High-throughput PIXE analysis of aerosol samples

G. Calzolai, M. Chiari, M. Giannoni, F. Lucarelli, S. Nava

Department of Physics and Astronomy, University of Florence and National Institute of Nuclear Physics (INFN), Florence, Italy
Outline

• Introduction on atmospheric aerosols and source apportionment

• The role of PIXE for aerosol analysis

• The PIXE set-up at LABEC

• Performances and measurement optimization for different kind of aerosol samples

• Some applications

• Conclusions and perspectives
Atmospheric aerosol (PM)

- Suspended particles solid and liquid, diameter < 100 µm
- Concentrations in air: from $\sim 10^2$ ng/m$^3$ up to $\sim 10^2$ µg/m$^3$
- Important effects on both human health and environment

Lung cancer, cardiopulmonary mortalities, premature mortality

Reduction of visibility, acid depositions, climatic forcing
Source apportionment

Different sources emit different elements with characteristic ratios that do not change during transport.

Measured PM mass and composition at the sampling site (receptor)

Aerosol source apportionment (identification of sources and their contribution to PM)

Pollution abatement policies to improve air quality

Climate models to assess the role of atmospheric aerosols in climatic forcing
What do we need to study aerosols?

Many good data concerning:

- PM concentration and composition
- size distribution
- time and space evolution
- optical properties
- ...

Pollution abatement policies to improve air quality

Aerosol source apportionment (identification of sources and their contribution to PM)

Climate models to assess the role of atmospheric aerosols in climatic forcing
Why PIXE?

Many good data concerning:

- PM concentration and composition
- Size distribution
- Time and space evolution

Aerosol sampling campaigns produce huge amounts of small samples (~10-300 µg/cm²)

Fast, high sensitive, quantitative, multi-elemental techniques are necessary

*PIXE technique is non destructive: further analysis by other techniques possible!*
PIXE for aerosols analysis

+ • 5-10 min bombardment to detect up to 20 elements (Na to Pb)
  • Good detection limits down to μg/g (ng/m³)
  • Possibility to analyze sample with little mass
  • High time resolution
  • Non-destructive analysis without any sample preparation
  • It can be complemented with other IBA techniques

- • PIXE provides only part of the desired information
  • Other competitive techniques: ICP-MS
    XRF
    SR-XRF
Non-IBA complementary techniques

PIXE provides only part of the desired information...

TC, EC, OC: THERMO-OPTICAL ANALYSER (SUNSET)

Aerosol campaings: an integrated approach involving different techniques is needed!
When PIXE on aerosols?

Other competitive techniques...

A prerequisite is the use of a proper experimental set-up which fully exploits PIXE potentialities.

PIXE must be used when its application can give unique information or can give final results in a far simpler way with respect to other competing techniques.

- Very short measuring time (~ 60 s instead of several m or h): hundreds of samples can be analyzed in one day
- Detection of all soil related elements: study of dust episodes
- Analysis of very low mass samples: samples collected with high time resolution (e.g. 1 hour)
- No sample pre-treatment: fundamental for very low mass samples (e.g. remote sites aerosol, mineral aerosol in polar ice cores)
Aerosol study at LABEC

External beam for aerosols

3 MV Tandetron Accelerator

Laboratory of nuclear techniques for the Environment and the Cultural Heritage

Different samplers for different temporal/size resolutions: different collection substrata and measurement optimizations.
External set-up

- Easy handling, positioning, changing and/or scanning of the samples
- Good heat dissipation: reduced loss of aerosol volatile components (Cl, Br) under beam irradiation
- No mechanical stress for transients to/from in-vacuum conditions
The PIXE-PIGE set-up

**HPGe Detector\(\gamma\)**
60 x 23 mm, 28%
1 keV @1.33 MeV

**Si(Li) “BIG” Detector**
\(X > 5 \text{ keV}\)
80 mm\(^2\), 3mm, 175 eV

**SDD “SMALL” Detector**
\(X < 6 \text{ keV}\)
10 mm\(^2\), 300 \(\mu\)m, 145 eV

**Faraday cup**

| low-Z elements | high \(\sigma_X\) | thin window |
| medium-high-Z elements | low \(\sigma_X\) | large solid angle |
|                     |                   | low-energy X-rays attenuated |

as it was presented at CAARI 2010
Which extraction window?

