

The chemical tiger in Diesel car exhaust : Search for fluorine-bearing highly acidic gases

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We report on a search for fluorine-bearing highly acidic and corrosive trace gases in Diesel car exhaust. Using an innovative, very sensitive and fast chemical ionization mass spectrometric method, we have made on-line and off-line measurements of highly acidic exhaust gases. The detected gases include sulphuric acid and several species, which most likely contain fluorine. Some of the F-bearing species also contain sulphur. We have also made a search for the source of exhaust fluorine. In commercial Diesel fuel we found highly variable F-mass fractions of up to 114 ppm and in lubricant oil up to 30 ppm. The detected F-bearing exhaust gases not only are highly acidic and corrosive, but include also ones having a highly toxic nature. One of the detected F-bearing gases has a very low volatility and therefore may become incorporated into exhaust nanoparticles. It is at least conceivable that exhaust fluorine may also undergo chemical conversion to toxic F-bearing dioxins and furans, but these are less stable than their chlorinated counterparts and may thermally decompose at typical exhaust temperatures. Presently fuel-fluorine is not explicitly regulated. However, we have found that certain catalytic Diesel particle filters, at least partially, remove the detected F-bearing highly acidic gases. Considering their corrosive and toxic nature, F-bearing exhaust species deserve increased future attention. In the chemistry literature Fluorine is often termed „The Tiger of Chemistry“ since it is extremely reactive

- Due to its large electronegativity, F tends to form very strong acids
- Some contain also S besides F
- Some have an extremely corrosive and toxic nature
- However, no information available on F-species in motorcar exhaust and fuel !

Screening of international literature

- German Federal Environment Agency
- German Fuel producers
- We have made a search for F in exhaust
- We have made a search for F in motor-car fuels and lubricant oils
- F-acids have been detected in exhaust
- Some undergo co-adsorption with H₂SO₄
- Likely F-source seems to be the fuel
- is F a Diesel OXICAT poison ?
- ATS efficiently removes organic F-species
- Is F contained only in fuels from certain refineries?
- Future fuel F-analyses are needed.

The chemical tiger in Diesel car exhaust :

Search for **fluorine**-bearing highly acidic gases

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Abstract

We report on a search for fluorine-bearing highly acidic and corrosive trace gases in Diesel car exhaust. Using an innovative, very sensitive and fast chemical ionization mass spectrometric method, we have made on-line and off-line measurements of highly acidic exhaust gases. The detected gases include sulphuric acid and several species, which most likely contain fluorine. Some of the F-bearing species also contain sulphur. We have also made a search for the source of exhaust fluorine. In commercial Diesel fuel we found highly variable F-mass fractions of up to 114 ppm and in lubricant oil up to 30 ppm. The detected F-bearing exhaust gases not only are highly acidic and corrosive, but include also ones having a highly toxic nature. One of the detected F-bearing gases has a very low volatility and therefore may become incorporated into exhaust nanoparticles. It is at least conceivable that exhaust fluorine may also undergo chemical conversion to toxic F-bearing dioxins and furans, but these are less stable than their chlorinated counterparts and may thermally decompose at typical exhaust temperatures. Presently fuel-fluorine is not explicitly regulated. However, we have found that certain catalytic Diesel particle filters, at least partially, remove the detected F-bearing highly acidic gases. Considering their corrosive and toxic nature, F-bearing exhaust species deserve increased future attention.

Background

- Motor-car exhaust still represents a major **air pollution** source in cities and near motorways
- Contains numerous **combustion** generated species (**gases** , **nanoparticles**)
- Some are related to **chemical elements** contained in the fuel only in **ultra-trace mass amounts**

Example

Sulphur (S)

