CLASSIFICATION OF NATURAL AIR IONS NEAR THE GROUND

U. Hõrrak, J. Salm, and H. Tammet

Institute of Environmental Physics, University of Tartu
18 Ülikooli St., Tartu, 51014, Estonia

ABSTRACT: The structure of air ion mobility spectrum recorded at Tahkuse Observatory, Estonia, during 14 months, is studied using factor analysis. The air ions in a mobility range of 0.00041–3.2 $cm^2 V^{-1} s^{-1}$ (diameters 0.36–80 nm) are divided into five classes: small and big cluster ions, intermediate ions, light and heavy large ions. The boundaries between the classes are 1.3 $cm^2 V^{-1} s^{-1}$, 0.5 $cm^2 V^{-1} s^{-1}$, 0.034 $cm^2 V^{-1} s^{-1}$, 0.0042 $cm^2 V^{-1} s^{-1}$. Five factors correlated with respective ion classes explain 92% of total variance. According to their physical nature, the intermediate and large ions are called aerosol ions. The classification of air ions according to their mobility leads to a correlated classification of atmospheric aerosol particles according to size. The 1.6 nm boundary diameter between clusters and aerosol particles is confirmed, and the boundary diameters between the nanometer particles, the ultrafine particles and the Aitken particles as classes of tropospheric aerosol are estimated to be 7.4 nm and 22 nm.

INTRODUCTION

The concepts of small and large air ions have a perceptible physical background. Problems arise when trying to specify the concept of intermediate ions and settle the mobility boundaries. The boundaries defined in atmospheric electricity textbooks are rather conventions. A natural classification is assumed to explain coherent behavior of air ions inside class intervals and relative independence of the ions of different classes. A requirement to measurements used in the verification of the classification is that the recorded air ion mobility fractions should be narrow when compared with mobility classes. The analysis of the statistical behavior of fraction concentrations requires thousands of mobility spectra recorded during at least one full year. First measurements that simultaneously satisfy both of these requirements have been carried out at Tahkuse Observatory where a 20-fraction air ion mobility spectrometer covering a mobility range of 0.00041–3.2 $cm^2 V^{-1} s^{-1}$ is running almost continuously since 1988 [*Hõrrak et al.*, 1994].

The large and intermediate ions are charged aerosol particles, and their mobility is correlated with the particle diameter. Thus the problem is related to the atmospheric aerosol particle size classification. As well as in the case of mobility measurements, the measurements of particle size distribution in a wide size range have been episodic and the boundaries between the particle size classes are conventional. Obviously the air ion mobility data contains the largest available statistical information about long term variations of tropospheric aerosol size spectrum. Thus the analysis of mobility spectra at Tahkuse Observatory could provide essential information about natural classification of atmospheric aerosol particles according to their size.

INSTRUMENTATION AND MEASUREMENTS

The instrumentation at Tahkuse Observatory consists of three original multichannel aspiration mobility analyzers. Air is sucked into the analyzers through an opening in the gable of a building at a height of about 5 m from the ground. High trees around the building shield the electric field and suppress the electrode effect asymmetry of polarities [*Hõrrak et al.,* 1994].

Table 1 describes the scheme of mobility fractions. All 20 fraction concentrations of positive air ions and 20 fraction concentrations of negative air ions were measured every 5 minutes. The hourly averages and standard deviations of air ion fraction concentrations inside the hourly periods were recorded together with simultaneously measured values of wind direction, wind speed, atmospheric pressure, temperature, relative humidity, and concentration of NO_2. The present analysis is based on the data collected during the period from September 1, 1993, to October 27, 1994. Due to occasional pauses in the measurements, about 16% of the possible measuring time was lost, and 8615 hourly mobility spectra of both signs are available.

TABLE 1. Air ion fractions, estimates of equivalent diameter ranges assuming single charged particles, and proposed classes of air ions.