- Progressive thinning of the 7.5 µm Upilex window, breaking after about 800-900 µC of integrated charge.
- Measuring with ~100 nA, replacement needed every ~ 2-3 h.
- Variation of the beam energy on the sample, which can complicate the quantitative analysis with the PIGE technique.

500 nm thick Si₃N₄ window by Silson.

After 5 months, >130 mC; no need to change it after almost 2y!
Silicon Drift Detectors

SDDs for IBA analysis:
• better resolution with respect to Si(Li)
• moderate cooling (-10/-40°C) achievable with Peltier cells
• high counting rates (up to ~50 kHz at 0.5 µs shaping time)

BUT
their use for a complete characterization of X-rays was limited by the small thickness and surface areas available

SDD was introduced only for low-energy X-rays detection

• 145 eV (FWHM at 5.9 keV)
• 300 µm thick, 10 mm² area, collimated to 7 mm²
• ultrathin window (8 µm Be)
• (+ He flow)
Magnetic proton deflector

When using PIXE detectors with thin entrance window the use of a magnetic proton deflector is mandatory as backscattering of protons from the target causes:

• pile-up increase
• energy resolution deterioration
• damage of the detector

The limit dose of $10^9$ protons/cm$^2$ (corresponding to a significant deterioration of the detector performance due to radiation damage) would be almost reached during the measurement of only 1 streaker sample!
New SDD “big”

- Dimensions: 450 $\mu$m thick, 113 mm$^2$ area, collimated to 80 mm$^2$

- Better resolution: 165 eV (FWHM a 5.9 keV @ t=1 $\mu$s)

- Detector closer to the entrance window: higher solid angle

- Possibility to manage high counting rates (up to 50 kHz at 0.5 $\mu$s shaping time).

- Smaller thickness: 450 $\mu$m (previous one: 3.5 mm) $\rightarrow$ less Compton background: very important for measurements on aerosol collected on Teflon filters (CF$_2$)
“Big”: SDD vs. Si(Li)
“Big”: SDD vs. Si(Li)

![Graph showing sensitivity vs. X-ray energy (KeV)]
2-SDD PIXE set-up

HPGe Detector(γ)

SDD “SMALL” Detector (E_x < 6 keV)

SDD “BIG” Detector (E_x > 4 keV)

F. Lucarelli et al., NIM B 318 (2014)
Samples with hourly resolution

- Most particulate emissions and atmospheric dilution processes change within a few hours. Daily samples can not track these rapid changes.
- Receptor models benefit of high inter-sample variability in the source contributions, which is enhanced when increasing the sampling time resolution.

![PM2.5 on Nuclepore](image1.png)

![PM2.5+10 on Kapton/Kimfol](image2.png)

beam size (1 x 2 mm\(^2\)) corresponding to 1h point

Only with PIXE!
“Big”: SDD vs. Si(Li)

\[ E_p = 2.5 \text{ MeV} \]
MDLs “Big”: SDD vs. Si(Li)

PIXE analysis of 1 week samplings: from 9h to 3-6h!

$E_p = 2.5$ MeV
Hourly samples: which energy?

Increasing the beam energy:
- X-ray emission cross-sections increase
- BUT: also the background increases

MDL study
Standard daily samples

PM1, PM2.5
or PM10

**Teflon filters:**

- Teflon (CF$_2$) is very clean
- It is possible to quantify Si.

**BUT**

- Strong Compton background due to $\gamma$-rays from F that worsen the MDLs
- With currents above 6-7 nA, the pile-up in the Si(Li) detector reaches unsustainable levels and saturation is reached in the preamplifier.
“Big”: SDD vs. Si(Li)

$E_p = 3.0$ MeV
MDLs “Big”: SDD vs. Si(Li)

Blank Teflon, $E_p = 3.0$ MeV

The thinner thickness of the SDD drastically reduces the problems due to Compton background and the possibility to manage higher counting rates allows the use higher currents.

i ~ 5 nA, $t = 500$ s
MDLs “Big”: SDD vs. Si(Li)

Blank Teflon, $E_p = 3.0$ MeV

PIXE analysis of 1 daily sample: from 400 s to 60 s!
Hundreds of samples may be analyzed in 1 day!
PIXE outstanding technique for the elemental analysis of aerosol samples
Daily samples: which energy?

