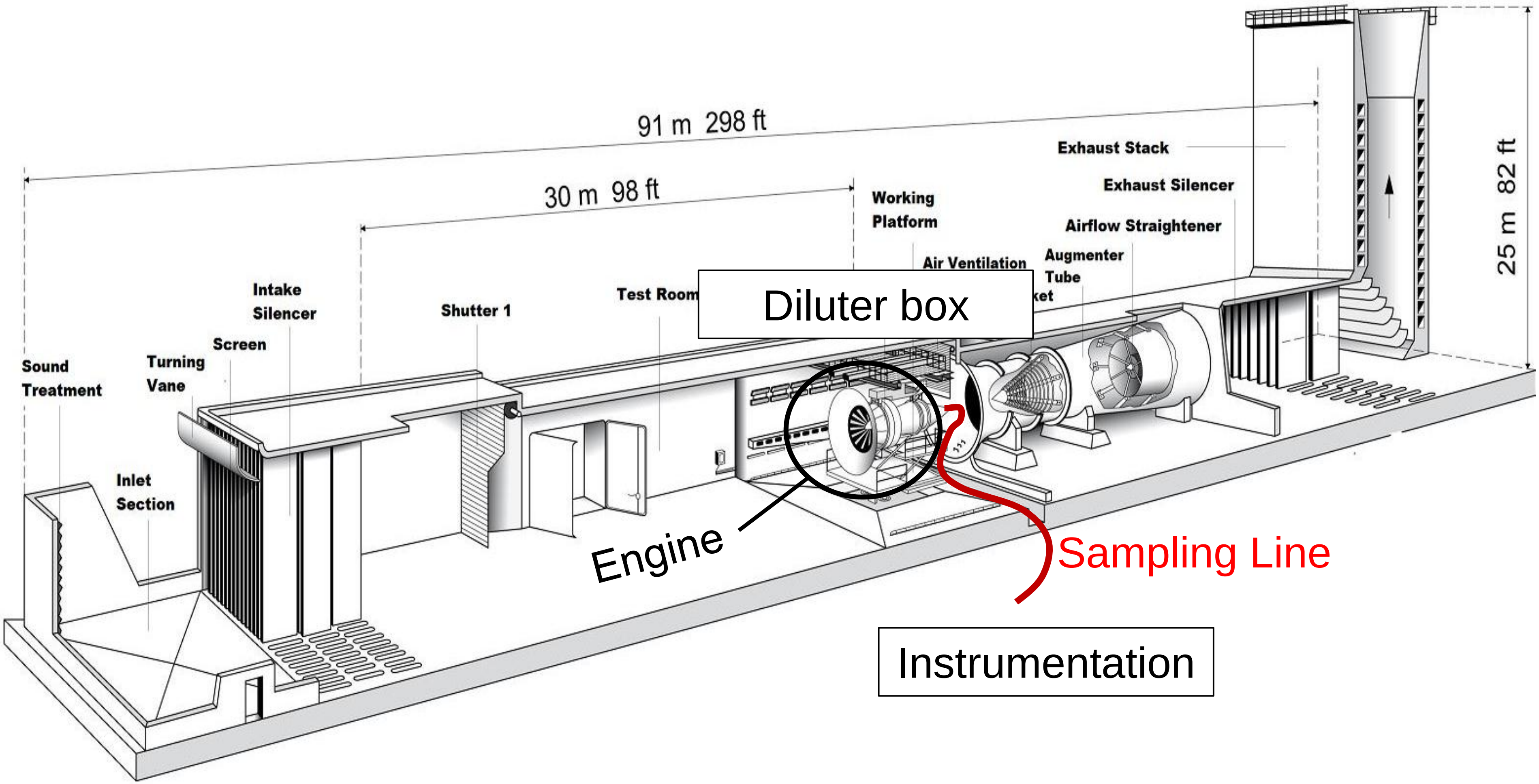
Health

- The emitted particles are ultrafine Particulate Matter ($PM_{0.1}$, mean diameter <100 nm)
- They are less likely to be removed from human respiratory system and can even enter the blood stream (Terzano et al., 2010)
- Respiratory health problems occur near airports (Keuken et al., 2015)
- Soot can act as carrier for toxic substances (Janssen et al., 2012)