Combustion

Exhaust flow

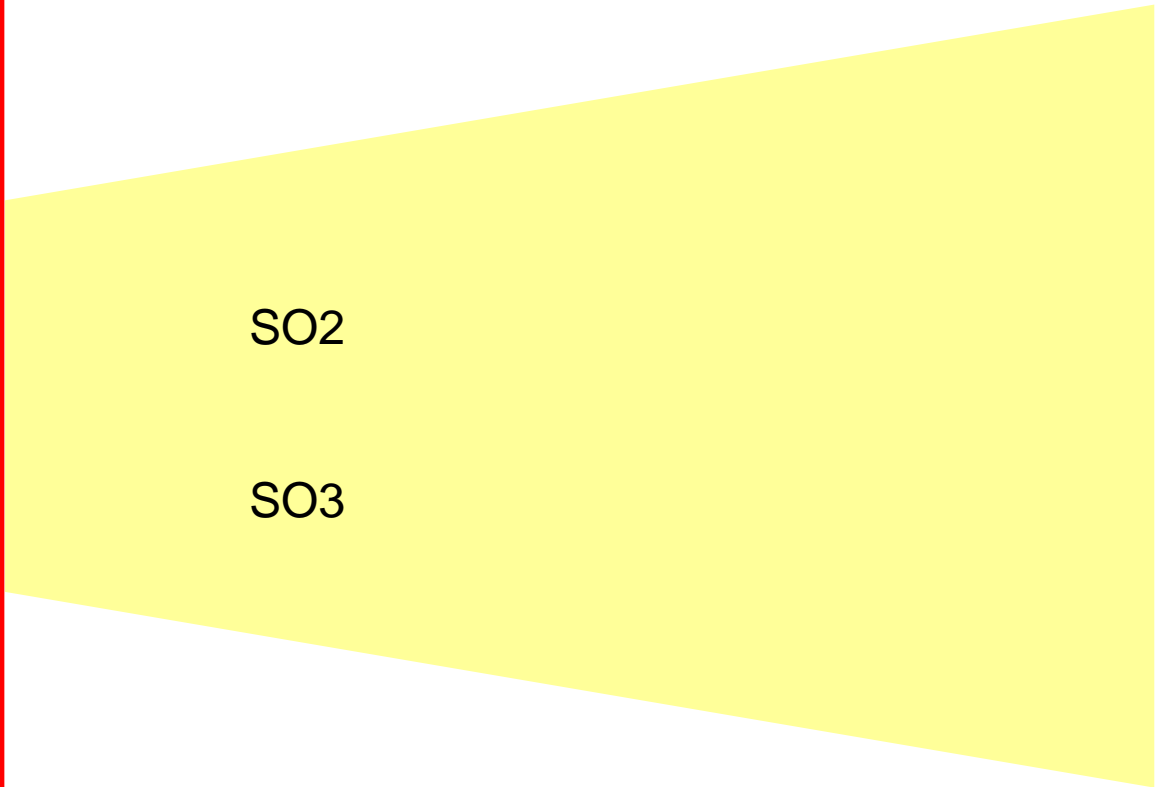
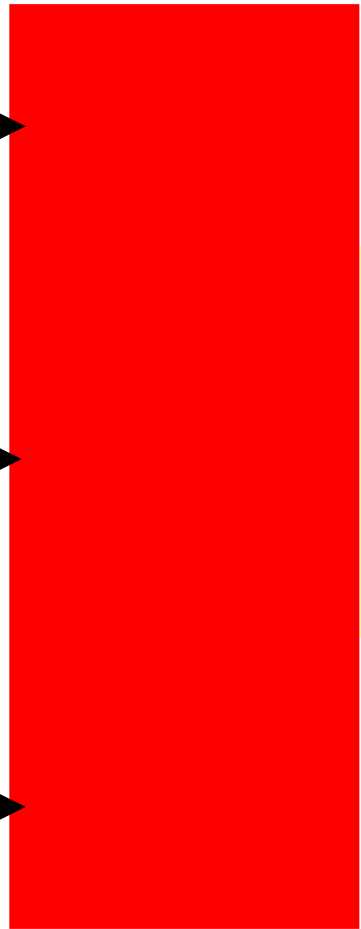
Air
O
N



