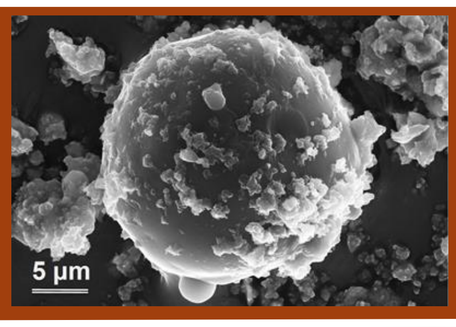
Design Project – SIE 2022

Students: Mageline Duquesne, Marie Pigneres

Unisanté Supervisors: David Vernez, Jean-Jacques Sauvain, Guillaume Suarez

EPFL Supervisors: Florien Breider, Satoshi Takahama

What are the sources linked to ambient air oxidative potential ?



Motivation: Key numbers

+ 2000 deaths

from particulate matter (PM*) exposure in Switzerland, 2016

10 times more deaths than car crashes

caused by PM* in Switzerland, 2016

Need to identify what makes a particle harmful to target the sources to reduce

Objectives

- Identify which functional groups and metals correlate with the oxidative potential of PM
- Assess the potential of a few protocoles for functional group analysis from PM collected on glass fiber filters

Working material

5 used sampling filters from Vaud'air official measuring station on which the OP has already been measured

What is the oxidative potential (OP) ?

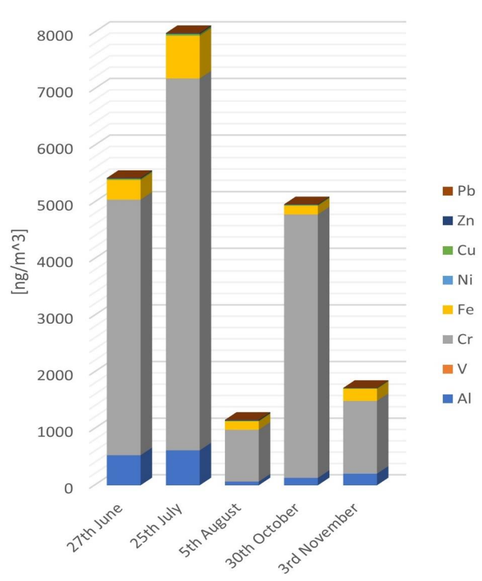
Measure of ability of a substance to oxidize a chemical / biological probe
Used to predict oxidative stress driven by PM

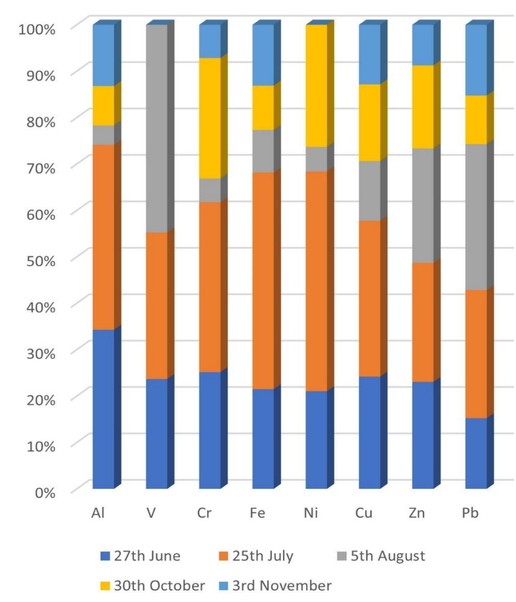
Methodology

1. Quantitative metal analysis with Inductively Coupled Mass Spectrometry (ICP-MS/MS)
2. Tests and comparison of different PM extraction and deposition methods of Attenuated Total Reflectance Fourrier-Transform Infrared Spectroscopy
3. Correlation analysis of the results obtained with the OP measured

