Acta Physica Universitatis Comenianae
Volume LIV (2019) 115–121

Analysis of Aluminum in Atmospheric Aerosols at Bratislava Using PIGE Technique*

M. Ješkovský[1], M. Doktor[1], J. Kaizer[1], I. Sýkora[1],
J. Zeman[1], J. Pánik[2], P. P. Povinec[1]

[1]Centre for Nuclear and Accelerator Technologies (CENTA), Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, 842 48 Bratislava, Slovakia
[2]Institute of Medical Physics, Biophysics, Informatics and Telemedicine, Faculty of Medicine, Comenius University, 81372 Bratislava, Slovakia

Abstract: First analysis of aluminum in atmospheric aerosol were performed by PIGE technique in CENTA laboratory in Bratislava. Method for extraction of inorganic aerosol from sampling filters and preparation of thin samples were developed. Using commercial available aerosol standard materials, calibration curves were constructed for aluminum determinations. Average concentration of aluminum with standard deviation in atmosphere of Bratislava from measured inorganic aerosol samples was determined to be 109±33 ng/m^3.

1. Introduction

Identification and characterization of fine particles in the urban atmosphere is important for identification of pollutants. Non-destructive analytical techniques such PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray Emission), with sensitivity down to few μg/g, have been widely used in aerosol science [1–3], as well as in other fields like art [4], archaeology [5, 6], environmental science [7], geology [8], astronomy [9] etc. Extraction of ion beam from vacuum to atmosphere significantly simplified analysis of big samples and samples of historical and cultural heritage. The development of this methods allows focusation of the ion beam down to micro scale size and construction of so called elemental maps, where elemental analysis of even single aerosol particle is possible [10].

PIGE is an analytical technique based on registration of prompt gamma-rays produced during interaction of high energy projectile with solid sample. It can be used for determination of concentration and even for depth profiling of usually light elements, because of lower Coulomb repulsion barrier. Since absorption of X-rays emitted by low Z (usually below phosphorus) elements by sample material, PIXE technique is not appropriate for this elements and emission of gamma-rays is preferable.

One of these lighter elements is also aluminium, that can be determined by PIXE as well as PIGE [11], however PIGE technique gives more accurate results that are not affected by attenuation in the sample. For the Al determination, usually reactions with protons ^{27}Al(p, p’)^{27}Al, with emission of E = 844, 1013 keV, and ^{27}Al(p,)^{24}Mg, with emission of E keV [12], are used. Even the reaction ^{27}Al(p, p’)^{27}Al with emission

*Dedicated to Professor Peter Prešnajder on the occasion of his 70th birthday

of 171 keV gamma [13] can be used, however the background radiation, due to Compton scattered gammas of higher energies, at this energy worsen the detection limit.

Since aluminium is most abundant metal in the Earth's crust it can easily enter the atmosphere due to natural processed like soil resuspension, but also by anthropogenic activities like mining, agriculture and automobile industry. Several authors analysed elemental composition of size distributed aerosols [14–17] under different conditions, while higher concentrations of aluminium was founded in particles with bigger size.

At the Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava the CENTA (Centre for Nuclear and Accelerator Technologies) was established [18]. The laboratory comprises the system for production of various ion beams from solid and gaseous samples, the energy and mass separation and the 3 MV tandem accelerator, that is used for acceleration of the ions up to tens of MeV. One part of the beam line is dedicated to IBA (Ion Beam Analysis) techniques like PIXE, PIGE and RBS (Rutherford back-scattering) [19]. In this work, we have focused on development of sample preparation for PIGE analysis of atmospheric aerosols and calibration of CENTA setup for analysis of light elements.

2. Methods

There is a long tradition and experience at the Department of Nuclear Physics and Biophysics of the Comenius University of atmospheric radioactivity monitoring in aerosols [20]. Aerosols sampled for radioactivity measurements [21] were used for elemental analysis by PIGE technique. The sampling device has been located next to the faculty building and the location has been close to the borders with Austria and Hungary. Atmospheric air has been pumped with sampling rate of about 80 m^3/h through 25 nitrocellulose membrane filters (PRAGOPOR 4), with 0.85 μm pore diameter, stacked next to each other. PM2.5 and PM10 aerosol fractions were together collected on the surface of the filters with area of about 0.5 m^2 and were also together analysed by PIGE technique. Filters were exchanged at weekly basis.