Fuel
H
C
S



Oil
M
S

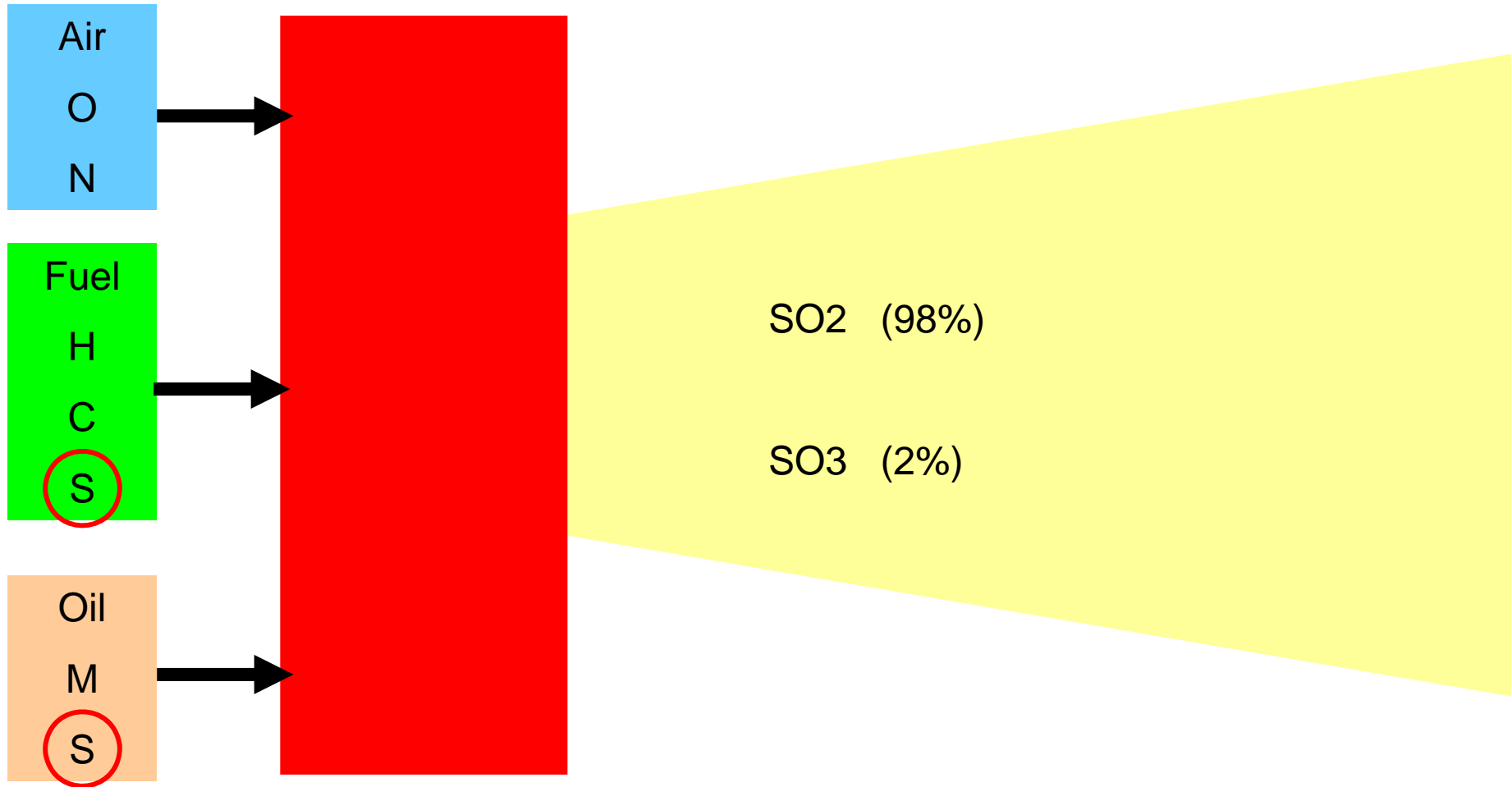


SO₂

SO₃

Combustion

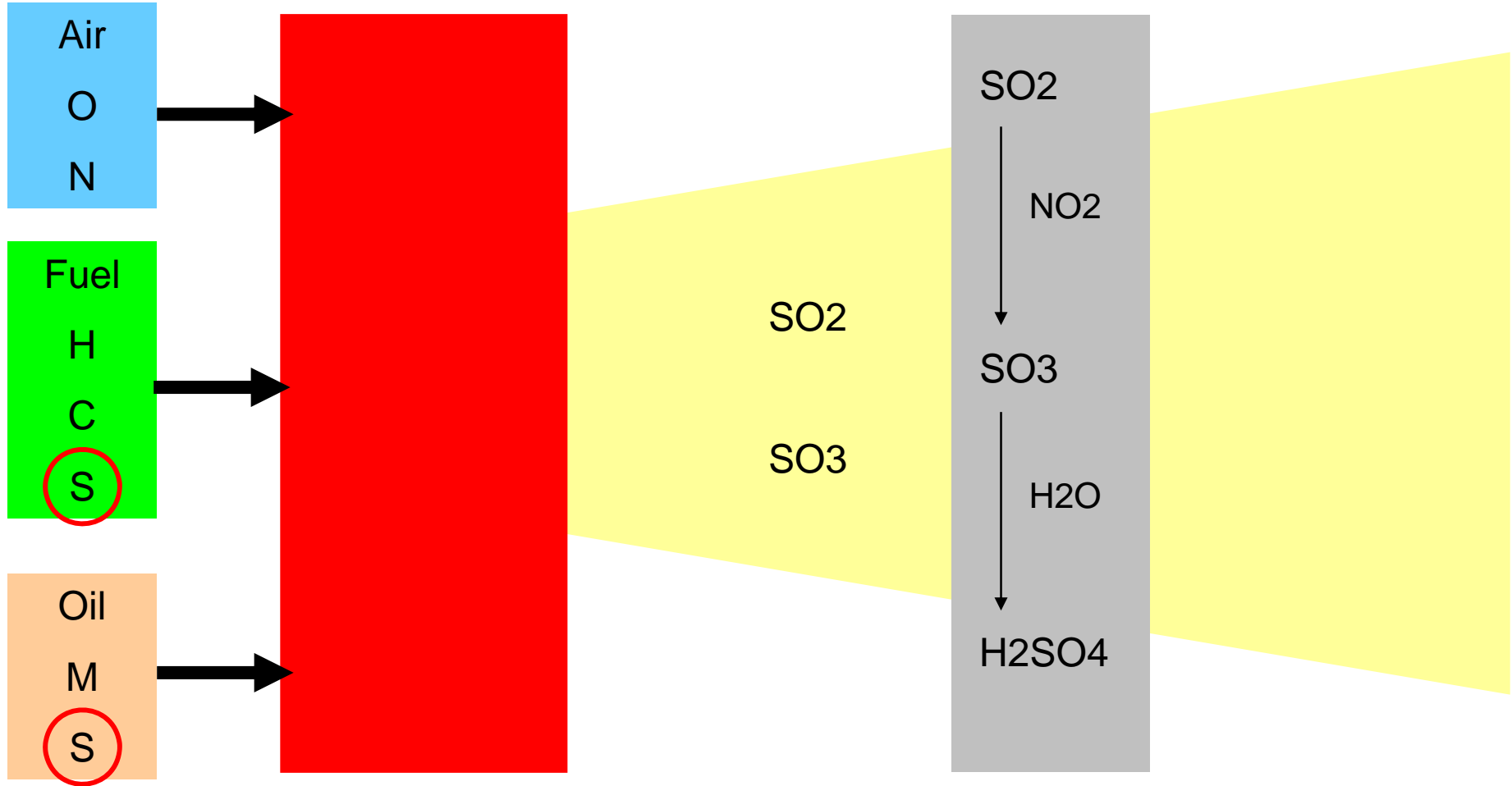
Exhaust flow