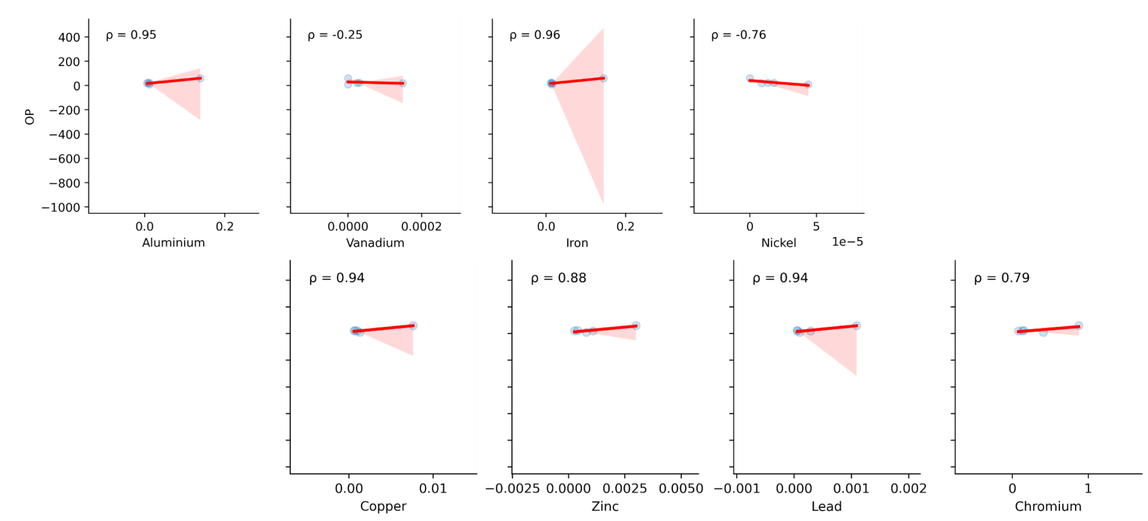
ICP-MS/MS: Results

Metal composition and concentrations





Correlations between metal concentrations and OP, normalized by PM mass



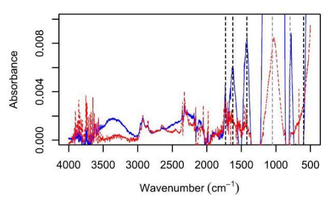
FTIR Spectroscopy: Results/ Method discussion

Single-bounce ATR-FTIR

Methods	Results	Interpretation/ Remarks

Mechanical deposition

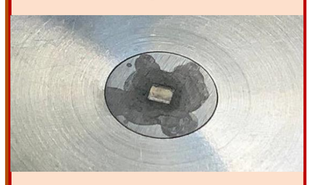
Pressing of the filter against the crystal with the ATR tool in grinding motion in order to deposit as much mass as possble onto the crystal

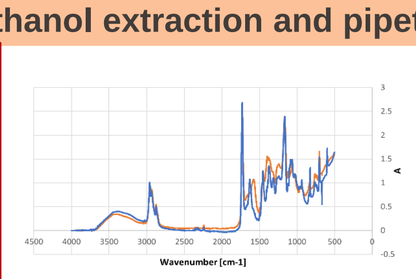


Fast method,very poor mass transfer to the crystal yielding hardly exploitable spectra (very low absobance), potential to increase mass transfer by inserting small ball of aluminium foil between filter and clamp

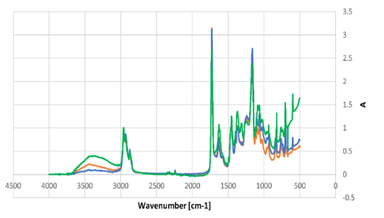
Methanol extraction and pipetting on FTIR crystal

Extraction of the organics by immerging the filter pieces in methanol and sonicating for better desorption. Evaporating resulting solution until reaching appropriate volume to pipette the remaining liquid directly onto the crystal and dry each drop with nitrogen flow.