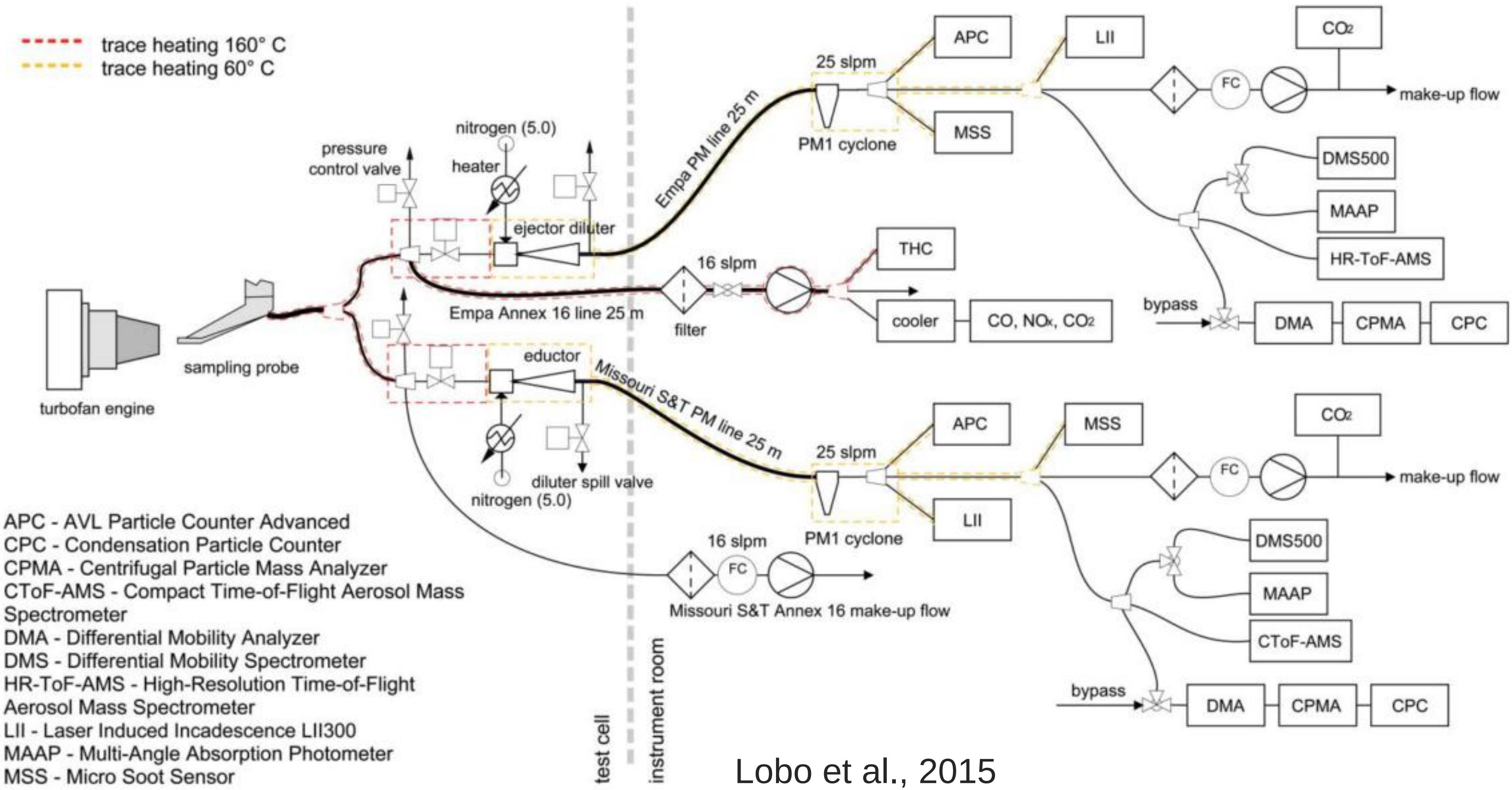
Measurements at the Zurich Airport

Campaign	Date	CPMA	ATOFMS
A-PRIDE 4	November 2012	✓	—
Piggyback	June 2013	✓	✓
A-PRIDE 5	July/June 2013	✓	✓
A-PRIDE 7	October 2014	—	✓
Piggyback	May 2015	—	✓