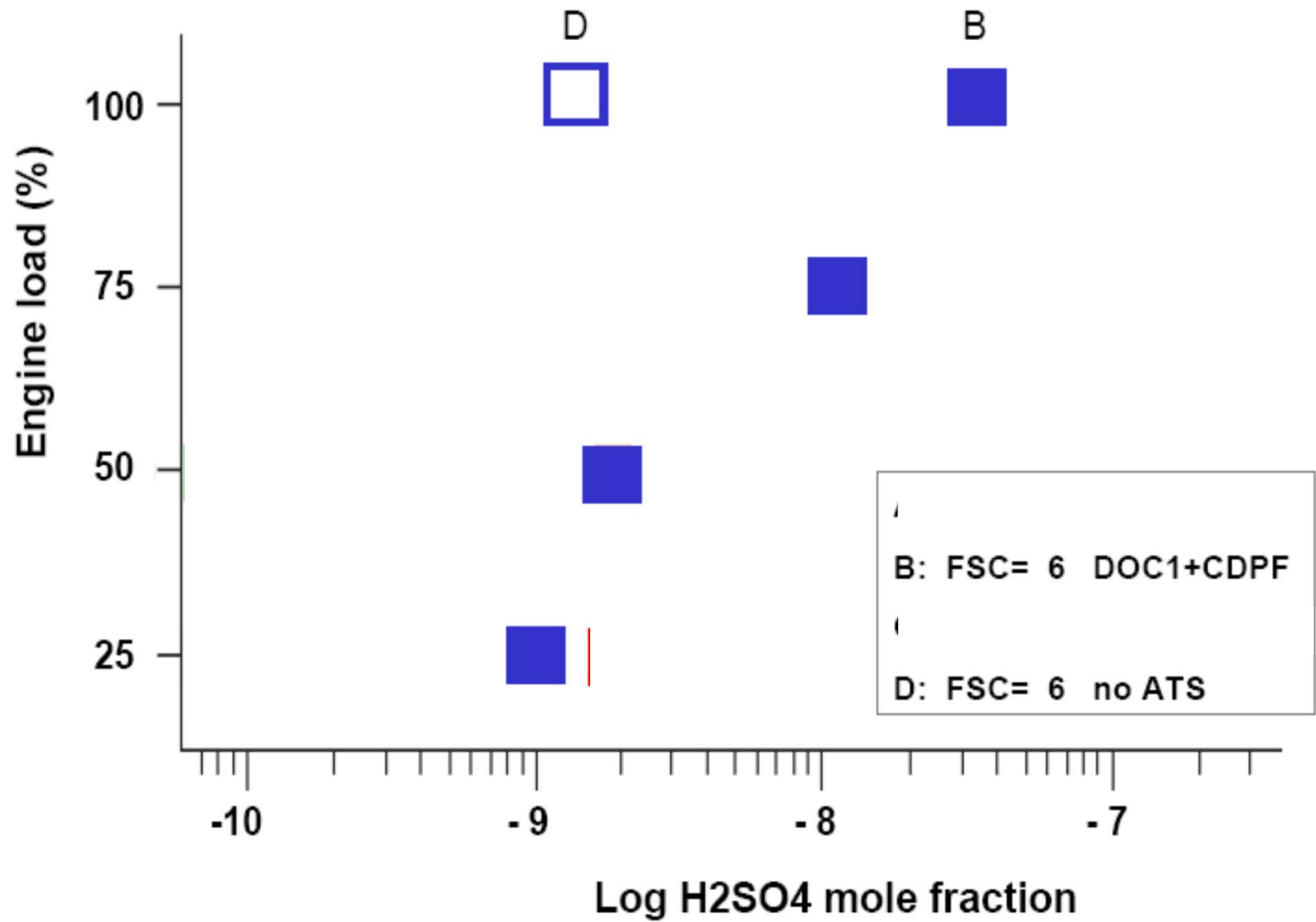


Combustion

Exhaust flow

Catalytic particle filter

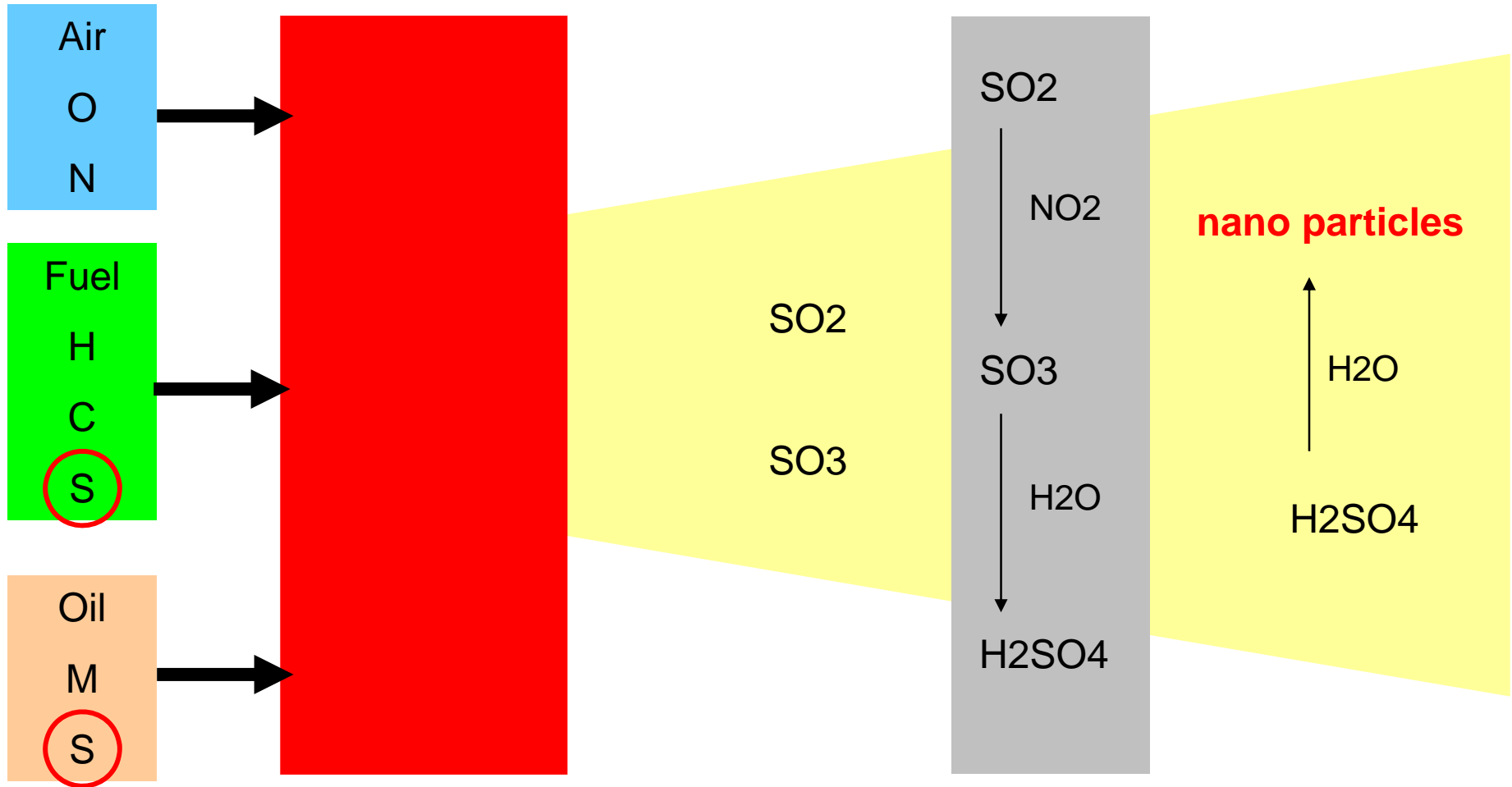




Combustion