For the PIGE analysis one of the 25 filters was separated and cut into half. Several ways of extraction of aerosols from the filter and preparation of thin samples for irradiation were tested. At the beginning the nitrocellulose filter itself was used for irradiation, but those filters are very combustible and were destroyed by used proton beam, even by low intensity, in high vacuum. Another option was mechanical separation of the aerosols from the filters, however this method suffers by a big loss of aerosols. The best results were obtained with dissolved filters in methanol. Since organic aerosols can be dissolved in the methanol, only inorganic fraction was afterwards separated from the solution by centrifugation, while the methanol was pipetted out and the remains were left evaporate.

Dried inorganic aerosols were weighted and in first attempts mixed with distilled water. 4 μL drop of the homogenized solution was dropped on 2 μm Mylar and left evaporate. However, during the PIGE measurement, as the result of the heat deposition from the proton beam, aerosol layer was cracked and fell off from the backing. Mixture of aerosols with 3% Formvar (chloroform was used as solvent) solution was therefore used for the thin sample preparation. After chloroform evaporation from the 3% solution, the thin layer of aerosols and Formvar mixture was formed.

Prepared thin targets were mounted on the sample holder for irradiation and placed inside the PIXE/PIGE chamber in the CENTA laboratory. In the CENTA laboratory, titanium hydride targets were used in MC-SNICS (Multi Cathode Source of Negative Ions by Cesium Sputtering) for production of negative proton beam. After energy and mass separation, negative protons were injected into 3MV Pelletron tandem accelerator and accelerated to 2.86 MeV energy. The energy of the protons was chosen from the calculated and measured cross-section for this reaction [12, 22], to be highest in the region and still low enough to suppress production of background from gammas produced by other elements. High energy protons were afterwards deflected and focused to the PIXE/PIGE chamber for sample irradiation. Proton beam at the sample plane had a rounded shape with diameter of about 2 mm and the angle between normal of the sample and incident beam was chosen to be about 10^{o}. BEGe detector (Canberra), with energy resolution of 1.9 keV for 1.33 Mev line of ^{60}Co, was used for spectrum acquisition and current integrator connected to the Faraday cup behind the thin samples was used for charge collection. Amptek digital pulse processor DP5 was used for data acquisition and measured spectra were analysed for presence of 843 keV and 1013 keV peaks. Non-linear curve fitting with background extraction was used for determination of peak area and obtained counts were normalized for collected proton charge.

3. Results and discussion

For the analysis of the Al in the samples, inelastic scattering reaction ^{27}Al(p, p')^{27}Al of 2.86 MeV protons with emission of the 843 keV and 1013 keV gammas was used. Absolute method, by using excitation functions, is still in development in CENTA laboratory and therefore relative method by using standard material was used in this work. From NIES CRM (National Institute for Environmental Studies Certified Reference Materials) No. 28 Urban Aerosol [23], twelve thin samples with known concentration of Al (from 45 to 0.5 mg/g) were prepared. Since RBS (Rutherford backscattering) analysis was not available at the CENTA laboratory, the thickness of the prepared samples was not experimentally confirmed. However, transmission of proton beam through samples, with known quantity of standard material, were simulated by using SRIM package [24] and energy losses of about 5% were estimated. Together with standard samples, two blank samples were produced. The first blank sample was clean Mylar backing without any preparation and represents machine background produced in the PIXE/PIGE chamber. Comparison of clean Mylar foil with the standard sample can be found in **Fig. 1**. The second one was procedural blank produced by evaporation of Formvar drop on Mylar backing. For measurement of the blank samples, 10 nA proton beam with 5 μC collected charge was used and the detection limit from background counts in the spectrum was estimated to be about 0.2 mg/g of Al in aerosols.

Calibration curves were constructed from known concentration of Al in the samples and fitted areas under gamma peaks of 843 keV and 1013 keV in measured spectrum, corrected for collected charge.

Four thin samples were prepared from aerosol filter A430 by method described before. To evaluate the losses of aerosols or dissolved aluminium in the methanol fraction (very fine fraction of aerosols can't be effectively separated by centrifugation), spectrum from