SR Technics – Aircraft Engine Test Cell



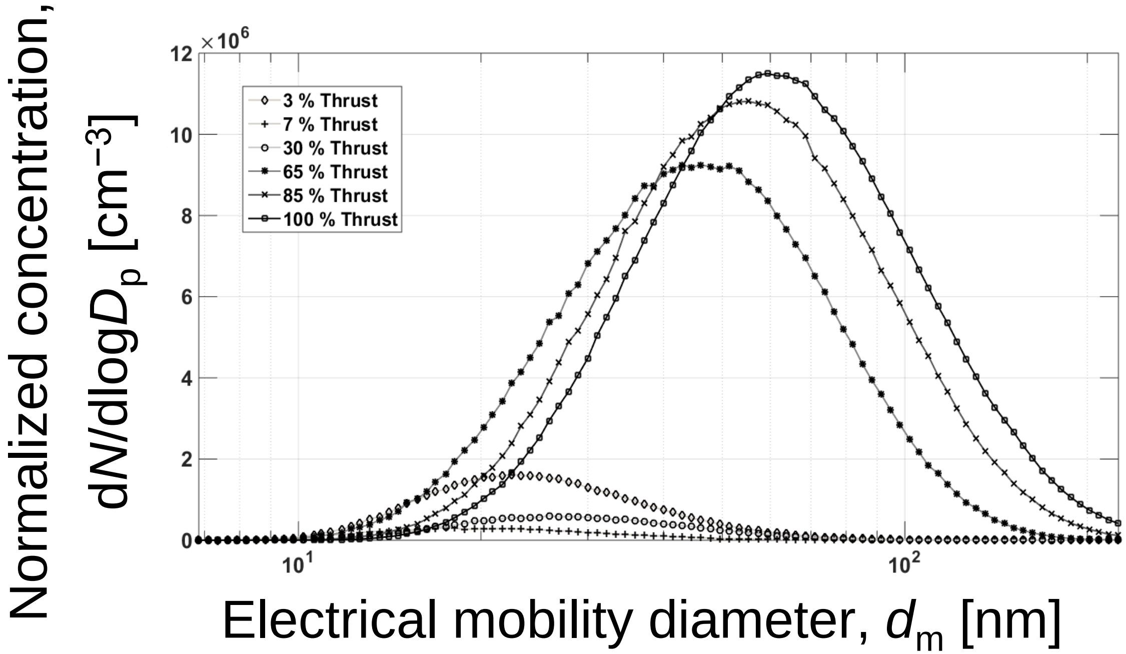
Experimental setup used in the A-PRIDE 4 campaign