1)Normalized overlapped spectra for most heavily loaded filter and blank filter presenting a baseline drift



2)Normalized spectra of the 3 different blanks, overlapped

Method

Very long deposition time (about 55 minutes per sample), uneven mass deposition that induces a bias with every deposition, formation of a slimy substance on the crystal which could inhibit propper drying and lead to unclear spectra, hiding useful peaks

Results

1) Would expect to see more differences in peak shapes since most heavily loaded filter supposed to bear many different species which the blank would not have. No clear peak shape inhetrently new within the sampling filter.
2) For normalized spectrum of a same material, one could expect less variations. Blue and orange were taken on the same day, and green on another day. Appears to be a bias induced by deposition process. Exhibit surprisingly high peaks for filters that did not get any air pumped through

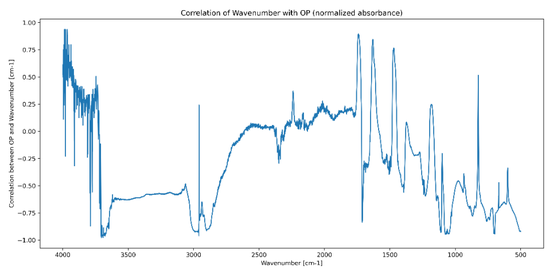
Interpretation

Low difference in magnitude between used samples and blanks:
- The evaporation could lead to a deposition of the compounds on the sides of the vials, leading to a decreased signal.
- The deposition was extremely uneven, only a small part of the deposition actually landed on the crystal.

High blank variation:
- Filters coming from different batches
- Manipulation artefacts

High peaks within the blanks:
- Product of desorption happening as the air gets through the filters,
- Destructive reactions with reactive atmospheric species like ozone.

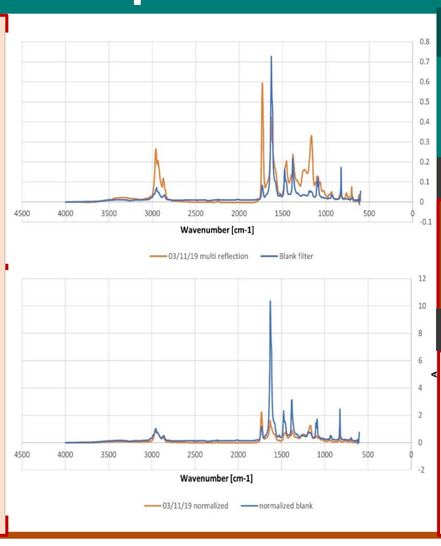
Correlations with OP



Negative correlation with some spikes of positive correlation in the '2000-500' band (do not disappear with smoothing so they don't seem to be an artifact of noise)
Those spikes are approximately in the 1800-1750, 1700-1650 (could be due to carbonyl, carboxylic, or carboxylate peaks) and 1500-1400 bands.

Multiple-reflection ATR-FTIR

Extraction of the organics within the PM embedded in the filter by immerging the filter pieces in methanol and sonicaing for better desorption. Deposition onto a 10-nodes crystal with an electrospray needle under a controlled environment



Method

Shorter than the pipette deposition followed by the drying, does require close attention due to handling of crystal, overall way less active time than pipette deposition

Resultss

No baseline drift, clear peak identification, higher absorbance values

Interpretation

Process under controlled environment which increases reproducibility significantly, filtrering of the solution before deposition on crystal and automatic deposition lower the risks of noise due to cross contamination or filter pieces deposition on the crystal, multiple nodes significantly increase sensitivity of the instrument which allows for a finer peak detection

Conclusion

ATR-FTIR method

Multi reflection ATR-FTIR appears to yield much better results in the sense that we can see an absence of baseline drift and enhanced peaks absorbance. Some peaks are detectable with this method and not with the single-bounce instrument. Both methods are probably perfectable but the electrospray on multiple reflection ATR-FTIR looks the more promising, and steps to perfect it might be more obvious than those for the single bounce ATR-FTIR. Furthermore, positive correlation seem to appear with peaks attributed to carbonyl/carboxyl/carboxylates

Metals analysis

A very high correlation is observed between OP and Copper as well as between OP and Iron. It has also been shown that a high correlation (0.95) is observed between these two metals. Meaning that the influence they have independently on OP is difficult to described.
Since Lead has a low correlation (0.4) with OP, it is possible that Lead has a reduced influence on the OP of particulate matters.

Sciences et ingénierie de l'environnement