Fraction number	Mobility cm^2 V^{-1} s^{-1}	Classes of ions	Diameter nm
1	2.51–3.14	Small cluster ions	0.36–0.45
2	2.01–2.51		0.45–0.56
3	1.60–2.01		0.56–0.70
4	1.28–1.60		0.70–0.85
5	1.02–1.28	Big cluster ions	0.85–1.03
6	0.79–1.02		1.03–1.24
7	0.63–0.79		1.24–1.42
8	0.50–0.63		1.42–1.60
9	0.40–0.50	Intermediate ions	1.6–1.8
10	0.32–0.40		1.8–2.0
11	0.25–0.32		2.0–2.3
12	0.150–0.293		2.1–3.2
13	0.074–0.150		3.2–4.8
14	0.034–0.074		4.8–7.4
15	0.016–0.034	Light large ions	7.4–11.0
16	0.0091–0.0205		9.7–14.8
17	0.0042–0.0091		15–22
18	0.00192–0.00420	Heavy large ions	22–34
19	0.00087–0.00192		34–52
20	0.00041–0.00087		52–79

Average concentrations of negative and positive small ions are 245 cm^{-3} and 274 cm^{-3}. The concentration of large ions diminishes towards higher mobilities due to a reduction of charging probability and concentration of aerosol particles. The shape of their mobility spectrum is in accordance with calculations based on the theory of bipolar charging of aerosol particles by diffusion of cluster ions. Average concentration of intermediate ions is about 50 cm^{-3}. Occasional bursts of intermediate ions up to about 900 cm^{-3} occur during daytime. The intermediate ions are formed probably by diffusion charging of nanometer aerosol particles generated by photochemical nucleation process. Another process responsible for the generation of intermediate ions is the growth of small ions under special environmental conditions. The variation coefficient of the hourly average values of concentration is about 50% for small ions, 70% for large ions, and up to 130% for intermediate ions. At night-time, intermediate and large air ions show a lower variation coefficient of 50–60%.

FACTOR ANALYSIS

Fraction concentrations of air ions are interpreted as a set of closely correlated variables. Greater part of the measurement information about correlated variables can be represented by a considerably smaller number of new variables, called the principal components, or factors. The analysis was carried out both in terms of the original values of the 20 fraction concentrations and of their logarithmically rescaled values, and the results are nearly the same. The eigenvalue problem was solved for the correlation matrix which is equivalent to preliminary standardization of variables, or analysis of relative variations. The principal components were transformed to well interpretable factors with dominating positive factor loadings using the VARIMAX procedure. The factor analysis was carried out separately for positive and negative ions. The results are presented in Figure 1 for positive ions, the results for negative ions being very similar.

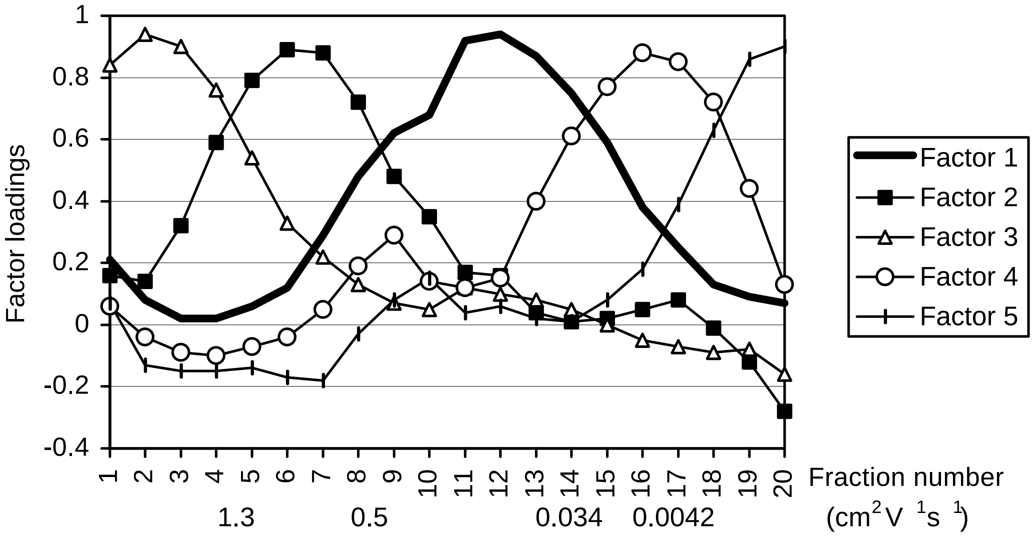

Figure 1. Factors of air ion mobility spectrum for positive ions.
The mobility and diameter boundaries of fractions are given in Table 1.