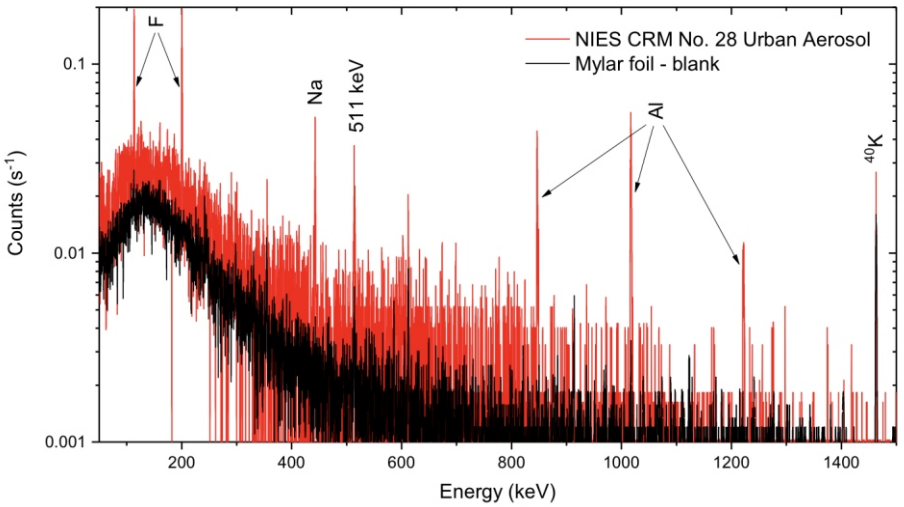

Fig. 1. PIGE spectrums of Al standard and used backing material as blank.

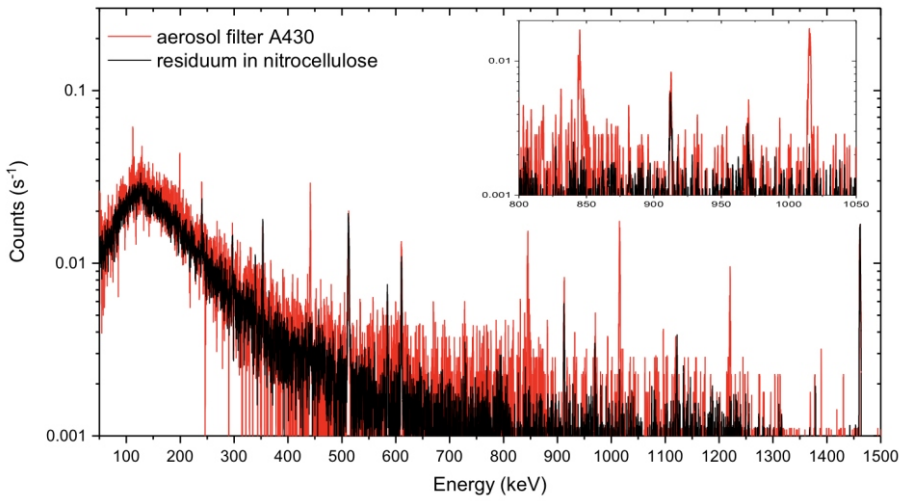

Fig. 2. PIGE spectrums of aerosols from A430 filter compared to spectrum of methanol residuum after aerosols separation.

irradiation of A430 sample and sample prepared from residuum in methanol fraction are compared in **Fig. 2**. As can be seen, no significant peaks above background were observed in spectrum of residuum sample, which means that the Al content in residuum sample was below detection limit correspond to 3 ng/m^3 of Al.

During the sample preparation, formation of "coffee ring effect" (small particles are concentrated at the edge of evaporated drop) was observed, therefore the thin samples were irradiated at several different positions to estimate the distribution of the Al in the evaporated droplet. By using the higher content of aerosol in the mixture with Formvar,

negligible formation of "coffee ring effect" was observed. Another five nitrocellulose filters (**Tab. 1**) were processed and two thin samples were produced for each filter. After irradiation, final Al concentration was calculated as arithmetic mean of measured values for 844 keV and 1013 keV for each thin sample. Uncertainty of Al concentrations were calculated as combination of statistical error and uncertainty of the calibration curve. From several measurements (at least two for each aerosol sample), standard deviation was calculated for each aerosol sample to determine the variation in surface distribution of the Al.

Table 1. List of measured aerosol filters with basic characteristics.

Filter	Sampling period	Volume (m^3)	Mass (mg)
A375	29.02.–07.03.2012	14719.6	174
A401	09.05.–16.05.2012	14108.4	65
A417	29.08.–05.09.2012	17106.1	129
A426	31.10.–07.11.2012	14357	233
A430	28.11.–05.12.2012	15150	221
A434	19.12.–26.12.2012	13613.7	240

Table 2. Concentrations of Al measured by PIGE and NAA technique.