Exhaust flow

Catalytic particle filter



Combustion

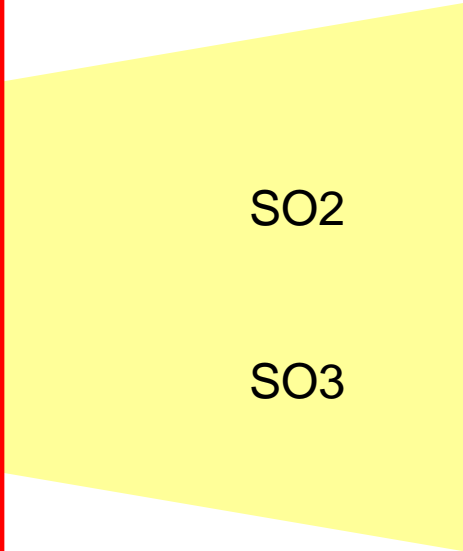
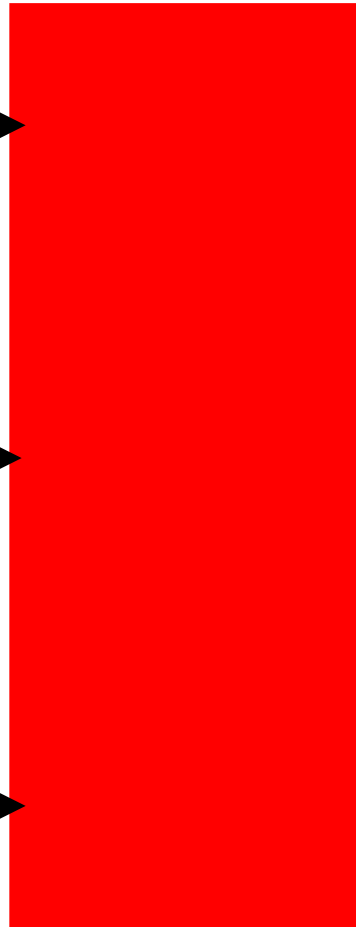
Exhaust flow

