Characterization of atmospheric aerosols using Synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) and Fe K-edge total reflection X-ray fluorescence (TXRF)-X-ray absorption near edge structure

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Why did I choose this topic?
Why do I chose this topic? (Contd.)

1. Rather than usual way of characterizing a readymade sample, why don’t we think about a little bit different way?

2. Also, is there any way to improve our global environment by using Synchrotron technique? Generally, people are accusing us (researchers) of polluting the atmosphere by radiation and other things.

3. Atmospheric aerosols have impact not only on human health but also on geo-ecological process such as nutrient transport into the oceans and cloud formation.

4. The atmospheric supply of iron, which is an important micro-nutrient to marine plankton, to the oceans has been studied intensively for a couple of years.
Overview of this Study

- Only a few techniques are capable to determine the species of metals from the sample of the order of pg. The amount of sample found in this study of aerosols is in between (34 – 920) pg of Fe.

\[ 1 \text{pg} = 10^{-15} \text{kg} \]

- Iron is the most abundant transition metal found in the atmosphere. However, its oxidation state is not properly known. The oxidation state of an element gives further important information towards toxicity.

- The uptake of Fe(II) is easy for the marine organism opposite to that of Fe(III). Thus, the change in oxidation state is important.
Overview of this Study (Contd.)

• A new technique of characterization of atmospheric aerosols down to the particle size of 0.015 μm by using Synchrotron total X-ray fluorescence (SR-TXRF).

• The potential of total reflection X-ray fluorescence – X-ray absorption near edge structure (TXRF-XANES) for the speciation of Fe (II) / Fe(III) down to the 34 pg is discussed.

• Also, the oxidation state of the Fe present in aerosols sample is determined.

• The results from the Fe K-edge Synchrotron radiation total reflection X-ray fluorescence (SR-TXRF)- X-ray absorption near edge structure analysis of aerosols prove that Fe(3) was mainly present in all particle size fractions.
What are atmospheric aerosols?

• Atmospheric aerosols (or particulate matter) are solid or liquid particles or both suspended in air with diameter usually less than 1 micrometer.

• An aerosols include both the particles and the suspending gas in air. For examples, mist, clouds, dust particles, smokes etc.

Figure: Pictures of aerosols taken from Scanning Electron Microscope (SEM), where the size of the particles are magnified by 2000 times. Source (Wikipedia)
Sample Collection

• The sample of aerosols were collected with a low pressure Berner impactor on Silicon carriers, that enables sampling of particles down to 15 nm, over the time period of 60 to 20 minute each.

• The surface roughness of the silicon carriers measured by atomic force microscopy was found to be smaller than those of glass carbon and quartz glass carriers, which are commonly used for TXRF analysis.

• The sedimentation and transport of aerosols were strongly depend on the particle size.

• The particles were collected in four and ten size fractions of (10.0-8.0)μm, (8.0-2.0)μm, (2.0-0.13) μm and (0.13-0.015)μm which were analyzed with both Fe K-edge TXRF-XANES and SR-TXRF. AND

(16-8) μm, (8-4) μm, (4-2)μm, (2-1) μm, (1-0.5) μm, (0.5-0.25) μm (0.25-0.130) μm, (0.130-0.060) μm (0.060-0.030) μm (0.030-0.015) μm which were analyzed by Fe K-edge TXRF-XANES.
Apparatus used for sample collection

Figure: (a) Low pressure Berner impactor with modified impaction plate. (b) Acrylic glass carries (c) Silicon-wafer carries
Figure: PM 2.5 aerosol inlet for atmospheric aerosol sampling and scanning tunneling microscope (SCM)
Experimental Technique:

• TXRF: Total Reflection X-ray Fluorescence is the surface elemental analysis technique generally used for the ultra trace analysis of particle, residues and impurities on the smooth surfaces.

• TXRF is basically an energy dispersive XRF technique in a special geometry.