Filter	C_{Al} PIGE (ng/m^3)	St. deviation	C_{Al} NAA (ng/m^3)
A375	108±12	8.8	–
A401	58.5±5.7	7.6	–
A417	73.9±8.4	7.6	–
A426	155±19	45.4	56.9±1.7
A430	124±5	27.8	123±4
A434	132±19	20.5	–

As can be seen from **Tab. 2**, standard deviation or values dispersion for filters A426 and A430 is much higher than uncertainty of measurements. This imply non-homogenic distribution of aerosols on the surface of the prepared samples and different concentrations of Al at measured points. Some of the filters were previously analysed by neutron activation analysis in Joint Institute for Nuclear Research Dubna [25] and in **Tab. 2**, results from PIGE and NAA can be compared. Al concentrations in A430 filter are in good agreement with both methods, however there is big difference for filter A426. This can be caused by analysing only one of 25 filters, where different mass distribution of aerosols is expected among the individual filters during the sampling or by higher content of organic aerosol in sample, that are dissolved in process of sample preparation and influence the total mass of the aerosol. Filters with enhanced coarse fraction of aerosol can contain higher concentration of Al [14, 16].

There is wide range of Al concentration in atmosphere, depending on urbanized area, agriculture and industrial activity. Obtained concentrations of Al in Bratislava are in good agreement with published data for urban area (e.g. 0.15–2.5 μg/m^3 in Massachusetts, US; 0.15–0.25 μg/m^3 in Chilton, UK; or 5.29–10.58 μg/m^3 in Munster, Germany), while for heavy industrialized locations, the concentrations can be orders of magnitude higher (e.g. 2.04 μg/m^3 in New York, US; 6.33–12.2 μg/m^3 in St. Petersburg, Russia; or 2.34–12.59 μg/m^3 in Keiyo, Japan) [26]. Low concentrations of Al were measured on Kerguelen Islands (1.84 ng/m^3), that are located far away from any human activities [27].

4. Conclusions

In this work, first results from the PIGE analysis of Bratislava atmospheric inorganic aerosols are presented. PIGE has proved to be useful tool to study light elements, like aluminium, in thin samples, while good agreement with NAA results was achieved. Method for inorganic aerosol extraction from the nitrocellulose filters and thin sample preparations were developed, to evaluate local concentrations of aluminium in the atmosphere. For our measurements, the detection limit is about 0.2 mg/g of Al in particulate matter, however by using more intensive proton beam, the limit could be lower. The average concentration of aluminium with standard deviation in several samples collected during the year 2012 in Bratislava atmosphere, was determined to be 109±33 ng/m^3. Next step in our research will be calibration for other PIGE elements like fluorine and sodium and determination of its content in atmospheric aerosols in Bratislava.

Acknowledgments

This work was supported by the EU Research and Development Operational Program funded by the ERDF (project No. 26240120012, 26240120026 and 26240220004), by the International Atomic Energy Agency (TC project RER7008 and SLR/1001) and by the Slovak Research and Development Agency under the contract APVV-15-0576.

References

[1] F. Lucarelli, G. Calzolai, M. Chiari et al.: Study of Atmospheric Aerosols by IBA Techniques. The LABEC Experience. Nucl. Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms, **417** (2018)121–127.

[2] T. Ivošević, E. Stelcer, I. Orlić et al.: Characterization and Source Apportionment of Fine Particulate Sources at Rijeka, Croatia from 2013 to 2015. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **371** (2016) 376–380.

[3] R. Mateus, M. A. Reis, A. P. Jesus, J. P. Ribeiro: Quantitative Analysis of Light Elements in Aerosol Samples by PIGE. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **249** (2006) 784–788.

[4] N. Grassi, A. Migliori, P. A. Mando, H. Calvo del Castillo: Identification of Lapis-lazuli Pigments in Paint Layers by PIGE Measurements. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **219–220** (2004) 48–52.

[5] Ž. Šmit, D. Jezeršek, T. Knific, J. Istenič: PIXE-PIGE Analysis of Carolingian Period Glass from Slovenia. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **267** (2009) 121–124.