Catalytic particle filter

Air
O
N

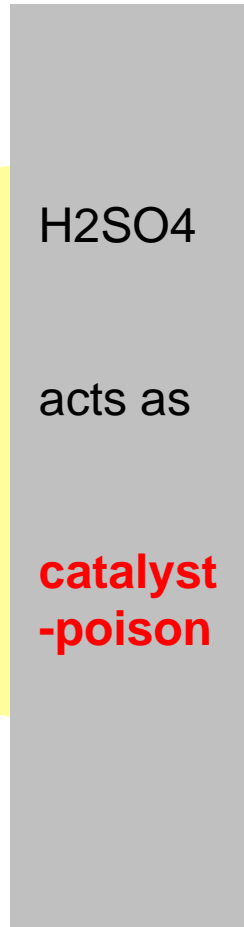
Fuel
H
C
S

Oil
M
S



SO₂

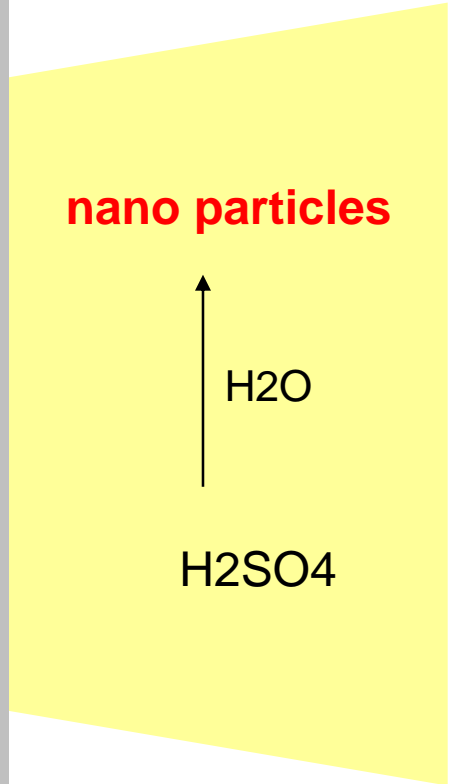
SO₃



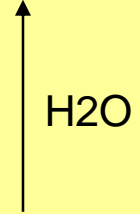
H₂SO₄

acts as

**catalyst
-poison**



nano particles



H₂SO₄

Example

Fluorine (F)
(the „Tiger of chemistry“)

Combustion

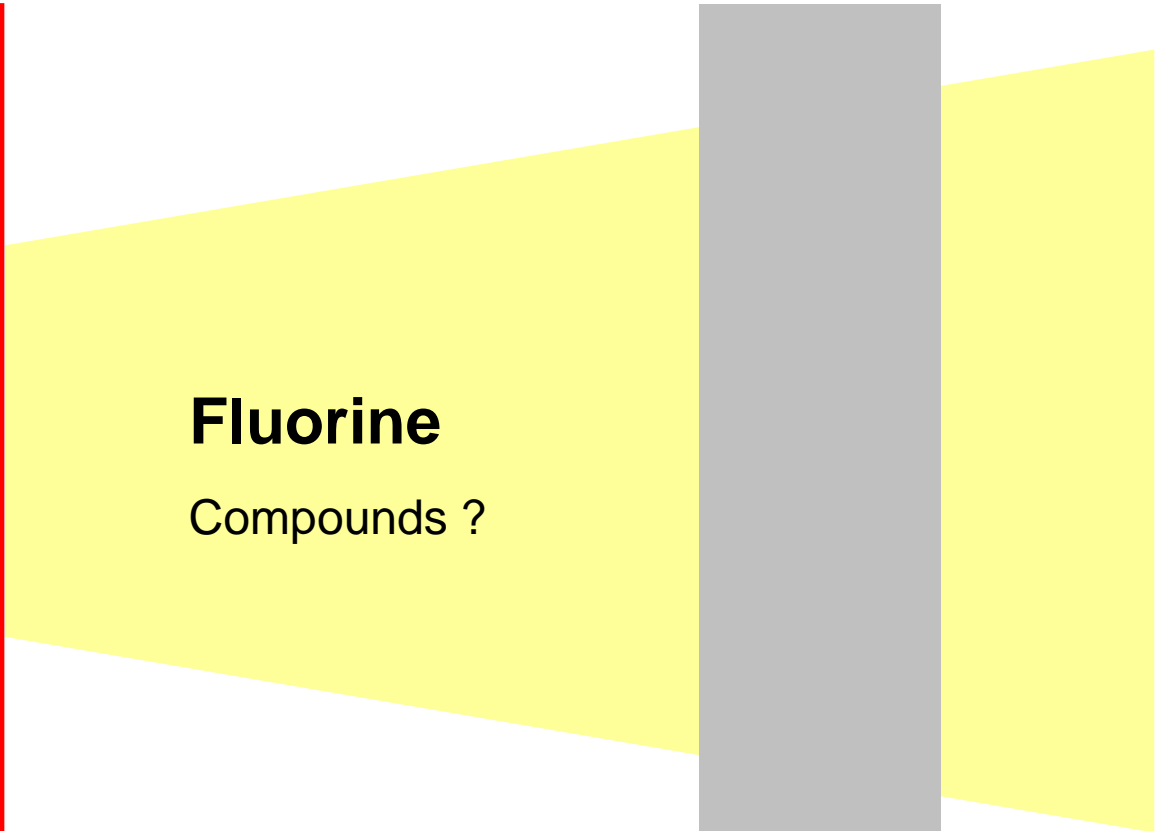
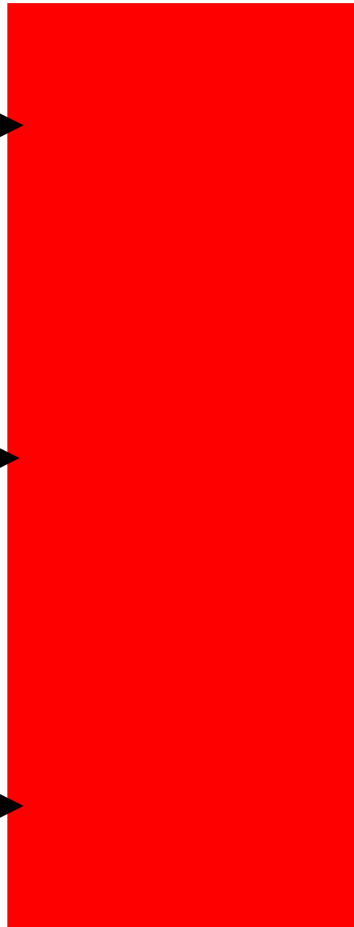
Exhaust flow

**Catalytic particle
filter**

Air
O
N

Fuel
H
C
S, F

Oil
M
S, F



Fluorine
Compounds ?

