

# Comparison of Aerosol Time of Flight Mass Spectrometer (ATOFMS) measurements with off-line techniques for determining metal concentration in atmospheric particles

Eoin McGillicuddy<sup>1</sup>, Robert Healy<sup>1</sup>, Manuel Dall'Osto<sup>2</sup>, Jean Sciare<sup>3</sup>, Franco Lucarelli<sup>4</sup>, Silvia Nava<sup>5</sup>, Xavier Querol<sup>2</sup>, Ian O'Connor<sup>1</sup>, Deborah Gross<sup>5</sup>, John Wenger<sup>1</sup>, John Sodeau<sup>1</sup>.

<sup>1</sup>Department of Chemistry and Environmental Research Institute, University College Cork, Ireland

<sup>2</sup>Institute for Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain

<sup>3</sup>LSCE, Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, Gif-sur-Yvette, France

<sup>4</sup>Dipartimento di Fisica e Scienze dello Spazio, Università degli Studi di Firenze, Via Sansone 1, 50019 Sesto Fiorentino, Italy

<sup>5</sup>INFN, Istituto Nazionale di Fisica Nucleare, Sezione di Firenze, Via Sansone 1, 50019 Sesto Fiorentino, Italy

<sup>6</sup>Department of Chemistry, Carleton College, 1 N. College Street, Northfield, MN 55057, USA

Keywords: ATOFMS, Aerosol Mass Spectrometry, Off-line, Metals.

Presenting author email: e.j.mcgillicuddy@mars.ucc.ie

Metals present in atmospheric particulate matter are associated with both natural and anthropogenic processes. Natural sources of metals in the atmosphere include volcanic activity and wind-blown dust, while anthropogenic sources include industrial processes, traffic emissions, incineration and fossil fuel combustion (Allen, Nemitz et al. 2001). The presence of certain metals in the atmosphere is of interest due to associated health effects.

The concentration of metals in atmospheric aerosols is traditionally measured using off-line techniques with particles being collected onto a substrate which is later analysed using techniques such as ICP-MS (Inductively Coupled Plasma - Mass Spectrometry), XRF (X-Ray Fluorescence) and IC (Ion Chromatography). These methods can quantitatively determine the metal component of particulate matter, but typically suffer from poor time resolution. This can lead to short-lived events being missed. More recent techniques such as PIXE (Particle induced X-ray Emission) allow samples to be analysed with an hourly temporal resolution (Chiari, Lucarelli et al. 2005). However, none of these off-line techniques can provide information on the mixing state of metals in the particles, which is useful for identification of their sources.

The interest in measuring the mixing state of individual aerosol particles has led to the development of single particle mass spectrometers. One such single particle instrument is the Aerosol Time of Flight Mass Spectrometer (ATOFMS), which provides size resolved single particle dual ion mass spectra of particles in the size range 100 nm to 3000 nm. This allows the characterisation of the primary composition of single particles (e.g. elemental/organic carbon and transition metals) along with the determination of secondary species present in the particle (such as nitrate and sulfate ions).

The ability of the ATOFMS to determine the presence of metals in ambient particles was utilised during several sampling campaigns to determine if ATOFMS can be used to measure metal concentrations in real-time. The comparisons were made during campaigns held in Cork (Ireland), Paris (France) and Barcelona (Spain). The ATOFMS ion signals for the

metals of interest were compared with measurements made using IC, PILS-IC and PIXE.

Several comparisons between the ATOFMS ion signal and the quantitative techniques provided poor correlations, with the ATOFMS ion signal intensity not being proportional to the ambient concentration. The reason for the poor correlations with the quantitative techniques may be due to the matrix effects associated with the mixing state of the particle being sampled. The mixing state can affect the ionisation of the metal in sampling with the ATOFMS. The strongest correlations were found for comparisons between the ATOFMS and PIXE measurements for several metals including Al, Fe, Zn, Mn and Pb. Fig. 1 shows the correlation between ATOFMS and PIXE measurements for aluminium. The improved correlations for these metals is likely due to them having a specific source, with several of the metals such as Pb, Zn and Mn also occurring in short sharp peaks in concentration these factors may result in the ATOFMS ion signal responding to changes in concentration in a more proportional fashion.

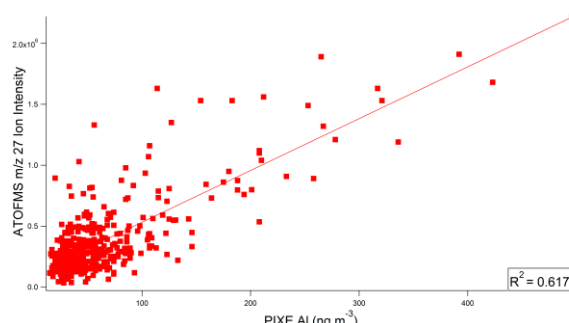


Fig. 1. Correlations between ATOFMS ion intensity (m/z 27) and PIXE mass concentrations for aluminium.

Allen, A. G., E. Nemitz, et al. (2001). "Size distributions of trace metals in atmospheric aerosols in the United Kingdom." *Atmospheric Environment* **35**(27): 4581-4591.

Chiari, M., F. Lucarelli, et al. (2005). "Characterization of airborne particulate matter in an industrial district near Florence by PIXE and PESA." *X-Ray Spectrometry* **34**(4): 323-329.

