J. Aerosol Sci., Vol. 23, Suppl. 1, pp. S373–S376, 1992
Printed in Great Britain.

0021–8502/92 $5.00 + 0.00
Pergamon Press Ltd

A new technique to measure trace elements in individual aerosol particles through scanning proton microprobe

P. Artaxo (*), M. L. C. Rabello (*), F. Watt (**), G. Grime (**), E. Swietlicki (***)
J. Knox (***), H-C. Hansson (***)

(*) Instituto de Física, Universidade de São Paulo, Caixa Postal 20516
CEP 01498-970, São Paulo, SP, Brazil.

(**) Department of Nuclear Physics, University of Oxford
Keble Road, Oxford OX1 3RH, England.

(***) Department of Nuclear Physics, Lund University
Sölvegatan 14, S-223 62 Lund, Sweden

Abstract

In atmospheric aerosol research, one key issue is to determine the sources of the airborne particles. Scanning Nuclear Microprobe (SNM) is a new micro analytical technique that gives unique information on individual aerosol particles. In the SNM analyses a 1.0 μm size 2.4 MeV proton beam from the Oxford SNM was used. The trace elements with Z>11 were measured by the Particle Induced X-ray Emission (PIXE) method with detection limits in the 1 to 10 ppm range. Carbon, nitrogen and oxygen are measured simultaneously using Rutherford Back Scattering Spectrometry (RBS). Atmospheric aerosol particles were collected at the Brazilian Antarctic Station and at several biomass burning sites in the Amazon basin tropical rain forest in Brazil. In the Antarctic aerosol samples, the sea-salt aerosol particles were clearly predominating, with NaCl and $CaSO_4$ as major compounds with several trace elements like Al, Si, P, K, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb. Factor analysis of the elemental data showed the presence of 4 components: 1) Soil dust particles; 2) NaCl particles; 3) $CaSO_4$ with Sr; 4) Br and Mg. The hierarchical cluster procedure gave results similar to the ones obtained through factor analysis. For the tropical rain forest biomass burning aerosol emissions, biogenic particles with high organic content dominate the particle population, while K, P, Ca, Mg, Zn, and Si are the dominant elements. Zinc at 10 to 200 ppm is present in biogenic particles rich in P and K. It was observed a better source resolution with SNM than with bulk PIXE with receptor modeling. The quantitative aspects and excellent detection limits make SNM analysis of individual aerosol particles a powerful analytical tool.

Keywords

Single Particle Analysis, Atmospheric Aerosols, Atmospheric Chemistry, Biological Particles, Measurements, Bioaerosol, Source/Receptor Modelling, Instrumentation.

Introduction

Most of the studies of elemental composition of aerosol particles and source apportionment were performed with bulk analytical methods like PIXE (Particle-Induced X-Ray Emission) (Johansson and Campbell, 1988), XRF (X-Ray Fluorescence), INAA (Instrumental Neutron Activation Analysis) and other techniques. In the bulk elemental analysis, the elemental composition represents averages over many different types of particles with different elemental composition, shapes and sizes. The

microanalysis of individual aerosol particles provides a very different and powerful view. The type and quality of the information obtained by individual particle analysis complements bulk measurements.

The development of the SNM (Scanning Nuclear Microprobe) technique has opened new possibilities for aerosol particle analysis (Artaxo *et al.*, 1990, Traxel and Wätjen, 1986). SNM is a novel technique that can provide detection limits of 2 to 20 ppm, for particles larger than 1 μm for most of the elements with Z>10. The SNM technique also allows the measurement of carbon, nitrogen and oxygen by the "Rutherford Back Scattering Spectrometry (RBS)" technique.

Scanning Nuclear Microprobe (SNM)

In the SNM analysis, a well-focused beam of high energy protons is scanned over the sample. One of the major advantages of this technique is the excellent detection limit, of the order of 5 to 20 ppm, depending on the SNM design. The proton beam with an energy of about 2.5 MeV is focused to a diameter of 0.5 to 2 μm, with beam currents of 50 to 100 picoamperes. A scanning system controls the beam positioning, with a computer system collecting data from several detectors. There are several processes occurring in the interaction of the proton beam with the sample. X-rays are generated by Particle Induced X-ray Emission (PIXE), allowing concentration measurements for elements heavier than sodium. Back scattered particles contain information on light elements like carbon, nitrogen and oxygen through the RBS technique. Normally PIXE and RBS analysis are done simultaneously, allowing the determination of carbon, nitrogen and oxygen together with 10 to 15 trace elements heavier than sodium (Artaxo *et al.*, 1990). The detection of light elements makes it possible to determine absolute elemental concentrations in ppm with good accuracy. The SNM analyses were performed at the Oxford SNM system, with an 1.0 μm size beam with a current of 50 to 100 pA. The aerosol particles were collected on polycarbonate filters and coated with a thin carbon layer to make the particles conductive. Qualitative analyses of several particles from Antarctica were also performed with the new Lund SNM. The elemental maps revealed many particles and particle agglomerates with complex and inhomogeneous elemental composition.