Fluorine

- In the chemistry literature often termed „The Tiger of Chemistry“ since it is extremely reactive
- Due to its large electronegativity, F tends to form very strong acids
- Some contain also S besides F
- Some have an extremely corrosive and toxic nature
- However, no information available on F-species in motorcar exhaust and fuel !
 - Screening of international literature
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Example

of acid bearing F and S

FSO₃H

Combustion

Exhaust flow

**Catalytic particle
filter**

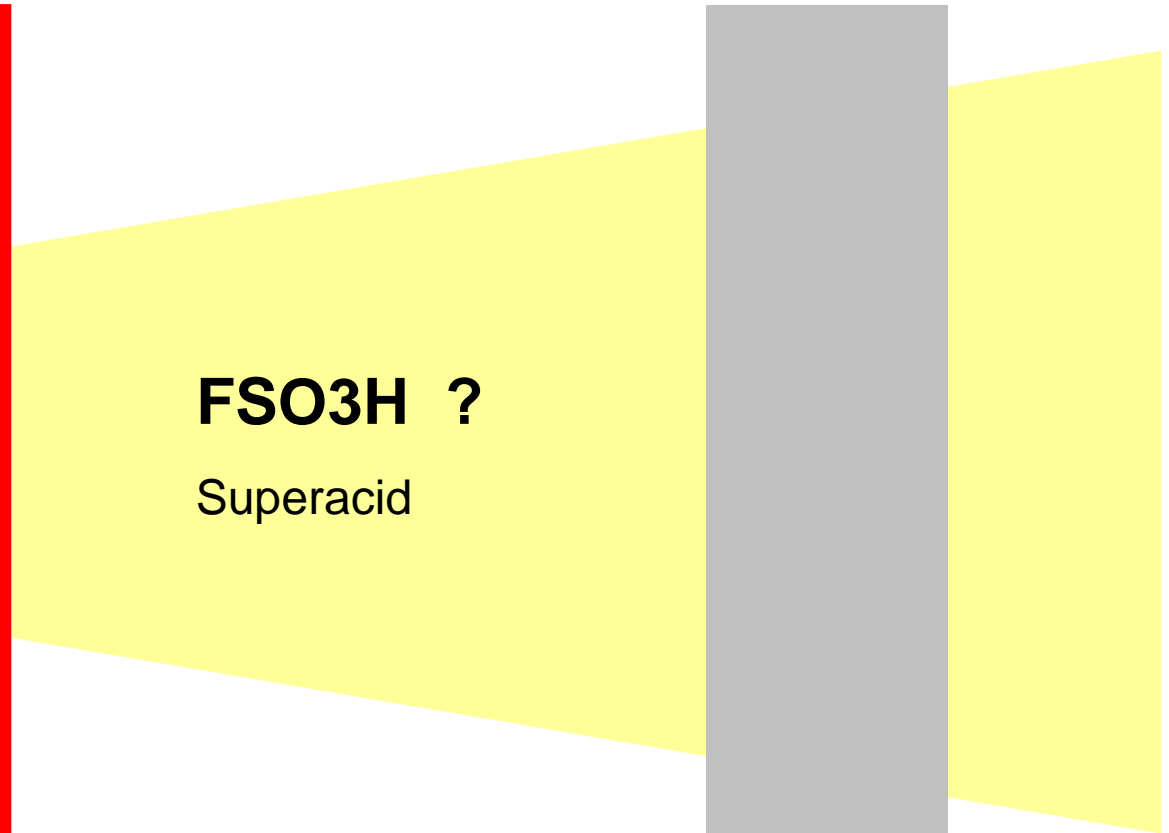
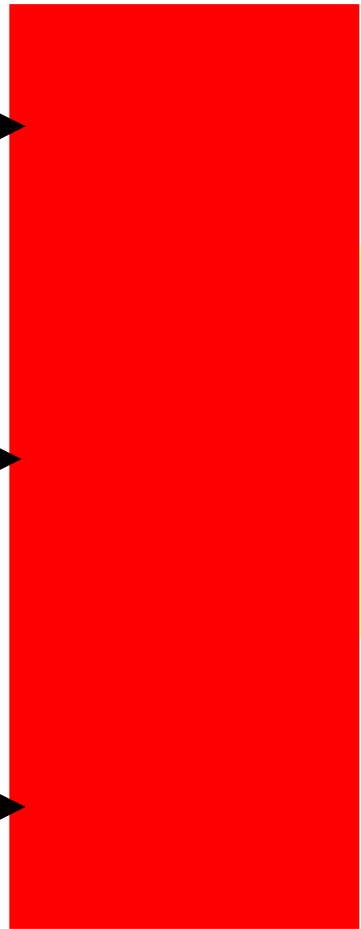
Air
O
N