• XRF geometry: The angle of incidence of X-rays is greater than the critical angle and the primary radiation penetrates into the sample.

• TXRF geometry: The angle of incidence is less than the critical angle and the primary radiation is reflected off of the sample surface.

• XAFS EXAFS and XANES: These are the spectroscopic technique that uses X-rays to probe the physical and chemical structure of matter at an atomic scale.
TXRF Technique

Figure: Schematic set up for TXRF analysis
Experimental measurements and Calculation

• The particles size are determined by scanning electron microscope (SEM).

• To confirm the oxidation state of Fe from SR-TXRF-XANES analysis, the iron containing compounds such as Fe(II) sulphide, Fe(II) oxalate, Fe(II) chloride, Fe(II) sulphate, Fe(III) sulphate, Fe(II)oxide, Fe(III)oxide, Fe(II) ammonium sulphate, Fe(III) ammonium sulphate as a reference.

• These reference compounds were prepared from suspensions in isopropanol and are pipette on the reflectors.

• The excitation energy was tuned with Si (111) monochromator from 6950eV to 7600eV as Fe has k-edge at 7111eV.

• To check the energy calibrations, Fe foil was recorded in transmission mode also.
Result and Discussion:

• Before the analysis of the aerosols blank values (aerosols that might originate from the internal structure and from the sampling device) were studied.

• Further, the loss of aerosols particles from the “bounce off” effect was also investigated.

• The results from the SR-TXRF analysis of the collected aerosols are shown in figure below:
Figure: Atmospheric aerosol’s amount determined from the three different samplings: (a) 60 minute day time, (b) 20min day time and (c) 60 min night time in four size fractions.
Result and Discussion (Contd.)

Iron and Lead in Aerosols

• It is found that the concentration of Iron and lead in the sample varied from (3-24)ng/m-3 and (0.045 – 4) ng/m-3 depending on the size of particles.

Table 1: Amounts of Iron and Lead found experimentally in four size fractions. (a) 60min, (b) 20min and (c) 60min at night.
• The scan of different Fe containing salts such as Fe(II) sulphide, Fe(II) oxalate, Fe(II) chloride, Fe(II) sulphate, Fe(III) sulphate, Fe(II)oxide, Fe(III)oxide, Fe(II) ammonium sulphate, Fe(III) ammonium sulphate as a reference, to determine weather Fe(II) or Fe(III) is mostly present in the atmospheric aerosols, is as shown in below:
Result and Discussion (Contd.)

• The energy calibration of these curves were done by using absorption edge of Fe as a reference.

• Also, these curves were fitted by using IFFEFIT Athena software.

• The XANES curves were pretty matched with standard curves, which confirms that the procedure used here to study TXRF-XANES analysis were correct.

• It is found from the XANES analysis that Fe was present in the oxidation state of (III) in all four sample size.

• By suspecting the oxidation state of Fe might change during the sampling, again the aerosols samples were collected in Ar-atmosphere and analyzed, the results are as shown below:
Figure: XANES spectra from different aerosol particle size from (16-8)μm to (30-15)nm. Beyond the aerosols one Fe XANES curve from Fe(II)sulphate and one from Fe(III) oxides are shown.
Result and Discussion (Contd.)

• This also proved that, all fractions of sample contains Fe in the oxidation state of (III).

• The repetitive scans of the sample shows the same XANES, which confirms that no oxidation occurs during the measurements.
• **References:**

• Characterization of atmospheric aerosols using Synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) and Fe K-edge total reflection X-ray fluorescence (TXRF)-X-ray absorption near edge structure by U.E.A. Fittschen and etal.


• Determination of phosphorus and other elements in atmospheric aerosols using SR-TXRF by U.E.A. Fittschen and etal.


• [http://xafs.org/](http://xafs.org/)

• Atmospheric analytical chemistry by Thorsten Hoffmann and Ru-Jin Huang.
Thank You