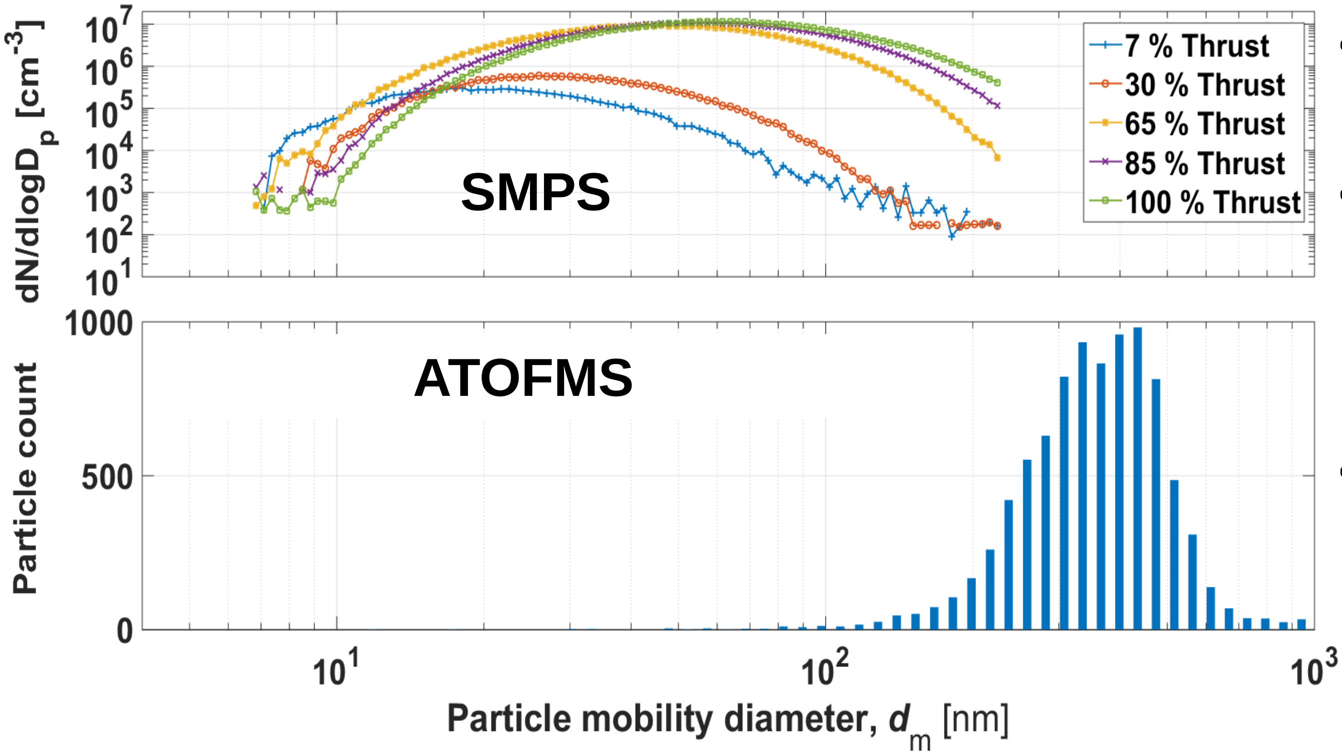
Lobo et al., 2015

Size Distribution

- Mean d_m increases with thrust
- Particle concentration increases with thrust
- Except at low thrust
- Smaller than exhaust particles emitted by diesel vehicles (e.g. Olfert et al., 2007)



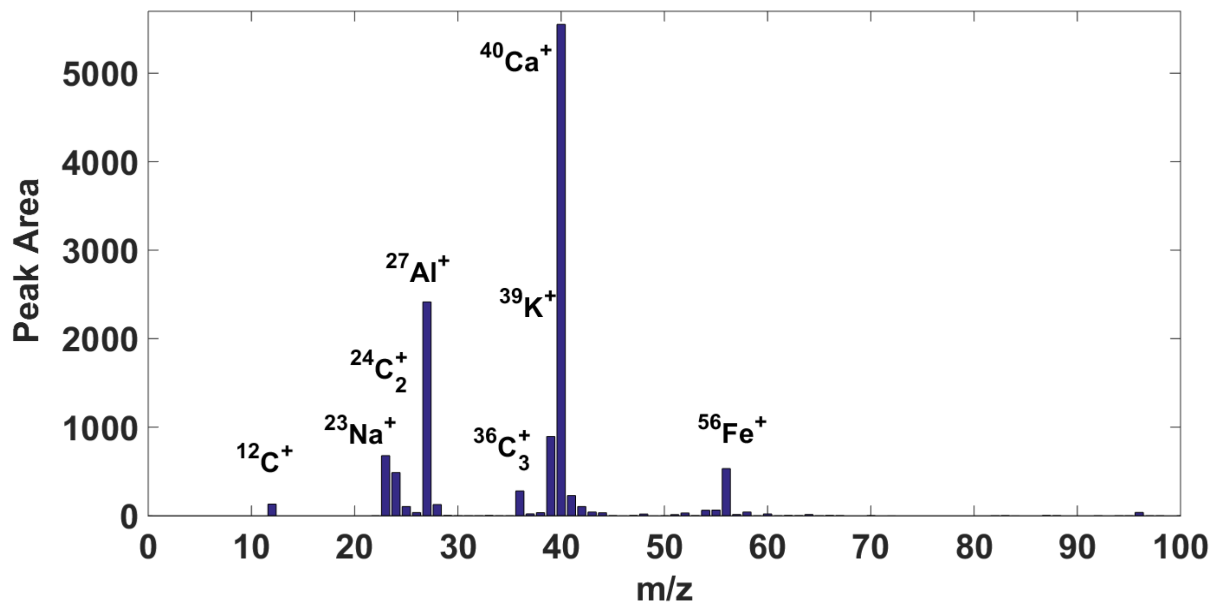
Results: Size of particles analyzed by the ATOFMS