Fuel
H
C
S, F



Oil
M
S, F



FSO₃H ?
Superacid

Combustion

Exhaust flow

**Catalytic particle
filter**

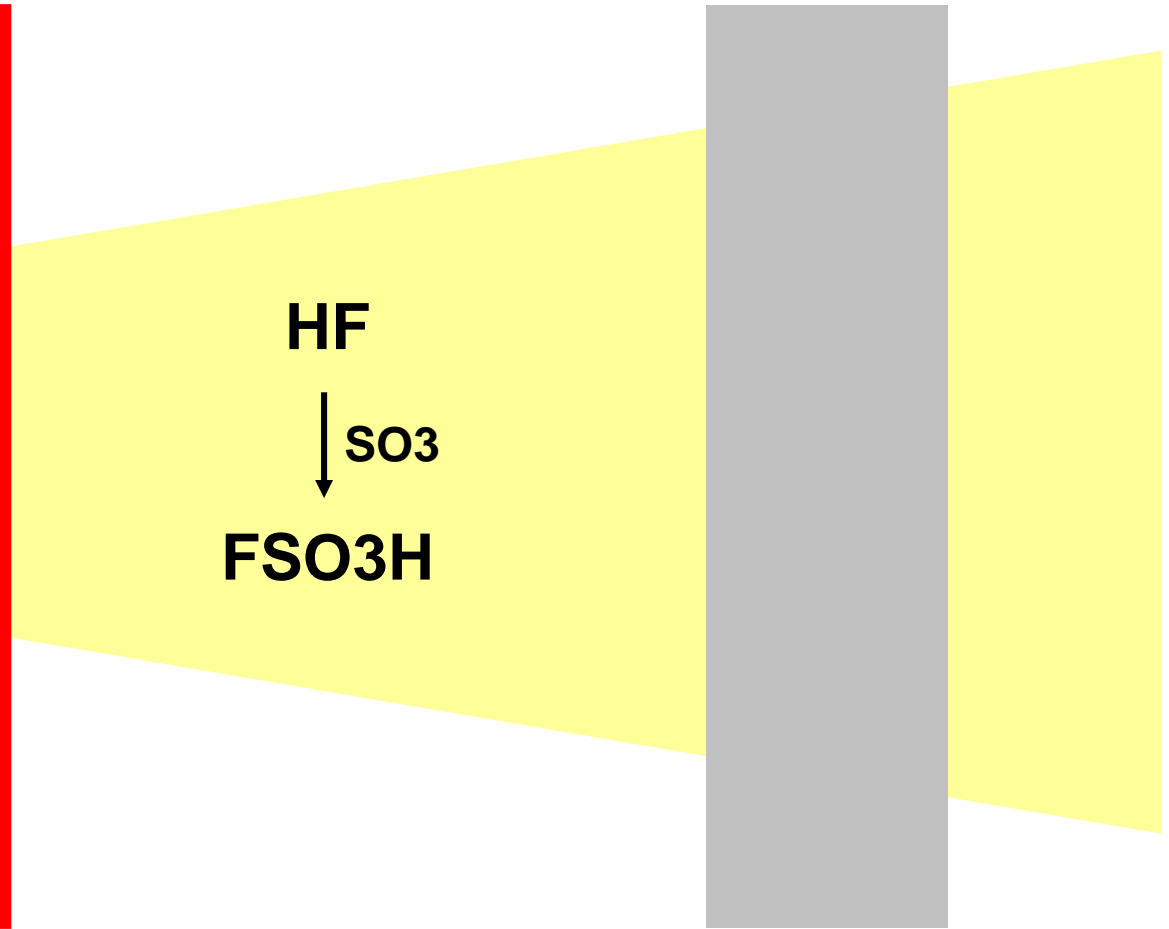
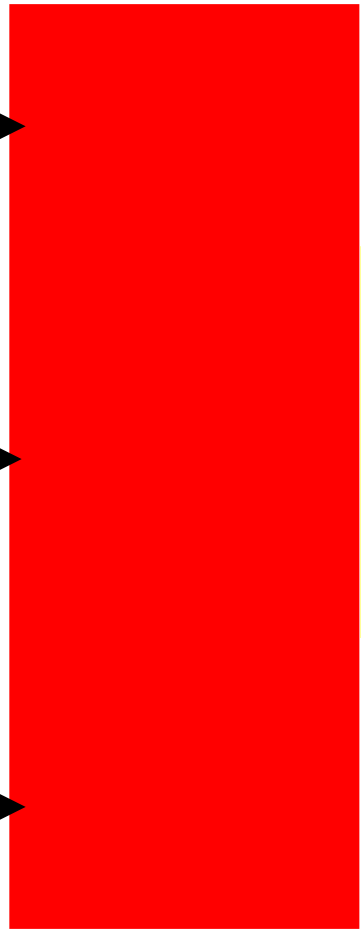
Air
O
N



Fuel
H
C
S, F



Oil
M
S, F



HF



SO₃

FSO₃H

FSO₃H

- Superacid
- highly toxic and highly corrosive
- hydrolyzes to release HF
- H₂O + FSO₃H is violent, similar to H₂O + H₂SO₄
- FSO₃H + H₂O much more violent than H₂SO₄ + H₂O
every single FSO₃H - drop makes a little explosion

Conclusions

- F-acids have been detected in **exhaust**
- Some undergo **co-adsorption with H₂SO₄**
- Likely F-source seems to be the **fuel**
- is F a Diesel **OXICAT poison** ?
- **ATS** efficiently **removes** organic F-species
- Future **fuel F-analyses** are needed. Is F contained only in fuels from **certain refineries**?

Acknowledgements

- Collaboration partners
 - Helsinki
 - Tampere
- DLR team
- MPIK team

Thank you
for your interest