

Characterization of soot particles coming from aircraft and ship emissions: unique properties and impact on the atmosphere

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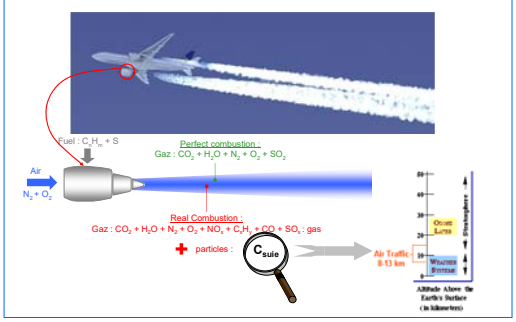
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Characterization of soot particles coming from aircraft and ship emissions: unique properties and impact on the atmosphere.

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FORMATION OF CARBON NANOPARTICLES (SOOT) IN THE ATMOSPHERE



THE SCIENTIFIC BACKGROUND

The low ability to predict climatic consequences (only qualitative estimates)

- The paucity of data about the physicochemical properties of aircraft engine soot

Most of studies, based on laboratory-generated soot particles

- show a large variation in their nucleation properties and reactivity.

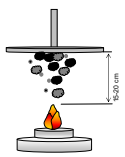
This study is devoted to the comparison of laboratory soot / engine soot:

- morphology,
- microstructure,
- chemical composition,
- hygroscopic properties

⇒ **determine the mechanisms responsible for the formation of CCN (contrails, clouds cirrus)**

SOOT PRODUCTION

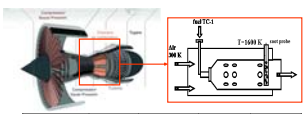
KEROSENE FLAME TC1 SOOT



Produced by burning aviation TC1 kerosene in a wick oil lamp



AIRCRAFT COMBUSTOR SOOT *(collab. Aviation Institute, Moscow)*



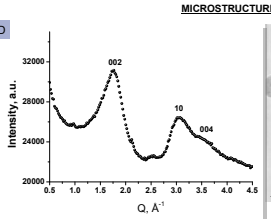
Aircraft engine	T_{inlet}(K)	T_{outlet}(K)	Air / fuel ratio	Pression (atm)
D30-KU	300	1250-1450	4 - 4.5	3 - 5

Aviation kerosene TC1 sulfur content: 1100 µg·g⁻¹

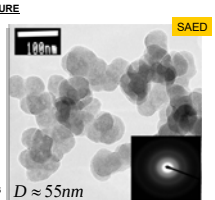
KEROSENE FLAME TC1 SOOT

MICROSTRUCTURE

ND



SAED



$d_{002} = 3.58 \pm 0.19$ Å $L_c = 13 \pm 2$ Å
$d_{10} = 2.05 \pm 0.09$ Å $L_a = 13 \pm 2$ Å
$d_{11} = 1.77 \pm 0.06$ Å

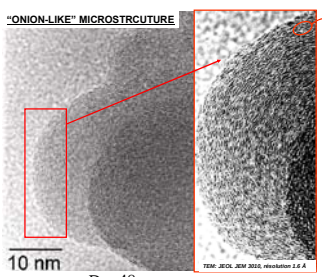
$d_{002} = 3.60 \pm 0.21$ Å $d_{10} = 2.07 \pm 0.11$ Å
$d_{11} = 1.23 \pm 0.06$ Å

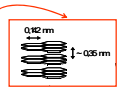
CHEMICAL COMPOSITION:

EDS:
carbon (95.0±0.6 wt%)
oxygen (5.0±0.3 wt%).