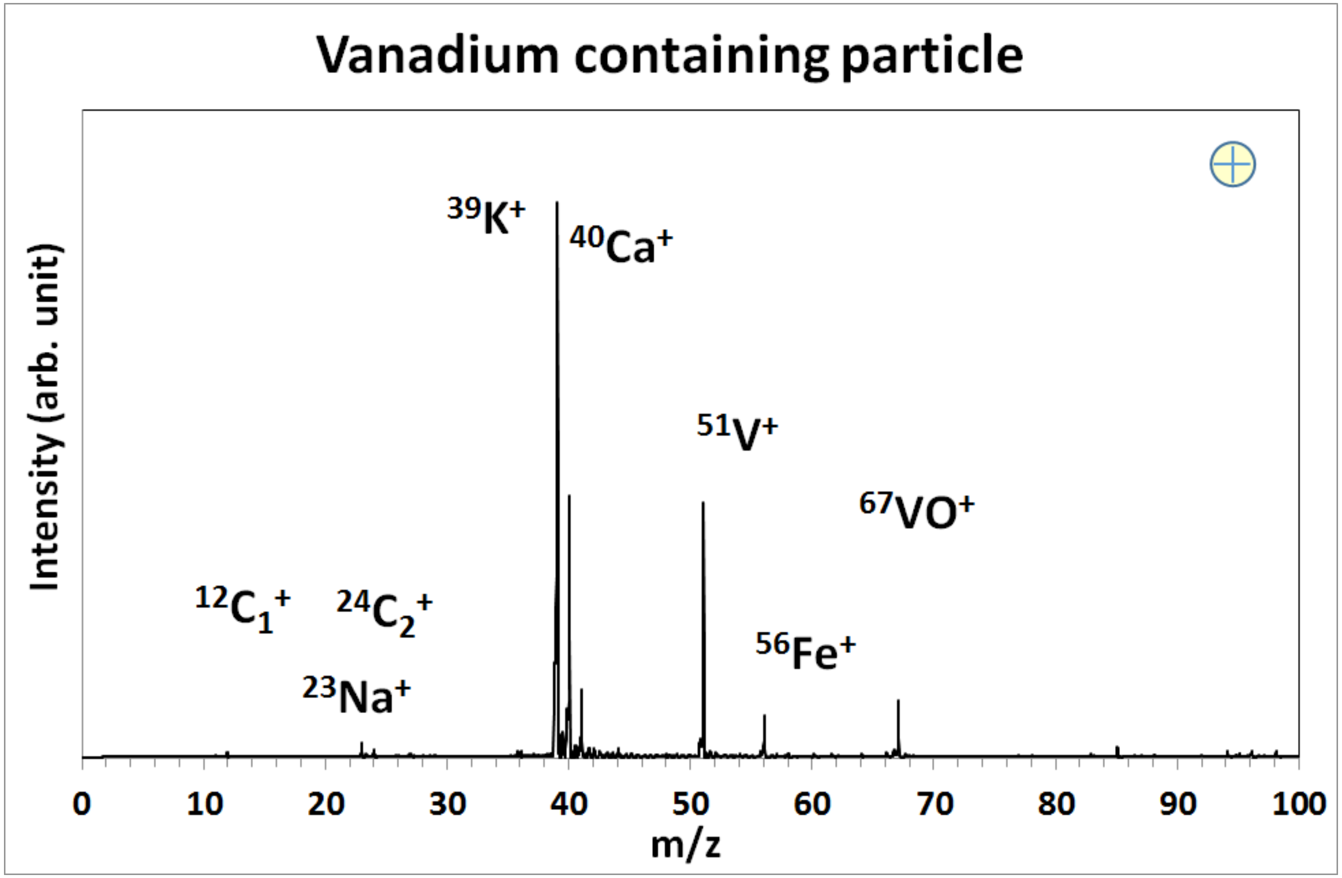
- d_{ae} (ATOFMS) was converted into d_m
- …using shape factors calculated from particle mass (Abegglen et al, 2015)
- → Only the largest particles could be analyzed