[6] B. Constantinescu, D. Cristea-Stan, Z. Szőkefalvi-Nagy et al.: PIXE and PGAA – Complementary Methods for Studies on Ancient Glass Artefacts (from Byzantine, Late Medieval to Modern Murano Glass). Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **417** (2018) 105–109.
[7] F. Marino, G. Calzolai, S. Caporali et al.: PIXE and PIGE Techniques for the Analysis of Antarctic Ice Dust and Continental Sediments. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **266** (2008) 2396–2400.
[8] J. Vogt, C. Wirth, H-E. Zschau, G. Otto: Elemental Analysis of Mineral Grains by Means of Simultaneous Use of PIXE, PIGE and Proton Backscattering. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **68** (1992) 285–288.
[9] A. Vasilescu, B. Constantinescu, R. Bugoi et al.: Micro-Elemental Analysis of Some Transylvanian Meteorites and Lunar Samples. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **267** (2009) 2233–2235.
[10] Z. Kertész, Z. Szikszai, Z. Szoboszlai et al.: Study of Individual Atmospheric Aerosol Particles at the Debrecen Ion Microprobe. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **267** (2009) 2236–2240.
[11] G. C. Ezeh, I. B. Obioh, O. I. Asubiojo et al.: Elemental Compositions of PM10-2.5 and PM2.5 Aerosols of a Nigerian Urban City Using Ion Beam Analytical Techniques. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **334** (2014) 28–33.
[12] A. Jokar, O. Kakuee, M. Lamehi-Rachti et al.: Differential Cross Section Measurements of ^{27}Al(p, p')^{27}Al and ^{27}Al(p,)^{24}Mg Reactions in the Energy Range of 1.6-3.0 MeV. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **362** (2015) 138–141.
[13] Á. Z. Kiss, E. Koltay, B. Nyakó et al.: Measurements of Relative Thick Target Yields for PIGE Analysis on Light Elements in the Proton Energy Interval 2.4–4.2 MeV. J Radioanal Nucl Chem Artic **89** (1985) 123–141.
[14] GC Ezeh, IB Obioh, OI Asubiojo et al.: The complementarity of PIXE and PIGE techniques: A case study of size segregated airborne particulates collected from a Nigeria city. Appl Radiat Isot **103** (2015) 82–92.
[15] M. Masiol, S. Squizzato, D. Ceccato, B. Pavoni: The Size Distribution of Chemical Elements of Atmospheric aerosol at a semi-rural coastal site in Venice (Italy). The Role of Atmospheric Circulation. Chemosphere **119** (2015) 400–406.
[16] H. Raclavská, A. Corsaro, S. Hartmann-Koval, D. Juchelková: Enrichment and Distribution of 24 Elements within the Sub-sieve Particle Size Distribution Ranges of Fly Ash from Wastes Incinerator Plants. J Environ Manage **203** (2017) 1169–1177.
[17] G. Zhang, H. Li, X. Wei, Z. Fu: Preliminary Assessment of Size Distribution of Airborne Metals and Metalloids in the Urban Aerosols of Guiyang, southwest China. Atmos Pollut Res **6** (2015) 635–643.
[18] P. P. Povinec, J. Masarik, P. Kúš et al.: A new IBA-AMS Laboratory at the Comenius University in Bratislava (Slovakia). Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **342** (2015) 321–326.
[19] J. Zeman, M. Ješkovský, R. Kaiser et al.: PIXE Beam Line at the CENTA Facility of the Comenius University in Bratislava: First Results. J Radioanal Nucl Chem **311** (2017) 1409–1415.
[20] P. Povinec, M. Chudý, I. Sýkora et al.: Aerosol Radioactivity Monitoring in Bratislava Following the Chernobyl Accident. J Radioanal Nucl Chem Lett **126** (1988) 467–478.
[21] I. Sýkora, K. Holý, M. Ješkovský et al.: Long-Term Variations of Radionuclides in the Bratislava Air. J Environ Radioact **166** (2017) 27–35.
[22] M. Chiari, B. Melon, L. Salvestrini et al. Measurement of Proton Induced -ray Emission Cross Sections on Al from 2.5 to 4.1 MeV. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **332** (2014) 355–358.
[23] I. Mori, Z. Sun, M. Ukachi et al.:Development and certification of the new NIES CRM 28: Urban Aerosols for the Determination of Multielements. Anal Bioanal Chem **391** (2008) 1997–2003.
[24] J. F. Ziegler, M. D. Ziegler, J. P. Biersack: SRIM - The Stopping and Range of Ions in Matter (2010). Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms **268** (2010) 1818–1823.
[25] J. Merešová, M. Florek, K. Holý et al.: Evaluation of Elemental Content in Air-borne Particulate Matter in Low-level Atmosphere of Bratislava. Atmos Environ **42** (2008) 8079–8085.
[26] J. R. J. Sorenson, I. R. Campbell, L. B. Tepper, RD Lingg: Aluminum in the Environment and Human Health. Environ Health Perspect **8** (1974) 3–95.
[27] A. Heimburger, R. Losno, S. Triquet et al.: Direct Measurements of Atmospheric Iron, Cobalt, and Aluminum-Derived Dust Deposition at Kerguelen Islands. Global Biogeochem Cycles **26** (2012) n/a-n/a.