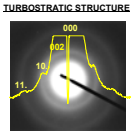
MAIN FRACTION OF AIRCRAFT ENGINE COMBUSTOR SOOT

"ONION-LIKE" MICROSTRCUTURE



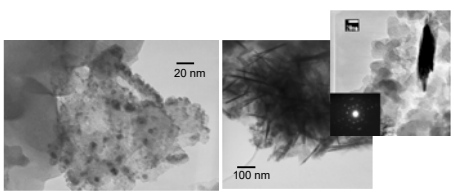


TURBOSTRATIC STRUCTURE



- d_{002} = 3,50 ± 0.18 Å *(graphite : d_{002} = 3,35 Å)*
- d_{10} = 2,07 ± 0.11 Å
- d_{11} = 1,19 ± 0.07 Å

AIRCRAFT ENGINE COMBUSTOR SOOT: FRACTION OF IMPURITIES

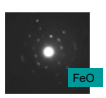


Sulfur-rich area

C=68,95 wt%
O=20,87 wt%
S=2,5 wt%

Iron-rich area

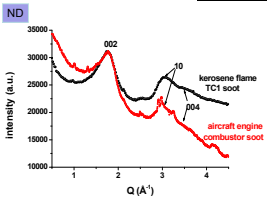
C=61,2 wt%
O=6,1 wt%
Fe=32 wt%
S=0,7 wt%



AIRCRAFT ENGINE COMBUSTOR SOOT

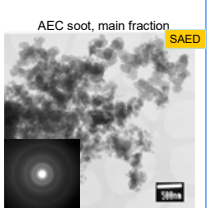
MICROSTRUCTURE

ND



AEC soot, main fraction

SAED



$d_{002} = 3.58 \pm 0.20$ Å $d_{10} = 2.07 \pm 0.10$ Å $L_c = 21 \pm 2$ Å

$d_{002} = 3.50 \pm 0.18$ Å

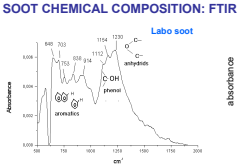
$d_{10} = 2.07 \pm 0.11$ Å $d_{11} = 1.19 \pm 0.07$ Å

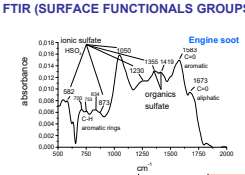
In fraction of impurities we observe iron-containing particles **FeO, Fe$_3$O(OH)$_x$**, copper containing **CuO, Cu$_2$O** and aluminum containing **Al(OH)$_3$**.

CHEMICAL COMPOSITION:

EDS:
C (96.6±0.7 wt%), O (3.1±0.5 wt%), S (0.3±0.1 wt%)

SOOT CHEMICAL COMPOSITION: FTIR (SURFACE FUNCTIONALS GROUPS)



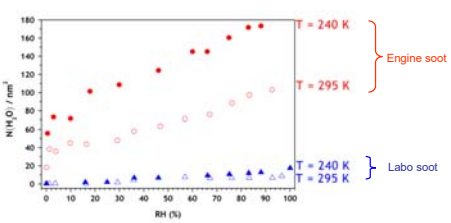


LABO SOOT ; ENGINE	Bands cm^{-1}	hydrophilicity
CH deformation, aromatics	650-920	Low
-C-O-C- anhydrids, aryls	1230	Medium
C-OH stretch, phenols	1154,1112	Medium
-O- aromatic ester	1154, 1112	Low
O-H stretch, hydroxyl	3290	High

ENGINE ONLY	Bands cm^{-1}	Hydrophilicity
C=O carbonyl, aliphatic	1673	High
C=O carbonyl, aromatic	1583	High
HSO_4^- ion	1355,1230 1050, 878, 582	High
Organic sulfates	1350, 1420	High

Engine soot has much more hydrophilic surface functional groups than the surrogate soot

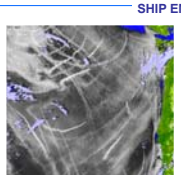
WATER UPTAKE ON SOOT PARTICLES



- Engine soot adsorbs big amounts of water at low RH and at T = 295 K
  → surface active sites (sulfates, carbonyls)
- Adsorption (engine soot) >> adsorption (labo soot)
  → Lamp soot relatively hydrophobic (isotherm shape)