The first five principal components explain 92% of the total variance and each of the five factors presents at least as much variance as the average for one fraction concentration. The subsequent 14 principal components explain only 8% of the total variance. A part of this variation is caused by instrument noise. Thus the mobility spectrum has five essential degrees of freedom, and the set of 20 fraction concentrations can be relatively well described by only five factors representing at least 92% of all the measurement information.

Factor 1 (see Figure 1) is highly correlated with intermediate ions (fractions 9–14) and thus can be called the “burst factor” of intermediate ions. It accounts for 24% of the total variance. Factor 2 is highly correlated with big cluster ions (fractions 4–8), Factor 3 with small cluster ions (fractions 1–4), and Factor 4 with light large ions (fractions 15–18). They account for approximately equal variances, 20%, 18% and 17%. The contribution of Factor 5, associated with heavy large ions (fractions 18–20), is the lowest, 13%. This factor is correlated inversely with cluster ions (fractions 2–7). Factor 2, correlated highly with big cluster ions (fractions 5–8), is correlated negatively with heavy large ions (fractions 19–20).

DISCUSSION AND CONCLUSIONS

The analysis of the correlations between the factors and air ion fraction concentrations shows that all the air ions can be divided into two wide classes: cluster ions with mobilities above 0.5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, and aerosol ions with mobilities below 0.5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Aerosol ions are particles with physical properties of macroscopic bodies. The cluster ions can be divided into two subclasses (small and big cluster ions), and the aerosol ions into three subclasses (intermediate ions, light and heavy large ions). This classification, given in Table 1, is still to a certain extent conventional and the boundaries are not exactly determined because the factors have crossloadings (any variable is correlated with more than one factor, see Figure 1).

A mobility of 0.5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ or a diameter of 1.6 nm is the same boundary, which has been considered physically as the boundary between molecular clusters and macroscopic particles [*Tammet*, 1995]. The same value of 0.5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ was also formerly considered as the lower boundary of small air ions [e.g., *Hõrrak et al.*, 1994].

The above classes of air ions could be physically characterized as follows:

- *Small cluster ions*: mobility 1.3–2.5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, estimated diameter 0.36–0.85 nm and mass 30–400 u. The core of a cluster could contain an inorganic molecule and be surrounded by one layer of water molecules. After recombination, the cluster would be destroyed and separated back to molecules.
- *Big cluster ions*: mobility 0.5–1.3 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, estimated diameter 0.85–1.6 nm and mass 400–2500 u. The core of a cluster could contain an organic molecule and be surrounded by a layer of water molecules. In the case of intensive nucleation events (bursts) the enhanced concentrations were recorded simultaneously with intermediate and light large ion concentrations. As distinct from aerosol ions, collisions between cluster ions and ambient gas molecules are considered to be elastic [*Tammet*, 1995].
- *Intermediate ions*: mobility 0.034–0.5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, diameter 1.6–7.4 nm. The corresponding class of aerosol particles: the *nanometer particles*. Some intermediate ions are a product of ion–induced nucleation: nucleating vapor condenses to cluster ions, which grow to the size of intermediate ions called the *primary aerosol ions*. Particles born in the neutral stage in the process of gas-to-particle conversion, or nucleation, and charged by attachment of cluster ions, are called the *secondary aerosol ions*.
- *Light large ions*: mobility 0.0042–0.034 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, diameter 7.4–22 nm. The corresponding class of aerosol particles: the *ultrafine particles*. They are often in a quasi-steady state of stochastic charging with cluster ions.
- *Heavy large ions*: mobility < 0.0042 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, diameter > 22 nm. The corresponding class of aerosol particles could be called the *Aitken particles*. They are, as a rule, in a quasi-steady state of stochastic charging with cluster ions, and some of them may carry multiple charges.

ACKNOWLEDGEMENTS: This research was supported by the Estonian Science Foundation grants nos. 1879, 3326, and 3050.

REFERENCES

Hõrrak, U., H. Iher, A. Luts, J. Salm, and H. Tammet, Mobility spectrum of air ions at Tahkuse Observatory, *J. Geophys. Res.,* ***99***, 10,679–10,700, 1994.

Tammet, H., Size and mobility of nanometer particles, clusters and ions, *J. Aerosol Sci.,* ***26,*** 459–475, 1995.