Multivariate statistical analysis was used to help in the data interpretation. Factor analysis was used to study the variability of elemental concentrations. Hierarchical cluster analysis was used as a classification method for the individual particles.

Results and Discussion

SNM results for biomass burning aerosol particles

A coarse mode (10 μm>d_p>2 μm) Nuclepore filter (sample CUI16G) was analyzed for 52 individual aerosol particles. This sample was collected in a background sampling station (Cuiabá) during the biomass burning season in the Amazon Basin. Absolute concentrations as low as 4 ppm was measured for Ni, Cu, Zn and others. A total of 21 elements were measured by PIXE in the particles (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Zr, and Pb), in addition to carbon, nitrogen and oxygen measured by RBS. Some elements (Na, Mn, Ni, Br, Rb, Sr, Zr and Pb) appeared in a very limited number of particles, not allowing an understanding of their sources. For the 13 remaining elements, factor analysis was used to study the relationship between the elemental concentrations. **Table 1** shows the VARIMAX rotated factor matrix for the 5 statistical significant factors. The high communalities on the last column of table 1 show the adequacy of the 5 factor model. The first factor has high loading for P, Mg, Zn and Cl. These elements have shown in previous works as biogenic related elements or emitted during biomass burning process. The second factor has high loading for K, Al and Si, indicating soil dust aerosol particles. The third factor represents $CaSO_4$ with Cl. The fourth factor represents Fe and As (maybe a soil dust component). The fifth factor has high loading for Cu, Ti and Al, representing a third soil dust component. The bulk PIXE and factor analysis

of many samples from the same site revealed only two components, identified as biogenic and soil dust (Artaxo *et al.*, 1988).

Hierarchical cluster analysis were performed and four clusters were analyzed. The first one with 38 % of the number of the particles consists of biogenic aerosol particles, with high P and S concentrations. This cluster 1 correspond to the factor 1, and has very homogeneous composition, as can be observed from the low dissimilarity between the particles in the cluster. The second cluster with 37 % of the number of particles is a soil dust group, with Al, Si, and Fe, and also rich in calcium. This cluster 2 represents a mixture of factor 2 (soil 1) and factor 3 ($CaSO_4$). Cluster 3 with 12 % of the number of particles is an aluminosilicate group with high Al and Si and low Fe, and is associated with factor 2. Cluster 4 (12 %) is a group with high Fe and As, similar to factor 4. The results obtained with cluster analysis are in general agreement with the factor analysis calculations, despite the different ways to look at elemental concentrations and particle composition.

Table 1 - Amazon Basin Biomass Burning Aerosol - Scanning Nuclear Microprobe Analysis of 52 Individual Aerosol Particles. VARIMAX Rotated Factor Matrix.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Element	Biogenic	Soil 1	$CaSO_4$	Fe+As	Soil 2	
Mg	**.85**	-.14	.12	-.09	.14	.79
Al	-.14	**.81**	.01	.15	**.43**	.89
Si	-.16	**.81**	-.06	.02	.18	.73
P	**.93**	.02	.13	-.04	-.01	.90
S	**.29**	.01	**.85**	-.08	-.12	.83
Cl	**.54**	.17	**.63**	-.03	-.23	.78
K	**.34**	**.85**	.08	.11	-.11	.87
Ca	.08	-.08	**.88**	-.01	.23	.85
Ti	-.10	.26	-.00	.09	**.77**	.68
Fe	-.08	.17	-.10	**.90**	.18	.90
Cu	.33	.05	.03	.04	**.80**	.76
Zn	**.83**	.05	**.31**	-.01	.09	.80
As	-.03	.03	.01	**.95**	-.02	.91

SNM results for Antarctic aerosol particles

Two coarse mode samples collected during summertime in the Antarctic Brazilian station in the Antarctic peninsula were analyzed for a total of 55 particles. **Table 2** presents the VARIMAX rotated factor matrix for the 11 elements and the 4 factor solution. The high communalities in the last column of Table 2, shows the adequacy of the factor model. The first factor has high loading for Si, Fe, Al and K, indicating soil dust aerosol particles. Factor 2 is a $CaSO_4$ factor with the presence of Sr. Factor 3 represents NaCl particles from sea-salt. Factor 4 has high loading for Br and Mg, and a moderate loading for K.