Cluster 3 (1.8 %): Ca-Al-K-Fe-Na (Metal Type Particle)

- Metals appear in the positive spectra
- Signature of EC/soot still obvious
- EC mixed with mainly inorganic compounds:
  - ^{23}Na
  - ^{27}Al
  - ^{39}K
  - ^{40}Ca
  - ^{56}Fe



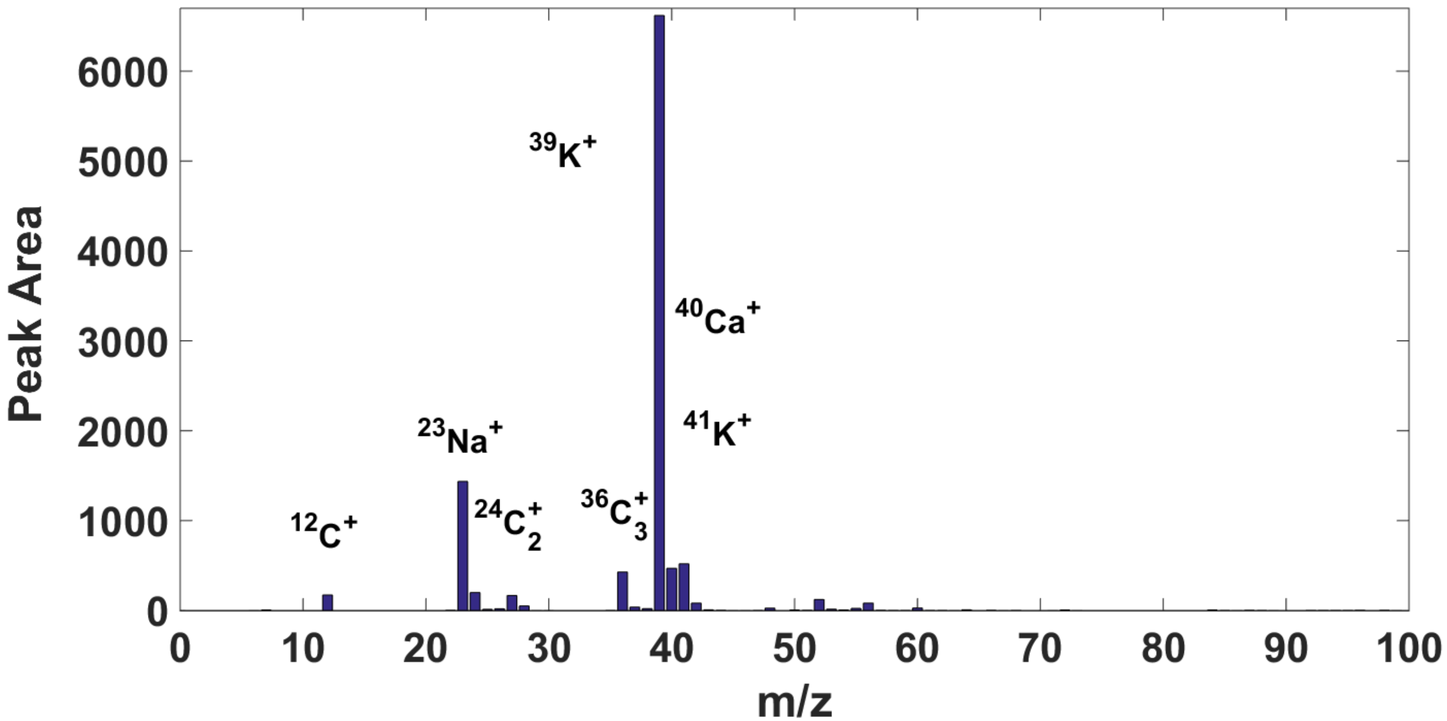
Results: Single particle spectra III



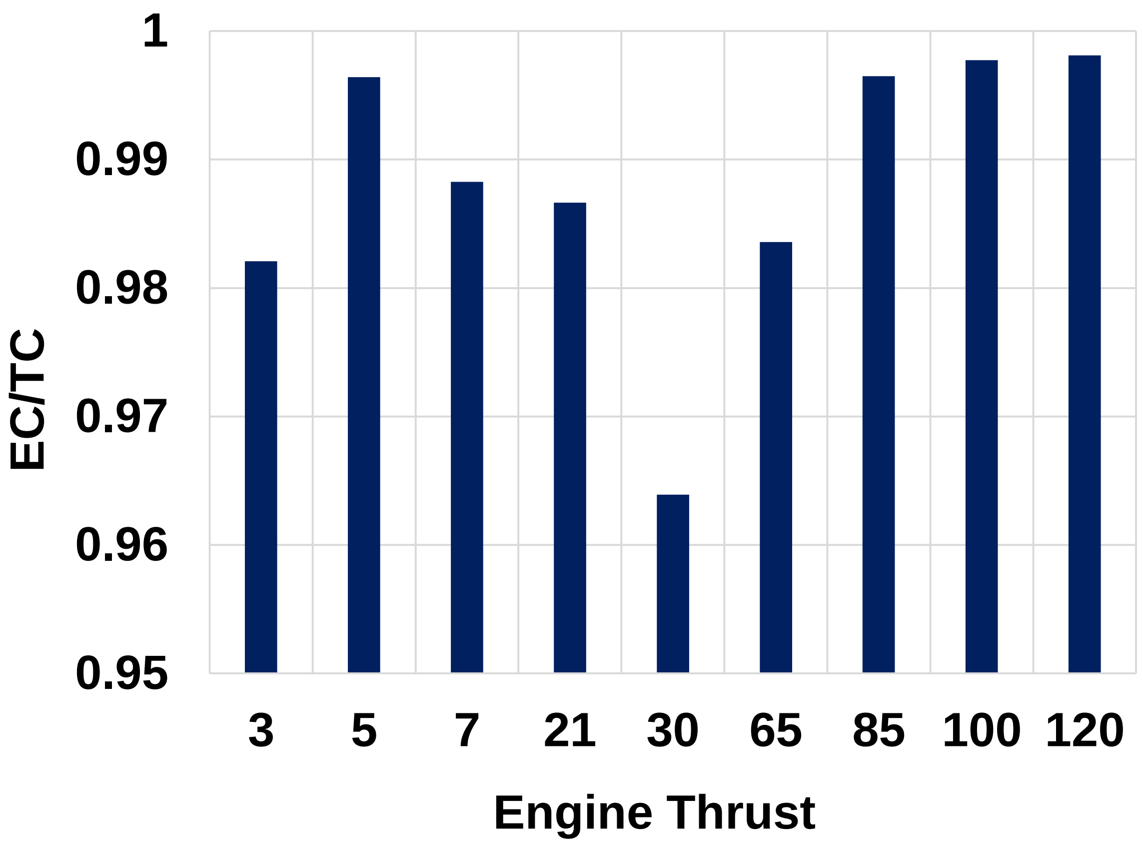
- Vanadium and Vanadium oxide
- Iron was found in a vast majority (up to 25 %) of the particles
- The ATOFMS is very sensitive to Potassium

Cluster 2 (4.5 %): K-Na-EC

- Very pronounced Potassium peak and Sodium with a weak ^{12}C pattern



Results: EC/TC-ratio



- Determination of EC/TC ratio according to method by Ferge et al. (2006) using relative peak areas
  - Prior subtraction of peaks from inorganic compounds
  - EC defined as m/z = C_x + n (n =1, 2, 3)
  - TC defined as rest
- →High EC content