The F of Teflon gives rise to a strong Compton background in PIXE spectra due to the emission of several \(\gamma\)-rays from the \(^{19}\text{F}(p,p'\ \gamma)^{19}\text{F}\) and \(^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}\) reactions.
Daily samples: which energy?

Comparison between two “good” energies for aerosol samples on Teflon analysis.

MDL (µg/cm²)

Elements

SDD 2200 KeV
SDD 3000 KeV
Examples of spectra

EMEP teflon MONTELIBRETTI 50nA 120s

EMEP teflon AUCH MOSS 100nA 240s

EMEP teflon MONTELIBRETTI 50nA 120s (x50)

EMEP teflon AUCH MOSS 100nA 240s (x50)
EMEP

EMEP (European Monitoring and Evaluation Programme) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution for international co-operation to solve transboundary air pollution problems.

EMEP periodically arrange intensive monitoring periods; in 2012-2013 one of the major focus was to measure chemical speciation in PM$_{10}$ with special emphasis on mineral dust, with daily samplings for two one-month periods in 14 sites.

The Chemical coordinating Centre decided to assign to LABEC the measurement of all the filters collected in the two intensive campaigns for the determination of all the soil-related elements to assess the contribution of natural episodes (like Saharan dust transport).

~ 1000 Teflon filters to be analyzed
Mineral dust (µg/m$^3$)

Mineral load: obtained by the addition of the SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ concentrations, and the dust contribution of Na$_2$O, K$_2$O, CaO and MgO after the subtraction of their marine contribution from the bulk concentrations.
Mineral affinity

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Mineral dust events

Mineral dust concentration graphs for different dates and locations.
Sea salt (µg/m³)

Courtesy A. Alastuey
Trace metals: heavy oil combustion (ng/m$^3$)
• Test existing and future mitigation measures for aerosol pollution

• Develop new strategies for the improvement of air quality in Southern European countries

• The project involves public and private institutions of Spain, UK, Portugal, Italy and Greece.

• AIRUSE will firstly harmonize PM monitoring and modeling methods to determine the contribution of air pollution sources

• Four urban areas have been selected for this purpose: Barcelona (Spain), Athens (Greece), Porto (Portugal), Florence (Italy).

\[\sim 1000 \text{ Teflon daily samples} \]
\[\sim 32 \text{ streaker samples (~5000 points)} \]
Traffic source

FIRENZE

NG/m³

PORTO

ng/m³
Biomass burning

FIRENZE

PORTO
Source apportionment with hourly samples

Average daily trend of a source

Polar plots: location of the source (correlation of the contributions of the source with wind speed and direction)
Multistage cascade impactors

- SDI (Small Deposit area Impactor)
  - 12 stages from 45 nm to 8.5 μm (11 l/min.)
  - Small particle collection area (< 8 mm)
- Developed to collect aerosol for PIXE in-vacuum analysis with large beams
- In an external set-up it is not possible to work with large beams
Multistage Cascade Impactors

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Homogeneous scanning of the deposit area
Arctic aerosol

Long range transport

Local dust event: crustal elements mode shifted to bigger particles
Conclusions

\( i \sim 50-100 \text{ nA} \)
Measuring time: \( \sim 0.5 - 3 \) minutes
Daily samples collected in 1 year  \( \rightarrow \) 1-2 days

\( i \sim 100 - 300 \text{ nA} \)
Measuring time: \( \sim 1-2 \) minutes/spot
1 sampling week with 1 h resolution: 168 spots!
1 week sampling  \( \rightarrow \) 3-6 hours

\( i \sim 50 - 300 \text{ nA} \)
12 stages sampling  \( \rightarrow \) 3-4 hours

Application in other fields foreseen: e.g., for cultural heritage where very low beam currents and doses are required to avoid damaging the artifacts.
Further (recent!) improvements

• Small: from a 10 mm$^2$ SDD to a 30 mm$^2$ SDD

• Big: a new SDD with same characteristics as the previous one in order to get a double statistics
Thanks for your attention!

Giulia Calzolai  calzolai@fi.infn.it  http://labec.fi.infn.it