Hierarchical cluster analysis shows the presence of four particle groups. The first cluster, responsible for 45 % of the number of particles represents sea-salt aerosol with predominance of NaCl, and corresponds to the factor 3. The second cluster (with 11 % of the number of particles) is also sea-salt, but richer in Br and soil dust related elements. The group number 4 responsible for 11 % of the number of particles is $CaSO_4$ with Sr, and the cluster number 3 is soil dust aerosol, rich in Al, Si and Fe, and responsible for 33 % of the number of particles. This cluster 3 has very homogeneous composition. The two sea-salt clusters have average Cl/Na ratio of 1.33 and 1.55, that compares quite well with the expected value (the molar ratio of NaCl is 1.54). For the $CaSO_4$ cluster, the Cl to Na ratio is 0.94, a low value probably because of the presence of sulfur that release chlorine in gas phase, leaving an enrichment of sodium in the particle. Br is present in all four particle groups at

concentrations of about 100 ppm. Sr is present in group 4 at concentrations of about 200 ppm. It is also possible to observe that sulfur was measured in all particles, even in soil dust aerosol particles. Possibly this is due to the fact that these particles have been transported for long distances and coated with sulfur species originating from oceanic biogenic sulfur.

Table 2 - Antarctic Aerosol - Scanning Nuclear Microprobe Analysis of Individual Particles. VARIMAX Rotated Factor Matrix of 55 particles.

	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Element	Soil Dust	$CaSO_4$+Sr	NaCl	Br+Mg+K	
Na	-.07	-.25	**.93**	.04	.95
Mg	-.04	-.11	.19	**.86**	.79
Al	**.95**	-.06	-.09	.03	.91
Si	**.99**	-.03	-.06	.02	.98
S	-.04	**.94**	-.19	-.02	.94
Cl	-.09	-.24	**.93**	.07	.95
K	**.40**	-.04	-.41	**.38**	.48
Ca	-.04	**.97**	-.12	-.10	.97
Fe	**.97**	-.02	-.05	.00	.95
Br	.05	-.01	-.08	**.89**	.81
Sr	-.04	**.95**	-.18	-.04	.95

It was possible to observe a better aerosol source apportionment using SNM analysis than with traditional bulk PIXE coupled with receptor modeling. SNM analysis was able to discriminate different particle types and clarify atmospheric processes in a unique way. This was clear for the Amazon basin samples, where the biogenic aerosol component was shown to consist of different particle types. For Antarctic aerosol particles the sea-salt component was split up in three particle types, revealing reactions of sulphur gases with NaCl particles and $CaSO_4$ particles, in addition to soil dust aerosol particles. Better spatial resolution of SNM analysis can improve the usefulness of this technique to study sub-micrometer aerosol particles.

Acknowledgments

We would like to acknowledge José Roberto Neme do Amorim, José Roberto Chagas, Alcides Camargo Ribeiro, Ana Lucia Loureiro, Alberto Setzer, Enio B. Pereira, Marcio Vilella, INPE and ICOMI for help with the sampling program in Antarctica and Amazon basin. This work has received financial support from FAPESP, Projeto Temático 90/2950-2, Projeto BID-USP 27.12, CNPq - Projeto Integrado 500539/91, and from the Swedish National Science Foundation.

References

Artaxo P., H. Storms, F. Bruynseels, R. Van Grieken and W. Maenhaut, Composition and sources of aerosols from the Amazon Basin, *J. Geophys. Res.*, 93 (1988) 1605-1615.

Artaxo, P., R. Van Grieken, F. Watt, M. Jaksic, The microanalysis of individual atmospheric aerosol particles by electron, proton and laser microprobe. Proceedings of the *Second world congress particle technology*, Society of Powder Technology, Kyoto, Japan, (1990) 421-426.

Johansson, S.A.E., J.L. Campbell, *PIXE - A Novel Technique for Elemental Analysis*, John Willey, New York, 1988.

Traxel K. and U. Wätjen, in: *Physical and chemical characterization of individual particles*, Ed. K.R. Spurny, John Wiley and Sons, New York, (1986) 298-326.