Fraction of impurities responsible of the high hydrophilicity

SHIP EMISSION AND SAMPLING



Satellite image of ship tracks

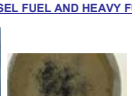
- Possible climate impacts which are still least defined in comparison with land-based transport
- Ship emission particulates can act as nuclei for the formation of cloud droplets
- Ships may produce ship tracks

The starting point for evaluating the effect of ship emission on environment is to characterize its properties (like structure, chemical composition etc)

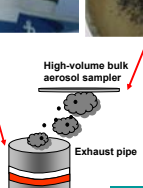
Water-soot interaction is one of the important parameters defining ability of the soot to form contrails and ship tracks

SAMPLING: MARINE DIESEL FUEL AND HEAVY FUEL OIL COMBUSTION RESIDUALS





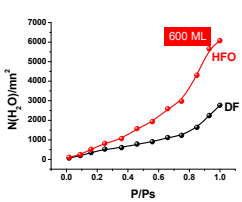
Sampled on the end-of the pipe on beard of marine conveyer ships burning diesel and heavy fuel oil.



Heavy Fuel Oil is a residual from crude oil refinement, after gasoline and distillate fuel oils are extracted through distillation. It typically contains **sulfur up to 3.5 wt%, ash 0.1 wt%, vanadium 0.02 wt%, calcium 0.003 wt%.**

Diesel fuel contains ash 0.01 wt% and sulfur 0.5 wt%

WATER UPTAKE ON DIESEL FUEL AND HEAVY FUEL OIL COMBUSTION PARTICLES



Significant uptake (up to 200, 275, and 600 ML at higher p/p_0) for HFO, DF-M, respectively and the presence of many hydrophilic functional groups on the surface of ship residuals indicate that the dominant mechanism of their water uptake is the water dissolution into the soluble coverage and the formation of a thick solution film surrounding the particles.



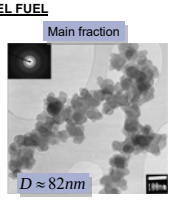
Water Soluble Fraction for DF and HFO are 19 and 44 wt%, respectively

S_{DF-M} =0.7 m²/g, S_{HFO} =5.4 m2/g

MICROSTRUCTURE AND CHEMICAL COMPOSITION OF DIESEL FUEL AND HEAVY FUEL OIL EMISSION RESIDUALS

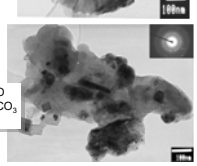
DIESEL FUEL

Main fraction



Impurities

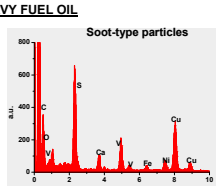


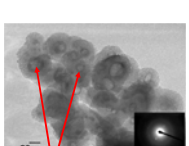


$d_{002} = 3.40 \pm 0.16$ Å
$d_{10} = 2.08 \pm 0.08$ Å
$d_{11} = 1.23 \pm 0.06$ Å

EDS of main fraction:
C=97.6±0.7 wt%
O=1.8±0.3 wt%
Fe=0.6±0.1 wt%

HEAVY FUEL OIL





dark core inside particles

EDS: Carbon (89.9±3.1 wt%), Oxygen (4.4±0.5 wt%), vanadium (2.4±0.3 wt%), and Sulfur (3.2±0.4 wt%); Nickel (0.3±0.1 wt%).

SAED+EDS:Ni_3S_2, $Na_6(CO_3)(SO_4)$, Ni_2Fe, Ni_3Fe, NiO, V_2O_3, NiS

$d_{002} = 3.65 \pm 0.17$ Å $d_{10} = 2.15 \pm 0.09$ Å $d_{11} = 1.17 \pm 0.05$ Å

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